Some Notes on the Chlorogenic Acids.
Part 4. Botanical Distribution of the Chlorogenic acids

Version 1 January 2017

Mike Clifford
Emeritus Professor of Food Safety
University of Surrey, Guildford GU2 5XH, Surrey, UK

Contents

	SUMMARY	Page 1
	ABBREVIATIONS	Page 3
	INTRODUCTION	Page 4
4.1.	BRYOPHYTA	Page 6
4.2.	PTERIDOPHYTA	Page 7
4.3.	GYMNOSPERMAE	Page 10
4.4.	ANGIOSPERMAE	Page 11
4.5.	CONCLUDING REMARKS	Page 145
4.6.	REFERENCES	Page 153

Summary

This compilation summarizes the compositional data found in the literature. Greater emphasis has been given to the more recent data — post-2000 — and especially that using modern methods of analysis and characterization, in particular LC–MS^n. Data have been obtained for over 400 acyl-quinic and acyl-shikimic acids in over 400 genera that fall within 44 Orders, but these represent just a fraction of the plant kingdom.

The objective was to provide a basis from which relationships of chemo-taxonomic interest and the summaries, highlighted in green, presented at various points throughout this document, attempt to do this. Unfortunately, there are at present too many gaps and inconsistencies in the literature, both analytical and taxonomic, to progress beyond the stage of highlighting areas that possibly merit further investigation. Accordingly these summaries in the text must be viewed only as work in progress.

One item that is clear, is that contrary to the generally held belief, there is good evidence for the occurrence of CQA in Bryophytes which lack vascular tissue. In the Pteridophyta there are reports also of *p*CoQA and diCQA, but reports of CSA are more numerous. Data for Gymnosperms are, surprisingly, more limited than for the Pteridophyta, but even here CQA have occasionally been reported along with *p*-coumaroyl esters of 2-hydroxy-quinic acid and *myo*-inositol.

For the Angiospermae, the general impression that forms from the comparatively limited data available, relative to the number of species known, is that the Magnolids have a fairly simple acyl-quinic acid acid profile. In the Commelinids, acyl-shikimic acids become more prominent. Galloylquinic acids appear first in the Eudicots and are more prominent in the Fabids. Profiles become more complex in the Malvids and galloyl-quinic acids remain

prominent. Campanulids tend to have complex profiles with a noticeable increase in quinic acids having two or more different substituents. Several aliphatic acids become obvious, whether or not 1-substituted dicaffeoylquinic acids are present seems to be taxonomically interesting, and the presence occasionally of acyl derivatives of one or more quinic acid epimers is another interesting feature. Hydroxyphenylacetyl-quinic acids also appear, but the GQA decline in prominence and may be absent. In the Lamiids hydroxybenzoylquinic acids other than gallic acid become more obvious.

Within the Angiospermae it seems clear that chlorogenic acids are not universally present, and even in families where some chlorogenic acids are found it seems that 5-CQA is not inevitably present. Also when 5-CQA, is present, it does not necessarily dominate its subgroup, and while it is quite likely that for any chlorogenic acid subgroup, all possible regio-isomers will somewhere be found, some species clearly favour a limited number of regio-isomers in at least some subgroups, a feature well illustrated by the presence or absence of esterification at C1 of (–)-quinic acid, but by no means restricted thereto. CQA and diCQA, while often the major subgroups, again are not inevitably so.

There are as yet insufficient data to judge the true distribution of the more recently discovered chlorogenic acids, those incorporating, aliphatic acids, dihydrocinnamic acids, the rarer cinnamic acids, the (hydroxy)benzoic acids, etc. but it seems distinctly possible that these will be of chemo-taxonomic interest.

Abbreviations

Cinnamoyl and Benzoyl Moieties

Bz	Benzoic acid
C	Caffeic acid [3′,4′dihydroxycinnamic acid]
Ci	Cinnamic acid
dhC	Dihydrocaffeic acid [3-(3′,4′-dihydroxyphenyl)propionic acid]
dhmC	3′,5′-Dihydroxy-4′-methoxycinnamic acid
D	3′,4′-Dimethoxycinnamic acid
Eud	Eudesmic acid (3,4,5-trimethoxybenzoic acid)
F	Ferulic acid [3′-methyoxy-4′-hydroxycinnamic acid]
G	Gallic acid [3,4,5-trihudroxybenzoic acid]
iF	Isoferulic acid [3-(3′-hydroxy-4′-methoxycinnamic acid]
*p*Co	*p*-Coumaric acid [4′-hydroxycinnamic acid]
Prot	Protocatechuic acid (3,4-dihydroxybenzoic acid)
Si	Sinapic acid [3′,5′-dimethoxy-4′-hydroxycinnamic acid]
Sy	Syringic acid [3,5-methoxy-4-hydroxybenzoic acid]
T	3′,4′,5′-Trimethoxycinnamic acid
V	Vanillic acid [3-methoxy-4-hydroxybenzoic acid]

Cyclitol Moiety

cisQA	*Cis*-quinic acid
deoQA	Deoxyquinic acid
epiQA	*Epi*-quinic acid
epiSA	*Epi*-shikimic acid
mucoQA	*Muco*-quinic acid
neoQA	*Neo*-quinic acid
Q	Quinate
QA	(–)-Quinic acid
QL	Quinic lactone
SA	Shikimic acid

Aliphatic Moiety

Ac	Acetic
Fum	Fumaric acid
Glut	(3-Hydroxy-3-methyl)glutaric acid
M	Methyl
Mal	Malic acid
Malo	Malonic acid
Mo	Methoxyoxalic acid
Suc	Succinic acid

Introduction

To make this document as useful as possible, and not merely a listing of some 1,100 papers, the published data have been examined critically. As a result, attention has been drawn to papers that did not use IUPAC numbering, and papers where it is unclear which numbering system has been used.

When it is clear that the authors of the work cited have not used the IUPAC numbering system this is noted **but the compounds reported are changed to the IUPAC system.**

When it is impossible to judge which system has been used this also is noted**, but the assignments are not altered.**

In some cases it is clear that authors have used IUPAC numbering but established the identity of the CGA reported by using standards identified using non-IUPAC numbering, and again this is noted. **All such comments appear in red.**

As discussed more extensively in Parts 1–3 the correct identification of individual CGA is fraught with difficulty, and where there is reason for doubt about the reliability of an assignment reported, attention is drawn to the nature of the problem and sometimes an alternative interpretation is suggested along with the basis on which the re-assignment is made. The nature of the uncertainties fall into several categories, including unexpected relative capacity factors for individual CGA, uncertain interpretation of NMR data, and uncertain interpretation of MS data as more fully discussed in Parts 2 and 3.

For convenience, the uncertainties possibly arising from MS interpretation are summarised below:

(i) the confusion in MS of FQA and methyl CQ, CFQA and methyl diCQ, etc.;

(ii) the confusion in MS of acyl derivatives of quinic acid methyl ethers with quinic acid methyl esters, or possibly with CGA where the cinnamic acid is a methyl ether;

(iii) the confusion of a hexose sugar residue with a caffeic acid residue, e.g. CQA-glucosides confused with diCQAs;

(iv) possible incorrect assignment of regio-chemistry when non-ion trap-MS instruments have been used and characteristic fragment ions are not present — also when high fragmentation energy has been used with ion trap instruments;

(v) possible incorrect assignment of regio-chemistry for tri- and tetra-acyl quinic acid derivatives with one or more dicarboxylic acid substituents even when ion trap-MS instruments have been used;

(vi) possible confusion of a *cis*-5-acyl quinic acid with the equivalent *trans*-1-acyl isomer;

(vii) possible confusion of acyl-quinic acids with acyl-isocitric acids..

The main uncertainty arising from NMR interpretation is the discrimination of the less common quinic acid epimers, especially the less common diCQA, as discussed in Part 2.

It has long been known that alkyl esters can form when samples are extracted in an alcoholic solvent and this potential problem has been highlighted again more recently.*(1-3)* Accordingly, the occurrence of CGA methyl esters in an extract prepared with methanol must always be treated with caution. The occurrence of alkyl esters other than methyl, e.g. *n*-butyl, *n*-propyl or ethyl, when methanol has been used suggests that these are genuine components.

For several reasons there has been no attempt to compile an exhaustive listing of quantitative data. It is clearly documented that significant differences in CGA content arise with variations in plant maturity, as well illustrated for the coffee bean,*(4, 5)* and artichoke,*(6, 7)* and with the organ analyzed as clearly observed for some *Ageratoides* spp.,*(8)* and artichoke.*(7)* Collectively, these factors seriously limit the value of such comparisons, especially when only a few samples have been analysed, although it may be of interest to know which CGA dominate the profile and whether the content is in the mg/kg or g/kg range. Further constraints arise from the use of different methods of quantification, and in particular, the choice of calibrant. The problem associated with the use of impure commercial standards as calibrants has been discussed in part 3 and will not be repeated here, but a few examples are mentioned in the text to illustrate the magnitude of this problem.

Because botanical classification changes over time, is currently sometimes uncertain, and because this monograph is likely to be used by those who are not specialists in taxonomy, a pragmatic approach has been taken to the sequence in which species are dealt with. The account begins with the Bryophyta, followed by the Pteridophyta, Gymnospermae and Angiospermae. For this latter group the order in which the Classes are presented follows the APG IV recommmendations of the Angiosperm Phylogeny Group.*(9)* Thereafter the Orders, Families, Tribes and Genera, as appropriate, are presented alphabetically, unless there is insufficient information to justify such a subdivision.

4.1. BRYOPHYTA

The Bryophyta are a division of nonflowering plants characterized by rhizoids rather than true roots and having little or no organized vascular tissue, and hence little or no lignification. Bryophyta have alternating generations of gamete-bearing forms and spore-bearing forms, and comprise true mosses (Bryopsida), liverworts (Hepaticopsida) and hornworts (Anthoceropsida). Reports of CGA have been located only for the mosses.

In 2008 Nam *et al*. reported 5-CQA in the Tree Moss, *Climacium dendroides*, following spectral characterisation of the isolate,*(10)* but did not use the IUPAC numbering. Erxleben *et al*. using GC–MS to characterise the secondary metabolites of *Physcomitrella patens* reported a caffeoylquinic acid in extracts of the upright gametophores but not in the protonema. The authors commented that from an evolutionary standpoint *P. patens* is the first plant to be recorded with the complete lignin biosynthesis pathway.*(11)*

There have been three other reports of CGA in mosses, but based solely on the matching of retention times in LC–DAD, as follows, and these must be viewed as tentative. In 2008 Jockovic *et al*. reported 4-CQA and 5-CQA in *Brachytheciastrum velutinum* (Hedw) Ignatov & Huttunen and *Kindbergia praelonga* (Hedw) Ochyra but these compounds were not detected in *Lunularia cruciata* (L.) Dumort.*(12)* In 2009 Montenegro *et al*. reported '*chlorogenic acid*', presumably 5-CQA, in *Sphagnum magellanicum*.*(13)*

4.2. PTERIDOPHYTA

The pteridophyta are vascular plants that produce spores rather than flowers and seeds. They include clubmosses (Lycopodiopsida), ferns and horsetails (Polypodiopsida = Polypodiidae),*(14)* but definitive studies of CGA have been located only for ferns and horsetails.

4.2.1. ORDER ATHYRIALES

4.2.1.1. Thelypteridaceae family

3-*p*CoSA has been isolated from *Phegopteris connectilis* and characterised by NMR.*(15)* 5-CSA has been isolated from *Wagneriopteris japonica* Loeve et Loeve,*(16)* and has been reported in *Thelypteris palustris* Schott, *Phegopteris conectilis* (Michaux) Watt and *Oreopteris limbsperma* (All.) Holub.*(17)*

4.2.2. ORDER CYATHEALES

4.2.2.1. Family Dicksoniaceae

Saito *et al*. isolated 4-CSA and 4-*p*CoSA from *Dicksoni antarctica* and characterised them by NMR.*(18)*

4.2.3. ORDER EQUISETALES

4.2.3.1. Equisetaceae family

5-CSA and 5-CQA occurs in the sporophytes and ganetophytes of *Equisetum arvense* and after isolation 5-CSA has been characterised spectroscopically. 5-CSA is also present in *E ×* littorale the hybrid between *E* arvense and *E. fluviatile*, *E × rothmaleri* and in the sporophytes of *E. ramossisimum* and *E. bogotense*, but absent from 16 other species including *E. fluviatile*.*(17)* Subsequently Holhfeld *et al*. isolated the hydroxy-cinnamoyltransferases for the synthesis of shikimic acid, quinic acid and *meso*-tartaric acid conjugates from *E. arvense*,*(19)* but a later screening by Petersen *et al*. failed to find 5-CQA in *E. arvense*.*(20)*

4.2.4. ORDER OSMUNDALES

4.2.4.1. Osmundaceae family

Osmunda regalis contains 5-CSA.*(17)*

4.2.5. Order Polypodiales

4.2.5.1. Athyriaceae family

Veit *et al.* isolated 5-CSA and characterised it spectroscopically, and reported its presence in *Athyrium filix-femina* (L.) Roth and *Cystopteris fragilis* (L.) Bemardi but apparent absence from *Matteucia strutkiopteris* (L.) Todaro and *Onoclea sensibilis* L.*(17)* Subsequently Adam reported chlorogenic acid, 5-CSA and 3,4-diCQA in *Athyrium felix-femina*,*(21)* but it is not clear whether IUPAC numbering has been used.

4.2.5.2. Blechnaceae family

Petersen *et al*. reported 5-CQA in *Blechnum arcuatum, B. brasiliense, B. gibbon* and *B. occidentale* but not in *B. polypodioides.(20)*

4.2.5.3. Pteridaceae family

5-CSA was found in Bracken, *Pteridium aquilinum* in 1962, and was at one time thought to be associated with its toxicity,*(22)* but there have been few recent studies. *Pteris ensiformis*, the Sword Brake Fern, contains 5-FQA, 3,4-diCQA and 4,5-diCQA,*(23)* and *Pteris multifida* contains the novel 4C-5MQA and 3,4-diCQA,*(24)* but note that the original paper did not use the IUPAC numbering, and that there is an error in the original paper with the novel compound sometimes described merely as 4-CQA. These authors characterized the novel 4C-5MQA by NMR and by hydrolysis with methanolic NaOH that yielded the methyl ester of 4-*O*-methyl quinic acid thus clearly demonstrating the location of the original methyl ether. Unfortunately, the NMR data reported for the methyl ester of 4-*O*-methyl quinic acid does not include any signals for either methyl residue,*(24)* but NMR of the parent compound shows a methoxyl δ_H = 3.34, essentially identical to the value reported by Zeller*(25)* for authentic 1M-5CQA (methoxyl δ_H =3.31). The coupling constants for H4 (7.8 and 5.3 Hz) are distinctly different from this associated with (–)-quinic acid.

Although the original identification of 1M-5CQA, and probably also 4M-5CQA, in *Phyllostachys edulis(26)* is now known to be incorrect,*(25)* this assignment of 4C-5MQA in *Pteris multifida* seems plausible, but would benefit from evaluation by LC–ion trap-MS.

Other reports include 5-CQA in *Cheilanthes farinosa (27)*, 5-CQA in *Pyrrosia petiolosa* and *P. davidii*,*(28, 29)* According to the abstract *P. calvata* contains 5-CQA, 1,5-diCQA, 3,5-diCQA and methyl-3-CQ,*(30)* but it is uncertain which numbering system has been used.

5-CQA plus three other uncharacterised CQA and an uncharacterised *p*CoQA have been reported in *Polypodium leucotomos*.*(31)* An undefined chlorogenic acid has been reported in *Metaxya rostrata*.*(32)* *Vittaria anguste-elongata* has been reported to contain methyl-4-*p*CoQA.*(33)*

4.2.6. ORDER SELAGINALES

4.2.6.1. Selaginaceae family

Selaginella species: Lin *et al*. have reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA, identified by FABMS, in Taiwanese *Selaginella delicatula*.*(34)*

4.3. GYMNOSPERMAE

Gymnospermae are the flowering plants that have 'naked seeds', i.e. the pines, cycads and Gingkgo. There are remarkably few studies of CGA in the Gymnospermae.

4.3.1. ORDER GINKGOALES

4.3.1.1. Ginkgoaceae family

Gingkgo biloba: *Ginkgo biloba* is the only surviving species and often referred to as a '*living fossil*'. Marques and Farah using LC–MS reported 5-CQA and traces of diCQA.*(35)* Szwajgier *et al*. reported 5-CQA.*(36)*

4.3.2. ORDER PINALES

4.3.2.1. Cuppresaceae family

Lesjak *et al.*report 5-CQA 209 mg/kg and 8 mg/kg dry basis in the leaves and cones, respectively, of *Juniperus foetidissima*.*(37)* (–)-Shikimic acid and the uncommon 3-*epi*-(–)-shikimic acid have been reported in *Sequoiadendron giganteum*.*(38)*

4.3.2.2. Pinaceae family

'*Chlorogenic acid*' has been reported in the needles of shade grown *Larix gmellini*,*(39)* and *Pseudotsuga menziesii*.*(40)* A caffeoylquinic acid, probably 5-CQA, has been reported in the juvenile needles of *Picea abies*,*(41)* and three uncharacterised CQA have been found in *Pinus pinaster*.*(42)* The novel 3-*p*-coumaroyl-(2-hydroxy-quinic) acid has been isolated from the needles of *Cedrus deodar* and characterised by NMR.*(43)*

4.3.2.3. Taxaceae family

Taxus baccata needles contain 2-O-(*p*-coumaroyl)-myo-inositol.*(44)* According to the English abstract *T. cuspidata* contains 1-*O*-methyl-2-O-(p-coumaroyl)-myo-inositol.*(45)*

4.4. ANGIOSPERMAE

4.4.1. ORDER AUSTROBAILEYALES

4.4.1.1. Schisandraceae family

Schisandra species: Mocan *et al*. reported 3-CQA, 4-CQA and 5-CQA (dominant), plus 3-*p*CoQA, 4-*p*CoQA and 5-*p*CoQA in the leaves and stems of *Schisandra chinensis* (Turcz.) Baill. *Cis-5*-p*CoQA* and 3-FQA were found only in the leaves and CGA could not be found in the fruit.*(46)*

4.4.2. ORDER MAGNOLIALES

4.4.2.1. Annonaceae family

The Annonaceae is a family of more than 130 genera and almost 2,500 species, including custard apples and cherimoyas.

Asimina species: Jimenez *et al.*using LC–MS^3 reported 5-CQA **35**, a diCQA and a component with M_r = 530 identified as 4F-5CQA in soursop (*Annona muricata*),*(47)* but the fragmentation of this supposed CFQA yielded *m/z* 161 at MS^3 suggesting that it should be assigned as a methyl diCQ. Three components with M_r = 368 which yielded *m/*z 179 at MS^2 are possibly methyl CQ isomers. These methyl esters might be artefacts associated with an extraction for two hours in methanol–0.1% HCl. Marques and Farah using a methanolic extract without added hydrochloric acid and LC–MS reported 3-CQA, 4-CQA and 5-CQA in *A. muricata*.*(35)*

Brannan *et al.* analysed the pulp of ten varieties of pawpaw (*A. triloba* [L.] Dunal) using LC–ion trap-MS and reported 5-*p*CoQA as the only CGA detectable. This was quantified in the range 13–592 mg/kg using *p*-coumaric acid as calibrant.*(48)* These data are presumably for fresh weight but, this is not explicitly stated.

Haribal *et al*. reported the novel 3-caffeoyl-*muco*-quinic acid as the dominant CGA in the leaves of the custard apple *Asimina triloba*, with 5-CQA not detected.*(49-51)* 3-CmucoQA was reported also in *A. parviflora* and *A. speciosa*.*(51)*. However, as discussed in Part 2 of these notes the NMR data used to assign the structure of the acyl-*muco*-quinic acid are incompletely resolved, and this constraint in association with the claim that 3-CmucoQA could be produced from 5-CQA by acyl migration in dilute base suggest that this assignment is not reliable.

4.4.3. ORDER LAURALES

4.4.3.1. Gomortegaceae family

Gomotega keule, the only species in this family, is an endangered Chilean tree that produces an edible fruit. Simirgiotis *et al*. using LC–TOF-MS reported 5-CQA, which was confirmed by spiking with a commercial standard, and a putative CoCQA,*(52)* this latter a doubtful assignment because of the reported λ_{max} at 343 nm.

4.4.3.2. Lauraceae family

The Lauraceae, commonly known as laurels, includes some 50 genera and some 3000 species. Most are aromatic evergreen trees and shrubs.

Cinnamomum species: 5-CQA (*ca* 0.12 mg/kg) and an uncharacterised diCQA have been reported in the bark of *Cinnamomum zeylanicum*.*(53)*

Laurus species: 5-CQA (*ca* 0.12 mg/kg) and an uncharacterised diCQA have been reported in the bark of *Laurus nobilis*.*(53)*

Machilus species: *Machilu zuihoensis* contains ethyl-5-CQ and methyl-5-CQ,*(54)* described with non-IUPAC numbering in the original paper.

Sassafras species: Carter *et al*. reported that the oviposition stimulant of the Spicebug Swallowtail butterfly, *Papilio troilus*, produced by *Sassafras albidum* is 3-CmQA.*(55)* This component was identical to that isolated from *Asimina triloba* by Haribal and Feeny and apparently could be produced from 5-CQA by isomerisation in base.*(50)* This latter factor places some doubt on the structural assignment, as discussed previously.

4.4.3.3. Monimiaceae family

Peumus boldus: Marques and Farah using LC–MS reported 5-CQA in *Peumus boldus*,*(35)* the only species in the genus.

4.4.4. ORDER PIPERALES

4.4.4.1. Piperaceae family

Piper species: Raniilla *et al*. reported 5-CQA in *Piper angustifolium* R.*(56)* Kamto *et al*. have isolated from *Piper guineense* Schum and Thonn, and characterised by NMR, a novel cyclitol derivative described as 4-O-caffeoyl-2-C-methoxycarbonyl-1-F-methyl-2,3,6-trihydroxycyclohexane carboxylic acid which is effectively a 2-hydroxy-4-deoxy-quinic acid with an additional carboxyl and methyl at C6. This was accompanied by 5-FQA and 5-CQA, presented with non-IUPAC numbering, plus components described as '3-*O*-caffeoyl-1-methylquinic acid' and 'ethyl-4-O-feruloylquinate' assigned by comparing experimental NMR with previously published data.*(57)* However, the structures presented for these two compounds are methyl 5-CQ and ethyl 4-feruloyl-*scyllo*-quinate, and these assignments must be viewed as tentative.

4.4.4.2. Saururaceae family

The Saururaceae comprise four genera and seven species. *Houttuynia cordata* Thunb. utilised in traditional Chinese medicine contains 3-CQA **33**, 4-CQA **39** and 5-CQA **35**, 4-pCoQA **56** and 3-FQA **68**. Unusually, 5-CQA **35** is present at a lower concentration than 3-CQA and 4-CQA.*(58)*

SUMMARY FOR CGA IN MAGNOLIIDS

According to APG IV the Magnoliids comprise the Magnoliales and Laurales, plus the Piperales and the Canellales,*(9)* for the last of which there are no reports regarding CGA. Collectively, the remaining orders in this grouping clearly contain the CQA, FQA and *p*CoQA with evidence for an unusual, currently unique, cyclohexane carboxylic acid derivative in the Piperaceae.

4.4.5. Order Chloranthales

4.4.5.1. Chloranthaceae family

The Chloranthaceae contains four genera but is of somewhat uncertain taxonomy. Wu *et al.* reported that *Sarcandra glabra* contains 5-CSA.*(59)* In contrast, Zhou *et al*. using LC–MS^2 and LC–TOF-MS, reported 3-CQA, 4-CQA and 5-CQA.*(60)* Petersen *et al*. reported 5-CQA in *Chloranthus officinalis* and *C. spicata*.*(20)*

4.4.6. Order Arecales

4.4.6.1. Arecaceae family

Arecaceae have previously been referred to as Palmae or Palmaceae, i.e. the palms, and include some 200 genera and 2,600 species.

Euterpe species: Garzon *et al*. using LC–MS^2 reported 5-CQA, two CSA and a novel hydroxyferuloylquinic acid in the fruit of *Euterpe oleracea* Mart.*(61)* The MS^2 fragmentation of the putative hydroxyferuloylquinic acid (*m/z* 385→*m/z* 191) is consistent with the extra hydroxyl being on the cinnamoyl moiety rather than on the quinic acid moiety, but the molecular mass (M_r = 386) corresponds to hydroxy-dihydroferuloylquinic acid and this assignment must be viewed as tentative. Brunschwig *et al*. using LC–MS reported 3-CQA, 4-CQA and 5-CQA (dominant) in the roots and leaves of *E. oleracea*, and 3-CSA, 4-CSA and 5-CSA only in the roots, but at an appreciably greater concentration than the quinic acid conjugates.*(62)*

Oenocarpus species: Leba *et al*. analysed the roots and leaflets of *Oenocarpus bacaba* and *O. bataua* and reported 3-CQA, 4-CQA and 5-CQA (dominant) in all samples plus 4-CSA, 5-CSA and a third CSA only in the roots.*(63)*

Phoenix dactylifera: It was from *Phoenix dactylifera*, a member of this family, that 5-CSA was first isolated and given the trivial name dactylifric acid.*(64, 65)* More recently three CSA isomers have been reported in the roots of *P. dactylifera* seedlings,*(66)* leaves,*(67)* and fruit, accompanied in the latter case by two caffeoylshikimic hexosides in the fruit.*(68)* Mansouri *et al* examined seven varieties of Algerian dates using positive ion LC–MS and reported three CSA in six varieties but absent from the variety Tazizaout. The varieties Tazerzait and Deglet-Nour apparently contained a *p*CoQA,*(69)* but the reported λ_{max} at 293 nm is not typical of such acyl quinic acids. Dhaouadi *et al*. similarly using positive ion LC–MS reported a caffeoylsinapoylquinic acid, a dicaffeoylquinic acid and 5-CSA in the syrup prepared from Tunisian dates (Rub El Tamer),*(70)* but again, the λ_{max} values are atypical and these assignments should be treated as tentative. A metabolomics study of the fruit from 21 varieities of Egyptian date palm using LC–QTOF-MS reported one diCQA, one diCSA and one CSA (dominant) plus an acetylated dicaffeoylshikimic acid in the fruit.*(71)* A similar study of 18 Saudi date palm cultivars reported a dominant CSA and a diCSA glycoside in the peel.*(72)*

Cocos nucifera: 'Chlorogenic acid' has been reported in the endocarp and mesocarp of *Cocos nucifera*.*(73-75)* Chakraborty *et al*. using LC–MS reported 5-CQA, a dicaffeoylquinic acid and three caffeoylshikimic acids in *C. nucifera* mesocarp.*(76)*

Other species: The only other recent reports are of 3-CSA and 5-CSA in the fruits of *Livistona chinensis*,*(77)* and 5-CQA **35** in *Salacca edulis*.*(78)*

4.4.7. ORDER POALES

The Poales include the grasses (Poaceae), sedges (Cyperaceae), rushes (Juncaceae) and the pineapple (Bromeliaceae).

4.4.7.1. Bromeliaceae family

Steingass *et al*. using LC–ion trap-MS^3 analysed commercial pineapples (*Ananas comosus* (L.) Merr. and reported 5-CQA which was confirmed by the use of a commercial standard. They also reported two isobaric compounds that by their fragmentation were tentatively identified as caffeic acid derivatives of isocitric acid. Two putative *p*-coumaric acid and one putative ferulic acid derivatives of isocitric acid also were detected.*(79)* Because stereoisomers would not be resolved on a reversed phase column packing, presumably these are geometric isomers.

Ma *et al* reported 5-CQA aand two *p*CoQA with identification based on LC–MS^2, plus several cinnamoyl-glycerols including a 5-hydroxycaffeic acid (3,4,5-trihydroxycinnamic acid) derivative. There was no mention of acyl-isocitric acid derivatives,*(80)* but both putative *p*CoQA yielded and MS^2 fragment ion at *m/z* 111 which is characteristic of acyl-isocitric acids rather than acyl-quinic acids.*(79)*

Such isocitric acid derivatives have previously been reported in *Amaranthus* cruentus (Amaranthaceae, Caryophyllales).*(81)* The assignment of the isocitric acid conjugates was by comparison of their MS^3 fragmentation with the MS^2 fragmentation of isocitric acid, which is distinct from that of citric acid and (–)-quinic acid, by virtue of a prominent ion at *m/z* 155.*(79)* This fragmentation is also different from that reported by Deshpande for *epi*-quinic acid, *muco*-quinic acid, *scyllo*-quinic acid and *cis*-quinic acid.*(82)*

4.4.7.2. Juncaceae family

Juncus species: Kim has reported methyl-3,4-diCQ, methyl-3,5-diCQ and methyl-4,5-diCQ in *Juncus diastrophanthus* following isolation and characterisation by NMR,*(83)* but did not use IUPAC numbering. Petersen *et al*. reported 5-CQA in *J. subnodulosus* but not in *J. effusus*.*(20)*

4.4.7.3. Poaceae (Gramineae) family

Brachiaria *species:* *Brachiaria ruziziensi* accumulates up to *ca* 30 g/kg dry basis of 1,3-diFQA **314** and a structurally related *p*Co-FQA, probably 1F-3*p*CoQA, in roots. Lesser concentrations were found in *B. procumbens*. *(84)* Perez *et al*. reported 3-CQA and 4-CQA in *B decumbens* and *B. brizantha*.*(85)*

Cymbopogon species: Ruiz *et al.* reported that European *Cymbopogon citratus* contained *ca* 100 mg/kg dry basis 5-CQA.*(86)* In contrast, Marques and Farah reported 3-CQA, 4-CQA and 5-CQA (449 mg/kg), 3-FQA, 4-FQA, 5-FQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA,*(35)* but the calibrants were not clearly stated.

Dactylis species: Orchard grass, *Dactylis glomerata*, contains 3-CQA, 4-CQA and 5-CQA (*cis* and *trans*).*(87)*

Echinochloa species: Barnyard Millet, *Echinochloa frumentacea* link, contained 3-CQA and 4-CQA but 5-CQA could not be detected.*(88)*.

Fargesia species: A possible FQA and 3-CQA have been reported in *Fargesia robusta*.*(89)*

Hordeum species: Piasecka *et al.* using LC–ion trap-MS have reported 3-CQA, 4-CQA, 5-CQA, 3-*p*CoQA, 3-FQA, 4-FQA and 3,4-diCQA plus a CQA glycoside and an FQA glycoside in the leaves of spring barley (*Hordeum vulgare* L.) with considerable variation of the profile with origin.*(90)* However, some of the fragments reported at MS^2 are unexpected, in particular *m/z* 355 for the FQA glycoside, *m/z* 277 and 163 for 5-CQA, and some UV spectral data were also atypical. Accordingly these assignments should be treated as tentative.

Indocalamus species: An undefined chlorogenic acid has been reported in the leaf of *Indocalamus latifolius* (Keng) McClure.*(91)*

Lolium species: Qawasmeh *et al.* reported 3-CQA, 4-CQA and 5-CQA in *Lolium perenne*.*(92)* 5-CQA was the dominant isomer in *L. arundinaceum* but not in *L. multiflorum*.

Lophatherum species: Tang *et al*. have reported 3-*p*CoQA and 4-*p*CoQA in *Lophatherum gracile* Brongn,*(93)* but did not use IUPAC numbering in the original paper.

Miscanthus species: The leaves and stems of the hybrid *Miscanthus x giganteus* contain *cis* and *trans* 3-CQA, 4-CQA and 5-CQA but in this grass they are accompanied by 3-*p*CoQA, *cis* and *trans* 4-*p*CoQA and 5-*p*CoQA, *cis* and *trans* 3-FQA, 4-FQA and 5-FQA, *cis* and *trans* 3-CSA, 4-CSA, plus 3,4-diCQA, 3,5-diCQA and 4,5-diCQA. 5-CQA dominated in the leaf, but the dominant product in the stem was a novel mandelonitrile-CQA conjugate. A novel *p*-hydroxy-phenylacetamide-CQA conjugate and CQA glycosides were also present.*(94, 95)*

Oryza species: Rice (*Oryza sativa*) contained 3-CQA but 5-CQA was not detected.*(96)*

Paspaulum species: Pinto *et al*. reported *trans*-3-CQA, *trans*-4-CQA and *trans*-5-CQA, plus *cis*- and *trans*-3-*p*CoQA in the mature leaves of *Paspalum atratum*.*(97)*

Phyllostachys species: *Phyllostachys edulis*, or moso bamboo, is a temperate species of giant timber bamboo from the leaves of which Kweon *et al*. reported 5-FQA and two unusual CQA derivatives, 4-methoxy-5CQA and 1-methoxy-5CQA.*(26)* Following the synthesis of authentic 1-methoxy-5CQA by Zeller *et al*.*(25)* it has become clear that the assignment by Kweon *et al*.*(26)* was incorrect (methoxyl δ_H = 3.70 ppm compared with 3.31 ppm in the authentic 1-methoxy-5CQA and 3.69 in methyl 5-CQ). That component of *Phyllostachys edulis* is probably methyl 5-CQ,*(25)* or possibly an FQA for which the aromatic methoxyl δ_H = 3.69.*(98)* Indeed, it is possible that the three components reported by Kweon *et al. (26)* are either all methyl CQs or all FQAs.

Yushania species: A possible FQA has been reported in *Yushania chungii*.*(89)*

4.4.8. ORDER ZINGIBERALES

Petersen *et al*. reported 5-CQA could not be found in the Costaceae, Heliconiaceae, Lowiaceae, Musaceae or Strelitziaceae that they surveyed.*(20)*

4.4.8.1. Cannaceae family

Petersen *et al*. reported 5-CQA in *Canna edulis* and *C. indica*.*(20)*

4.4.8.2. Marantaceae family

Petersen *et al*. reported 5-CQA in *Maranta depressa* and *M. leuconeura*, but absent from the *Ataenidia* spp., *Calathea* spp., *Ctenantae* spp., *Marantochloa* spp. *Megaphrynium* spp., *Pleiostachya* spp. *and Thalia* spp. that they surveyed.*(20, 99)*

4.4.8.3. Zingiberaceae family

The Zingiberaceae are commonly known as the ginger family, characterised by aromatic horizontally creeping tuberous rhizomes. Petersen *et al*. reported 5-CQA could not be found in *Curcuma longa*, *Globba marantina or Zingiber officinale*.*(20)*

Elettera species: 4,5-DiCQA has been reported in *Elettera cardamomum*.*(100)*

Etlingera species: Chan *et al*. using NMR identified 3-CQA, 5-CQA and methyl 5-CQ in the leaves of *Etlingera elatior*, *E. fulgens*, *E. ribrostriata*, *E. littoralis* and *E. maingayi*.*(101, 102)*

SUMMARY FOR CGA IN COMMELINIDS

According to APG IV the Commelinids comprise Arecales, Poales, Commelinales and Zingiberales.*(9)* There are no data regarding CGA in the Commelinales.

The Arecales clearly contain the CQA accompanied by CSA (dactyliferic acids) which sometimes dominate.

The Poales generally contain CQA (but 5-CQA sometimes not found), FQA and *p*CoQA, with diCQA and methyl CQ sometimes reported, and the uncommon 1,3-diFQA in *Brachiaria*. Novel mandelonitrile-CQA and *p*-hydroxy-phenylacetamide-CQA conjugates, and CSA, have been reported in *Miscanthus*.

The Zingiberales includes some species in which 5-CQA is present, and others in which it was sought but could not be found. There are some reports of methyl CQ.

4.4.9. ORDER ASPARAGALES

4.4.9.1. Asparagaceae family

Knittel *et al*. using LC–ion trap-MS have reported 3-CQA and 5-CQA in the leaves and inflorescences of sea squill, *Drimia maritime* L. Stearn but they were not present in the bulb. What appear to be 4-CQA, *cis* and *trans* 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, 3-FQA and 4-FQA were tentatively identified.*(103)*

4.4.9.2. Asphodelaceae family

Asphodelus species: Di Petrillo *et al*. using LC–quadrupole-MS^2 reported 3-CQA and 5-CQA in *Asphodelus microcarpus*.*(104)* Note that some authorities place *Asphodelus* in the Liliaceae.

4.4.9.3. Orchidaceae family

Acccording to the abstract γ-quinide has been reported in the orchid *Dendrobium nobil* Lidl.*(105)*

4.4.9.4. Xanthorrhoeaceae family

The Xanthorrhoeaceae is a family of uncertain taxonomy in which *Hemerocallis* or Day Lily is now placed: formerly it was part of the Liliaceae, which includes true lilies. Clifford *et al*. using LC–ion trap-MS reported 3-CQA, 4-CQA, 5-CQA, 3FQA, 4-FQA, 3-*p*CoQA, 4-*p*CoQA and 5-*p*CoQA in *Hemerocallis*. Di-acyl-quinic acids were not detected. The 4-acyl-quinic acids dominated each subgroup, with the 5-acyl regio-isomer being the minor member of each group.*(106)* Lin *et al.* additionally reported *n*-butyl 4-CQ and methyl 5-CQ in the flowers of *H. fulva.(107)*

Aloe vera (L.) Burm. f. (*Aloe barbadensis* Mill.) can be placed in the Asphodeloideae, a subfamilly of the Xanthorrhoeaceae, but some authorities assign it to a separate family, Asphodelaceae. Analysis of a flower extract by LC–ion trap-MS^2 detected *cis* and *trans* 5-*p*CoQA, 5-CQA, 5-FQA and an uncharacterised CSA.*(108)* These flowers have been used as a herbal tea and in cosmetics, but these preparations are not the same as the emetic preparation obtained from the leaves.

A survey by El Sayed *et al*. using LC–ion trap-MS of the leaves of eight species of Aloe reported 5-CQA, 3,4-diCQA, malonoyl-3,4-diCQA, 3C,4FQA, 3C,5*p*CoQA, 4-succinoyl-3,4-diCQA, 3,4-di-*p*CoQA, malonoyl-4,5-diCQA plus an acetyl-diCQA, CQA glycoside and several trihydroxycinnamoyl derivatives.*(109)* However, it must be noted that the retention times and reported MS^2 fragments reported are not typical of acylquinic acids and these assignments must be viewed as unconvincing.

4.4.10. ORDER LILIALES

Note that at one time the Xanthoraceae and Asphodelaceae were placed in the Liliales but have been dealt with under the Asparagales.

4.4.10.1. Liliaceae family

Asparagus species: Lin and Harnly using LC–MS reported that the 3-*p*CoQA, 3-CQA and 3-FQA dominate their respective subgroups in *Asparagus officinalis* L.*(110)* Jimenez-Sanchez *et al*. using LC–TOF-MS^2 reported six CGA in *A. officinalis*.*(111)* They describe 3-CQA as chlorogenic acid and 5-CQA as neochlorogenic acid, i.e. using non-IUPAC numbering, but the mass fragmentation associated with the peak designated 5-CQA corresponds to that for 5-CQA IUPAC and it elutes later than the peak designated 3-CQA, the fragmentation of which is very similar to that reported for 3-CQA IUPAC. Accordingly these assignments have to be treated as tentative. The other four CGA are described as 3-*p*CoQA, 3-FQA plus two with identical fragmentation both described as 4-FQA, all of which are plausible based on the reported fragmentation.

4.4.10.2. Smilacaceae family

Smilax species: Ivanova *et al*. and Khaligh *et al.* isolated 5-CSA from the air dried rhizomes of *Smilax excelsa*,*(112, 113)* and Zheng *et al.* and Zhang *et al.* using LC–MS^2 and NMR reported 5-CSA in the rhizomes of *S. chinense* and *S. glabra*.*(114-117)* Gu *et al*. using LC–MS^2 reported in Smilacis Galbrae Rhizoma 3-CSA, 5-CSA and a third incompletely characterised CSA and four novel caffeoyl-formyl-shikimic acids thought to include 3-caffeoyl, 4-formylshikimic acid or 3-caffeoyl, 5-formylshikimic acid and 5-caffeoyl, 3-formyl shikimic acid and 5-caffeoyl, 4-formylshikimic acid and possibly including a *cis* isomer.*(118)*

4.4.11. ORDER DIOSCOREALES

4.4.11.1 Dioscoreaceae family

Tacca species: Acccording to the abstract *Tacca integrifolia* contains 3-CQA,*(119)* but it is not known which numbering system was used.

4.4.12. ORDER PANDANALES

4.4.12.1. Pandanaceae family

Pandanus species: The fruits of *Pandanus tectorius* have been analysed using UHPLC–QTOF-MS and reported to contain all four CQA, all six diCQA, 1,3-diCepiQA, 3,5-diCepiQA, methyl 1,3-diCQ, methyl 3,4-diCQ and 3,4,5-triCQA.

The authors state '*The 1, 4-di-O-caffeoylquinic acid, the 3, 4-di-O-caffeoylquinic acid, and the 3, 5-di-O-caffeoylquinic acid were designated as the major components of the PTF-b (Figure 1)*', *(120)* but an examination of Figure 1 clearly shows the major peaks at 325 nm as 4-CQA and 3,4-diCQA.

The authors state that these components were identified by their LC–MS behaviour and comparison with commercial standards and literature data,*(120, 121)* but the sources of the standards are not stated. The CQA elute in the sequence 1-CQA, 3-CQA, 4-CQA and 5-CQA as seen on many reversed phase column packings. The diCQA elute as follows: the putative 1,3-diCepiQA, 3,4-diCQA, 3,5-diCepiQA and 1,3-diCQA. On a reversed phase packing, 1,3-diCQA is usually the first diCQA to elute.*(122)* The behaviour reported here is unexpected, and the identification of the diCQA at regio-isomer level must be viewed as tentative.

In contrast to the foregoing, Liu *et al*. reported 3-CQA (described as chlorogenic acid thus implying non-IUPAC numbering), 4-CQA, 5-CQA, 1,3-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3,4,5-tri-CQA, methyl 3,5-diCQ and methyl 3,4-diCQ, all characterised by NMR after isolation.*(123)* An examination of the NMR data for 1,3-diCQA (H5 *J* = 10.8, 9.6, 3.2 Hz) suggests that this compound has been reported using IUPAC numbering whereas methyl 3,4-diCQ is possibly methyl 4,5-diCQ (H3 *J* = 12.0, 7.2 Hz; H5 *J* = 6.4, 3.2 Hz).

4.4.12.2. Stemonaceae family

The Stemonaceae are of mainly south-east Asian origin. There are four genera and some 30 species.

Stemona species: Ge *et al*. characterised 3-FQA, 4-FQA, methyl 3-FQ, methyl 4-FQ, ethyl 3-FQ, ethyl 4-FQ and methyl 5-CQ by NMR and MS in extracts from *Stemona japonica*.*(124)* LC–ion trap-MS^n of Stemonae Radix, the dried root of *S. japonica, S. tuberosa* and *S. sessiliflora* identified 3-CQA, 4-CQA, 5-CQA, 3-*p*CoQA, 5-*p*CoQA, 3-FQA, 4-FQA and 5-FQA with the *p*CoQA only in *S. tuberosa* which lacked the FQA. *S. parviflora* contained only a small amount of 3-FQA.*(125)*

4.4.12.3. Velloziaceae family

Nanuza species: *Nanuza plicata*, a Brazilian endemic, has been reported to contain methyl-5-CQ and 3,5-diCQA.*(126)*

Barbacenia species: Sugiyama *et al*. reported 3-CQA, 4-CQA and 5-CQA in the Brazilian Resurrection Plant, *Barbacenia purpurea* Hook.*(127)*

4.4.13. ORDER ALISMATALES

4.4.13.1. Araceae family

The Araceae include over 100 genera and some 3,700 species, of mainly tropical habitat, but with some found in northern temperate regions.

Alocasia species: Champagne *et al*. using HPLC with standards but without MS reported 3,5-diCQA in the tuber of *Alocasia esculenta*, but 5-CQA was not found.*(128)*

Arum species: Petersen *et al*. reported 5-CQA could not be found in *Arum italicum*.*(20)*

Colocasia species: Ferreres *et al.* using LC–ion trap-MS and a 5-CQA calibrant quantified two dhCQAs (421 and 310 mg/kg dry basis) in the leaves of the red variety of taro, *Colocasia esculenta*, but not in the giant white variety. Both dhCQA produced an MS^2 base peak at *m/z* 191.*(129)* Champagne *et al*. using HPLC with standards but without MS reported 3,5-diCQA in *C. esculenta*. However, 5-CQA was not found in the tuber.*(128)*

Juncaginaceae species: Petersen *et al*. reported 5-CQA could not be found in *Triglochin striatum*.*(20)*

SUMMARY FOR CGA IN REMAINING MONOCOTS

According to APG IV the remaining Monocots comprise Asparagales, Liliales, Dioscoreales, Pandanales and Alismatales, plus Petrosaviales and Acorales.*(9)* There are no records for CGA in the Petrosaviales and Acorales.

Asparagales collectively have CQA, FQA and *p*CoQA.

Liliales: CQA, FQA and *p*CoQA occur in the Liliaceae with 3-acyl dominant, but only CSA and formyl-CSA have ben reported in the in Smilacaceae. Very limited data.

Dioscoreales have only one report of an incompletely characterised CQA.

Pandanales have CQA and diCQA, possibly including 1-acyl quinic acids, plus triCQA, methyl diCQ and ethyl diCQ.

Alismatales: 5-CQA not found in *Arum, Alocasia, Colocasia* and *Triglochin*, but diCQA in *Alocasia* and *Colocasia* plus the rarer dhCQA at least in *Colocasia*.

SUMMARY FOR CGA IN MONOCOTS

According to APG IV the Monocots embrace 11 orders, four of which are split off into the Commeliniids.*(9)* Of these 11, data are available for eight.

CQA are quite widely, but not universally distributed. There are fewer reports of *p*CoQA, FQA and diCQA. CSA can occur, as can the rare 1,3-diFQA, and a dihydrocinnamoylquinic acid, all of which have possibly been overlooked. More LC–MS profiling required.

4.4.14. ORDER RANUNCULALES

4.4.14.1. Berberidaceae family

The Berberidaceae are 15 genera of trees, shrubs and herbaceous species, commonly referred to as Barbary, and in which Berberis is perhaps the best known.

Berberis species: Ruiz *et al.,* have analysed the ripe berries of Calafate, *Berberis microphylla* G. Forst, and have reported *cis* and *trans* 4-CQA and 5-CQA, 3,5-diCQA, 4,5-diCQA, two further CQA, one further diCQA, a *p*CoQA, two FQA, and a putative CFQA which from its fragmentation appears more likely to be methyl caffeoylquinate and methyl dicaffeoylquinate. There are also several caffeoyl and dicaffeoyl-glucaric acids.*(130)*

Epimedium species: According to the abstract 3-*p*CoQA has been isolated from *Epimedium diphyllum*,*(131)* but it is not known which numbering system has been used.

Mahonia species: *Mahonia repens* contains 5-CQA,*(132)* but note that the authors do not use the IUPAC numbering.

4.4.14.2. Lardizabalaceae family

The Lardizabalaceae family consists of only five genera, mostly lianas. Jin *et al*. have isolated 5-CQA and methyl 5CQ from the stem of *Akebia quinata,(133, 134)* but note that the authors do not use the IUPAC numbering. According to the English abstract Wang *et al*. located methyl-3-CQ, methyl-4-CQ, methyl-5-CQ, methyl-3,4-diCQ, methyl-3,5-diCQ and methyl-4,5-diCQ in the stems of *A. trifoliata*.*(135)*

4.4.14.3. Papaveraceae family

The Papaveraceae family, commonly referred to as Poppies, includes some 40 genera and over 700 species. Pauli *et al*. *(136)* used *Macleaya microcarpa* as a convenient source of 3-FQA as originally reported in Bögge's thesis.*(137)* Unfortunately, it has not been possible to access this thesis which may provide more information on the CGA of this otherwise unstudied family, but according to the English abstract Liu *et al.* reported 3-FQA and methyl 3-FQ in this species,*(138)* but is not known whether or not they used IUPAC numbering.

4.4.14.4. Ranunculaceae family

The Ranunculaceae, buttercup or crowfoot family, includes 60 genera and some 1,700 species.

Aconitum species: The roots of *Aconitum koreanum* contain 3,5-diCQA, 4,5-diCQA, methyl 3,5-diCQ and 3,4,5-triCQA, all characterised by NMR.*(139, 140)*

Coptis species: Rhizoma coptidis is a traditional Chinese preparation derived from the rhizomes of the Goldthreads, *Coptis chinensis* Franch, *C. deltoidea* C. Y. Cheng et Hsiao, and *C. teeta* Wall. '*Chlorogenic acid*' detected by ^{1}H-NMR profiling (δ = 2.04 ppm) was one of the components that contributed to the differentiation of the three species. According to the abstracts methyl-4-FQ and methyl 5-FQ have been isolated from the root of *Coptis japonica* var. *dissecta*,*(141)* and methyl-5-FQ and ethyl-5-FQ have been reported in *C. chinensis*,*(142)* but it is not known which numbering system has been used.

Hydrastis species: McNamara *et al*. reported a 4-CQA, 5-CQA, 5-FQA glycoside, *n*-butyl 4-FQ and *n*-butyl 5-FQ from the roots and rhizome of goldenseal (*Hydrastis canadensis*), a medicinal plant.*(143)* These butyl esters were first reported by Gentry *et al*. using *n*-butanol/HCl in the extraction procedure and might be artefacts.*(144)*

Nigella species: *Nigella sativa* callus contains 3-CQA, 5-CQA, 5-FQA, a second incompletely characterised FQA and a *p*CoQA identified using LC–QTOF-MS.*(145)*

SUMMARY FOR RANUNCULALES

CQA, *p*CoQA and diCQA all occur, often accompanied by methyl CQ and methyl diCQ or butyl diCQ. Sometimes FQA and triCQA have been reported.

4.4.15. ORDER GUNNERALES

4.4.15.1. Myrothamnaceae family

The genus *Myrothamnus* contains four species and is currently assigned to the Myrothamnaceae but the Gunnerales has previously been assigned to the Hammamelidales. An investigation of the Resurrection Plant, *Myrothamnus flabellifolius*, established the presence of 3,4,5-triGQA as the sole polyphenol in leaves of plants grown in Namibia, whereas South African plants also contained a broad spectrum of higher mass derivatives containing additional gallic acid or ellagic acid moieties up to and including decaGQA.*(146)*

4.4.15.2. Gunneraceae family

Profiling of an extract of *Gunnera manicata* L. by LC–MS failed to find any CGA.*(147)*

SUMMARY FOR GUNNERALES

The data are too limited to draw any useful conclusions but the Myrothamnaceae are the first genus in which GQA are prominent.

SUMMARY FOR EUDICOTS NOT FABIDS

According to APG IV the Eudicots placed above the Fabids encompass five orders,*(9)* with data available only for Ranunculales and Gunnerales. The data are too limited to draw any useful generalisations, but the Myrothamnaceae (Gunnerales), are the first family in which GQA have been reported.

4.4.16. ORDER FABALES

4.4.16.1. Fabaceae family

The Fabaceae, formerly Leguminosae, commonly known as the pea, bean or legume family, is the third largest family of flowering plants. It is of great commercial importance as food and feed but has been little studied with regard to CGA content.

Adesmia species: 5-CQA **35** has been sought but not found in *Adesmia emarginata* but it was reported to contain a putative trihydroxycinnamoylquinic acid which yielded MS^2 fragments at *m/z* 311, 268, 195 and 191,*(148)* suggesting that the additional hydroxyl is in the cinnamic acid residue.

Arachis species: The wild groundnut, *Arachis paraguariensis* (Chod et Hassl.) contains 3-CQA, 5-CQA and the unusual 1C-4deoQA,*(149, 150)* but a more recent analysis of peanut (*A. hypogea*) skins failed to find any CGA, although several conjugates of tartaric acid were present.*(151)*

Bauhinia species: Liu *et al*. using LC–TOF-MS^3 reported in *Bauhinia blakeana* Dunn a novel compound tentatively identified as a caffeoyl-hydroxyquinic acid which yielded a base peak at *m/z* 369, MS^2 fragments at *m/z* 189 and 207, an MS^3 fragment at *m/z* 127 and an MS^4 fragment at *m/z* 83 which are consistent with this assignment. They also reported 3,5-diCQA and 4,5-diCQA accompanied by four CQA described as 5-CQA, 1-CQA, 3-CQA and 4-CQA in order of elution, these mono-acyl CGA characterised by fragmentation and comparison with commercial standards.*(152)* This sequence of elution is unexpected and re-examination of their supplementary fragmentation data suggests that the supplied standards may have been described using non-IUPAC numbering whereas the authors have used IUPAC numbering. It is uncertain whether or not 1-CQA is present, or whether this has been confused with *cis*-5-CQA.

Hedysarum species: Two incompletely characterised CQA have been reported in the fodder crop *Hedysarum coronarium*.*(153)*

Caesalpinia spp. were once important commercial sources of Tara tannin used in leather manufacture, and in which the dominant tanning agent is a complex mixture of GQA where gallic acid residues are not only attached to the quinic acid moiety, but attached depsidically to the directly attached gallic acids. Early studies established the presence of 4,5-diGQA, 3,4,5-triGQA and 1,3,4,5-tetraGQA.*(154-156)* It was only with the advent of LC–MS^8 that the complexity of this tannin became fully apparent. Controlled methanolysis established that the 'core' units are 5-GQA, 3,5-diGQA, 4,5-diGQA, 3,4,5-triGQA and 1,3,4,5-tetraGQA and that some high mass components contained at least one chain of up to four gallic acid residues. The largest components detected were octa-GQA: penta-GQA to octa-GQA consisted primarily of two subgroups, one based on 3,4,5-triGQA and the other on 1,3,4,5-tetraGQA. The following components were characterised: 1-GQA, 4-(diG)QA, 5-(diG)QA, 3G-5(diG)QA or 3(diG)-5GQA, 4G-5(diG)QA, 5G-4(diG)QA, 3(diG)-4,5diGQA, 4(diG)-3,5diGQA, 5(diG)-3,4diGQA, 1,3,4-triGQA, 1,3,5-triGQA, and 1,4,5-triGQA.*(157)* It was not possible to assign the *para* or *meta* linkage of depsidic galloyl residues in the absence of MS^n fragments at *m/z* 321 [(diG)–H^+].*(157)* In addition to the foregoing Kondo *et al*. reported methyl 3,4,5-triGQ and methyl 3,4-diGQ,*(158)* but note that these authors used the non-IUPAC numbering.

Caragana species: 3-CQA, 5-CQA and 3,5-diCQA have been reported in the shoots of *Caragana arborescens*.*(159)*

Cicer species: 5-CQA in the chickpea *Cicer arietinum*.*(160)*

Copaifera species: LC–MS analysis of extracts of the leaves of *Copaifera langsdorffii* has located 26 GQA, some of which are methylated, including one GQA, three monomethyl GQA, three monomethyl diGQA, five dimethyl diGQA, one dimethyl triGQA and one trimethyl triGQA.*(161)* Noguiera *et al*. reported the novel 3-(3-methlgalloyl)quinic acid in the leaves of *C. langsdorffii* Desf. accompanied by 3,4-di-(3-methylgalloyl)quinic acid, 3,5-digalloyl-4-(3-methylgalloyl)quinic acid and 3,5-di(3-methylgalloyl)-4-galloylquinic acid.*(162)*

Cytisus species: CGA have been sought but not found in *Cytisus multiflorus*.*(163)*

Erythrina species: *Erythrina velutina* contains 3-CQA, 4-CQA and 5-CQA.*(35)*

Onobrychis species: *Onobrychis vicifolia*, a traditional fodder legume plant, contains all four CQA, 3-*p*CoQA, 4-*p*CoQA and 5-*p*CoQA, but apparently only 4-FQA. In many cases both the *cis* and *trans* isomers were reported along with several esters with malic acid. Depending on the organ analysed, leaf, petiole, stem, flower stalk or flower bud, the material analysed contained 0.14–0.97 g/kg of 3-CQA dominant, 0.03–0.66 g/kg of 5-CQA and 0.01–0.04 g/kg of 3-*p*CoQA on a dry basis.*(164)* 5-CQA was used as calibrant.

Pterospartum species: 5-CQA has been sought but not found in *Pterospartum tridentatum*.*(86)*

Tamarindus species: CGA have been sought but not found in *Tamarindus indica*.*(165)*

SUMMARY FOR FABALES

The data currently available for the Fabaceae indicate a clear split between *Caesalpinia* and *Copaifera* with significant GQA contents, reminiscent of the Myrothamnaceae (Gunnerales) and most other families where the hydroxycinnamoylquinic acids are reported. Generally CQA (sometimes 3-CQA dominant), *p*CoQA and diCQA occur, with novel acyl-deoxyquinic acid in at least some *Arachis*, acyl-hydroxy-quinic acid in *Bauhinia* and possibly in *Adesmia* although this latter might be a trihydroxycinnaoylquinic acid.

Currently there are several families (*Adesmia*, Cytisus and *Tamarindus)* where 5-CQA and / or CGA generally have been sought but not found, but these species have not been thoroughly profiled.

4.4.17. ORDER ROSALES

4.4.17.1. Rhamnaceae family

Rhamnaceae are the buckthorn family of some 50 to 60 genera and approaching 800 species. *Ziziphus jujuba* Miller fruits are used in herbal medicines, food and for cooking.

Colubrina species: Ali using LC–MS^2 was unable to detect CGA in an extract of *Colubrina asiatica*.*(166)*

Ziziphus species: The analysis of the fruits of several varieties of *Ziziphus jujuba* has identified 5-CQA **35**,*(167)* and an incompletely characterised CQA has been reported in *Ziziphus mouritiana.(168)* The fruits and leaves of *Ziziphus jujuba* contain 1.1–2.7 mg/kg fresh weight and 7.0–69.0 mg/kg dry weight, respectively, of 5-CQA.*(169)* 5-CQA was used as calibrant.

4.4.17.2. Rosaceae Family

The Rosaceae contains 95 genera and in excess of 2,800 species but much taxonomic work remains to be completed.

4.4.17.2.1. Tribe Amygdaleae

Prunus species: It has long been reported that in the stone fruits (*Prunus* spp.) 3-CQA dominates the CQA subgroup,*(170-172)* but it is now clear that this trait is not shared by all species of *Prunus*.

Takeoka *et al*. reported that 3-CQA dominated in almond (*P. dulcis*) hulls.*(173)* The situation in apricots (*Prunus armeniaca*) is variable. Ruiz *et al*. analysed the peel and flesh of a large number of cultivars: in some cultivars 3-CQA dominated in both peel and flesh, but in some 5-CQA dominated in both tissues, and elsewhere 3-CQA dominated in one tissue but not the other. Overall this study found Apricot peels contained 70–670 mg/kg of 5-CQA and 70–731 mg/kg of 3-CQA while the flesh contained 30–161 mg/kg of 5-CQA and 10–160 mg/kg of 3-CQA on a dry basis with 5-CQA as calibrant.*(174)* Schmitzer *et al*. analysed 13 cultivars of *P. armeniaca* and reported 3-CQA, 4-CQA, 5-CQA (dominant), and 3-*p*CoQA in the peel and pulp.*(175)*

In the flesh and peel of nectarines (smooth skinned *Prunus persica*) and peaches (fluffy skinned *P. persica*) 5-CQA exceeded 3-CQA but the reverse was found in plums (*P. domestica*).*(176, 177) (178)* Analysis by LC–MS^2 of extracts prepared from the insoluble residue remaining after commercial peach juice extraction detected 3-CQA, 4-CQA and 5-CQA (dominant).*(179)*

In the Ecuadoran plum (*P. salicina* Lindl.) Vasco *et al*. reported 3-CQA (76–92 mg/kg fresh weight) and 5-CQA (40 mg/kg fresh weight) *(180)* but they describe 5-CQA (188 mg/kg fresh weight) as dominant in *P. serotina*. 4-CQA was not found

in *P. salicina*, the authors suggesting that in some earlier reports a cinnamic acid-sugar conjugate may have been misidentified as 4-CQA.*(180)*

Tomas-Barberan *et al*. also reported that 4-CQA could not be found in plums (*P. domestica*),*(176)* but an LC–MS^2 analysis of *P. spinosa* fruits by Guimaraes *et al.* detected 3-CQA, 3-*p*CoQA, 3-FQA, 4-CQA and 4-*p*CoQA, but not the related 5-acyl isomers.*(181)*

Jaiswal *et al*. using LC–ion trap-MS analysed fruits of *P. salicina* (Japanese Plum), *P. domestica* (Plum), *P. spinosa* (Blackthorn or Sloe), *P. cerasifera* (Black Cherry) and several hybrids. They reported *cis* and *trans* 3-CQA,4-CQA and 5-CQA, 3-FQA, 4-FQA, 5-FQA, methyl 3CQ, methyl 4CQ, methyl 5CQ, *cis* and *trans* 3-*p*CoQA *cis* and *trans* 4-*p*CoQA, methyl 3*p*CoQ, 3-CSA and the novel 3-(*p*-methoxycinnamoyl)quinic acid. A second CSA was also detected, differing in behavior from those previously encounter in maté, but it was not fully assigned. There were considerable differences in profile, even between closely related material, for example the *p*CoQA and methyl 5-CQ were restricted to *P. salicina*, but note that the flesh and skin were extracted together whereas for the other species only flesh was extracted.*(541)* In contrast to the earlier reports 4-CQA was found in some but not all *P. salicina* and *P. domestica*, and 5-CQA was found in *P. spinosa*. In *P. domestica* flesh the 3-acyl *p*CoQA, CQA and FQA clearly dominate their respective subgroups, but 3-CQA is very low or undetectable in the flesh of *P. cerasifera* and its hybrids.

An LC–MS^2 profiling of pitted prunes, i.e. semi-dried plums (*P. domestica* L.) reported six CQAs, two FQAs, four *p*CoQAs and two novel trihydroxycinnamoylQAs. With the exception of 3-CQA (dominant), 4-CQA and 5-CQA, these were not identified to regio-isomer level, but yielded MS^2 fragments at *m/z* 195, 191, and 151 indicating that the additional hydroxyl is on the cinnamic acid residue, but the position (ring or sidechain) of the third hydroxyl in the trihydroxy-cinnamoylquinic acids was not determined.*(182)* This dominance of 3-CQA was confirmed by Donovan *et al*.*(172)* More recently Nakatani *et al*. found in prunes 1.2–1.5 g/kg of 3-CQA, 0.3–0.4 g/kg of 4-CQA and 53–77 mg/kg of 5-CQA on a fresh weight basis.*(183)* Note that 3-CQA and 4-CQA were prepared from commercial 5-CQA and these were used as calibrants, but the response factors were not reported.

Olszewska *et al*. reported 5-CQA in the leaves and flowers of *P. padus* L (Bird Cherry or Hackberry),*(184)* but did not comment on the other isomers. An LC–MS^2 analysis of the fruits of *P. avium* (Bird cherry or Gean) detected three CQA, three FQA , 3-*p*CoQA, 4-*p*CoQA, *cis* 5-FQA, 3*p*Co-5CQA, 3-CSA, 4-CSA and an uncharacterized diCQA in the cultivar Pu-DM2b *(185)* that yielded an unexpected *m/z* 169. In contrast, the cultivar Pu-DR2b in which 5-CQA and 3-pCoQA dominated, contained 5-*p*CoQA but not 4-*p*CoQA, the CSAs, the diCQA or the *p*Co-CQA. *(185)* Mozetic *et al*. analysed Sweet Cherries from Slovenia, which they described as the fruit of *P. avium*, and reported that 3-*p*CoQA and 3-CQA were the dominant CGA as characterised by LC–MS.*(186-188)* Usenik *et al*. subsequently reported 3-CQA**,** 5-CQA**,** a *p*CoQA and a diCQA, probably 3,5-diCQA, in the fruit of *P. avium*.*(189)*

There have been several investigations of *P. mume,* Japanese Apricot. Using NMR Mitane *et al*. characterized 3-CQA and 5-CQA after isolation from the fruit.*(190)* Similarly Fujimoto *et al*. reported 5-*p*CoQA, 5-CQA, methyl 5-*p*CoQ, methyl 5-FQ, methyl 5-CQ and ethyl 5-CQ plus the novel 4Bz-5CQA (Mumeic acid A) and methyl 4Bz-5CQ from the

flowerbuds,*(191)* and this group later reported ethyl 5-*p*CoQ.*(192)* Zhang *et al*. using LC–QTOF-MS^3 reported 1-CQA, 3-CQA, 4-CQA, 5-CQA and methyl-5-CQ, 3-FQA, 5-FQA and 5-*p*CoQA plus 3-CSA, 4F-5CQA and 4Bz-5CQA (Mumeic acid A) in the edible flowers of *P. mume*.*(193)* On the basis of the retention time it seems likely that the reported 1-CQA is *cis*-5-CQA.

Sorbus species: Olszewska reported that leaf extracts of *Sorbus aria* (L.) Crantz contained 3-CQA and 5-CQA in equal concentration.*(194)* Hukkanen *et al*. reported that the concentration of 5-CQA exceeded that of 3-CQA in orange-fruited rowan berry (*S. aucuparia*) hybrid cultivars (cvs. Kubovaja, Rosina, and Zholtaja) and cvs Dessertnaja and Rubinovaja, but 3-CQA dominated in hybrid cvs Burka, Eliit, Granatnaja and Titan.*(195)* Gaivelyte *et al*. reported 3-CQA (1–11 g/kg and 1–5 g/kg) and 5-CQA (3–22 g/kg and 3–7.8 g/kg) in the leaves and fruits of *Sorbus* spp. from Lithuania. In the fruit of eight species 3-CQA **33** exceeded 5-CQA, in six species 5-CQA dominated, and in the remaining three they were essentially equal in concentration.*(196)* Commercial 3-CQA and 5-CQA were used as calibrants, but the response factors were not reported. Becerra-Herrera *et* al. using positive ion LC–MS reported that 3-CQA exceeded 5-CQA in the fruits of *S. Americana*.*(197)* Although the structures shown follow IUPAC numbering, the chromatograms shown have the putative 5-CQA eluting before the putative 3-CQA strongly suggesting that the assignments have been reversed. Unfortunately, these authors did not use any commercial standards, and because in positive ion mode both compounds showed identical fragmentation, it is not possible to confirm their assignments.

Termentzi *et al*. analysed the fruit of *S. domestica* using LC–MS^2 but chose the positive ion mode, severely limiting the structural assignments that could be made. Four CQA including 5-CQA, two CQA glycosides, three FQA and one *p*CoCQA were reported.*(198)* The late-eluting CQA is plausibly *cis* 5-CQA. However, it has since been reported that the mature fruit of *S. domestica* contain 5-CepiQA, preferentially extracted in *n*-butanol, isolated and characterised by MS and NMR,*(199)* but a critical examination of the NMR data suggests that this may be a mis-assignment of 3-CQA, as fully discussed in Part 2 of these notes concerned with NMR of Chlorogenic Acids.

Cao *et al*. using LC–triple quadrupole-MS and commercial standards analysed the cherries of four *Prunus* species grown in China. Red-fruited *P. tomentosa* contained 3-CQA, 4-CQA and an incompletely characterised *p*CoQA, but 5-CQA was not detected: only the *p*CoQA was found in cherries from a white fruited variety. These three CGA, plus 5-CQA and 3,5-diCQA were found in the cherries of *P. avium* (two varieties), *P. cerasus* (two varieties) and *P. pseudocerasus* (one variety): 3,5-diCQA was absent from a second variety. 3-CQA dominated in *P. avium*, red-fruited *P. tomentosa*, and *P. cerasus* cv Erdi Bottermo, but 5-CQA dominated in *P. cerasus* cv Aode. These two isomers occurred at much the same concentration in both cultivars of *P. pseudocerasus*.*(200)*

4.4.17.2.2. Tribe Maleae

Amelanchier species: Ozga *et al*. quantified 5-CQA (0.44–0.58 g/kg fresh weight) and 3-CQA (0.10–0.11 g/kg fresh weight) in Saskatoon fruits (*Amelanchier alnifolia* Nutt.) and the data are expressed in 5-CQA-equivalents.*(201)*

Aronia species: The dominance of 3-CQA has also been reported in black chokeberries (*Aronia melanocarpa*) which contain 1.2 g/kg of 3-CQA and 0.6 g/kg of 5-CQA,*(202)* and some but not all *Aronia* × *Sorbus* hybrids.*(195)* Lee *et al*. reported two incompletely characterized CQA and a diCQA in *A melanocarpa*.*(203)* McDougall *et al*. reported 3-CQA and 5-CQA in *A melanocarpa*.*(204)* According to the abstract Romani *et al*. have made the first observation of 4-CQA in *A. melanocarpa*.*(205)* Grunovaite *et al*. using commercial standards and LC–HRMS reported 1-CQA, 3-CQA, 4-CQA and 5-CQA in *A. melanocarpa*.*(206)* In contrast to the foregoing Esatbeyoglu *et al*. have also claimed the first report of 4-CQA in the juice and pomace of *A. melanocarpa*, but clearly extending the range reported with the 3-acyl and 5-acyl regio-isomers of *p*CoQA and FQA, plus 3,5-diCQA.*(207)*

Chaenomeles species: Du *et al*. using LC–MS reported 5-CQA (dominant) and a second CQA, probably 3-CQA, were reported in fruit of *Chaenomeles sinensis*, *C. japonica*, *C. thibetica*, *C. speciosa* and *C. cathayensis*.*(208)*

Cotoneaster species: Kicel *et al*. reported 3-CQA, 4-CQA and 5-CQA, 5-*p*CoQA and three incompletely characterised diCQA in the leaves of *Cotoneaster zabelii, C. splendens, C. bullatus, C. divaricatus, C. hjelmqvistii* and *C. lucidus*.*(209)* However, one of the putative diCQA eluted between 3-CQA and 5-CQA and is more likely to be CQA glycoside.

Crategeus species: Barros *et al*. using LC–MS reported 3-CQA (0.18 g/kg), 4-CQA (0.21 g/kg), 5-CQA (2.33 g/kg), 4-*p*CoQA (1.66 g/kg), 5-*p*CoQA (0.61 g/kg) and 3,5-diCQA (0.55 g/kg), plus *cis* 3-CQA (0.02 g/kg), *cis* 4-*p*CoQA (0.22 g/kg), *cis* 5-*p*CoQA (0.39 g/kg) in the flowers of *Cratageus monogyna*, a medicinal plant from Portugal.*(163)* The dominance of 5-CQA **35** but 4-pCoQA in their respective subgroups is noteworthy. The apparently greater content of *cis*-4-CQA than *trans*-4-CQA is unexpected and noteworthy, but might be a typographical error. Commercial 5-CQA was used as calibrant for all CGA thus over-estimating diacyl quinic acid derivatives by *ca* 40%. The fruits of *C. grayana* contain two isomers of CQA, reported as 3-CQA (0.2–0.5 g/kg) and 5-CQA (0.5–1.0 g/kg),*(210)* quantified using commercial 5-CQA **35** as calibrant, but note that these authors used non-IUPAC numbering. Chinese hawthorn (*C. pinnatifida*) fruits used in Chinese herbal medicines contain 0.12–0.54 g/kg dry weight and an extract prepared therefrom 0.8–12.1 g/kg dry weight of a single uncharacterized chlorogenic acid.*(211, 212)*

Cydonia species: Pontes *et al.* reported 5-CQA in the peel, pulp and seeds of *Cydonia oblonga* (1.5 g/kg, 1.7 g/kg and 0.06 g/kg dry matter, respectively) but 4-CQA was not detectable.*(165)* Fiorentino *et al*. reported 3-CQA, 5-CQA, 3-*p*CoQA and 5-*p*CoQA in quince (*C. vulgaris*) peels: the associated 4-isomers were not mentioned.*(213)* In contrast, Silva *et al*. using LC–MS reported 3-CQA, 4-CQA, 5-CQA and 3,5-diCQA but did not detect *p*CoQAs,*(214)* whereas Wojdylo *et al*. analysed quince fruits using LC–MS^2 and reported 3-CQA, 4-CQA, 5-CQA, 4-*p*CoQA and 3,5-diCQA plus a CSA, a second *p*CoQA and a fourth CQA. Quantitative data are reported for 20 varieties that demonstrate 5-CQA is dominant in its sub-group, 1.7–3.2 g/kg dry weight, but unfortunately the equivalent data for the *p*CoQAs are not presented.*(215)* In a subsequent paper from this group, Carbonell-Barrachina *et al*. reported quantitative data for the same CGA in quince liquors. Commercial standards were used as the calibrants for the CQA and diCQA, but caffeic acid for 4-pCoQA.*(216)* The response factors were not reported. Marques and Farah using LC–MS provide quantitative data for the major CGA in *C. oblonga*,*(35)* but the calibrants are not clearly stated.

Branca *et al*. reported 3-CQA, 4-CQA, 5-CQA and 3,5-diCQA in quince seeds and pulp.*(217)* Karer *et al.*using LC–ion trap-MS reported *cis* and *trans* 5-CQA, 3-CSA, 4-*p*CoQA, 5-*p*CoQA, methyl 5-CQ and an incompletely characterised quinic acid derivative M_r = 533 in quince fruit.*(218)*

Eriobotrya species: Analysis of Loquat fruit (*Eriobotrya japonica* (Thunb.) Lindl. revealed 3-CQA, 4-CQA, 5-CQA and 5-FQA.*(219)*

Malus species: In *Malus domestica*, the well-known apple, and the associated alcoholic beverage (UK cider, USA applejack) 5-CQA dominates the CQA subgroup but 4-*p*CoQA dominates the *p*CoQA subgroup,*(220-222)* a phenomenon that has led sometimes to the misidentification of 4-*p*CoQA as 5-*p*CoQA. An analysis of the flowers of *M. sylvestris* reported only an incompletely characterized CQA.*(163)* Sommella *et al*. reported two CQA and two *p*CoQA in *M. pumila* Miller cv *Anurca (223)* but the reported retention times and fragmentations do not entirely support their assignments (3-CQA, 5-CQA, 4-pCoQA and 5-pCoQA) at regio-isomeric level.

Ramirez-Ambrosi *et al*. using LC–QTOF-MS reported two *p*CoQAs and four CQAs in apples, apple pomace and apple juice but, apart from 5-CQA for which a standard was available, these could not be assigned at regio-isomeric level because the fragmentation was identical.*(224)*. An LC–ion trap-MS analysis of apple seeds located 5-CQA, 4-*p*CoQA and 5-*p*CoQA.*(225) (178)* Analysis by LC–MS^2 of extracts prepared from the insoluble residue remaining after commercial juice extraction detected 5-CQA, 5-*p*CoQA and 4-*p*CoQA, this latter exceeding the concentration of 5-*p*CoQA.*(179)*

Pyrus species: Early studies on pears (*Pyrus communis*) established the presence of 5-CQA and 3,5-diCQA.*(226-228)* Lin and Harnly reported 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 1,3,5-triCQA and 3,4,5-triCQA and an incompletely characterised F-diCQA in pear (*Pyrus* spp.) skins. Some *cis* isomers were detected as a consequence of the relatively intense exposure of this tissue to UV light. The profiles of CGAs in pear skins could be used to define the origin of the fruit.*(178)* Analysis by LC–MS^2 of extracts prepared from the insoluble residue remaining after commercial juice extraction detected 3-CQA, 5-CQA and small amounts of 5-*p*CoQA **52** but no 4-*p*CoQA.*(179)* Lee *et al*. reported methyl-3-*p*CoQ, methyl-*cis*-3-*p*CoQ, methyl-3-CQ, 3-*p*CoQA and 3,5-diCQA in the immature fruit of *P. pyriformis* Nakai after isolation and characterisation by NMR,*(229)* but did not use IUPAC numbering.

4.4.17.2.3. Tribe Potentilleae

Alchemilla species: Uncharacterised 'chlorogenic acids' have been found in *Alchemilla vulgaris* and *A. mollis*.*(230)*

Fragaria species: Bagdonaite *et al.*have quantified 'chlorogenic acid' in the leaves and fruits of *Fragaria vesca*¸ *F. viridis* and *F. moschata*, but the constituent CGA were not identified.*(231)*

Potentilla species: Fecka *et al*. reported 3-GQA in the rhizomes of *Potentilla tomentosa*. Commercial tinctures prepared from them also contained 4-GQA and 5-GQA.*(232)*

4.4.17.2.4. Tribe Roseae

Rosa species: Ieri *et al.* using LC–MS reported two incompletely characterised GQA and one diGQA in the leaves and buds of *Rosa canina.(233)*

4.4.17.2.5. Tribe Rubeae

Rubus species: Ruiz *et al.* using LC–MS^2 have analysed the berries of *Rubus geoides* but it is not clear whether or not they are using the IUPAC numbering system. Dall'aqua *et al*. isolated 3-CQA, 4-CQA and 5-CQA from extracts of *R. ulmifolius* and characterised them by MS and NMR.*(234)* They reported one incompletely characterised GQA.*(235)* Martins *et al*. using LC–ion trap-MS analysed a decoction of the flower buds of *R. ulmifolius* and reported 3-*p*CoQA, 3-CQA, 3-FQA and 3,5-diCQA. 3-CQA was the main phenolic acid.*(236)* LC–ion trap-MS analysis of *R. grandifolius* Lowe has identified 3-CQA, 5-CQA, 1-*p*CoQA (tentative), and 1,5-diCQA.*(237)* The relatively late elution of the putative 1-*p*CoQA relative to 5-*p*CoQA, which was not reported in this extract, might suggest that it is *cis* 5-*p*CoQA, but the presence of a *cis* isomer in the absence of the corresponding *trans* isomer is unexpected.

4.4.17.2.6. Tribe Sanguisorbeae

Agrimonia family: Granica *et al.*using LC–MS^3 analysed Agrimonia eupatoriae herba, a pharmaceutical material prepared from *A. eupatoria*, and reported 3-CQA, 4-CQA and 3-*p*CoQA, but 5-CQA, used as calibrant, was not present.*(238)*

4.4.17.3. Moraceae family

The Moraceae encompass some 40 genera and over 1000 species of which the best known are figs (*Ficus* spp) and mulberries (*Morus* spp.).

Ficus species: Figs (*Ficus carica* L.) contain 2.0–5.8 g/kg of 5-CQA in skin, 0.3–1.3 g/kg of 5-CQA in pulp,*(239)* and 5-CQA has been detected in the leaves of *F. carica*.*(240)* and *F. cyathistipula* Warb.*(241)* Russo *et al*. reported an uncharacterised CQA in the peel of Italian figs but could not detect it in the pulp.*(242)* Omar *et al*. reported 4-*p*CoQA from *F. deltoidea*, a Malaysian herbal tea. No other CGA were detected, and the dominance of a 4-acyl quinic acids is noteworthy.*(243)* Farag *et al*. detected three incompletely characterised CQA and one incompletely characterised *p*CoQA in the fruit and leaves of *F. lyrata*.*(244)* An uncharacterised 'chlorogenic acid' has been reported in the roots and stems of *F. benjamina* but was not found in the leaves.*(245)* Jahan *et al*. reported 5-CQA in *F. racemosa* fruits,*(246)* but did not use IUPAC numbering. El-Sakhawy *et al*. reported 3-CQA and a second incompletely characterised isomer in the leaves of *F. cyathistipula* Warb.*(100)*

Morus species: The fruits and leaves of *Morus alba* and *M. nigra* contain 3-CQA and dominant 5-CQA, but with both greatly exceeded by the content of ferulic acid. However, it is unclear from this investigation whether or not FQA might also be present.*(247)* In contrast Zhang *et al*. reported that *Morus alba* L. used in traditional Chinese medicines contained 4-CQA and 5-CQA, totalling 5.2–32 mg/kg, and 2.5–8 mg/kg of 3,5-diCQA but with marked variation between cultivars,*(248)* expressed as 5-CQA equivalents, thus over-estimating 3,5-diCQA by *ca* 40%. Sanchez-Salcedo *et* al. reported 3-CQA, 4-CQA and 5-CQA (dominant) in the leaves of *M. alba* and *M. nigra*, plus a fourth isomer designated 1-CQA,*(249, 250)* but its late elution suggests that it might be *cis*-5-CQA. An early eluting putative diCQA is probably a CQA glycioside. Seo *et al*. reported 3-CQA, 4-CQA and 5-CQA in Mori Cortex Radicis.*(251)*

4.4.17.4. Urticaceae family

The Urticaceae encompass some 50 to 80 genera and some 2,600 species of which the best known are the nettles. There are reports of 5-CQA in *Cecropia glaziovii* Sneth,*(252) Pilea microphylla*,*(253) Pipturus albidus*,*(254) Urtica circularis (255)* and *Urtica urens*.*(256) Urtica dioica* contains 5-CQA, a second uncharacterised CQA and 2-caffeoyl-malic acid.*(257, 258)* Lopes-Lutz *et al*. reported 3-CQA, 5-CQA, 5-FQA and 4,5-diCQA in the pulp and peel of Amazon grape fruit (*Pourouma cecropiifolia* Martius). The pulp and peel contained 0.2 g/kg and 0.7 g/kg of 5-CQA, respectively.*(259)*

SUMMARY FOR ROSALES

Rhamnaceae: Currently insufficient data — one genus with no CGA, and one with CQA

Rosaceae: Amygdaleae contain CGA, predominantly CQA but also *p*CoQA and FQA, some methyl CQ and occassional ethyl CQ, and there are occasional reports of diCQA and *p*CoCQA. There is pronounced variation in which regio-isomer dominates, some 3-acyl, some 5-acyl, and occasionally 4-acyl missing. Also sometimes 5-acyl missing, or 3-acyl very low or missing. Sometimes CSA are present. Some of these inconsistencies might reflect incorrect assignments at regio-isomer level, but it is also distinctly possible that selective breeding of food relevant species has accentuated certain compositional peculiarities. The uncommon Bz-CQA, trihydroxycinnamoylquinic acids and 3-(*p*-methoxycinnamoyl)quinic acid deserve further investigation as they may well have been overlooked.

Maleae: CQA present, some also with *p*CoQA, with 4-*p*CoQA dominant in *Cratageus* as also seen in *Malus*. A few reports of diCQA and occasionally triCQA, at least in pears.

Potentilleae: Few data but interestingly some reports of GQA which certainly don't seem to be universal in Rosales.

Rubeae: Few data, but CQA, *p*CoQA, FQA, diCQA, and again GQA.

Sanguisorbeae: Very few data but 5-CQA absent despite other CQA being observed.

Moraceae. Limited data, with CQA consistently reported but sometimes apparently only 5-CQA. Possible that 4-*p*CoQA dominant in *Ficus*.

Urticaceae: Few data, mainly CQA, but one report of FQA and diCQA.

4.4.18. ORDER FAGALES

4.4.18.1. Betulaceae family

The Betulaceae family includes the alders, birches, hazels and hornbeams. 3-CQA, 5-CQA, 3-*p*CoQA and 5-*p*CoQA have been reported in the leaves of *Betula pubescens*,*(260, 261)* with 3-*p*CoQA and 5-*p*CoQA exceeding the contents of the equivalent CQA by approximately three-fold.*(262)* 5-CSA-4-glucoside has been reported in *Alnus sibrica* Fisch ex Turcz,*(263)* and 5-GSA has been reports in *Alnus japonica*.*(264)*

4.4.18.2. Corylaceae family

The leaves of *Corylus avellana* contain 5-CQA and in some varieties also 3-CQA.*(265)*

4.4.18.3. Fagaceae family

The Fagaceae or beech family comprises some 900 species, many of which are commercially important sources of wood, such as the oaks (*Quercus* spp), chestnuts (*Castanea* spp), and beeches (*Fagus* spp.).

3-CQA **33** and 5-CQA **35** have been reported in the leaves of *Fagus sylvatica*,*(266)* and 5-CQA in the leaves of *Castanea sativa*.*(267)* Nishimura *et al*. reported 3-GQA, 4-GQA, 5-GQA, 3,5-diGQA, 4,5-diGQA and 3,4,5-triGQA from *Quercus stenophylla*,*(268)* which also produces galloyl esters of *proto*-quercitol.*(269, 270)*

An early study of the leaves of *Castanopsis cuspidata* var. *Sieboldii* Nakai led to the isolation and charcaterisation by NMR of the novel galloyl esters of (–)-shikimic acid, as follows: 5-GSA, depsidic 5-(diG)SA, depsidic 5-(triG)SA 3,5-diGSA and 4,5-diGSA.*(271)* A more extensive study of the leaves of the evergreen *Castanopsis fissa* has revealed 3-GQA, 1,3-diGQA, 1,4-diGQA, 3,4-diGQA, 3,5-diGQA, 1,3,4-triGQA, 1,3,5-triGQA, 3,4,5-triGQA, 1,3,4,5-tetraGQA, 3-*p*CoQA, 4-*p*CoQA, 5-CQA and a novel 3,4diG-1purpurogalloylQA all characterised by NMR and high resolution MS.*(272)* The purpurogalloyl moiety is reminiscent of the theaflagallins of black tea,*(273)* and probably forms through the interaction of a gallic acid quinone with the 1-galloquinone form of 1,3,4-triGQA.

4.4.18.4. Juglandaceae family

The Juglandaceae are trees and shrubs, commonly known as walnuts, and of importance for nuts and timber. Amaral *et al*. reported 3-CQA, 3-*p*CoQA and 4-*p*CoQA in *Juglans regia* leaves, *(274)* and Gawlik-Dziki *et al*. using LC–MS^2 found these same CGA plus 4-CQA **39** in the fruit.*(275)* In contrast, Regueiro *et al*. using LC–MS^2 and non-IUPAC numbering reported 3-CQA **33**, 5-CQA, 4-*p*CoQA and 5-*p*CoQA in the nut.*(276)* Kulisic-Bilusic *et al* reported 3-CQA, 5-CQA and 3-*p*CoQA in the dried flowers and leaves of walnut.

FAGALES SUMMARY

Very interesting differences regarding the presence or absence of galloyl esters, and no reports of diCQA

Betulaceae: *Betula* has CQA and dominant *p*CoQA, but *Alnus* has CSA and GSA

Corylaceae: 5-CQA, sometimes 3-CQA

Fagaceae: *Fagus* and *Castanea* have 5-CQA. In contrast *Quercus* has GQA, diGQA and triGQA. *Castanopsis* has GSA, diGSA and triGSA including depsides, plus GQA, diGQA, triGQA, tetraGQA and a possibly unique diG-purpurogalloylQA, but also CQA and *p*CoQA.

Juglandaceae: CQA and *p*CoQA but no reports of GQA or GSA.

4.4.19. ORDER CUCURBITALES

4.4.19.1. Cucurbitaceae family

Citrullus species: Abu-Reidah *et al.* using LC–QTOF-MS reported one triCSA, four diCSA, two CSA and an FQL in water melon, *Citrullus vulgaris*, but these were not assigned to regio-isomeric level.*(277)* The triCSA presumably must be 3,4,5-triCSA: presumably one of the diCSA is a *cis*-isomer. The putative FQL is unexpected, and its identification is supposedly based on a study by Belles *et al*.*(278)* who in fact reported an FSA in melon and cucumber and not an FQL as claimed by Abu-Reidah *et al*.

Cucurbita species: Peteresen *et al*. failed to find 5-CQA in *Cucurbita pepo*.*(20)*

Momordica species: Madala *et al*. using LC–MS reported the *cis* and *trans* isomers of 4-CQA, 4-*p*CoQA and 4-FQA in the leaves of *Momordica balsamica*.*(279)* Yasir *et al*. using LC–ion trap-MS^2 reported 4-FQA in the seeds of *M. dioica* but did not refer to any other acyl-quinic acids.*(280)*

CUCURBITALES SUMMARY

Limited data but shikimic acid utilised in some and quinic in others.

No reports of diCQA

Citrullus has CSA, diCSA, triCSA and probably FSA

Cucurbita no 5-CQA

Momordica CQA, pCoQA and FQA

4.4.20. ORDER OXALIDALES

4.4.20.1. Elaeocarpaceae family

The Elaeocarpaceae consists of 12 genera and about 600 species.

Aristotelia species: Ruiz *et al*. reported a GQA, tentatively assigned as 5-GQA, in *Aristotelia chinensis* fruit and sought but could not detect any CQA.*(281)*

Sloanea species: *Sloanea rhodantha* is a little studied Madagascan rainforest plant in which Cao *et al*. reported 3,5-diGQA, 3,4,5-triGQA and the novel 1-eudQA which was characterized by NMR.*(282)*

OXALIDALES SUMMARY

Very limited data, but once again have GQA, diGQA and triGQA, plus the novel eudesmoylQA

No CQA or diCQA

4.4.21. ORDER MALPIGHIALES

4.4.21.1. Erythroxylaceae

The Erythroxylaceae are commponly referred to as the coca family, consisting of four genera and some 200 species of trees and shrubs. The leaves of *Erythroxylon coca* contain 5-CQA and 5-*p*CoQA and it is thought that there might be *in vivo* complexation with the tropane alkaloids, e.g. cocaine, produced by this plant.*(283)*

4.4.21.2. Calophyllaceae and Clusiacea or Guttiferae family

The Calophyllaceae are flowering plants previously considered part of the Clusiaceae, also known as the Guttiferae, and together containing over 1,500 species. Some classifications incorporate the St John's Worts (*Hypericum* spp.) whereas others place these in the Hypericaceae.

Cratoxylum species: Yingngam *et al*. report the isolation from the leaves of *Cratoxylum formosum* ssp. *formosum* of 5-CQA and its characterisation using LC–MS and comparison with a commercial standard.*(284)* However, the structure shown corresponds to 3-CQA IUPAC but the mass fragmentation presented corresponds to 5-CQA IUPAC and it is not clear which is correct.

Hypericum species: The presence of an incompletely characterised chlorogenic acid has been reported several times in *Hypericum* spp. A more thorough analysis of *Hypericum perforatum* L. identified 3-CQA, 1,3,5-triCQA and 3,4,5-triCQA but made no mention of 5-CQA.*(285)* Extracts of hairy root cultures of *H. perforatum* L. grown under photoperiod conditions and analysed by LC–MS^2 contain a *p*CoQA and an FQA,*(286)* probably the 5-acyl isomers. Tusevski *et al*. reported 3-CQA, 4-CQA, 5-CQA, 5-*p*CoQA, 5-FQA, 3,5-diCQA and 4.5-diCQA in the callus culture of *H. perforatum*, and with the exception of 5-FQA these were also present in wild growing plants.*(287)* These authors used non-IUPAC numbering.

Demirkiran *et* al. reported 5-CQA, methyl-5-CQ and 5-*p*CoQA in the arial parts of *H. montbretii*,*(288)* but appear to have named these three CGA using the IUPAC system but show the structures using non-IUPAC numbering. Capriolo *et al*. using LC–DAD reported 3-CQA, 5-CQA and 3,5-diCQA in the berries of *H. androsaemum* L, with 3,5-diCQA found only in red berries and not in black.*(289)* Jabeur *et al*. reported 3-CQA, 5-CQA and 3-*p*CoQA in *H. androssaenum.(290)* An analysis of Herba Hyperici prepared from the flowerheads of *H. perforatum* L. revealed 3-CQA, 4-CQA, *cis* and *trans* 3-*p*CoQA all identified by comparison with standards (of unstated origin) and the authors comment that 4-CQA was not resolved from 5-CQA.*(291, 292)*

3-CQA and 5-CQA were reported in *H. richeri* Vill.*(293)* and 5-CQA and *n*-butyl 5-CQ in *H. calycinum*,*(294)* but note that the original publication did not use the IUPAC numbering system. Rainha *et al*. using LC–MS identified 3-CQA, 4-CQA and 5-CQA in *H. undulatum* accompanied by a *p*CoQA and an FQA,*(295)* and 3-CQA and 5-CQA in *H. foliosum*, *H. androsaemum* and *H. undulatum*.*(296)*

Caraipa species: *Caraipa densifolia* is used in Brazilian folk medicines and its leaves contain 3-CQA (0.23–0.71 g/kg) and 5-CQA (0.33–1.67 g/kg). An incompletely characterised *p*CoQA was also reported in the range 0.66–2.58 g/kg.*(297)* It appears from its fragmentation to be 5-*p*CoQA. Commercial 3-CQA and 5-CQA were used as calibrants.

4.4.21.3. Euphorbiaceae family

The Euphorbiaceae is a large family of 300 genera and some 7,500 species, but they have been little studied with regard to CGA.

Cnidoscolus species: '*Chlorogenic acid*' has been reported in *Cnidoscolus chayamansa*.*(298)*

Euphorbia species: Chen reported 3,4-diGQA in *Euphorbia hirta* L,*(299)* whereas Yoshida *et al*. reported 5-CQA and 3,4-diGQA.*(300)* It is uncertain whether these are IUPAC or non-IUPAC descriptions. At least three, and possibly four, GQA have been detected by LC–MS in Poinsettia, *E. pulcherrima*.*(301)*

According to the English abstract 3-GSA has been reported in *E. pekinensis*,*(302)* and, similarly, 4-GSA and 5-GSA have been reported in *E. helioscopa*,*(303)* but it is unclear whether or not IUPAC numbering has been used in these publications.

Falsone reported the novel 3-(hydroxymethylglutaroyl)-shikimic acid and 5-(hydroxymethylglutaroyl)-shikimic acid in the latex of *E. biglandulodsa* Desf.*(304, 305)*

Sapium species: Devkota *et al*. reported 3-CQA in *Sapium insigne* (ROYLE) BENTH. ex HOOK. Fil,*(306)* and 5-CQA has been reported also in *S. insigne*,*(307)* but it is unclear whether or not IUPAC numbering has been used.

4.4.21.4. Linaceae family

Linaceae species: Simirgiotis *et al*. using LC–ion trap-MS examined an extract of *Linum chamissonis* and failed to obtain unequivocal evidence for the presence of CGA. Tentative assignment of a putative diCQA and a putative triC-sucQA,*(148)* must be viewed as unproven.

4.4.21.5. Malpighiaceae family

The Malpighiaceae includes some 75 genera and some 1300 species.

Byrsonima species: The dried bark of *Byrsonima crassifolia* L. contains 14.79 g/kg of 3-GQA, 11.29 g/kg of 5-GQA, 5.59 g/kg of 3,4-diGQA, 3.85 g/kg of 3,5-diGQA and 1.31 g/kg of 3,4,5-triGQA.*(308)* Quantification employed purified isolates and an internal standard of 5-CQA, with measurement of specific MS transitions. A more extensive LC–MS^2

study detected three GQAs, four diGQAs, one triGQA, four tetraGQAs and at least six pentaGQAs.*(309)* From a re-examination of the fragmentation data presented it appears that one of the diGQA might be a depside, and at least three of the four tetraGQA must be, but more detailed characterisation requires higher order ion trap-MS spectra.*(157)* Mariutti *et al.* using LC–MS^3 reported one incompletely characterised diGQA, one triGQA and one tetraGQA in the fruit (murici) of *B. crassifolia*.*(310)* Reexamination of the published mass fragmentation data suggests that these might be 3,5-diGQA and 1,3,4,5-tetraGQA, plus 1,3,5-triGQA *(157)* rather than 3,4,5-triGQA reported in the bark.

De Sousa *et al*. using NMR characterised 3,5-diGQA **179**, 5-GQA, 5-(3-methylG)QA and 3,4,5-triGQA in extracts prepared from the leaves and stems of *B. coccolobifolia* Kunth.*(311)*

Galphimia species: The major CGA in *Galphimia glauca* is a tetraGQA,*(312, 313)* accompanied by four diGQA and four triGQA,*(314)* among which is 3,4,5-triGQA.

Heteropterys species: Bezerra *et al*. using LC–quadrupole-MS^2 reported in *Heteropterys tomentosa* A. Juss a 3-CQA malonyl pentoside, 3,4-diCQA, 3,5-diCQA and a triCQA described at different points in the text as both 1,3,4-triCQA and 3,4,5-triCQA.*(315)* In the absence of comparable data for standards these assignments at regio-isomeric level must be viewed as tentative.

4.4.21.6. Phyllanthaceae family

Baccourea species: Yang *et al.* reported 4M-5CQA and methyl 5-CQ in the leaves of *Baccaurea ramiflora* based solely on previously reported data *(316)* presumably indicating that IUPAC numbering has not been used for the MQA. As discussed elsewhere, the assignment of 4M-5CQA must be treated as uncertain.

Bridelia species; Cimanga *et al.*isolated 3,5-diCQA and 1,3,4,5-tetraCQA from the stem bark of *Bridelia ferruginea* and characterised them by NMR and MS.*(317)*

Phyllanthus species: Agyare *et al*. reported 5-CQA and 3,5-diCQA in *Phyllanthus muellerianus* (Kuntze) Exell.*(318)*

4.4.21.7. Salicaceae family

The Salicaceae or willow family includes 55 genera.

Laetia species: Estork *et al*. have isolated 3-CQA, 4-CQA and 5-FQA from the leaves and stem of *Laetia suaveolens,(319)* a species previously assigned to the now defunct Flacourtiaceae family.

Flacourtia species: Jayasinghe *et al*. isolated and characterised methyl 3-CQ, methyl 4-CQ, methyl 5-CQ, *n*-butyl 3-CQ and *n*-butyl 5-CQ from the juice of *Flacourtia inermis*. *(320)* Subsequently, Alakolanga *et al*. using LC–ion trap-MS

reported in *F. inermis* and *F. indica* 3-CQA, 4-CQA, *cis* and *trans 5-CQA*, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3-FQA, 5-*p*CoQA, 3-CSA, 3C-4glucosylQA, 3C-5glucosylQA, 3-glucosyl-4CQA, 4-glucosyl-5CQA plus two incompletely characterised CSA that are different from those previously reported in maté, and the three methyl CQ.*(321)*

MALPIGHIALES SUMMARY

Presence or absence of GQA seems important.

Erythroxylaceae and Calophyllaceae, Clusiacea or Guttiferae, Phyllanthaceae and Salicaceae have CQA, *p*CoQA, FQA and in some cases diCQA. *Flacourtia* (Salicaceae) has some uncommon glycosyl-QA derivatives. Phyllanthaceae also has comparatively rare tetraCQA,

Euphorbiaceae family are mixed. Clear evidence of GQA and GSA, plus uncommon aliphatic only QA, and CQA in *Euphorbia* whereas *Cnidosculus* and *Sapium* on limited data apparently have only CQA

Linaceae: On a single report Liinaceae seem not to have CGA

Malpighiaceae has GQA, including depsides and *O*-methyl-gallic acid esters in *Bysonimia*, and *Galphimia* has GQA but CQA in *Heteropterys*

4.4.22. ORDER CELASTRALES

4.4.22.1. Celastraceae family

Euonymus species: According to the English abstract, Lee *et al*. have found 3-CQA, 4-CQA, 5-CQA, 1,5-diCQA, 3,4-diCQA and 3,5-diCQA in the heartwood of *Euonymus japonica*, Japanese Spindle.*(322)* The structures presented follow IUPAC numbering and the NMR presented are consistent with the presence of a 1-acyl-quinic acid. Peteresen *et al*. reported 5-CQA was not found in *E. verrucosus*.*(20)*

Maytenus species: Marques and Farah using LC–MS reported 3-CQA, 4-CQA and 5-CQA (dominant) in *Maytenus ilicifolia*.*(35)*

Salacia species: 5-CQA was reported in the leaves of *Salacia chinensis, S. fruticose* and *S. oblonga*.*(323)*

4.4.22.2. Lepidobotryaceae family

The Lepidobotryacea family is somewhat unusual in that there are only two species**,** *Lepidobotrys staudtii* and *Ruptiliocarpon caracolito*. Bokesch *et al*. reported 1,3,4,5-tetraGQA, 3,4,5-triGQA and methyl 3,4,5-triGQA from *Lepidobotrys staudtii*.*(324)*

CELASTRALES SUMMARY

Limited data, but presence or absence of GQA seems important.

Celastraceae has CQA and diCQA

Lepidobotryaceae has triGQA and tetraGQA

4.4.23. ORDER ZYGOPHYLLALES

4.4.23.1. Zygophyllaceae family

The Zygophyllaceae include over 20 genera and nearly 300 species.

Tribulus species: Hammoda *et al*. isolated *cis* and *trans* 4,5-di*p*CoQA from the aerial parts of *Tribulus terrestris* and characterised them by NMR. *Cis* and *trans* 5-*p*CoQA were also present.*(325)*

ZYGOPHYLLALES SUMMARY

Insufficient data but the comparatively rare di*p*CoQA is noteworthy.

FABIDS SUMMARY

According to APG IV ther Fabids encompasses eight orders, Fabales, Rosales, Fagales, Cucrbitales, Oxalidales, Malpighiales, Celastrales and Zygophyllales, and while some data are available for each thereof, they are often too limited to permit sound generalisations.

GQA have not been reported in Cucurbitales or Zygophyllales but are quite prominent in the other six orders, although not recorded in every family. Shikimic acid noticeably more prominent in one family of the Cucurbitales.

Fabales has the only report so far of actl-deoxyquinic acids, and Rosles the only report so far of *p*-methoxy-cinnamoyl-quinic acid.

4.4.24. ORDER GERANIALES

4.4.24.1. Geraniaceae family

Erodium species: Lin and Lin isolated 5-GSA, 4,5-diGSA and 3,5-diGSA from *Erodium moschatum* (L.) L'Her. And characterised them by NMR.*(326)* Fecka and Cisowski reported 5-CSA in *E. cicutarium*.*(327)* None of the authors used the IUPAC numbering. Petersen *et al*. reported 5-CQA could not be found in *E. manescavii*.*(20)*

Geranium species: Tuominen *et al.* using LC–MS reported several incompletely characterised CGA, as follows: three GQA (dominant), three diGQA, one triGQA, two CQA and one GSA in various organs of *Geranium sylvaticum*.*(328)* Petersen *et al*. reported 5-CQA in *G. sylvaticum*, but not in *G. sanguineum* or *G. swaticum*.*(20)* Miliasuskas *et al*. isolated and NMR characterised 4-GQA from *G. macrorhizum*.*(329)*

GERANIALES SUMMARY

Erodium GSA diGSA and CSA but negative CQA

Geranium GQA, CQA GSA, one negative CQA

4.4.25. Order Myrtales

4.4.25.1. Combretaceae family

The Combretaceae is a small family of 18 genera and about 600 species.

Guiera species: Bouchet *et al*. reported 3-GQA, 4-GQA, 5-GQA, 1,3-diGQA, 3,4-diGQA, 3,5-diGQA, 4,5-diGQA, 3,4,5-triGQA, 1,3,4-triGQA and 1,3,4,5-tetraGQA from *Guiera senegalensis (330-332)*

Terminalia species: According to the English abstract 5-GSA and 3,5-diGSA have been found in *Terminalia arborea*.*(333)* Pfundstein *et al*. reported 3,4,5-GSA in *T. chebula* but only traces were found in *T. bellerica* and it could not be detected in *T. horrida*.*(334)*

4.4.25.2. Lythraceae

Peteresen *et al*. failed to find 5-CQA in the Lythraceae that they surveyed, i.e. *Cuphea procumbens, Lythrum alatum* and *L. hyssopifolia*.*(20)*

4.4.25.3. Myrtaceae family

The Myrtaceae include over 130 genera and over 5,500 species, many of which are noted for their essential oils, e.g. Eucalyptus.

Eucalyptus species; An incompletely characterised CQA has been reported in the wood of *Eucalyptus grandis*, *E. urograndis* and *E. maidenii*,*(335)* the bark of *Eucalyptus globulus* Labill,*(336)* and the leaf of *E. camaldulensis* Dehnh., which also contains two GQA and one GSA.*(337)*

Heteroplexis species: *Heteroplexis micocephal* has been reported to contain several CQA and diCQA, including some methyl esters, but it is not clear if this report uses the IUPAC numbering system.*(338)*

Myrtus species: The leaves of *Myrtus communis* contain 3,5-diGQA,*(339, 340)* plus three incompletely characterised GQA.*(341, 342)*

Myrteolus species: Ruiz *et al.* using LC–MS^2 have analysed the berries of *Myrteola nummularia* but it is not clear whether or not they are using the IUPAC numbering system. They reported one incompletely characterised GQA and an incompletely characterised CQA.*(235)*

Psidium species; Pontes *et al*. screened 22 Brazilian species for CGA and failed to find 4-CQA and 5-CQA of in the peel, pulp, or seeds of *Psidium guava*, while detecting one or both in 18 other species.*(165)*

Syzigium species: Marques and Farah reported 5-CQA in Brazilian *Syzigium cuminii* plus traces of the other CQA and diCQA,*(35)* whereas Nikhat *et al*. reported a novel glycoside, 4-pentosyl-5-caffeoylquinic acid, from the roots of *S. cuminii* L. Skeel, a medicinal plant from Asia.*(343)*

4.4.25.4. Onagraceae family

The Onagraceae consists of 17 genera and over 600 species includintg the Evening Primroses, Willowherbs and Fuchsias. Peteresen *et al*. failed to find 5-CQA in the Onagraceae that they surveyed, i.e. *Gaura biennis, Oenothera missouriensis* and *Lopezia racemosa*.*(20)*

Fuchsia species: Ruiz *et al.* using LC–MS^2 have analysed the berries of *Fuchsia magellanica* but it is not clear whether or not they are using the IUPAC numbering system. They reported one incompletely characterised CQA and one incompletely characterised *p*CoQA.*(235)*

MYRTALES SUMMARY

Few data

Combretaceae has GQA, diGQA, triGQA, tetraGQA and GSA

Lythraceae 5-CQA negative

Myrtaceae

- *Eucalyptus* GQA, CQA, GSA
- *Heteroplexis* CQA, diCQA
- *Myrtus* GQA, diGQA
- *Myrteolus* GQA, CQA
- *Psidium* CQA negative
- *Syzigium* CQA diCQA and a pentosyl derivative

Onagraceae limited data but some 5-CQA negative, some positive

4.4.26. ORDER MALVALES

4.4.26.1. Malvaceae family

The Malvaceae or mallows consist of some 200 genera and over 4,000 species including cotton, okra, hibiscus and cocoa.

Corchorus species: 5-CQA, a second CQA and three diCQA have been reported in *Corchorus olitorius*,*(344)* but the QTOF-MS fragmentations reported are inadequate to define the other CGA at regio-isomeric level. An earlier report identified 3,5-diCQA in *C. olitorius*.*(345)* Taiwo *et al.* isolated a methyl triCQ from *C. olitorius* and using NMR defined it as methyl 1,3,4-triCQ,*(346)* but did not use IUPAC numbering.

Hibiscus species: Petersen *et al* failed to find 5-CQA in *Hibiscus cannabinus* and *H. rosa-sinensis*.*(20)* However, *H. sabdariffa* calyces and leaves contain 3-CQA, 4-CQA and 5-CQA.*(347, 348)* Ifie *et al*. analysed red and white varieties of *H sabdariffa* and reported the foregoing (3-CQA dominant) in red varieties. White varieites contained two additional CQA, presumably *cis* isomers, but lacked 4-CQA.*(349)* A *p*CoQA and several methylCQ and ethylCQ have also been reported but not characterised to regio-isomeric level.*(350)*

Theorbroma species: Petersen *et al* reported 5-CQA in cocoa (*Theobroma cacao*).*(20)*

4.4.26.2. Tiliaceae family

Tilia species: Petersen *et al*. reported 5-CQA in *Tilia cordata, T. platyphyllos* and *T. japonica* but not in *T. americana* or *T. tomentosa*.*(20)* In contrast, Ieri *et al*. using LC–MS reported two incompletely characterised *p*CoQAs, 3-CQA, 4-CQA and 5-CQA in the buds of Silver Linden, *T. tomentosa*, but with considerable variation depending on source.*(233)*

4.4.26.3. Thymelaceae family

Daphne species: Petersen *et al*. did not find 5-CQA in *Daphne mezereum*.*(20)*

MALVALES SUMMARY

Malvaceae, Tiliaceae, Thymelaceae all have CQA but not many data

4.4.27. ORDER BRASSICALES

4.4.27.1. Brassicaceae family

The Brassicaceae, formerly Cruciferae, consists of over 350 genera and over 3,500 species, including many vegetables such as broccoli, cabbages, cauliflower, radishes, sprouts, swedes and turnips.

Anastatica species: AlGamdi *et al*. using LC–MS^2 reported 5-CQA, 3,4-diCQA and 4,5-diCQA in a medicinal tea prepared from the seeds of *Anastatica hirerochuntica* L..*(351)*

Brassica species: Early studies demonstrated the presence of 3-CQA and 5-CQA in many edible brassicas.*(352)* Three pCoQA have been reported in the leaves of wild *Brassica napus*.*(353)* Harbaum *et al.* using LC–ion trap-MS examined the leaf blade and petiole of Pak Choi (*Brassica campestris* L. ssp. *Chinensis* var. *communis* and reported what appears to be 3-CQA, 4-CQA, *cis* and *trans* 3-*p*CoQA and 3-FQA,*(354)* but these were not assigned by the authors. Interestingly, a novel 3',4'-dihydroxy-5'-methoxycinnamoyl-malic (hydroxy-feruloyl-malic) acid conjugate was characterised. The equivalent quinic acid conjugate was not detected in Pak Choi, but a hydroxyferuloyl-feruloylquinic acid has been tentatively identified in green robusta coffees.*(355)*

Lin and Harnly using LC–MS^2 characterised the CGA in 17 brassicaceous vegetables on sale in Maryland (USA) and found CQA, FQA and pCoQA in one or more of the species studied. 3-CQA and 4-pCoQA were absent from mustard greens, baby mustard greens, baby gai choy and gay choi, but present in the remaining 13 vegetables. In contrast, 5-CQA was absent from yu choy, yu choy tip and turnip greens, but present in the remaining 14 samples. Gay choi was very similar to mustard greens, baby mustard greens and baby gay choi but lacked 5-*p*CoQA and 5-FQA. The reasons for these variations and their significance, if any, are far from clear.*(356)* Note that the component assigned as 4-*p*CoQA did not at MS^2 show the expected *m/z* 173 fragment.

Lin and Harnly also analysed Collard Greens, Kale, and Chinese Broccoli, reporting 3-CQA, 4-CQA, 5-CQA, 3-*p*CoQA, 5-*p*CoQA, 3-FQA and 5-FQA: The 3-acyl isomers always exceeded the 5-acyl isomers,*(357)* a feature also observed in some Rosaceae — see **4.4.17.2.**

Cakile species: LC–MS analysis of extracts from Sea Rocket, *Cakile maritima*, failed to locate any CGA.*(358)*

4.4.27.2 Capparaceae family

The Capparaceae, embracing some 30 genera and some 700 species. are commonly known as the capers. The taxonmomy is rather uncertain.

Capparis species: Siracusa *et al.* using LC–MS reported 5-CQA, 4-CQA, 4-FQA and 5-*p*CoQA in an extract of caper (*Capparis spinosa* L.)*(359)* Bakr *et al*. reported 5-CQA and an incompletely characterised *p*CoQA the in aerial parts of *Capparis spinosa* var. *aegyptia* (Lam.) Boiss.*(360)*

4.4.27.3 Caricaceae family

Carica species: Zunjar *et al* have reported 5-CQA plus a series of unusual acyl-quinic acids in *Carica papaya*.*(361)* Unfortunately the reported mass fragmentations, even for 5-CQA, are not typical of acyl-quinic acids, and these assignments must be viewed as doubtful.

4.4.27.4. Moringaceae family

There is only one genus, *Moringa*, in this family. *Moringa oleifera* (English names: moringa and drumstick) is the well-known and most cultivated species in the family Moringaceae. Kashiwada *et al*. detected 3-CQA, 4-CQA, 5-CQA and two 4-CQA glucosides, 4-*O*-(4'-*O*-caffeoyl glucosyl)quinic acid and 4-*O*-(3'-*O*-caffeoyl glucosyl)quinic acid in leaves of *Moringa oleifera.(362)* Khoza *et al*. have also reported *p*-CoQA and FQA including several *cis* isomers.*(363)* Nouman *et al*. reported 3-CQA, 5-CQA, 3-*p*CoQA plus an incompletely characterised FQA and an early-eluting diCQA in *M. oleifera*.*(364)* this latter more likley to be a CQA glycoside.

Makita *et al*. using UPLC–QTOF-MS reported the *cis* and *trans* isomers of 3-acyl, 4-acyl and 5-acyl p-coumaroylquinic, caffeoylquinic and feruloylquinic acids, plus a single isomer of 3,5-diCQA , a 3-CQA-glycoside and the 3'- and 4'-glycosides of 4-CQA in *M. ovalifolia*.*(365)* In addition to the foregoing Rodriquez-Perez *et al*. reported a CSA.*(366)*

BRASSICALES SUMMARY

Brassicaceae: *Anastatica* and *Brassica* have CQA, pCoQA and FQA, sometimes with 3-CQA dominant in *Brassica*. In contrast, *Cakile* does not have any CGA

Capparaceae: CQA and diCQA have been reported, but limited data

Caricaceae: no reliable data

Moringaceae: CQA, diCQA, FQA and pCoQA have all been reported

4.4.28. ORDER SAPINDALES

4.4.28.1. Anacardiaceae family

The Anacardiaceae include the sumacs, mangoes, poison ivies, and pistachios, and are well known for their contents of distinctive long chain alkyl- or alkenyl-resorcinols and catechols,*(367)*.

Anacardium species: Pontes *et al.* found only a trace of 5-CQA in the peel of *Anacardium occidentale*.*(165)*

Mangifera species: Pontes *et al.* using HPLC and isolated CGA standards and surrogate standards quantified 4-CQA and 5-CQA in mango peel, pulp and seeds. 4-CQA 47 mg/kg was detected only in peel: 5-CQA **35** was found in all three tissues, 45 and 29 and 29 mg/kg, respectively.*(165)* Pontes *et al*. used commercial 5-CQA **35** as calibrant and corrected for differences in molecular mass and molar absorbance. More recently it has been reported that Mango (*Mangifera indica*) contains 5-CQA as a major phenolic compound with the amount 0.28–30 g/kg dry basis.*(368)* The authors' criteria for this assignment were '*Chlorogenic acid was identified as a [M–H]$^-$ deprotonated molecule (**m/z 356**) with an UV spectrum (**λ_{max} = 286, 240 nm**)…*' which on fragmentation yielded ions at '***55, 161, 173, 295, 313***'. *(368)* This assignment is clearly incorrect: the negative ion should be *m/z* 353 and λ_{max} *ca* 325 nm.

Pistacia species: According to the English abstract Hou *et al*. isolated from the leaves of *Pistacia weinmannifolia* the novel Pistafolin A and B, and by spectral means characterised them as the depsides 5-(triG)QA and 5-(diG)QA, respectively,*(369, 370)* subsequently confirmed by Zhao *et al*.*(371)* The ^{1}H-NMR showed clearly that only one quinic acid hydroxyl was acylated and therefore these two compounds were depsides. Note however, the authors did not use the IUPAC numbering. Minami *et al.* reported also the presence of 3-GQA characterised by NMR,*(372)* but it is not clear whether or not these authors used the IUPAC nomenclature. Ben Ahmed *et al*. reported one GSA, one GQA, one diGQA and one tetraGQA in the leaves of *P. atlantica*, but they were unable to judge whether or note these were depsides.*(373)*

Bampouli *et al*. reported two incompletely characterised GQA in the leaves of *P. lentiscus* var. *chia*.*(374)* At least two GQA, at least four diGQA and at least one triGQA have been identified in in the leaves of *P. lentiscus*, known variously as pistachio, mastic(k) or lentisk.*(375-377)* Isolation and NMR characterisation allowed the quantification of 5-GQA (9.6 g/kg), 3,5-diGQA (26.8 g/kg) and of 3,4,5-triGQA (10.3 g/kg) from the dried leaves of *P. lentiscus* L. Romani *et al*. used gallic acid as calibrant with correction for molecular mass,*(376)* and it is clear from the ^{1}H-NMR that the compounds identified as 3,5-diGQA and 3,4,5-triGQA are not depsides in contrast to those isolated from *P. wienmannifolia*.

Foddai *et al*. using LC–single quadrupole-MS reported 3-GQA, 5-GQA, 3,5-diGQA, 1,5-diGQA in both *P. terebinthus* and *P. lentiscus* fruits and leaves from Sardinia, but 3,4,5-triGQA was found only in *P. terebinthus*.*(378)* It is not clear whether or not the IUPAC numbering has been used.

Ersan *et al*. using LC–ion trap-MS^3 analysed the hulls (exocarp and mesocarp) of *P. vera* and reported three GSA, two diGSA, one GQA, one diGQA and one triGQA.*(379)*

Rhus species: Abu-Reidah *et al*. using LC–accurate mass-MS reported two isomers of quinic acid, a diC-sucQA, two GQAs and a CQA in *Rhus coriaria* fruits, but the positive ion spectra could not be assigned to regio-isomer level.*(380)*

Schinus species: Marzouk *et al.* isolated a 'chlorogenic acid' from *Schinus molle* and characterised it spectroscopically but do not further define its structure.*(381)* Feuereisen *et al*. have reported galloylshikimic acids in the exocarp of *Schinus terebinthfolius* Raddi (Brazilian Pepper) including three GSA, four diGSA, two triGSA, two tetraGSA, one pentaGSA and one hexaGSA, those with four to six galloyl units being new to nature.*(382)*

Spondias species: Pontes *et al.*using HPLC reported 4-CQA 5 mg/kg in peel and 5-CQA in peel, and pulp of *Spondias cytherea* at 2.1 g/kg and 132 mg/kg, respectively.*(165)* Pontes *et al*. used commercial 5-CQA as calibrant and corrected for differences in molecular mass and molar absorbance.

4.4.28.2. Burseraceae family

The Burseraceae family encompasses about 18 genera some 500 species including frankincense and myrrh. He *et al*. reported butyl 5-GQ from the Chinese olive (*Canarium album* L.), a tropical fruit tree in southeast China.*(383)*

4.4.28.3. Rutaceae family

The Rutaceae is a large family of uncertain classification including many ornamental shrubs but probably best known for the citrus fruits.

Citrus species: Citrus fruits are well known for their content of cinnamic and benzoic acid conjugates of glucaric acid and galactaric acid which are located mainly in the peel.*(384-386)* There are several reports that claim '*chlorogenic acid*' is one of the major polyphenols in citrus fruits, based solely on co-chromatography with 5-CQA.*(387-389)* More recently a caffeoylquinic acid in the pulp (5.4–8.9 mg/kg) and peel (8.8–18.7 mg/kg) of some citrus hybrids has been detected using GC–MS,*(390)* but the calibrant is not clearly stated. An LC–MS^2 analysis of citrus pulp by Tao *et al*. reports the presence of 5-CQA and an FQA derivative (M_r =530).*(391)* An LC–MS^2 analysis by Girones-Vilaplana *et al.* of the whole fruit of lemon (*Citrus limon*), orange (*C. sinensis*), lime (*C. aurantifolia*), mandarin (*C. reticulata*) and grapefruit (*C. paradisi*) detected 3-CQA, 5-CQA, 4-*p*CoQA, two diCQA, 3C-4FQA, 3,5-diFQA, a '*hydrated 3-FQA*' and a '*hydrated 5-FQA*', plus ferulic acid and sinapic acid. 3-CQA and 5-CQA were found in all five species but there were also significant differences in profile.*(392)* Nogota *et al*. reported 4F-5CQA and methyl 4F-5CQ in the peel of *C. reticulata*.*(393)*

Tao *et al*. used a commercial 5-CQA standard and its identification in citrus pulp seems to be sound,*(178)* but a study by Delpino-Ruis *et al*. who analysed by LC–MS^2 extracts prepared from the insoluble residue remaining after commercial orange, tangerine and lemon juice extraction failed to detect any CGA.*(179)* Girones-Vilaplana *et al.* do not state whether or not standards were used in their study, but the presence of 3-CQA and 5-CQA is plausibly supported by the MS^2 fragmentations. However these authors claim that two components (M_r = 516) and a third

component (M_r = 338) that elute from a C_{18} column packing before 3-CQA are two diCQAs and 4-*p*CoQA, respectively.*(392)* This is unexpected,*(221)* and casts doubt on the assignments, the putative diCQA possibly being CQA glycosides.

In view of the earlier studies it would be plausible that the hydrated FQA are the isobaric feruloyl-glucaric acids rather than quinic acid derivatives, but the quoted MS^2 fragment ions (*m/z* 367 and 173) do not match those previously reported (*m/z* 209 and 191) for glucaric acid conjugates.*(130)* DiFQA have M_r = 544 rather than 562 as tabulated by Girones-Vilaplana *et al.* and plausibly this compound is related to the hydrated feruloylquinic acids.

It seems likely that the FQA derivative of Tao *et al*. is the same as the CFQA of Girones-Vilaplana *et al.* but the fragmentation is not a good match for the CFQA as determined by Clifford *et al.,(221)* and this assignment is uncertain. Clearly further investigation is required, but note that tomato cotyledons can convert 5-CQA **35** to a caffeoyl-glucaric acid,*(394)* and this pathway might be more widespread.

Fagara species: The root bark of *Fagara zanthoxyloides* Lam. contains the novel 3,4-diVQA, 3,5-diVQA and 4,5-diVQA also referred to as Burkinabin A–C.*(395)*

Ruta species: Pacifico *et al.* using LC–ion trap MS^3 reported 4-*p*CoQA and 4-FQA in *Ruta graveolens*.*(396)* It is, however, unusual to see only single regio-isomers and the possibility that these are acyl-isocitric acids should be considered.

Zanthoxylum species: Yang *et al.* using LC–triple-quadrupole-MS^2 quantified 5-CQA (2.5 g/kg) and 5-FQA (17 mg/kg) in the deciduous shrub *Zanthoxylum bungeanum*,*(397)* using MRM and commercial 5-CQA as calibrant. Braguine *et al*. reported 5-CSA in *Z. naranjillo*.*(398)*

4.4.28.4 Sapindaceae family

Aesculus species: Oszmianski *et al*. analysed the leaf tissue of *Aesculus hippocastanum* L. and *A.carea* H. and reported 5-CQA and a putative trihydroxycinnamoylquinic acid which gave *m/z* 369 and *m/z* 189 at MS^1 and MS^2, respectively,*(399)* possibly suggesting that the extra hydroxyl is on the quinic acid moiety, but this assignment must be viewed as tentative.

Koelreuteria species: Chen *et al*. isolated 1,3,4,5-tetraGQA from *Koelreuteria henryi*, and characterised it by NMR and LC–ion trap-MS.*(400)*

Litchi species: 5-CQA has been reported in *Litchi chinensis*.*(401, 402)*

SAPINDALES SUMMARY

Anacardiaceae: *Anacardia* and *Mangifera* probably have traces of CQA but few good data. *Pistacia* has GQA. *Rhus* might have two QA isomers? GQA, CQA and suc-diCQA also reported, possibly the earliest report of a succinic acid derivative. *Schinus* has GSA upto hex-GSA whereas *Spondias* has CQA

Burseraeae: Contains relatively uncommon butyl GQ

Rutaceae: *Citrus* has CQA, FQA, diCQA, CFQA pCoQA and diFQA but some peculiar hydrated FQA that have been reported may be glucaric acid conjugates.

Fagara has the rare diVQA whereas *Ruta* apparently has 4-*p*CoQA and 4FQA but the presenc of only single regio-isomer may indicate that these are acyl-isocitric acids

Zanthoxylum has CQA CSA

Sapindaceae: *Aesculus* has CQA and a possible hydroxy-quinic but very few data. *Koelreuteria* has GQA whereas *Litchi* has CQA

SUMMARY FOR MALVIDS

The Malvids embraces eight orders but there are no data for the Crossosomatales, Picramniales or Huertales.*(9)* The data available for the Geraniales, Myrtales, Malvales, Brassicales and Sapindales are summarised below.

There is a clear presence of gallic acid esters of both quinic acid and shikimic acid in the Geraniales, Myrtales and Sapindales. There are several examples within these three orders of samples where CQA were not found, but generally CQA and diCQA are reported. There is a single report of a succinoyl-dicaffeoylquinic acid in the Sapindales (*Rhus*) where two free quinic acids have also been reported, and a novel pentosyl derivative has been reported in the Myrtales (*Syzigium*).

Although the data are limited there are no reports of gallic acid esters in the Malvales or Brassicales, but CQA have been reported in both, and *p*CoQA, FQA and diCQA in Brassicales.

The overall impression is of considerable variation, and this increasing markedly in the Sapindales. Further LC–MS profiling is required and thedistribution of GQA seems quite important.

4.4.29. ORDER VITALES

4.4.29.1. Vitaceae family

Tetrastigma species: Sun *et al*. using LC–MS^2 and a commercial 5-CQA standard reported 1-CQA, 3-CQA, 5-CQA, 1-*p*CoQA and 5-*p*CoQA in an extract of *Tetrastigma hemsleyanum* leaves.*(403)* The assignment of the putative 1-acyl quinic acids is uncertain because they eluted from a reversed phase column packing after the corresponding 5-acyl quinic acids, and might therefore be *cis* 5-acyl quinic acids. Note also that the structures shown do not follow the IUPAC numbering system despite the commercial standard used being described as 5-CQA**.**

Vitis species: Handoussa *et al*. using LC–QTOF-MSMS profiled the polyphenols in the leaves of *V. vinifera* and did not report any CGA.*(344)*

VITALES SUMMARY

Limited data. CQA present in Tetrastigma but not Vitis

4.4.30. ORDER SAXIFRAGALES

4.4.30.1. Grossulariaceae family

Grossulariaceae include the currants and gooseberries, but must not be confused with the currants prepared by drying grapes.

Ribes species: Ruiz *et al.* using LC–MS^2 have analysed the berries of *Ribes magellanicum* and *R. cucullum* but it is not clear whether or not they are using the IUPAC numbering system. They reported incompletely characterised CQA, *p*CoQA and FQA.*(235)* Anttonen and Karjalainen using LC–ion trap-MS reported 3-CQA and 3-*p*CoQA but found no significant difference in content in organically grown fruit compared with conventionally grown fruit, 2.89–4.51 mg/kg and 2.73–3.84 mg/kg, respectively for 3-CQA **39** and 3.28–3.67 and 3.42–4.35 mg/kg, respectively, for 3-*p*CoQA.*(404)* Ieri *et al*. using LC–MS reported 3-CQA, 4-CQA and 5-CQA, plus three incompletely characterised *p*CoQA in the leaves and buds of *R. nigrum*.*(233)* Makila *et al*. reported 3-CQA, 5-CQA and 3-*p*CoQA in the stored juice from *R. nigrum*.*(405)* Jimenez-Espee *et al*. reported 3-CQA, 3-*p*CoQA, 5-*p*CoQA, 3-FQA, 5-FQA plus 4-CQA and two incompletely characterised CQA in *R. cucllatum*, *R. magellanicun*, *R. punctatum* and *R. trilobum* with considerable variation in the relative contents.*(406)*

4.4.30.2. Hamamelidaceae family

The Hamamelidaceae are commonly known as the witch hazel family. Duckstein *et al*. reported 3-CQA, 4-CQA, 5-CQA and 3-*p*CoQA, 5-*p*CoQA and a CSA in the leaves of *Hamamelis virginiana* L., a plant used to treat dermatological disorders.*(407)*

4.4.30.3. Saxifragaceae family

Salminen *et al*. reported a CQA and a GQA in the leaves of *Bergenia crassifolia* L.*(408)*

SAXIFRAGALES SUMMARY

Very limited data with only a single species per family, but again split between GQA and CQA

Grossulariaceae — *Ribes:* CQA, pCoQA FQA.

Hamamelidaceae — *Hammamelis* CQA and CSA.

Saxifragaceae — *Bergenia* CQA and GQA.

4.4.31. ORDER SANTALALES

4.4.31.1. Loranthaceae family

Tristerix species: Simirgiotis *et al*. reported 3-CQA, 5-CQA, 5-FQA and 5-*p*CoQA in *Tristerix tetandrus*,*(409)* but did not use IUPAC numbering.

4.4.31.2. Schoepfiaceae family

Quinchamalium species: Simirgiotis *et al*. using LC–ion trap-MS examined an extract of *Quinchamalium chilensis* but failed to obtain unequivocal evidence for the presence of CGA. Tentative assignments were made of a putative diCQA and a putative triC-MoQA*,(148)* but the atypical MS^2 fragmentations make them uncertain.

4.4.31.3. Viscaceae family

The Viscaceae are commonly referred to as Mistletoes.

Phoradendron species: Furbacher reported the isolation and characterisation of 5-CepiQA from *Phoradendron juniperum*, this being the first report of any CGA from this family. The isolate was characterised by NMR, LC–APCI-MS and FTIR.*(410)* The evidence presented by Furbacher in support of this assignment has been discussed in Part 2 of these notes, and it seems certain that Furbacher was misled by previously published data where IUPAC and non-IUPAC data have been confused. Furbacher's isolate is likely to be 3-CQA IUPAC.

Viscum species: Abdallah *et al*. using LC–MS reported in *Viscum schimperi* four CQA including 1-CQA, one SiQA, one FQA and a component described as a feruloylquinic acid methyl ether (M_r = 398, yielding *m*/*z* 367 at MS^2).*(411)* The order of elution of the CQA is atypical, and it might be that the putative 1-CQA is *cis*-5-CQA. The basis of the description '*FQA methyl ether'* is not discussed and this assignment should be treated as tentative.

SANTALES SUMMARY

Loranthaceae: CQA pCoQA FQA single report

Schoepfiaceae: single report of doubtful quality

Viscaceae: CQA (not CepiQA), pCoQA and FQA but need more data

4.4.32. ORDER CARYOPHYLLALES

4.4.32.1. Aizoaceae family

Carpobrotus species: Meddeb *et al*. have reported 5-CQA and 1,3-diCQA in aqueous acetone extracts of the leaves of *Carpobrotus edulis* using HPLC with UV detection, but do not appear to have used standards,*(412)* and the criteria for identification are unclear.

4.4.32.2. Amaranthaceae family

The Amaranthaceae, now incorporating the Chenopdiaceae (Goosefoots) contains approximately 180 genera and 2,500 species, some of which are used as food, feed or herbal medicines.

Amaranthus species: A noteable feature of *Amaranthus* is the ability to produce acyl-isocitric acids which at unit mass precision are isobaric with the commoner acyl-quinic acids. Strack *et al*. observed *cis* and *trans* caffeoyl-isocitric acid along with the corresponding feruloyl- and *p*-coumaroyl-isocitric acids in Amaranthus *cruentus.(81)* There is also a web reference to a University of Braunschweig study in which an acyl-isocitric acid was detected in *A. tricolor* (Chinese spinach). This component, characterised by NMR, is recorded as 'p-*caffeoyl-isocitric acid*' which is presumably a typographical error for either *p*-coumaroyl- or caffeoyl-isocitric acid'.[1] Many investigators seem not to be aware of this early and thorough work, including *de novo* synthesis, by Strack *et al*.

For example, Stintzing *et al*., using LC–ion trap-MS^2 and the hierarchical keys developed by the Clifford research group, reported two CQA, two *p*CoQA and two FQA in *A. spinosus*.*(413)* However, close inspection of the fragmentation data indicates that these are indeed acyl-isoctric acids as discussed more fully in Part 3 of these notes discussing LC–MS of chlorogenic acids. Similarly, Li *et al.* report 'chlorogenic acid', presumably 5-CQA in the flowers of *A. hypocondriachus* and *A. caudatus*, but apparently absent from the flowers of *A. cruentus*.*(414)* These authors used a commercial chlorogenic acid standard but close inspection of their published chromatograms shows that it is not a perfect match to the peak assigned as 5-CQA. Maroli *et al*. and Paucar-Menacho *et al*. reported 4-CQA and 4-FQA in *A. palmeri,(415)* and *A. caudatus*,*(416)* respectively. None of these authors make reference to acyl-isocitric acids or the study by Strack *et al*.

Beta species: Arens *et al*. reported 5-FQA in the leaves of sugar beet (*Beta vulgaris*).*(417)*

Gomphrema species: LC–MS profiling failed to detect any CGA in extracts of *Gomphrena globose*.*(86)*

Suaeda and *Salicornia* species: These species are characteristic of saltmarshes and both produce the uncommon dihydrocaffeoyl derivatives of quinic acid. 3,5-DiCQA and its methyl ester have been reported in the saltmarsh plants *Suaeda glauca,(418)* and *Salicornia herbacea* L.,*(419)* which also contains 3,4-diCQA plus the novel 4dihC-5CQA

---

1 http://gepris.dfg.de/gepris/OCTOPUS;jsessionid=9D2DA1B6FC8B51A31EF0DF72BC480C7A?context=projekt&fontSize=2&id=5410659&language=en&selectedSubTab=2&task=showDetail

(tungtungmadic acid) **55**,*(420)* and methyl 4C-3dhCQ (salicornate) which were characterised by NMR*(421)* Subsequent investigation by LC–QTOF-MS of HSCCC extracts prepared from *Salicornia gaudichaudiana* has identified three diCQA, two dhC-CQA, and a novel dhC-CFQA but it was not possible to assign these to regio-isomeric level.*(422)*

Tuan *et al*. isolated the novel 3-caffeoyl, 5-dihydrocaffeoylquinic acid and and 4,5-di-(dihydrocaffeoyl)quinic acid from *S. hederacea* and characterised them by NMR, accompanied by 3,5-diCQA, methyl 3,5-diCQ, 2,3-diCQA and 3,5-di-(dihydrocaffeoyl)quinic acid.*(423)* The reference to 2,3-diCQA is presumably a typographical error. Cho *et al*. reported 3-CQA and methyl 3CQ which they present with the correct IUPAC structures but describe as '*chlorogenic acid*' and '*methyl chlorogenate*' respectively. Accordingly, it is not possible to judge whether or not the following novel compounds have been described by the IUPAC numbering system — 3-caffeoyl-5-dihydrocaffeoylquinic acid, methyl 3-caffeoyl-5-dihydrocaffeoylquinate, methyl 3-caffeoyl-4-dihydrocaffeoylquinate and methyl 3-dihydrocaffeoyl-5-caffeoylquinate.*(424)*

4.4.32.3. Polygonaceae family

Bistorta species: Some authorities equate *Bistorta* with either *Persicaria* or *Polygonum*. *Bistorta manshuriensis* has been reported to contain methyl-5CQ and methyl 3,5-diCQ.*(425)*

Fagopyrum species: Chlorogenic acid has been reported in Tartary Buckwheat (*Fagopyrum tataricum*).*(426)* A more extensive study using positive ion LC–FTICR-MS of *F. tataricum* Gaerth. identified 5-CQA by comparison with a standard, and suggested tentatively the presence of a *p*CoQA, a methyl-*p*CoQ and an FQA.*(427)*

Li *et al*. also analysed Tartary Buckwheat (*F. tataricum* Gaerth.) and reported chlorogenic acid and an early eluting dicaffeoylquinic acid, designated '*Compound 4*' about which they say:

'*Compound 4 (m/z 515) was tentatively assigned as dicaffeoylquinic acid derivatives, which were concretely identified as 3,4-di-O-caffeoylquinic acid (m/z, 515), 1,5-di-Ocaffeoylquinic acid (m/z, 515), 3,5-di-O-caffeoylquinic acid (m/ z, 515) and 4,5-di-O-caffeoylquinic acid (m/z, 515) according to the previous reports*'.*(428)* This statement indicates some confusion and this compound is more likely to be a CQA glycoside.

Karamac *et al.* reported 5-CQA in *F. esculentum* Moench.*(429)*

Polygonum species: Kutia *et al*. isolated 3-CQA from the leaves of *Polygonum cuspidatum* and characterised it by NMR and specific rotation.*(430)*

CARYOPHYLLALES SUMMARY

Aizoaceae: single report of CQA and diCQA must be viewed as tentative

Amaranthaceae:

Amaranthus acyl-isocitric rather than acyl-quinic

Beta single report 5-FQA

Gomphrema profiling negative for CGA

Suadea and Salicornia uncommon dihydrocaffeoylquinic acids plus some triacyl and diCQA

Polygonaceae

Bistorta methyl CQ and methyl diCQ single report

Fagopyrum CQA FQA diCQA

SUPERASTERIDS SUMMARY

According to APG IV the Superasterids embraces three orders,*(9)* with data available for the Santalales and Caryophyllales but not the Berberidales.

Limited data preclude useful generalisations, but there are records of CQA, pCoQA, FQA and diCQA. The appearance of dihydrocinnamoylquinic acids and acyl-isocitric acids are noteworthy.

4.4.33. ORDER CORNALES

4.4.33.1. Hydrangaceae family

Hydrangea species: *Hydrangea* is a genus of approximately 75 species, including some well-known cultivated shrubs, small trees and lianas. The flowers of the decorative *Hydrangea macrophylla* var. *Thunbergii* contain 3-CQA, 5-CQA, *cis* and *trans* 3-*p*CoQA, and methyl 5-CQ.*(431)*

CORNALES SUMMARY

Single report.

4.4.34. ORDER ERICALES

4.4.33.1. Actinidiaceae family

The Actinidaceae includes three genera and some 350 species and is perhaps best known for the Chineses gooseberry. Zhao *et al*. using LC–MS^2 have reported all four CQA, all four *p*CoQA plus 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in the root extract of *Actinidia chinensis*,*(432)* but the original paper used non-IUPAC numbering, and the late eluting 1-acyl-quinic acids are more likely to be *cis*-5-acyl-quinic acids.

4.4.34.2. Clethraceae family

Llorent-Martinez *et al*. using LC–MS could not detect any CGA in leaf extracts from *Clethra arborea*.*(433)*

4.4.34.3. Ericaceae family

The Ericaceae is a large family of plants that are associated with poor acidic soils, including heathers, rhododendrons and many edible berries.

Anthopterus species: Dastmalchi *et al*. reported 5-CQA in the fruits of *Anthopterus wardii* Ball.*(434)*

Arbutus species: The fruits of the Strawberry tree, *Arbutus unedo*, contain 3-GQA, 5-GQA, 3-GSA and 5-GSA, all characterised by LC–MS and NMR.*(435)* Mosele *et al*. additionally reported incompletely characterised diGQA, triGQA, tetraGQA plus GSA and diGSA.*(436)*

Cavendishia species: Dastmalchi *et al*. reported 5-CQA in the fruits of *Cavendishia grandifolia* Hoerold.*(434)*

Gaultheria species: Ruiz *et al.* using LC–MS^2 have analysed the berries of *Gaultheria mucronata* and *G. antartica* but it is not clear whether or not they are using the IUPAC numbering system. They reported one incompletely characterised CQA in *G. mucronata* that was not found in *G. antartica*.*(235)* Although this component produced a parent ion at *m/z* 353, the MS^2 fragments at *m/z* 195 and 177, and the λ_{max} at 312 nm are not consistent with the assignment as a CQA.

McDougall *et al*. reported an incompletely characterised CQA in *G. shallon*.*(204)*

Macleania species: Dastmalchi *et al*. reported 5-CQA in the fruits of *Macleania coccoloboides* A. C. Smith.*(434)*

Rhododendron species: An LC–ion trap-MS investigation of leaves from 16 taxa of *Rhododendron* spp. identified *cis* and *trans* 3-CQA, 5-CQA and *cis* and *trans* 3-*p*CoQA, 4-*p*CoQA and 5-*p*CoQA in some but not all. Of particular interest was the apparent absence of 4-CQA **39** and the occurrence in *Rhododendron* 'Catawbiense Grandiflorum' of 3-

*p*CoQA as the only representative of this class of CGA, and its absence from *Rhododendron calophytum* and *Rhododendron ungernii*, where the only representative of this class was 5-*p*CoQA.*(437)*

Sphyrospermum species: Dastmalchi *et al*. reported 5-CQA in the fruits of *Sphyrospermum buxifolium* Poeppig & Endlicher, and *S. cordifolium* Benth.*(434)*

Vaccinium species: It has been reported that there are considerable amounts of 5-CQA **35** in the fruits of European bilberries (*Vaccinium myrtillus* L.),*(438)* Lowbush Blueberries (*V. angustifolium*) Northern Highbush Blueberries (*V. corymbosum* L.)*(438, 439) V. arctystaphylos* from Turkey*(440)* and related neotropic species such as *Vaccinium virgatum*,*(434)* but these studies did not fully characterise the CGA profiles.

Ieri *et al.*using LC–MS^2 reported *cis* 5-CQA, *trans* 5-CQA **35** (dominant), a *p*CoQA and a CSA in bilberries (*V. myrtilus*), whereas lingonberries (*V. vitis-idaea* L.) contained 4-CQA and 5-CQA at modest concentration with a novel caffeoyl-arbutin dominating.*(441)* In addition to the two CQAs Mane *et al.*using LC–MS^2 subsequently reported a CSA in a commercial lingonberry extract. *(442)* An extensive study employing UPLC–TOF-MS compared the composition of the leaves of *V myrtillus* L., *V. vitis-idaea* L. and their hybrid *Vaccinium × intermedium* Rothe L. This study revealed four CQA, including *cis* and *trans* 5-CQA, four *p*CoQA, one FQA and a CSA, but these could not be assigned at the regio-isomeric level.*(443)* Bujor *et al*. using LC–MS^2 analysed the leaves, stems and fruit of *V. myrtillus* and reported a 5-CQA-4-glucoside, 5-CQA confirmed with a standard, *cis*-5-CQA, *cis*- and *trans*-5-*p*CoQA and a CSA plus several incompletely characterised putative acyl-quinic acids, as follows. Four components with M_r = 708 and several fragments characteristic of CQA but a λ_{max} =282 were tentatively thought to be CQA dimers in which the cinnamic acid side chain conjugation had been lost. Two components with M_r = 706 and λ_{max} = 322 were thought to be related to the foregoing.*(444)*

Ecuadorean montiño berries, *V. floribundum* Kunth, contain 3-CQA, 5-CQA and a CSA,*(445)* and a more thorough study of bluberries (*V. corymbosum*) has identified two malo-CQA and one malo-diCQA only in the variety Legacy, but these were not characterised to regio-isomer level.*(446)* Kim *et al*. reported that 5-CQA was present in the leaves of *V. corymbosum* in the range 37 to 76 g/kg dry basis depending upon variety, but much higher concentrations than found in the fruits,*(447)* and 3-CQA, 5-CQA and an FQA have been reported in the fruits analysed by LC–QTOF-MS.*(448)* Feng *et al*. using a LC–quadrupole ion trap-MS^2 reported 5-CQA, two malonoyl-CQA and an additional putative late-eluting CGA with M_r = 434 in the fruit and leaf of *V. glaucoalbum*. There are reports also of two incompletely characterised pCoCQA in some poorly defined Blueberry cultivars.*(449)*

Li *et al*. using LC–MS^2 reported that the predominant polyphenols in *V. ashei* leaves were 3-CQA **33**, 5-CQA, 3,4-diCQA and 3,5-diCQA,*(450)* but it is not clear whether or not they are using the IUPAC numbering and these assignments must be viewed as tentative. Stefkov *et al*. using LC–MS^2 reported in *V. myrtillus* fruits 3-CQA, 5-CQA, an incompletely characterised *p*CoQA and FQA, plus a second FQA that yielded *m/z* 179 and *m/z* 161 at MS^2,*(451)* clearly indicating that it was a methyl CQ.

Feng *et al*. using a LC–quadrupole ion trap-MS^2 reported 5-CQA, two malonoyl-CQA and an additional putative late-eluting CGA with M_r = 434 in the fruit and leaf of *V. glaucoalbum*.

4.4.34.4. Lecythidaceae family

Pontes *et al*. screened 22 Brazilian species for CGA and failed to find 4-CQA and 5-CQA of in the peel, pulp, or seeds of *Couroupita guyanensis*, while detecting one or both in 18 other species.*(165)*

4.4.34.5. Primulaceae family

Llorent-Martinez *et al*. using LC–MS could not detect any CGA in leaf extracts from *Heberdenia excelsa*.*(433)*

4.4.34.6. Sapotaceae family

Manilkara species: Ma *et al.*analysed the fruit of *Manilkara zapota* (Sapodilla) and characterized two novel CGA, methyl 4G-5CQ and 4G-5CQA, in addition to the previously reported 5-CQA and methyl 5-CQ.*(452)*

4.4.34.7. Theaceae family

The Theaceae is a family of complex and uncertain taxonomy, including the genus *Camellia* to which tea belongs. Leaves of *Camellia sinensis* var. *sinensis* and var. *assamica* characteristically contain theogallin or 5-GQA. They also contain 3-CQA, 4-CQA, 5-CQA, 5-*p*CoQA, 4-*p*CoQA, 3-*p*CoQA, 3-GQA and 4-GQA.*(157, 453-457)* The relative intensity of CQA and *p*CoQA varies with cultivar,*(457)* but note that Fang *et al*. did not use IUPAC numbering. According to Marques and Farah 4-CQA dominates this group in both green and black tea.*(35)* 5-GQA has also been reported in *Camellia irrawadiensis*.*(458)*

Camellia crassicolumna var. *multiplex* has been reported to contain 5-CQA, 5-GQA, this latter at a greater concentration than *C. sinensis*, and the novel 4-CcisQA, in which the hydroxyl at C5 is axial, at a greater concentration than 5-CQA. It was suggested that a GQA epimer might also be present, and caffeine was not detected.*(459)* The identification in 4-CcQA by NMR spectroscopy had previously been reported,*(460)* but in the absence of coupling constants it is not possible to distinguish this component from 4-CQA.

ERICALES SUMMARY

Actinidiaceae: CQA, pCoQA, FQA, diCQA but single report

Clethraceae: Profiled and negative for CGA, but only a single report

Ericaceae

Anthopterus single report CQA

Cavendihii single report CQA

Macleania single report CQA

Rhododendron CQA pCoQA with significant variation at cv level

Sphyrospermum single report CQA

Vaccinium extensively studied CQA, pCoQA, FQA, CSA and malonoyl

Gaultheria – unclear poor quality reports

Arbutus GQA and GSA

Lecythidaceae: single report negative CQA

Primulaceae: single report negative CGA

Sapotaceae: single report of novel G-CQA and CQA

Theaceae: CQA, pCoQA, GQA

More profiling required to assess the distribution of GQA and especially the unusual CGQA

4.4.35. ORDER AQUIFOLIALES

4.4.35.1. Aquifoliaceae family

Some accounts consider the Aquifoliaceae to consist of a single genus, *Ilex*, containing some 600 species, better known as Holly. In this family the emphasis has been on Yerba maté, or matte, a traditional South American beverage, now popular all over the world, and Kudingcha, a beverage which is a popular in China and some other countries of Southeastern Asia (e.g., Singapore, Malaysia and Vietnam).

Maté is prepared from the leaves primarily of *Ilex paraguariensis* which has long been known rich in CQA and diCQA.*(461)* The leaves of *I. brevicuspis* Reisseck, *I. theezans* C. Martius ex Reisseck, *I. dumosa* Reisseck var. *dumosa, I. microdonta* Reisseck, *I. pseudobuxus* Reisseck, *I. taubertiana* Loes and *I. argentina* Lillo have a similar profile but much smaller content of CGA,*(462)* as do the leaves of *I. brasiliensis*.*(463, 464)*

In a much more exhaustive study of commercial maté Jaiswal *et al*. using LC–ion trap-MS identified 3-CQA, 4-CQA, 5-CQA, 3-FQA, 4-FQA, 5-FQA, 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, methyl 3-CQ, methyl 5-CQ, 1,3-diCQA, 3,4-diCQA, 4,5-diCQA, 1,4-diFQA, 4,5-diFQA, 3,4,5-triCQA, 3,4diC-5FQA, 3-CSA, 4-CSA, 3,4-diCSA, 3,5-diCSA, 3,4,5-triCSA, 1C-3FQA, 3F-5CQA, 4F-5CQA, 4C-5FQA, 3C-5*p*CoQA, 4*p*Co-5CQA, 4C-5*p*CoQA, 3C-4SiQA, 3Si-5CQA and 4Si-5CQA in green dried and roasted leaves of yerba maté. The authors cautioned that 1C-3FQA might be an artefact of the work-up procedure. Two novel CQA and a novel CFQA were detected and tentatively identified by their disitinctive fragmentation as acyl derivatives of a quinic acid epimer, but the isomer was not fully characterised. *(465)* These observations have been largely confirmed by de Souza *et al*.,*(466)* and Dugo *et al.*,*(467)* who also reported 1-CQA and 1,5-diCQA. The dominant CGA in the beverage have been quantified by Peres *et al*. *(468)* and Marques and Farah.*(35)* Souza *et al*. provide quantitative data for the three CQA and three diCQA in the whole plant, leaves and stems of *I. paraguraiensis*.*(469)*

Kudingcha is prepared from the leaves of several species including *I. kudingcha* C.J. Tseng, *I. latifolia* Thunb and *I. cornuta* Lindl. ex Paxt. *I. latifolia* is rich in 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA.*(470)* Thuong *et al*. report in addition methyl 4-CQ, methyl 3,4-diCQ, methyl 3,5-diCQ and methyl 4,5-diCQ plus *n*-butyl 3,5-diCeQ.*(471)* At least two diCQA have been reported in *I. hainanensis*.*(472)* Jiang *et al*. have reported methyl 3,4-diCQ and methyl 3,4,5-triCQ in *I. pubescens*.*(473)* A detailed LC–ion trap-MS study of Kudingcha by Che *et al* has located 68 chlorogenic acids which can be summarised as follows: three *p*CoQAs, four CQAs, three FQAs, three QA glycosides, seven *p*CoCQAs, seven diCQAs, nine CQA glycosides, nine CFQAs, six triCQAs, nine diCQA glycosides, five CQA diglycosides, and three CFQA glycosides. Standards were available for 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA and the remaining 62 components were assigned tentatively by their fragmentation pattern at MS^3 for the six major components but only at MS^2 for the remainder.*(474)* The minor components included 1-acyl-diCQA and presumably some *cis* isomers. Targetted MS^3 and MS^4 fragmentations are necessary to confirm some of these assignments.

Jaiswal *et al*. using LC–ion trap-MS have detected 4-CQA, 5-CQA, 5-FQA, 5-*p*CoQA, 3,5-diCQA, 4,5-diCQA, 4F,5CQA, 5-ProtQA, 5-*O*-(4'-*O*-caffeoyl glucosyl)quinic acid and 5-*O*-(3'-*O*-caffeoyl glucosyl)quinic acid in the leaves of *I. glabra* L. Gray.*(475)*

Llorent-Martinez *et al*. using LC–ion trap-MS analysed extracts prepared from the leaves of *I. perado* ssp. *perado* endemic to the laurel forest of Madeira.*(433)* They reported three CQA, two of which were characterised as 3-CQA and 5-CQA. The third appears to be *cis* 3-CQA by its early elution and fragmentation identical to 3-CQA.

Four diCQA were observed, including 3,4-diCQA, 3,5-diCQA and 4,5-diCQA which were confirmed with commercial standards, plus a fourth isomer that eluted later, gave an MS^3 base peak at *m/z* 173 and which was not fully characterised. It seems unlikely that the fourth isomer is 1,4-diCQA because it lacks its characteristic fragment ions. However, its fragmentation is rather different from that seen for the other three isomers making it unlikely that it is a *cis*-diCQA, thus raising the possibility that it is derived from a quinic acid epimer similar to that reported by Jaiswal *et al*. in commercial maté.*(465)* 4-*p*CoQA and 3*p*Co-4CQA were also detected.

Eight CGA, a mixture of CQA and diCQA, including 3,5-diCQA, have been reported in *I. kaushue*.*(476)*

AQUIFOLIALES SUMMARY

Extensively studied and profiled, significant content and range of CGA in the leaves.

Ilex: CQA, pCoQA, FQA, diCQA diFQA CFQA, pCoCQA, CSiQA including some 1-acyl. CSA diCSA triCSA

Good evidence for quinic acid epimer and novel protQA

4.4.36. ORDER ASTERALES

4.4.36.1. Asteraceae Family

The Asteraceae, formerly Compositae, is considered to be the largest family of flowering plants and contains over 1600 genera and over 24,000 species,*(477)* some of which are used for food, as flavourings, or in traditional medicine. The classification is complex with seven subfamilies, but data for the CGA content are available only for four, Asteroideae, Carduoideae, Cichorioideae and Mutisioideae.*(477)*

4.4.36.1.1. MUTISIOIDEAE Subfamilly

4.4.36.1.1.1. Mutisieae Tribe (254 spp)

Ainsliaea species: It has been reported by Nugroho *et al.* that *Ainsliaea acerifolia* contains 3-CQA 7.0 g/kg, 5-CQA 6.2 g/kg, 3,4-diCQA 3.4 g/kg, 3,5-diCQA 3.9 g/kg, 4,5-diCQA 2.2 g/kg and 3,5-diCepiQA 0.8 mg/kg but 3-*p*CoQA was not present.*(478)* Note that, as discussed above under *Aster scaber,* these quantitative data may not be reliable because the calibrants were impure, and there is some doubt whether it is 3,5-diCepiQA or 3,5-diCmucoQA.

Wang and Liu, and Chen *et al*. isolated 3,5-diCQA and 4,5-diCQA from *A. fragrans (479, 480)* and a more recent study reported 1,5-diCQA in *A. acerifolia* and *A. apiculata,(481)* but neither makes any reference to the *Epi*QA derivative reported by Nugroho *et al.* However, Kim *et al*. analysing *A. acerifolia* reported 3-CQA, 3,4-diCQA, 4,5-diCQA, methyl 4,5-diCQA plus 3,5-di*Cepi*QA and methyl 3,5-di*Cepi*Q, having isolated and characterised the acyl *epi*-quinic acids by NMR.*(482)* Note that these authors did not use IUPAC numbering. Note also that the ^{3}J coupling constant for H4 (3.0, 9.0 Hz) is not consistent with an acyl *epi*-quinic acid and reminiscent of (–)-quinic acid as discussed in Part 2 of these notes.

4.4.36.1.2. CARDUOIDEAE sub-family

4.4.36.1.2.1. Cardueae tribe (Cynareae tribe) (2500 spp)

Arctium species: Burdock (*Arctium lappa* L.) roots are used in folk medicine and as a vegetable in Asia, especially in Japan, Korea and Thailand. Maruta *et al*. reported 1,5-diCQA; 1,5diC-3SucQA 1,5diC-4SucQA, 1.5diC-3,4diSucQA and 1,3,5triC-4SucQA in the roots of *A. lappa*.*(483)* Lin *et al*. using LC–MS^2 with NMR-characterised in-house isolated standards and surrogate standards such as green coffee extract and artichoke extract made a thorough study of the CGA in burdock roots (*Arctium lappa*). In addition to the CGA reported by Maruta *et al.* they reported 1-CQA, 3-CQA, 4-CQA, 5-CQA, 1,3-diCQA, 1,4-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3,4,5-triCQA, 1,3,5-triCQA and several uncharacterised CGA, some of which might have a *p*-coumaroyl substituent.*(110)* Saleem *et al*. reported four incompletely characterised CQA and three incompletely characterised diCQA,*(484)* and da Silva *et al*. reported two CQA, three diCQA, one diC-sucQA and a triCQA in the roots of *A. lappa*.*(485)* Haghi *et al*. reported 3-CQA, 4-CQA, 5-CQA (dominant), 1,3-diCQA (minor) and 1,5-diCQA (dominant) in the leaves and roots of wild and commercial *A. lappa*.*(486)* Carlotto *et al*. using LC–ion trap-MS^n reported all four CQA, 1,3-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and two incompletely characterised maloyl-diCQA,*(487)* but did not use IUPAC numbering.

Jaiswal *et al. (488)* using LC-ion trap-MS confirmed the presence of the previously reported CGA and made some additional discoveries, as follows, including the first observations of malic acid-containing CGA: 3,4-diCQA, 1,5diC-4FumQA, 1,5diC-3MalQA, 1,4diC-3MalQA , 1,5diC-4MalQA, 1,5diC-3Fum-4SucQA, 1Fum-3,5diC4-SucQA, 3Suc-4,5diCQA or 1Suc-3,4diCQA, 1,3diC-5FumQA or 1Fum-3,5diCQA, 1,3diC-4,5diMalQA or 1,4diMal-3,5diCQA and 1,5diC-3Suc-4MalQA. Liu *et al*. analysed burdock root and seeds, confirming the observations made by Jaiswal *et al*. and providing quantitative data. The major CGA in seeds were 5-CQA (13.2 g/kg), 1,3-diCQA (20.7 g/kg) and 1,5-diCQA (8.6 g/kg), whereas in the root 5-CQA (5.3 g/kg), 1,5diC-3MalQA (7.6 g/kg) and 1,5diC-3SucQA (6.0 g/kg) dominated.*(489)* 5-CQA **35** was used as the calibrant but, because the authors do not report any correction for the molecular mass of the individual CGA, it is likely that those components containing two caffeic acid residues have been over-estimated by *ca* 40%.

Tousch *et al*. analysed a dried burdock root extract in which 1,5diC-4MalQA accounted for 44% of the total CGA content. CGA were characterised by LC–MS (accurate mass) and by comparison with surrogate standards including coffee, maté and artichoke. Twenty-seven CGA were detected and 19 characterised to regio-isomer level, including all four CQA, 1,4-diCQA, 1,5-diCQA, 3,5-diCQA, 1,3,5-triCQA, 4Mal-1,3,5-triCQA, 1,5diC-3SucQA, 1,5diC-4SucQA, 1.5diC-3,4diSucQA, 1,3,5triC-4SucQA, 1,5diC-3MalQA, 1,4diC-3MalQA, 1,3diC-4,5diMalQA, 1,4diMal-3,5diCQA, 1,5diC-3Suc-4MalQA. The partially characterised CGA included two diC-Suc-MaloQA, i.e at least one not previously reported, two additional diMal-diCQA, one additional Mal-triCQA and one additional Suc-triCQA.*(490)*

According to the English abstract Bai *et al* reported 1,5-diC-3-(malic acid methylester)quinic acid, methyl 3,4-diCQ, methyl 3,5-diCQ, methyl 4,5-diCQ and methyl 5-CQ in *A lappa*,*(491, 492)*

Jiang *et al.* isolated and characterised by NMR three novel tri-acyl quinic acids from the roots of *A lappa* L. as 1-(5-hydroxypentanoyl)-4,5-diCQA, 1-(methyl maloyl)-4,5-diCQA and 1-(methyl succinoyl)-4,5-diCQA.*(493)*,

Carduncellus species: Shabana *et al*. isolated 3,5-diCQA from *Carduncellus eriocephalus* Boiss. var. *albiflora* Gauba.*(494)* Some authorities consider this species to be synonymous with *Carthamus eriocephalus (Boiss.) Greuter* in the tribe Cardueae *syn.* Cynareae.

Carduus species: Li *et al.* using LC–QTOF-MS and commercial standards identified 3-CQA, 4-CQA and 5-CQA, plus 4-*p*CoQA and 5-*p*CoQA in the Tibetan herb, *Carduus acanthoides*. Two additional CQA, four additional *p*CoQA and two FQA were also observed, *(495)* but note that one of the putative FQA produced a prominent ion at *m/z* 179 and might be a methyl CQ.

Carlina species: Jaiswal *et al*. using LC–ion trap-MS reported 3-CQA, 4-CQA, 5-CQA, 3-FQA, 4-FQA, 5-FQA, 3-*p*CoQA, 5-*p*CoQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3C-4FQA and 4F-5CQA in the leaves of *Carlina acaulis*. An epimeric CQA was also present, identical to that found in *Helianthus tuberosus*, but different from that in *Rudbeckia hirta*. *(496)*

Centaurea secies: Petersen *et al*. reported 5-CQA in *Centaurea macrocephala*.*(20)* Flamini *et al*. reported methyl 3-CQ, 5-CQA and 3,4-diCQA in the aerial parts of *C. bracteata*,*(497)* but it is not known which numbering system was used.

Cirsium species: Abbet *et al*. reported 5-CQA, methyl 3-CQ and methyl 3-*p*CoQ in *Cirsium spinosissimum*.*(498)* Nugrohu *et al*. have reported 5-CQA and 3,5-diCQA in *Hemisteptia lyrata*,*(499)* which is also known as *Cirsium lyratum* Bunge. According to the abstract Nugroho *et al*. reported '*chlorogenic acid*' and 3,4-diCQA in *C. setidens*,*(500)* but it is not clear which numbering system was used.

Cnicus species: Jaiswal *et al*. using LC–ion trap-MS reported 5-CQA, 3-FQA and 5-FQA in the leaves of *Cnicus Benedictus*, but did not detect any other CGA.*(501)*

Cynara species: 1,3-diCQA and 1,5-diCQA have been reported in the leaves of cardoon, *C. cardunculus*,*(502)* and 1,5-diCQA has been reported in the heads of wild cardoon from Crete, but no CGA were found in wild cardoon from Sicily or in the cultivated variety Altilis.*(503)* An LC–ion trap-MS analysis of the leaves of commercial *C. cardunculus* var. *scolymus* (artichoke) and wild *C. cardunculus* var. *ferocissima* (Madeira cardoon) from Madeira recorded 3-CQA, 5-CQA, 1,5-diCQA and 3,5-diCQA in both plants. A third late-eluting incompletely characterised CQA (possibly *cis* 5-CQA), 5-FQA, 1,3-diCQA, 3,4-diCQA, 4,5-diCQA **and** a CQA-diglycoside were found only in artichoke.*(504)*

A UHPLC–ion trap-MS analysis detected 1-CQA, 3.CQA, 5-CQA, 1,3-diCQA, 1,4-diCQA and 1,5-diCQA. A 1.5diC-sucQA and two isomers thereof (one of which is possibly 4,5diC-sucQA) plus a diC-disucQA were also detected *Cynara cardunculus* L. var. *altilis* (DC),*(505)* this latter CGA having a distinctly different fragmentation to the 1,5diC-3,4disucQA identified tentatively by Jaiswal *et al*. in Burdock.*(488)* Ramos *et al.* provide extensive quantitative data obtained using commercial 5-CQA and 1,5-diCQA as calibrants. The dominant CGA wre 5-CQA (15–21 g/kg), 1,5-diCQA (14–15 g/kg) and 1,5-diC-sucQA (11–12 g/kg as 1,5-diCQA equivalents) in the stalks, capitula and bracts, these being much richer than the leaves.*(505)*

Schütz *et al*. using LC-ion trap-MS quantified CGA in artichoke heads (Green Globe), pomace and juice, reporting for heads as follows: 1-CQA (0.8 g/kg), 3-CQA (0.2 g/kg), 4-CQA (0.1 g/kg), 5-CQA 3.1 g/kg, 1,3-diCQA (0.09 g/kg), 1,5-diCQA (3.9 g/kg), 3,4-diCQA (0.17 g/kg|), 3,5-diCQA (0.76 g/kg), 4,5-diCQA (0.12 g/kg) and what appears to be 1,4-diCQA (0.24 g/kg). The same profile was reported in the pomace and juice.*(506)* In contrast, Zhu *et al*. isolated the dominant diCQA from *C. scolymus* flower heads and characterised them as 1,3-diCQA, 3,5-diCQA and 4,5-diCQA.*(507)* In addition to CQA and diCQA Pereira *et al*. using LC–ion trap-MS^2 have reported 3-*p*CoQA, 4-*p*CoQA and *cis* and *trans* 5-*p*CoQA in *C. scolymus*.*(508)*.

The heads of Cimiciusa variety artichokes contained 71 mg/kg 1,5-diCQA, whereas Tondo di Paestum contained 5-CQA and 1,5-diCQA (0.95 g/kg and 0.33 g/kg, respectively) and Violetto di Sicilia contained 1.98 g/kg 5-CQA and 0.54 g/kg 1,5-diCQA plus a trace of 1-CQA.*(503)* Schütz *et al*. and Pandino *et al*. utilised commercial 5-CQA and 1,3-diCQA as calibrants but the response factors were not reported. All four CQA and all six diCQA were found in canned artichokes.*(509)*

Using LC–ion trap-MS Jaiswal *et al.* reported 1-CQA, 3-CQA, 5-CQA, 5-FQA, 5-*p*CoQA, 1,4-diCQA, 1,5-diCQA, 3,5-diCQA, 1*p*Co-5CQA and 1,5diC-3SucQA from the leaves of *C. scolymus*. *(501)*

Pandino *et al.* have demonstrated elegantly how not only the content, expressed as 5-CQA and 1,3-diCQA equivalents, but also the profile and relative content of CGA in the receptacle of *C. scolymus*, particularly 5-CQA and 1,5-diCQA, vary with time of harvest. 1-CQA, 4-CQA and 3,5-diCQA were only detectable at certain discrete periods. The equivalent data were also presented for floral stem, leaves and bracts. In all tissues 1,5-diCQA always dominates, followed by 5-CQA, but by far the most complex profile (four CQA and four diCQA) is found in the floral stem in March and April.*(7)*

Dolomiaea species: Wei *et al*. reported methyl 5-CQ and methyl 3,4-diCQ in *Dilomiaea soulei*,*(510)* but it is not known what numbering system was used.

Echinops species: Jaiswal *et al*. using LC–ion trap-MS reported 3-CQA, 5-CQA, 5-FQA, 5-*p*CoQA, 3,5-diCQA, 4,5-diCQA, 3C-5*p*CoQA and 1*p*Co-3CQA in the leaves of *Echinops humilis*. *(501)* Abdallah *et al.* reported 1,3-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA, characterised by NMR, in the aerial parts of *E. galaensis*.*(511)* Note that the original publication did not use the IUPAC numbering.

Leuzea species: See *Rhaponticum*.

Onopordum species: Verotta *et al*. extracted *Onopordum Illyricum*, a plant used as a salad vegetable, and by NMR characterisation reported 1,5-diCQA, 3,5-diCQA and a diC-sucQA tentatively assigned as 1suc-3,5diCQA. Alkaline hydroclysis released 3,5-diCQA and molecular mechanics modelling placed the succinoyl residue axial with its distal carboxyl hydrogen bonded to the 5-O-caffeoyl carbonyl moiety. 5-CQA was clearly present, plus two further diCQA and a second diC-sucQA which were detected by LC–MS but not fully characterised.*(512)*

Rhaponticum species: Some authorities consider *Rhaponticum* to be synonymous with *Leuzea*. Skala *et al*. reported 3-CQA, 4-CQA and 5-CQA, 1,3-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA, plus 1,4,5-triCQA and two incompletely characterised triCQA derivatives (M_r = 794),*(513)* possibly tricaffeoyl-maloyl-QA, in the roots of *Rhaponticum carthamoides* (Maral root).

Saussurea species: 5-CQA and 1,5-diCQA have been quantified in several species and show marked variation with geographic origin. *Saussurea laniceps* contained 2.3–7.0 g/kg 5-CQA and 0.9–3.0 g/kg 1,5-diCQA.*(514) S. medusa* (0.02–0.35 and 0.1–0.68 g/kg) *(514)* and *S. 73haracteris* (3.7–14.4 g/kg and 0.5–1.7 g/kg) *(515)* and if extracted in water there is an increased tendency for 1,5-diCQA to convert to 1,3-diCQA.*(516)* Quantification used commercial 5-CQA and a purified isolate of 1,3-diCQA, but the response factors were not reported. Yi *et al*. subsequently reported 1,5-diCQA (dominant), 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *S. laniceps*.*(517)*

It has been reported by Nugroho *et al.* that *S. grandifolia* contains 3-*p*CoQA 16.6 g/kg, 3-CQA 5.5 g/kg, 5-CQA 14.4 g/kg, 3,4-diCQA 10.6 g/kg, 3,5-diCQA 7.7 g/kg but 4,5-diCQA and 3,5-diCepiQA were not present.*(478)* Note that, as discussed above under *Aster scaber,* these quantitative data may not be reliable because the in house prepared and characterised calibrants were impure, and there is some doubt whether it is 3,5-diCepiQA or 3,5-diCmucoQA, and whether either assignment is correct Nugroho *et al*. using commercial standards subsequently repoted only 5-CQA and 3,5-diCQA in *S grandifolia,(518)* and Kim *et al.* reported 1,5-diCQA in *S. grandifolia* but neither group referred to the presence of any other CGA.*(481)*

S. stella, *S. odontolepis*, *S. gracilis* and *S. ussuriensis* also contain 1,5-diCQA *(481, 519)* and *S. 73haracteris* contains 3-CQA, methyl 4CQ and methyl 5CQ.*(520, 521)*

A more extensive ion trap-MS analysis of *S. 73haracteris* revealed 3-CQA, 4-CQA, 5-CQA, 1,3-diCQA, 1,4-diCQA, 1,5-diCQA, 4,5-diCQA, 1,5diC-3sucQA, 1,5diC-4sucQA and 1,5diC-3,4disucQA, plus one diC-MalQA, one diC-sucQA and two triC-MalQA that were incompletely characterized.*(522)* Subsequent studies of CGA isolated from cultured cells of *S. 73haracteris* led to the identification by NMR and LC–MS of the previously reported 1-CQA, 3-CQA, 4-CQA, 5-CQA, 3-FQA, 5-*p*CoQA, 1,3-diCQA, 1,4-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and 1,5diC-3MalQA plus the novel 3,5-diC-1-(2-O-caffeoyl-4-maloyl)-QA and 1,3-diC-5-(2-O-caffeoyl-4-maloyl)-QA,*(523)* and 1,3-diC-5-(1-methoxyl-2-O-caffeoyl-4-maloyl)-QA.*(524)*

Serratula species: Lech *et al*. using LC–MS^2 reported three CQA and three methyl CQ in the coloured extract from *Serratula tinctoria* but it is possible that the methyl esters were artefacts of the extraction procedure using acidified methanol.*(2)*

Silybum species: LC–ion trap-MS^2 analysis of extracts of *Silybum marianum* (Milk Thistle) yielded 3-CQA, 5-CQ 3-*p*CoQA, *cis* and *trans* 5-*p*CoQA and 3,5-diCQA.*(508, 525)*

Synurus species: Kim *et al*. have reported 1,5-diCQA in *Synurus excelsus* flowers,*(481)* but note that in the original text the name is misprinted as *Synulus*.

4.4.36.1.3. CICHORIOIDEAE subfamily

4.4.35.1.3.1 Arctotideae tribe

Gazania species: According to the abstract Soliman *et al*. analysed the flowers and other aerial parts of *H. bracteatum* (Vent.) Andrews, *Gazania nivea* DC. and *Dimorphotheca ecklonis* DC. and reported 3-CQA, 1,5-diCQA, 3,5-diCQA, 1,4,5-triCQA, methyl 3,4-diCQ and methyl 3,5-diCQ,*(526)* but it is not known which numbering system was used or which compounds were in which species.

4.4.36.1.3.2 Cichorieae (Lactuceae) tribe (1400+ spp)

Andryala species: Gouveia *et al.* have analysed extracts of *Andryala glandulosa* ssp. *varia* and reported a novel early eluting CGA (M_r = 500) which produces an MS^2 base peak at *m/z* 191 plus several secondary peaks including *m/z* 353, which they assigned as a *p*Co-CQA in which a *p*-coumaric acid residue is attached depsidically to a caffeic acid residue which is in turn attached to C5 of the quinic acid, i.e. 5-(*p*Co-C)QA. This is the first report of a depsidic hydroxycinnamic acid derivative. 5-CQA, 3,5-diCQA 4,5-diCQA and a diC-sucQA were also present, with 3,5-diCQA dominant at *ca* 0.6 g/kg dry basis plus 5-CQA **35** at *ca* 0.2 g/kg dry basis.*(527)* However, the calibrants were not defined

Cicerbita species: Fusani and Zidorn reported 5-CQA and 3,5-diCQA in the edible shoots of *Cicerbita* (L.) Wallroth.*(528)*

Cichorium species: *Cichorium endivia* and *C. intybus* are leafy vegetables that can be used raw for salad or cooked. Goupy *et al.* reported two CSA in *C. endivia* L. cv. Geante Maraichere) leaves.*(529)* Mascherpa *et al*. using LC–MS^2 analysed *C.* endivia var. crispum and var. *latifolium* and reported significant differences in profile. 3-CQA was detected only in var. *crispum* but 5-CQA in both. They also reported *cia* and *trans* 5-FQA, 1,3-diCQA, 1,4-diCQA, 3,4-diCQA and 3,5-diCQA but the phrasing of the text makes their distribution in the two varieties unclear.*(530)* The assignment of the four diCQA is questionable because all eluted very close together (69.9 to 72.2 min), with the fragmentation clearly indicating two 4-acyl and two that are not 4-acyl-quini acids. The fragmentation is very similar to that previously observed in the hierarchical keys developed by Clifford *et al*., but there are small differences that also raise some uncertainty.

Jaiswal *et al*. using LC–ion trap-MS detected 3-CQA, 5-CQA, 5-FQA, 5-*p*CoQA, 3,5-diCQA, 1C-3FQA, 3C-5*p*CoQA and 1*p*Co-3CQA in the leaves of *C. intybus*.*(501)* A rather superficial study of the leaves of *C. intybus* from Anatolia using LC–quadrupole-MS reports 4-CQA as the main CGA, accompanied by 5-CQA,*(531)* but it is uncertain whether or not the IUPAC numbering has been used.

Petropoulos *et al*. using LC–ion tap-MS^3 reported 5-CQA in the saline-tolerant *C. spinosum*.*(532)* Note that these authors reported an atypical fragmentation having used 5 Kv ionisation potential rather than 3.5 Kv used to prepare the hierarchical keys. In a more extensive study Brieudes *et al*. reported 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA (tentative) and 4,5-diCQA in *C. spinosum* (and *C. intybus*) but made no reference to any 1-acyl-quinic acids.*(533)* These

authors appear to be confused about the quinic acid numbering, describing 3-CQA as '*chlorogenic acid*' but assigning that as the first eluting CQA, followed by 5-CQA ('*neochlorogenic acid*') and 4-CQA ('*cryptochlorogenic acid*').

Tong *et al*. characterised 3,5-diCQA by NMR *(534)* and identified tentatively 5-CQA, 1,3-diCQA, 3,4-diCQA and 4,5-diCQA in the *n*-butanol extract of *C. glandulosum* Boiss. et Huet by positive ion LC–MS.

Crepidiastrum species: Lee *et al*. reported 3,5-diCQA in *Crepidiastrum denticulatum* and made no reference to any other CGA.*(535)*

Crepis species: 5-CQA and 3,5-diCQA have been reported in the flowering heads of *Crepis capillaris* (L.) Wallr. and 14 other taxa.*(536, 537)*

Hedypnois species: Enke *et al*. using LC–MS reported 5-CQA and 3,5-diCQA in *Hedypnois cretica*.*(538)*

Hieracium species: Zidorn *et al*. were able to use 1,5-diCQA as an internal standard for quantitative analysis of the CGA in extracts from an extensive range of *Hieracium* taxa *sensu lato* (84 samples from 7s taxa belonging to 66 species) demonstrating elegantly that it is absent therefrom — 5-CQA, 3,5-diCQA *dominant) and 4,5-diCQA were present in all.*(539)* Petrovic *et al*. analysed the arial parts of *Hieracium gymnocephalum*, *H. suborienii*, *H. blecicii*, *H. coloriscapum*, *H. guentheri-beckii*, *H. naegelianum* and *H. rotundatum* and reported 5-CQA and 3,5-diCQA in all samples.*(540)*

Svehlikova *et al*. reported 5-CQA and 3,5-diCQA in the leaves of *Hieracium rohacsense*, *H. borsanum, H*. *ratezaticum* and *H*. *pseudocaesium*.*(541)* Zidorn *et al*. analysed the flowerheads of 84 samples of 76 taxa belonging to 66 species of *Hieracium*, all from central Europe, and reported a comparatively simple CGA profile consisting of 5-CQA, 3,5-diCQA (dominant) and 4,5-diCQA. Quantitative data were obtained using 1,3-diCQA as calibrant, which will have underestimated the 5-CQA **35** content. A PCA analysis that took account of CGA and flavonoid contents was able to discriminate between members of the subgenera *Hieracium* and *Pilosella*, but the differences were small and considered insufficient to require a split into two genera,*(539)* but the presence of 4,5-diCQA distinguished this species from *Crepis capillaris*.*(536)*

Hypochaeris species: Enke *et al*. using LC–MS reported 5-CQA and 3,5-diCQA in *Hypochaeris cretensis*, *H. 75haracte* and *H. laevigata*.*(538)* Zidorn *et al*. reported 5-CQA and 3,5-diCQA in eight samples of *H. radicata* with small amounts of 4,5-diCQA only in two of these.*(536)*

Ixeris species: According to the English abstract Liu *et al*. reported 1-CQA, 3-CQA and 4-CQA, 3-*p*CoQA, 5-*p*CoQA, 3-FQA, 4-FQA, 3,4-diCQA, and 3,5-diCQA in *Ixeris sonchifolia*.*(542)* The apparent presence of 1-CQA, but apparent absence of 5-CQA is sufficiently unusual to suggest that an incorrect assignment has been made. It is also unclear whether or not the authors used the IUPAC nomenclature.

Lactuca species: Jaiswal *et al*. using LC–ion trap-MS reported 5-CQA, 5-*p*CoQA and 3,5-diCQA in the leaves of *Lactuca sativa*,*(501)* exactly as reported by Ribas-Agusti *et al*. using LC–triple quadrupole-MS. Similarly, Luna *et al*. reported 5-CQA and 3,5-diCQA in *Romaine* lettuce,*(543)* as did Romani *et al*. in cv *Audran*.*(544)* None of these investigations located the corresponding *muco*-quinic acid derivative reported in *L. indica*.*(545)* However, as discussed in Part 2, the

correct assignment of 3,5-diacylQA from NMR data is problematic, and some doubt remains about the validity of this assignment.

An extremely detailed LC–QTOF-MS study of several *L. sativa* cultivars by Abu-Reidah *et al*. detected at least four CQA, three *p*CoQA, at least two diCQA and at least one *p*CoCQA but these were not characterised to regio-isomeric level.*(546)* Pepe *et al*. using LC–IT-TOF-MS reported one CQA, two FQAs and a CFQA in *L. sativa* L. var. *Maravilla de Verano*. They did not report any diCQAs.*(547)* However, the putative FQAs gave a prominent fragment ion at *m/z* 179 suggesting that they are methyl CQs. There are insufficient data to fully characterise the putative CFQA, but this might be a methyl diCQ.

Stojakowska *et al*. reported 5-CQA and 3,5-diCQA by matching to 'in house' or commercial standards in the roots of *L. tuberosa*.*(548)*

Kim *et al*. reported 3-CQA, 5-CQA, 5-*p*CoQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and 3,5-diCmucoQA in *Lactuca indica*,*(549)* and isolated and purified all seven of the reported CGA. These seven isolates were used as standards by Nugroho *et al.* for their studies on Asteraceae, but note, as discussed above, in two papers Nugroho *et al.* refer to these seven isolates as including 3,5-diCepiQA rather than 3,5-diCmucoQA. Subsequently, Park *et al*. analysed seven cultivars of *L. sativa* L. and reported 3,4-diCQA (2.72–4.78 g/kg) and 3-*p*CoQA (8.07–23.26 g/kg).*(550)*

Leontodon species: Zidorn isolated 3,5-diCQA from *Leontodon hispidus*, and this compound was subsequently quantified in 13 samples of *L. helveticus*, 19 samples of *L. autumnalis*, and 61 samples of *L. hispidus*, with comparatively little variation associated with the altitude at which the plants were growing.*(551)* The same group reported 5-CQA and 3,5-diCQA in *L. rosani*, *L. siculus* and *L. villarsii*.*(538)* Similarly 5-CQA and 3,5-diCQA were reported in *L. croceus, L. duboisii, L. montaniformis, L. montanus* subsp. *melanotrichus*, *L. montanus* subsp. montanus, *L. pyrenaicus* and *L. rilaensis*.*(552)*

Picris species: Enke *et al*. using LC–MS reported 5-CQA and 3,5-diCQA in *Picris hieracioides* subsp. *villarsii*.*(538)*

Podospermum species: Zidorn *et al.* isolated from *Podospermum laciniatum* the novel 1,3,5-tri-dhCQA and characterised it by NMR,*(553)* and reported 5-CQA and 3,5-diCQA in *P. canum* and *P. laciniatum*.*(554)*

Prenanthes species: Enke *et al*. using LC–MS reported 5-CQA and 3,5-diCQA in *Prenanthes purpurea*. *(538)*

Reichardia species: Recio *et al.* reported 5-CQA and two incompletely characterised diCQA in several *Reichardia* spp.*(555)*

Rhagadiolus species: Krimplstatter *et al*. using LC–MS reported 5-CQA and 3,5-diCQA in *Rhagadiolus stellatus* Gaertn., a Mediterranean food plant. The structure shown is non-IUPAC but the text states that identification was made '*in comparison with authentic reference compounds using an established system*' and it remains uncertain whether or not it should be 3-CQA rather than 5-CQA.

Robertia species: Enke *et al*. using LC–MS reported 5-CQA and 3,5-diCQA in *Robertia taraxacoides*.*(538)*

Scorzonera species: Zidorn *et al.* reported that 5-CQA and 3,5-diCQA were present in all ten *Scorzonera* spp. investigated (*S. aristata, S. austriaca, S. baetica, S. hispanica, S. aff. hispanica, S. humilis, S. parviflora, S. purpurea, S. rosea* and *S. trachysperma*).*(554)* They later reported 5-CQA, 4,5-diCQA and 3,5-diCQA in the aerial parts of *S. aristata* but only 3,5-diCQA in the sub-aerial parts.*(556)* In a subsequent LC–MS^n study this group reported that 3-CQA, 4-CQA, 5-CQA, 1,5-diCQA, 3,5-diCQA and 4,5-diCQA were present in the aerial and sub-aerial parts of *S. hispanica*. 5-CQA and 3,5-diCQA were dominant.*(557)* Tsevegsuren *et al.* identified by NMR 1,5di-dhC-3FQA (feruloyl-podospermic acid A) and tentatively 1,4di-dhC-3FQA (feruloyl-podospermic acid B) in the aerial parts of *S. divaricata* and *S. pseudodivaricata*,*(558)* but only 3,5-diCQA and 4,5-diCQA were reported in *S. aristata*.*(556)* Subsequently, 3-FQA, *n*-butyl 3FQ, 1,4diF-3dhCQA, 1F-4dhCQA, 3,5-diFQA, 1F-3dhCQA and 1F-5dhCQA were also isolated from *S. divaricata*.*(559)* Sari using accurate mass and NMR spectra reported 5-CQA, 4-CQA, methyl 5-CQ, 3,5-diCQA, 4,5-diCQA and methyl 4,5-diCQ in both *S. veratrifolia* Fenzl and *S. latifolia* (Fisch and Mey.) DC plus 5-CQA and 4-CQA in the former.*(560, 561)* Wang *et al*. prepared extracts of the aerial parts of *S. radiata*, a Mongolian species used medicinally, and using 600 MHz NMR and LC–MS characterised *cis* and *trans* 5-*p*CoQA, 5-CQA, 3,5-diCQA, 4,5-diCQA, methyl 3,5-diCQ (Macranthoin F), methyl 4,5-diCQ (Macranthoin G), 3,5-diCepiQA and 4,5-diCepiQA.*(562)* The 4,5-diCepiQA showed a clear negative optical rotation $[-32°]_D^{20}$ and an NMR spectrum distinctly different from 4,5-diCQA As previously reported both diCepiQAs had very low solubility in methanol, clearly distinguishing them from the better known 3,5-diCQA and 4,5-diCQA.*(562, 563)* However, the authors do caution that the coupling constants for H3 of the putative *epi*-quinic acid moiety are unusual, but explainable by their being possibly three conformers in equilibrium at room temperature.

Acikara *et al*. HPLC on an amide column and commercial standards reported 5-CQA, 3,5-diCQA and 4,5-diCQA in several Turkish species — *S. latifolia* (Fisch. & Mey.) DC*., S. cana* (C.A. Meyer) Hoffm. var. *jacquiniana* (W. Koch) Chamb., *S. tomentosa* L., *S. mollis* Bieb. ssp. *szowitzii* (DC.) Chamb., *S. eriophora* DC*., S. incisa* DC., *S. cinerea* Boiss. and *S. parviflora* Jocq.*(564)*

Sonchus species: Xu *et al*. extracted and characterised three *p*-hydroxyphenylacetylquinic acids found in *Sonchus arvensis*. Extensive NMR investigation identified these as the novel 1,3,4,5-tetra-*p*HPAQA, 3,4,5-tri-*p*HPAQA and methyl 3,4,5-tri-*p*HPAQA.*(565)* Similar derivatives have been found in *Hubertia*.*(566)*

Tragopogon species: Sareedenchai *et al*. reported 5-CQA, 3,5-diCQA and 4,5-diCQA in *Tragopogon porrifolius* L.*(567)* Granica *et al*. reported 3-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *T. tommasinii*.*(568)* Zidorn *et al*. reported 5-CQA and 3,5-diCQA in *T. dubius, T. orientalis, T. porrifoliu, T.preatensis* and *T. samaitani*.*(554)*

Urospermum species: Enke *et al*. using LC–MS reported 5-CQA and 3,5-diCQA in *Urospermum picroides* F.W. Schmidt.*(538)*

4.4.36.1.3.3. Vernonieae tribe (1500+ spp)

Elephantopus species: According to the English abstract Li *et al.* reported 3,5-diCQA and 4,5-diCQA in *Elephantopus tomentosus*,*(569)* but it is not known which numbering system was used. Ooi *et al*. isolated 4.5-diCQA from *E mollis*,*(570)* having used non-IUPAC numbering. Geng *et al.* reported the novel dicaffeoyl-cyclopentanol, along with 3,4-diCQA, 4,5-diCQA, methyl 3,4-diCQ and methyl 4,5-diCQ, all characterised by NMR, in the rhzomes of *E. scaber*.*(571)*

Eremanthus species: Silva *et al*. reported 5-CQA, methyl 5-CQ, ethyl 3-CQ, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, ethyl 3,5-diCQ, ethyl 4,5-diCQ, *n*-butyl 3,5-diCQ and *n*-butyl 4,5-diCQ in *Eremanthus crotonoides*.*(572)*

Lychnophora species: Brazilian Arnica (*Lychnophora ericoides* Mart.) is a medicinal plant endemic to Brazil. Gobbo-Netto *et al*. *(573)* reported it contains 3-CQA, 4-CQA, 5-CQA, 3-FQA, 4-FQA, 5-FQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3,4-diFQA and 3,4,5-triCQA. Dos Santos *et al*. reported that 3,5-diCQA, 4,5-diCQA and 3,4,5-triCQA were the dominant CGA in *L. ericoides*.*(574)*

Vernonia species: According to the English abstract Wang *et al*. reported 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA and the novel 3,4-diCisoQA in *Vernonia anthelmintica* with structure determined by NMR.*(575)* The authors subsequently reported that 3,4-diCisoQA eluted appreciably earlier from a reversed phase column packing than 3,4-diCQA and that both yielded *m/z* 353 as the MS^2 base peak,*(576)* but no further fragmentation data. It is not clear whether or not the IUPAC numbering was used by Wang *et al*. According to the English abstract Liu *et al*. found methyl 3,4-diCQ, methyl 3,5-diCQ, methyl 3,4,5-triCQ and ethyl 3,4-diCQ in *V. cumingiana*,*(577)* but it is not known whether or not IUPAC numbering was used.

In contrast Igual *et al*. isolated 3,5-diCQA and 4,5-diCQA from *V. polyanthes* and characterised them by NMR.*(578)* Johnson *et al*. reported 1-CQA, 3-CQA, 4-CQA, 5-CQA, 1,3-diCQA, 1,4-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 1,3,5-triCQA, 1,4,5-triCQA and 3,4,5-triCQA plus an F-diCQA in *V. amygdalina* leaves using LC–MS with commercial and in house-isolated standards, including some from the laboratory of Lin and Harnly.*(579)* Lin and Harnly reported traces of all four CQA, all six diCQA (3,4-diCQA and 4,5-diCQA dominant) plus 1,3,5-triCQA, 1,4,5-triCQA and 3,4,5-triCQA in the leaves of *V. amygdalina*.*(580)*

4.4.36.1.4. ASTEROIDEAE sub-family

4.4.36.1.4.1. Anthemideae tribe (1800 spp)

Achillea species: *Achillea millefolium* is a complex aggregate of polymorphic species varying in ploidy. Benedek *et al*. reported initially that *Achillea millefolium* contained 3,4-diCQA, 3,5-diCQA and 4,5-diCQA,*(581)* but later examined nine species belonging to the aggregate and quantified those diCQA plus 1,5-diCQA, and 5-CQA but note that the 5-CQA structure is shown using non-IUPAC numbering and the diCQA structures shown using IUPAC numbering.

There was considerable quantitative variation and some samples did not contain 1,5-diCQA **57**.*(582)* It was concluded that diploid species *A. asplenifolia, A. roseoalba and a diploid* A. ceretanica lacked 1,5-diCQA this compound generally being found only in species of higher ploidy such as a tetraploid *A. ceretanica, A. pratensis, A. collina,* and *A. styriaca*, hexaploid *A.millefolium s. str*. and *A. millefolium* ssp. *sudetica*, and octaploid *A. pannonica* but with the exception of one sample of *A. styriaca* and one of *A. pratensis*. 3,5-diCQA dominated all samples.

Jaiswal *et al.* using LC–ion trap-MS reported 1-CQA, 3-CQA, 4-CQA, 5-CQA, 5-FQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and 1C-3FQA.*(501)* Vitalini *et al*. (2011) who contemporaneously used LC–ion trap-MS reported also the presence of 1,3-diCQA and 1,4-diCQA, but not 1,5-diCQA, and surprisingly claimed that theirs was the first report of 3,4-diCQA and 3,5-diCQA in this species.*(583)* Note that only putative 3,4-diCQA and 3,5-diCQA IUPAC were characterised by NMR and the structures assigned by comparison with the data of Wang and Liu who characterised 3,5-diCQA and 4,5-diCQA IUPAC,*(479)* leaving some uncertainty about these assignments.

Further evidence of variation is provided by Radulovic *et al.* who isolated 5-CQA, 3,5-diCQA, 3F-5CQA and 3F-4CQA from the roots of *A. holoserica* and characterised them by NMR.*(584)*

Kundakovic *et al.* reported 3,4-diCQA also in *A alexandri-regis*,*(585)* but it is unclear which numbering system has been used.

Dias *et al.*, using LC-Qtrap-MS^2, reported 3-CQA, 4-CQA, 5-CQA plus four diCQA in wild and commercial samples of *A millefolium*. These include 3,4-diCQA, 3,5-diCQA and 4,5-diCQA plus a putative *cis* 3,5-diCQA with a fragmentation pattern similar to 3,5-diCQA. The *cis* and *trans* 3,5-diCQA were the dominant CGA.*(586)* It seems unlikely that only a single *cis*-isomer would be present, and the putative *cis* isomer might be 1,5-diCQA, especially as it was clearly exceeding the equilibrium concentration for a *cis*-isomer.*(587)*

Anthemis species: Pavlovic *et al.* extracted the aerial flowering parts of *Anthemis triumfetti* L. DC and characterised the CGA by NMR, which data were compared with previously published data. They reported 5-CQA, 3,5-diCQA and 3,4-diCQA.*(588)* The identitiy of the putative 3,4-diCQA is uncertain because the authors compare their data with data from Morishita *et al., (589)* who did not use IUPAC numbering, and Iwai *et al., (590)* who used IUPAC numbering, and the authors do not appear to be aware of these differences.

Artemisia species: *Artemisia* are widely used medicinally, and many species have been investigated and screened for bioactive components in numerous assay systems, but in many cases the CGA profiles are almost certainly

incomplete, and usually presented only for the most efficacious sample examined. *Artemisia alba,* in particular, has been described *as 'a taxonomically problematic species, characterised by common polymorphism leading to a quite high variability in secondary metabolites content'(591)* and this tendency is clearly borne out by the data below for all members of the genus.

For example, Niranjan *et al*. reported 5-CQA (130 mg/kg) in *A. pallens* L., an Indian traditional medicinal plant,*(592)* Fiamegos *et al.(593)* reported 5-CQA, 3,5-diCQA and 4,5-diCQA in *A. absinthum*, but it is uncertain which numbering system was used and whether other diCQA were present. Lee *et al*. have reported 3,4-diCQA, 3,5-diCQA (dominant), 4,5-diCQA, methyl 3,4-diCQ and methyl 3,5-diCQ in *A. dubia.(594)* Note, Lee *et al*. did not use IUPAC numbering.

Similar studies of *A. capillaris* have revealed 3-CQA, 4-CQA, 5-CQA, methyl 3-CQA, methyl 4-CQA, methyl 5-CQA, 1,3-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA and methyl 3,5-diC,**.***(595-597)* but note that Nurul *et al* uses non-IUPAC numbering for 5-CQA and IUPAC numbering for the diCQA. Zhao *et al*. have additionally reported 3-CQA, 4-CQA, methyl 3-CQ, methyl 4-CQ and methyl 5-CQ,*(598)* but did not use IUPAC numbering.

In *A. princeps* 3,5-diCQA (dominant) and 4,5-diCQA have been reported,*(599, 600)* plus 5-CQA, *n*-butyl 5-CQ, *n*-butyl 4-CQ, 3,4-diCQA, methyl 3,5-diCQ and methyl 4,5-diCQ in the MeOH extract of moxa, the processed leaves of *A. princeps* Pamp., identified by comparison with previously published data.*(601)* Note that the data for moxa did not use the IUPAC numbering.

The analysis of *A. argyi* revealed 3,5-diCQA and its methyl, ethyl and *n*-propyl esters,*(602)* but only 3-CQA was reported in *A. arborescens*.*(603)* 3,5-DiCQA has been isolated from *A. ludoviciana* Nutt.*(604)*

Könczöl *et al.(605)* reported 4-CQA, 5-CQA, 3,5-diCQA and ethyl 3,5-diCQ in *Artemisia gmelinii* Webb., a medicinal plant used in south and south-east Asia to treat many inflammatory diseases. These authors discuss elegantly the difficulty inherent in distinguishing between 3,5-diCQA and 3,5-diCepiQA by NMR in DMSO and conclude that in the absence of X-ray structural data it was not possible to make a certain assignment, but suggest tentatively that EpiQA derivatives are not present. Accordingly they caution that other reports purporting to describe 3,5-diCepiQA in this and other species might not be reliable, but when two all-*trans*-3,5-diacyl-quinic acids are isolated from the same sample, as in *Chrysanthemum morifolium*,*(606)* further investigation is required.

Zhang *et al.* using LC–MS^2 and commercial standards reported three CQA, one *p*CoQA and three diCQA in *A. selengensis* Turcz,*(607)* but it is not clear whether or not they use the IUPAC numbering. A subsequent study of the leaves of *A. selengensis* by LC–QTOF-MS reported 1-CQA, 3-CQA, 4-CQA and 5-CQA, plus 3,4-diCQA, 3,5-diCQA and 4,5-diCQA, and 3,4,5-triCQA.*(608)* However, the elution of the putative 1-CQA after 5-CQA strongly suggests that it is *cis* 5-CQA**,** and the early eluting putative 3,4,5-triCQA yielding a characteristic *m/z* 341 is probably a diCQA glucoside. In a third publication from this group 4-*p*CoQA, 5-*p*CoQA and 1,5-diCQA also were reported.*(609)*

Dahmani-Hamzouai *et al.* isolated 5-CQA, 3,5-diCQA**,** 4,5-diCQA and 3,4,5-triCQA from the leaves of *A. herba-alba*.*(610)* Boudjelal *et al*, reported 3-CQA, 4-CQA, 5-CQA, 4-*p*CoQA, 4-FQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *A.*

herba-alba following identification by LC–MS^2.*(611)* The identity of the CQA was confirmed with standards but the other CGA were supposedly identified by their fragmentation. However, the tabulated data presented are inadequate for this purpose and these assignments at regio-isomer level must be viewed as tentative. The same problem is encountered with the data for *A. herba-alba* which Younsi *et al*. reported as containing 'chlorogenic acid', 1,4-diCQA, 3,4-diCQA and 3,4,5-triCQA,*(612)* but iin this case it is unclear which numbering system has been used.

The most comprehensive, and almost certainly the most reliable, data have been obtained using LC– ion trap-MS methods. Gu *et al*.*(613)* reported 1-*p*CoQA , 5-*p*CoQA, 4-FQA, 5-FQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3F-4CQA, 3C-4FQA, 3F-5CQA, 3C-5FQA, 4F-5CQA, and 4C-5FQA and either 1-CQA or 5-CQA in *A. rupestris*, a Chinese medicinal herb.

Gouveia *et al*. reported 3-CQA, 4-CQA, 5-CQA, 3-FQA 5-FQA, 3,4-diCQA, 1,5-diCQA (dominant), 3,5-diCQA, 4,5-diCQA and an incompletely characterised diCQA, 3*p*Co-5CQA, 1C-5FQA, 3F-5CQA, an incompletely characterised CFQA, 3,4-diFQA, 3,5-diFQA and 3,4,5-triCQA in *A. annua*.*(614)* Carbonara *et al*. analysed by LC–MS^2 the beverage prepared from *A. annua* and reported additionally 4-FQA, 4,5-diFQA and an incompletely characterised C-disucQA, but only one CFQA and no 1-acyl diCQA. 5-CQA and 4,5-diCQA dominated their respective CGA subgroups.*(615)*

Han *et al*. using LC–ion trap-MS^3 reprted two CQA, one FQA, five diCQA, eight CFQA, three diFQA, one triCQA and one diC-FQA in *A. annua* but because the ion spray voltage was set at 4.5 Kv, rather than 3.5 Kv, the fragmentations do not match those utilised in the hierarchical keys. The authors assignments are 3-CQA, 5-CQA, 5-FQA, followed by 3,4-diCQA, 3,5-diCQA, 4,5-diCQA plus two incompletely characterised diCQA which all elute close together, possibly suggesting that 1,3-diCQA was not present. The CFQA are assigned as 3F-4CQA, 4F-5CQA, 1F-5CQA, 1C-5FQA, 3F-5CQA, 3C-5FQA, 4C-5FQA, 3C-4FQA in order of elution but late elution of a 3,4-diacyl-quinic acid and early elution of a 4,5-diacyl-quinic acid is unusual and might be incorrect. These were followed by 3,4-diFQA, 3,5-diFQA and 4,5-diFQA and 3,4,5-triCQA plus the incompletely characterised diC-FQA.*(616)*

Li *et al.* reported the *cis* and trans isomers of 3-CQA, 4-CQA and 5-CQA, plus 1,3-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *A.* annua,*(617)* but did not use IUPAC numbering. According to the English abstract Zhao *et al*. found 5-CQA, 1,3-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, methyl 3,4-diCQ and methyl 3,5-diCQ in dried whole plants of *A. annua*,*(618)* but it is not possible to judge whether or not IUPAC numbering was used. Zhao *et al*. using LC–triple quadrupole-MS^2 to analyse extracts of *A. annua* subsequently reported 1-CQA, 3-CQA, 4-CQA and *cis*- and *trans*-5-CQA, 3-FQA, 4-FQA and *cis*- and *trans*-5-FQA, 3-*p*CoQA, 1,5-diCQA, 3,4-diCQA, one *cis*- and di-*trans*-3,5-diCQA, two *cis*- and di-*trans* 4,5-diCQA, 1C-3FQA, 1F-5CQA, 1C-5FQA, 3C-4FQA, one *cis*- and di-*trans*-4C-5FQA, 4F-5CQA, 3,4,5-triCQA, 3,4-diFQA, 3,5-diFQA, 4,5-diFQA, and two compounds described as 3D-5CQA plus 4D-5CQA.*(619)* Note that the order of elution of the diacyl-quinic acids is atypical, with late elution of a 3,4-diacyl-quinic acid and early elution of a 4,5-diacyl-quinic acid. This observation, coupled with the use of ion trap-MS hierarchical keys to interpret data from a triple quadrupole MS suggests that some assignments at regio-isomer level may be incorrect.

In *A. argentea* L'Her Gouveia *et al*. reported 3-CQA **33**, 5-CQA, *cis* 5-*p*CoQA, 5-FQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3C-4*p*CoQA, 5C-4FQA, plus an incompletely characterised 3*p*Co-CQA.*(620)* The presence of a *cis* isomer but not the

trans isomer is unusual and it appears that this is likely to be the *trans* isomer based upon the report of both in *Helichrysum monizii*.*(621)*

Ma *et al*. analysed *A. 82haracter* and reported 3-CQA, 4-CQA, 5-CQA and *cis*-5-CQA, 1,3-diCQA, 1,4-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and a mono- or di-*cis* diCQA isomer, and at least six peaks that are very probably CQA glycosides, methyl 1,5-diCQ, methyl 3,5-diCQ, and four CFQA including 3F-4CQA . In addition to the foregoing, diCQA glycosides, CQA-diglycosides and triCQA were also detected.*(622)*

Jaiswal *et al*. *(501)* using LC–ion trap-MS reported 3-CQA, 4-CQA, 5-CQA, 4-FQA, 5-FQA, 5-*p*CoQA, 1,3-diCQA, 3,5-diCQA, 4,5-diCQA and 1C,4FQA in the leaves of *A. dracunculus*. Melguizo-Melguizo *et al.* using LC–ion trap-MS reported 3-CQA, 5-CQA, 5-FQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA (dominant), 4,5-diCQA plus traces of another incompletely characterised late-eluting diCQA in the leaves of *A vulgaris*.*(623)* Carnat *et al*. reported that 1,5-diCQA and 3,5-diCQA are the dominant diCQA in *A vulgaris* flowering tops.*(624)*

Lin and Harnly using LC–MS^2 reported all four CQA and five of the six diCQA (1,3-diCQA was not found) plus 3C-5FQA and 3,4,5-triCQA in flowers of Tarragon, *A. dracunculus*.*(625)* These assignments were made by '*comparison to standards or positively identified compounds in reference plant samples*' and the report of 1,4-diCQA should be treated with caution because of the absence of the diagnostic MS fragments associated with 1,4-diCQA and the absence of 1,3-diCQA that rapidly forms from it during sample preparation.

Jung *et al*. reported 3-CQA, 4-CQA, 5-CQA and 3,5-diCQA in *A. montana*,*(626)* by isolation and NMR characterisation. Ornano *et al*. isolated 5-CQA and 3F5CQA from *A. caerulescens* subsp *densiflora* (Viv.)*(627)* but note that in the original paper the authors used non-IUPAC numbering. According to the English abstract Lin *et al*. reported methyl 3,4-diCQ and methyl 3,5-diCQ in *A. lactiflora*,*(628)* but it is not known which numbering system was used.

Yan *et al*. reported methyl 5-CQ and 4,5-diCisoQA in *A. iwayomogi*,*(629)* but no physical data are provided for this latter compound. The structures shown in the original paper have the IUPAC structure but in the text the latter is incorrectly described as 3,4-diCisoQA. Nugroho *et al* reported 'chlorogenic acid' and 3,4-diCQA but the criteria used for identification are not stated,*(630)* and it is unclear which numbering system was used.

Calea species: Lima *et al*. reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *Calea pinnatifida* (R. Br.) Less.*(631)* Torres-Rodriguez *etal*. reported two CQA, two putative CQA derivatives (M_r = 388 and 378), three FQA, and three diCQA in *C. urticifolia*.*(632)*

Chrysanthemum species: Chrysanthemum is a genus of flowering plants used ornamentally, as a component of herbal and folk medicines in Asia, and, in some cases, to prepare tea, wine, soup and salad. It is of particular interest because of the unusual range of CGA reported, and because of confusing inconsistencies in the literature. Particular points of contention are whether or not acylated *epi*-quinic acids are present, and whether these include (+)-enantiomers as well as (–)-enantiomers. Variation in the reporting of succinic acid- and / or methoxyoxalic acid-containing CGA is also noteable.

Chuda *et al*. reported 5-CQA, 3,5-diCQA and 3,5diC-4SucQA in Garland (*Chrysanthemum coronarium*) and characterised them by CD and NMR spectroscopy. 5-CQA was not characterised to this extent.*(633)* Hosni *et al.* using LC–MS^2 reported 5-CQA **35** and two incompletely characterised diCQA in *C. coronarium*,*(634)* whereas Murayama *et al.* using cochromatography with diCQA isolated from the coffee bean reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA.*(635)* Lai *et al*. reported 5-CQA, 3,5-diCQA and 3,5diC-4SucQA**,** 1,3-diCQA and 4,5-diCQA in *C. coronarium*,*(636)* but present the structures with some cinnamic acid residues in the *cis* configuration, and show a *muco*-quinic acid residue rather than a (–)-quinic acid residue. These peculiarities are not discussed in the paper, and the assignments at regio-isomer level should be viewed as tentative.

3-CQA, 5-CQA, methyl 5-CQ, 3,5-diCQA, 4,5-diCQA, methyl 3,5-diCQ and methyl 4,5-diCQ have been reported in the Vietnamese medicinal plant *C. sinense (637)* following isolation and comparison of spectral data with literature values.

NMR characterisation of extracts identified 3-CQA, 5-CQA and 5-FQA in *C. grandflora* (also known as *Dendranthema grandiflora*).*(638)*

C. morifolium (*Dendranthema morifolium or Dendranthema grandiflora* Tzvelev) has been more extensively investigated. Lai *et al*. reported chlorogenic acid but present the structure with a *muco*-quinic acid residue rather than a (–)-quinic acid residue and the caffeic acid residue in the *cis* configuration.*(636)* These peculiarities are not discussed in the paper. Beninger *et al.* confirmed the presence of 5-CQA and 3,5-diCQA.*(639)* In a more extensive study Kim and Lee investigated *C. morifolium* Ramat from Korea and after isolation characterised by NMR spectroscopy 1,5-diCQA, 3,5-diCQA, methyl 3,5-diCQ and methyl 4,5-diCQ, accompanied by the novel 3,5-diCepiQA and 1,3-diCepiQA. CD spectroscopy clearly demonstrated positive first Cotton effects at 289 nm for 1,5-diCQA, 3,5-diCepiQA and 1,3-diCepiQA but a negative first Cotton effect for 3,5-diCQA.*(640)* The published NMR data for both the putative 3,5-diCQA and 3,5-diCepiQA clearly show the 3,5-di-substitution and the presence only of *trans* cinnamoyl residues thus implying that one of these is not a typical (–)-quinic acid derivative. Note that an incorrect structure for 1,3-diCepiQA was shown in the original publication and later corrected.

Xie *et al.* subsequently reported 3,5-diCQA, 1,3-diCepiQA**,** methyl 3,5-diCQ (Macranthoin F) and 5-CQA identified by comparing their NMR and MS spectra with published data. These authors also stated that 3,5-diCQA and 1,3-diCepiQA are incompletely separated, have identical UV spectra and produce identical MS^2 fragments. A third later-eluting uncharacterised diCQA also had the same fragmentation.*(641)*

Könczöl *et al.* consider the NMR-based assignment of 1,3-diCepiQA as unproven,*(605)* and certainly it should be treated as tentative. There does however, appear to be two all-*trans*-3,5-diacyl-quinic acids in some samples of *C. morifolium* as judged from the NMR data of Kim and Lee,*(640)* and further study is necessary. Note that a diacyl derivative of *epi*-quinic acid has been reported in *Psiadia*, *Inulanthera, Tessaria* and *Tussilago*.

Lin and Harnly analysed the flowers of *C. morifolium* Ramat by LC–MS^2 and reported 1-CQA, 3-CQA, 4-CQA, 5-CQA, 1,3-diCQA, 1,4-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA, but did not detect any *epi*-quinic acid derivatives.*(642)* Lin and Harnly also reported 5-SiQA, 3Mo-1,5diCQA, 4C5FQA and an isomer thereof, plus 3,4,5-

triCQA and two diCQA glycosides.*(642)* This is the first report of an SiQA in *Chrysanthemum*, and only the second report in Asterales.

An LC–ion trap-MS study of four samples of herbal *C. morifolium* from China by Clifford *et al*. reported four mono CQAs, six diCQAs, 3-*p*CoQA, 4-*p*CoQA**,** 5-*p*CoQA, 3-FQA, 4-FQA**,** 5-FQA and 3,4,5-triCQA, but not the *epi*-quinic acid derivatives,*(643)* which as discussed in Part 3 would have distinctive fragmentation spectra if present.*(82, 465, 496)* Niu *et al.* examined *C. morifolium* var *jiji* by LC–TOF-MS^2 and reported 4-CQA, 5-CQA, 1,5-diCQA, 3,5-diCQA and 4,5-diCQA but also failed to detect any *epi*-quinic acid derivatives.*(644)* Wang *et al*. using LC–MS compared the composition of eight samples of Chrysanthemum Flos derived from *C. morifolium* plus one each from *C. nankingense* and *C. indicum*. Collectively 1-CQA or 3-CQA, 4-CQA, 5-CQA, 5-SiQA, 1,4-diCQA, 1,5-diCQA, 3,5-diCQA, 4,5-diCQA and 3Mo-1,5diCQA were detected. There were several significant differences, with 4,5-diCQA found only in four samples and 3Mo-1,5diCQA only in five.*(645)* If correct, this is only the third report of a SiQA in Asterales, but note that the molecular mass is given as 388 rather than 398. He *et al*. reported 4-CQA, 5-CQA (dominant), 3,4-diCQA, 3,5-diCQA (dominant) and 4,5-diCQA in *C. indicum* flowers.*(646)*

Wang *et al*. analysed 12 samples of *C. morifolium* Ramat cv Hangju from different geographic origins and provide quantitative data for 5-CQA and 3,5-diCQA illustrating marked variations in content with inflorescence age.*(647)*

A more extensive study of *C indicum* reported 1,3-diCQA, 3,4-diCQA and 3,5-diCQA but it is not clear whether or not the IUPAC numbering was used.*(648)* According to the English abstract Sun *et al*. reported the novel dicaffeoyl-eriodictyol, 1,3-diCQA, 1,5-diCQA and 3,5-diCQA plus a *cis* isomer thereof.*(649)* Farag *et al*. using LC–QTOF-MS reported 3-CQA, 5-CQA, 1,3-diCQA and 3,5-diCQA in *C. pacificum* Nakai, with the CGA being present at higher concentrations in the flowers and aerial parts than in the roots.*(650)* Note that the authors appear to use IUPAC numbering in the text (chlorogenic acid is described as 5-CQA) but show structures using non-IUPAC numbering.

Nugroho *et al*. reported 5-CQA and 3,5-diCQA in the flowers of *C. boreale.(651)*

Coleostophus species: Bessada *et al* reported 3-CQA, 5-CQA, 3,5-diCQA and 4,5-diCQA in the aerial parts of *Coleostophus myconis* (L.) Rchb.f. using LC–ion trap-MS^2 with a high spray voltage (5 Kv) *(652)* which precluded use of the hierarchical keys developed by Clifford *et al.* who used only 3.5 Kv.

Eriocephalus species: LC–ion trap-MS analysis of extracts of the dried stems and leaves of *Eriocephalus africanus* revealed 1-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA and 1,4-diCQA.*(653)* Note that the authors did not use the IUPAC numbering system and there is some doubt about the reliability of the 1-CQA and 1,4-diCQA assignments which seem more likely to be 3-CQA and 4,5-diCQA, respectively.

Inulanthera species: Gafner *et al.* using LC–MS and 'in house' standards reported '*chlorogenic acid*', 3,4-diCQA, 1,5-diCQA, 4,5-diCQA and 3,4-diCisoQA (= 3,4-di*Cepi*QA) *i n* the aerial parts of *Inulanthera nuda*,*(654)* but the authors do not state whether or not the IUPAC numbering system has been used. This group previously reported 4,5-diCisoQA (IUPAC) in *Psiadia* and this appears to be the same compound.

Laggera species: Shi *et al*. isolated 3,4-diCQA, 3,5-diCQA and 4,5-diCQA from *Laggera pterodonta* and characterised them by NMR.*(655)*

Matricaria species: Lin and Harnly using LC–MS^2 reported 3-CQA, 4-CQA, 5-CQA, 1,5-diCQA and 4,5-diCQA in Chamomile flowers (*M. chamomilla* L.). Although detected in Tarragon leaves analysed simultaneously, the other four diCQA regio-isomers were not detected in Chamomile flowers.*(625)* Petrulova *et al*. reported 5-CQA and 1,3-diCQA in *M. chamomilla* leaves, and demonstrated a rapid increase, especially in 1,3-diCQA, after exposure to UVB, the magnitude of the response varying with ploidy of the samples,*(656)* but note that the authors do not use the IUPAC numbering. Ganzara *et al.* reported significant increases in the contents of 5-CQA and 3,5-diCQA in the flower heads of *M. chamomilla* as the altitude increased from 590 to 2230 m. 1,3-DiCQA was used as an internal standard therefore absent, and 1,5-diCQA was not mentioned.*(657)* In a study of the effect of methyl jasmonate on the secondary metabolite content of *M. chamomilla* leaves Ducaiova *et al*. reported 5-CQA and 1,5-diCQA as the dominant CGA.*(658)*

Raal *et al*. using LC–ion trap-MS^2 reported 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in the aerial parts of *Chamomilla suaveolens* (= *Matricaria discoidea*) from Estonia.*(659)*

Tanacetum species: Wu *et al*. using LC–QTOF-MS and NMR reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in dried Golden Feverfew (*Tanacetum parthenium*).*(660)* Jaiswal *et al*. using LC–ion trap-MS reported 3-CQA, 4-CQA, 5-CQA, 3,5-diCQA, 4,5-diCQA and 3,4,5-triCQA in the leaves of *T. parthenium*.*(501)*

4.4.36.1.4.2. Astereae tribe (3080 spp)

Aster species: Members of this species are frequently referred to as Asters or Michaelmas Daisies valued for their decorative flowers. In south-east Asia, particularly Korea, the leaves of several Aster species are known as 'mountain vegetables' or Chwinamul and used boiled. Aster species have received quite a lot of attention with regard to the profile and content of CGA with considerable variation in the data generated, particularly with regard to the diCQA profiles, and whether or not diacyl *muco*-quinic or diacyl *epi*-quinic acids are present. However, it is also clear that for a given species there are marked variations with the tissue analysed, as well illustrated for *A. ageratoides*.*(8)*

Kwon *et al*. *(661)* isolated the novel 3,5-diCmucoQA from *Aster scaber* Thunb., and characterised it by NMR, but stressed that the assignment was tentative and recommended that it should be confirmed by X-ray crystallography. This never seems to have been done, and as discussed in Part 2 of these notes the correct assignment of 3,5-diacylquinic acids by NMR is problematic, and some doubt remains about the validity of this assignment. 5-CQA, 3,5-diCQA and 4,5-diCQA were also present but, 3,4-diCQA was not found.

The novel 3,5-diCmucoQA was subsequently also found in and isolated from *Lactuca indica* by Kim *et al.* along with 3-CQA, 5-CQA 5-pCoQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA,*(549)* but they did not report any NMR data for the new isolates. These isolates have been used as standards in a number of later studies of various Asteraceae. One such study by Nugroho *et al*. of several species included *A. scaber* and *A. yomena* (= *Kalimeris yomena*). In direct contrast with the original study by Kwon *et al*. they concluded that 3,5-diCmucoQA was not present in *A. scaber* or *A. yomena* but confusingly Nugroho *et al.* referred to this compound as 3,5-diCepiQA.*(478)*

Nugroho *et al*., again using the same seven standards originally isolated from *Lactuca indica*,*(549)* later reported that 3,5-diCmucoQA (*sic*) could not be found in extracts of *A. glehni (662)* and they made no reference to 3,5-diCepiQA.

Ko *et al.* isolated from extracts of *A. subulatus* Michx. two CGA which they described as 3,5-diCQA and 3,5-diCepiQA, and referred to them as having previously been characterised but did not report any physical data.*(663)*

Most of the studies reporting 3,5-diCmucoQA or 3,5-diCepiQA have been obtained using a set of in house isolated and characterised standards supplied by Professor Kang Ro Lee (see Kwon *et al. (661)*) which do not include 3,4-diCQA, but include two components with NMR data consistent with both being all *trans* 3,5-dicaffeoylquinic acids. While this suggests that one must be an ester of a quinic acid isomer this has never been confirmed and these inconsistent results have never been clarified.

However, an LC–ion trap-MS investigation by Clifford *et al*. located in the flower buds of *A. ageratoides* Turcz. 3-CQA, 4-CQA, 5-CQA and the corresponding *p*CoQA and FQA, three diCQA, three diFQA, six CFQA, six *p*Co-CQA and six *p*Co-FQA but no 1-acyl-CGA, no aliphatic acid-containing CGA, and no *muco*-quinic or *epi*-quinic acid derivatives despite specifically searching for them. Unusually, the FQA and diFQA dominated the mono-acyl and di-acyl quinic acid fractions.*(8)*

Whatever the status of 3,5-diCmucoQA and 3,5-diCepiQA there is considerable variation in the diCQA profiles reported for various *Aster* spp. and while this variation might be of chemotaxonomic significance it is possible that there have been some mis-identifications. It should be noted that the quinic acid moiety of 3,5-diCmucoQA**,** 3,5-diCepiQA, 3,4-diCQA, 3,5-diCQA, 1,5-diCQA and 1,4-diCQA has one free equatorial hydroxyl and one free axial hydroxyl with the result that one would expect them all to elute close together from reverse phase HPLC packings, a recipe for easy confusion. For example, see Clifford *et al*.,*(122)* where 3,4-diCQA, 3,5-diCQA, 1,5-diCQA and 1,4-diCQA elute from both phenylhexyl and C_{18} column packings in a five minute period about half way through a 90 minute analysis.

The LC–ion trap-MS study of *A. ageratoides* Turcz. that reported only 3,4-diCQA, 3,5-diCQA and 4,5-diCQA can be taken as reliable because it has been established that this procedure can resolve and discriminate the six diCQA*(8)* and the unique fragmentation patterns associated with *muco*-quinic or *epi*-quinic acid isomers would also have been recognised even if they were not chromatographically resolved in the UV.*(465, 496, 664, 665)*

Note that the 33 chlorogenic acids detected by Clifford *et al*. in flower buds of *A*. *ageratoides* Turcz. could not be found in the leaves or stem of *A*. *ageratoides* Turcz., or in the flower buds of *A*. *ageratoides* Turcz. var. Gerla or *A. kalimeris indica* (L) Sch. Bip.*(8)*

An independent analysis by LC–QTOF-MS^2 of extracts of whole *Kalimeris indica* plants detected 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 1,5-diCQA, and 1Malo-3,5diCQA, all assignments at regio-isomer level being tentative.*(666)* These authors did not refer to the study by Nugroho *et al.(478)* or make any reference to CGA containing a quinic acid epimer, but had strong evidence for four diCQA in contrast to Clifford *et al*. who found only three.

There are several studies to report only two diCQA. Wubshet *et al*. reported only 3,5-diCQA and 4,5-diCQA, accompanied by 5-CQA, in A*. tripolium* L.,*.(358)* Similarly, *A. altaicus* var. *uchiyamae* Kitamura contains 3-CQA, 5-CQA and only two diCQA — 3,5-diCQA and 4,5-diCQA. The putative 3,5-diCepiQA was explicitly stated not to be present.*(667)* Note that the sequence of elution as previously mentioned, was peculiar, with 3,4-diCQA (*ca* 2.5 min, 5-CQA *ca* 4.5 min, 3-CQA *ca* 9.5 min, 3,5-diCepiQA *ca* 10.5 min, 3,5-diCQA *ca* 14 min and 4,5-diCQA *ca* 17.5 min. In contrast, Kim *et al*. reported 1,5-diCQA was present in *A. altaicus* var. *uchiyamae* Kitamura.*(481)*

Using LC–QTOF-MS Zhao *et al*. reported 1-CQA, 3-CQA, 4-CQA, 5-CQA, two incompletely characterised FQAs, 3,5-diCQA, 4,5-diCQA and one early eluting incompletely characterised putative diCQA, plus two putative diCQA derivatives (M_r = 602) in the root of *A. tataricus*.*(668)* but did not use IUPAC numbering. The putative 1-CQA eluted after *trans* 5-CQA **35** (identified by an authentic standard) and appears to be *cis* 5-CQA. The early eluting putative diCQA eluted before the CQAs and might well be a CQA-glycoside. The two diCQA derivatives are presumably either diC-MaloQA or diC-MoQA. Kim *et al*. reported 1,5-diCQA was not present in *A. tataricus*.*(481)*

Choi *et al*. also reported only two diCQA, but not the same pair — 3,4-diCQA, 3,5-diCQA accompanied by methyl 3,5-diCQ in *A. oharai*.*(669)* Clearly, there is great variation and additional work is required.

Some quantitative data are available, but should be interpreted with care. Nugroho *et al*. reported 3-CQA 5.0 g/kg, 5-CQA 9.34 g/kg 3-*p*CoQA 9.9 g/kg, 3,4-diCQA 5.60 g/kg and 3,5-diCQA 3.9 g/kg in *A. scaber*.*(478)* *A. yomena* (also

known as *Kalimeris yomena*) contained 3-*p*CoQA 4.8 g/kg, 3-CQA 16.5 g/kg, 5-CQA 18.8 g/kg, 3,4-diCQA 5.6 g/kg, 3,5-diCQA 12.1 g/kg and 4,5-diCQA 3.9 g/kg,*(478)* but subsequently Kim *et al*. reported 1,5-diCQA was present in *A. yomena* (0.22 g/kg), *A. ciliosus* (0.071 g/kg) and the flower of *A. koraiensis* (0.15 g/kg) but confusingly not in the whole plant.*(481)*

A. glehni contained 3-CQA, 5-CQA 3-*p*CoQA and 3,5-diCQA, but the profile, particularly of the diCQA, differed markedly with the solvent used for extraction. The ethanol extract of *A. glehni* also contained 3,4-diCQA and the 30% aqueous ethanol extract also contained 4,5-diCQA suggesting that acyl migration had occurred in the more aqueous solvents.*(662)*

Quantification made use of calibration curves prepared from seven standards isolated by Kim *et al*. from *Lactuca indica*, *(549)* for which Nugroho *et al*. reported response factors of 241 and 301 for 5-CQA and 3-CQA, respectively, 23 for 3-*p*CoQA, and 67, 383, 114 and 142 for 3,4-diCQA, 3,5-diCepiQA, 3,5-diCQA and 4,5-diCQA, respectively. As discussed in Part 2 the molar absorbance values are expected to differ by very little for regio-isomers containing the same cinnamic acid, and the marked variation in the response factors reported by Nugroho *et al.* strongly suggests that the standards were impure, probably containing non-UV-absorbing salts and solvents because the published chromatogram (246 nm) shows only minor impurities. Although the quantitative data must have been distorted by the use of these response factors, visual comparison of the published chromatograms should give a reasonable indication of the relative contents of the individual mono-acyl and diacyl quinic acids.

A more recent study reports the quantification of 1,5-diCQA in the aerial parts of 11 species of *Aster,(481)* but makes no reference to any other CGA. The content in the six species not already referred to ranged from 0.07 g/kg to 0.26 g/kg, with 0.47 g/kg in *A. glehni*, 0.86 g/kg in *A. tripolium*, 1.35 g/kg in *A. incise*, 1.63 g/kg in *A. pekinensis*, 2.57 g/kg in *A. ageratoides*, 3.3 g/kg in *A. hayatae* and 78.35 g/kg in *A. pilosus*. Quantification used 1,5-diCQA isolated by the authors.

Baccharis species: Aboy *et al.(670)* analysed *Baccharis trimera*, a medicinal herb used in South America, collected at different seasons from several locations and reported 0.08-0.59 g/kg of 5-CQA, 0.27–12.52 g/kg of 3,4-diCQA, 0.79–14.46 g/kg of 3,5-diCQA and 0.70–10.51 g/kg of 4,5-diCQA, and 1.38–8.93 g/kg 3,4,5-triCQA. Quantification employed commercial 5-CQA **35**, purified 4,5-diCQA and purified 3,4,5-triCQA, with response factors of 59771, 67246 and 67035, respectively. However, as discussed in Part 3 the molar absorbance of caffeic acid-containing mono-, di-, and tri-acyl quinic acids should increase in ratios approximating 1 : 2 : 3. Accordingly it is likely that the preparations of 4,5-diCQA and 3,4,5-triCQA contain non-UV absorbing impurities that will result in the reported content of the diacyl and triacyl quinic acids being over-estimates. The same diCQA have been reported in *B. uncinella (671)*, 5-CQA and 3,5-diCQA in *B. chilco*,*(672)* and an uncharacterised range of CGA recorded in *B. 88haracteri*,*(673)* but including 4,5-diCQA **57**,*(674)* although it is unclear what numbering system has been used. dos Greco *et al*. reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *B. retusa* D.C.*(675)*

Marques and Farah analysed *B. genistelloides* using LC–MS and reported 3-CQA **33** 2.3 g/kg, 4-CQA 1.8 g/kg, 5-CQA 3.6 g/kg, 3-FQA 131 mg/kg, 4-FQA 56 mg/kg, 5-FQA 44 mg/kg, 3,4-diCQA 1.2 g/kg, 3,5-diCQA 3.0 g/kg and 4,5-diCQA

1.9 g/kg,*(35)* but the calibrants were not clearly stated. Simões-Pires *et al*. analysed *B. trimera* (Less.) DC, *B. crispa* Spreng and *B. usteri* Heering and characterized isolated components by NMR. They reported 3-CQA, 5-CQA, 4C-1MQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA.*(676)* Note that these authors did not use the IUPAC numbering system, and that the compound named as 4-caffeoyl-1-methyl-quinic acid is actually showm as methyl 4CQ. This is consistent with the reported δ_H = 3.80 in contrast to the value obtained by Zeller (δ_H = 3.31) for an authentic methyl ether of quinic acid (1M-5CQA **65**).*(25)*

Centipeda species: Chan *et al*. using LC–QTOF-MS reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *Centipeda minima*.*(677)*

Chrysothamnus species: Timmermann *et al*. using NMR characterised 3,4,5-triCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA isolated from *Chrysothamnus paniculatus*, this being the first report of a triCQA.*(678)* They did not use IUPAC numbering.

Dichrocephala species: Using NMR Lin *et al*. reported 5-CQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, ethyl 4,5-diCQ and methyl 3,5-diCQ in Taiwanese *Dichrocephala bicolor*. The authors comment that the ethyl and methyl esters might be artifacts of isolation.*(679)*

Erigeron species: Yue *et al*. reported 4,5-diCQA, 3,5-diCQA, methyl 4,5-diCQ and methyl 3,5-diCQ in *Erigeron breviscapus*,*(680)* but used non-IUPAC numbering. According to the English abstract Zhang *et* al. reported methyl 3,5-diCQ and methyl 4,5-diCQ in *E. breviscapus*, but is not known whether or not IUPAC numbering was used. Li *et al*. reported 1,3-diCQA and 1,5-diCQA in *E. breviscapus*,*(681)* but although structures are shown with non-IUPAC numbering, putative IUPAC 1,5-diCQA elutes well before putative 1,3-diCQA, which is contrary to what would be expected. Ju *et al*. reported 1,3-diCQA, 3,5-diCQA and 4,5-diCQA.*(682)*

Wang *et al*. using isolated standards purified to UV chromatographic homogeneity quantified 5-CQA, 4,5-diCQA and 3,5-diCQA in *E. breviscapus* in the range 2.1–4.7, 1.4–3.6 and 1.9–4.1 g/kg, respectively.*(683)* The reported response factors of 37, 53 and 59, respectively, suggest that, as discussed above, at least the diCQA preparation contained non-UV-absorbing impurities and accordingly their contents will have been over-estimated.

This Chinese herbal medicine also contains 1-CQA, 3-CQA, 4-CQA, 1,3-diCQA, 1,4-diCQA, 1,5-diCQA, 3,4-diCQA, 1,3,4-triCQA, 1,3,5-triCQA, 1,4,5-triCQA, 3,4,5-triCQA, 1Malo-3,5diCQA, 4Malo-3,5diCQA **,** 4Malo-1,3,5triCQA, plus one glycoside of each diCQA except 1,4-diCQA, two 5-CQA glycosides and two incompletely characterised MaloCQA.*(684-688)* According to the English abstract Li *et al*.*(689)* also isolated the rather unusual 3-CQL. The criteria for this assignment are not stated in the abstract and it is possible that this is a CSA. Jang *et al*. reported the isolation from *E. annuus* leaves of 5-CQA, methyl 3,5-diCQ and 3,5-diCepiQA.*(690)* However, note that the structure shown for this last component is 3,5-diCQA and the authors do not use IUPAC numbering or provide any spectral data in support of the identification.

Berto *et al*. using LC–MS^4 reported in *E. floribundus* 3-CQA, 5-CQA, 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, 5-FQA, 3,5-diCQA, 4,5-diCQA, 3C-5FQA, 3,4,5-triCQA plus an early-eluting component described as 3,4-diCQA and a late-eluting component described as 1,3-diCQA glycoside,*(691)* which may be 1,3-diCQA and a triCQA, respectively.

Zahoor *et al*. reported methyl 3,5-diCQ and methyl 4,5-diCQ in *E. bonariensis(692)* but present the structures as IUPAC methyl 3,4-diCQ and methyl 3,5-diCQ.

Grindelia species: Ferreres *et al*. using LC–MS^3 reported 4-CQA, 5-CQA, 3-FQA, 4-FQA, 5-FQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and 3,5-diFQA in *Grindelia robusta*.*(693)*

Haplopappus species: Schmeda-Hirschmann *et al*. using LC–tandem-MS reported one FQA, 5-CQA, 4,5-diCQA, 3,5-diCQA, three CFQA, two diFQA and one diF-CQA in the herbal tea, baylahuen, prepared from *Haplopappus multuifolius*, *H. taeda*, *H. baylahuen* and *H. rigidus*. Only 3,5-diCQA was found in all five species, and 5-CQA was apparently absent from *H. baylahuen* and *H. rigidus*. the ferulic acid-containing CGA were absent from *H deserticola* and *H. taeda*.*(694)* The original paper used non-IUPAC numbering. The putative diF-CQA eluted comparatively early, well in advance of the diFQA and CFQA, suggesting that it might be a diFQA glycoside.

Heterotheca species: Lin and Harnly using LC–MS^2 reported all four CQA and five of the six diCQA (1,3-diCQA was not found) plus 3C-5FQA and 3,4,5-triCQA in flowers of Mexican arnica, *Heterotheca inuoides*.*(625)* These assignments were made by '*comparison to standards or positively identified compounds in reference plant samples'* but the assignment of 1,4-diCQA should be treated with caution because of the absence of the diagnostic MS fragments associated with 1,4-diCQA and the absence of 1,3-diCQA that rapidly forms from it.

Psiadia species: Wang *et al*. reported 3,5-diCQA, 4,5-diCQA, and the novel 4,5-diCisoQA in *Psiadia trinervia*.*(695)* This novel compound was characterized by circular dichroism (positive first and negative second Cotton effects) as 1*S*,3*R*,4*R*,5*R*-1,3,4,5-tetrahydroxycyclohexane carboxylic acid,*(695)* rather than the usual 1*R*,3*R*,4*S*,5*R* isomer. The quinic acid moiety in this novel CGA was released by saponification and shown to be chromatographically disitinct from (–)-quinic acid. Note that the authors did not use the IUPAC numbering, and their designation as '*iso*-quinic acid' corresponds to the previously reported '*epi*-quinic acid'.

Solidago species: Nugroho *et al.* reported 3-CQA 12.7 g/kg, 5-CQA 22.5 g/kg, 3,4-diCQA 6.6 g/kg, 3,5-diCQA 13.3 g/kg and 4,5-diCQA 5.3 g/kg in the leaves (Chwinamul) of *Solidago virga* var. *90haracter* as sold in South Korea. 3,5-DiCepiQA and 3-pCoQA were not detected. The corresponding data for *S. virga-aurea* var. *asiatica* (= *S. japonica*) are 3-CQA 6.2 g/kg, 5-CQA 12.4 g/kg, 3,4-diCQA 11.0 g/kg, 3,5-diCQA 4.2 g/kg but 3,5-diCepiQA, 3-pCoQA and 4,5-diCQA were not detected. Note that, as discussed above under *Aster scaber,* these quantitative data may not be reliable because the calibrants used were impure, and there is some doubt whether it is 3,5-diCepiQA or 3,5-diCmucoQA. Kim *et al*. reported 1,5-diCQA characterised by NMR after isolation in *S. virga-aurea* var. *90haracter*, *S. virga-aurea* var. *asiatica* and *S. 90haracte* but did not refer to any other CGA.*(481)*

Choi *et al*. isolated 3,5-diCQA and methyl 3,5-diCQ from var. *90haracter* and characterised them by NMR,*(696)* but Jaiswal *et al*. using LC–ion trap-MS reported only 5-CQA, 5-*p*CoQA and 3,5-diCQA in the leaves of *S. virga-aurea* for

which the variety was not defined,*(501)* whereas according to the abstract Abdel-Motal *et al*. reported 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and 3,4,5-triCQA.*(697)* According to the abstract 5-CQA and 3,5-diCQA were isolated from *S. virgaurea* and *S. graminifolia* and characterised by NMR.*(698)*

Methyl 3,5-diCQ,*(699)* 5-CQA, 3,4-diCQA and 4,5-diCQA *(700)* have been reported in *S. chilensis*.

Symphyotrichum species: Jaiswal *et al*. using LC–ion trap-MS reported 3-CQA, 4-CQA, 5-CQA, 3-FQA, 4-FQA, 5-FQA, 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3F-5CQA, 4F-5CQA, 3C-4FQA, 3C-5*p*CoQA, 3C-4*p*CoQA, 4*p*Co-5CQA, 4C-5*p*CoQA, 3,4-diFQA, 3,5-diFQA, 4,5-diFQA, 3,4,5-triCQA and 3,5diC-4FQA in the leaves of *Symphyotrichum novae angliae*.*(496)*

4.4.36.1.4.3. Calenduleae tribe (120 spp)

Calendula species: Olennikov and Kashchenko have reported 3,5-diCQA in the leaves of *Calendula officinalis*,*(701)* plus 4-CQA, 5-CQA, 3,4-diCQA, 1,3-diFQA and the novel 1,3-di-Ifqa in its pollen identified by NMR and the release of isoferulic acid after hydrolysis.*(702)* Fernandes *et al.* also reported 3-CQA,*(703)* but note that none of these reports used IUPAC numbering. Engel *et al*. reported 5-CQA and one incompletely characterised diCQA.*(704)*

Osteospermum species: *Osteospermum* is considered synonymous with *Dimorphotheca.* According to the abstract Soliman *et al*. analysed the flowers and other aerial parts of *H. bracteatum* (Vent.) Andrews, *Gazania nivea* DC. and *Dimorphotheca ecklonis* DC. and reported 3-CQA, 1,5-diCQA, 3,5-diCQA, 1,4,5-triCQA, methyl 3,4-diCQ and methyl 3,5-diCQ,*(526)* but it is not known which numbering system was used or which compounds were in which species.

4.4.36.1.4.4. Coreopsideae tribe (550 spp)

Bidens species: Silva *et al.* using LC–MS^2 identified 5-CQA, 3,5-diCQA, 4,5-diCQA and methyl 5-CQ, this latter confirmed by NMR, in the aerial parts of *Bidens gardneri*.*(705)* The diCQA assignments at regio-isomer level should be viewed as tentative because the fragmentation conditions employed do not correspond to those used to prepare the hierarchical keys. Ping *et al*. reported methyl 3,4-diCQ, methyl 3,5-diCQ and methyl 4,5-diCQ in *B. pilosa*,*(706)* but note that the authors show the structure of methyl 3,4-diCQA as the 4-epimer, i.e. as methyl 3,4-diC-*epi*-quinic acid. Liang *et al*. reported 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and a triCQA, probably 3,4,5-triCQA in *B. pilosa*.*(707)* Gbashi *et al*. using LC–MS^2 reported 3,4-diCQA, 3,5-diCQA, one *cis* isomer of 3,5-diCQA and 4,5-diCQA in the aerial parts of *B. pilosa*.*(708)*

Coreopsis species: Chen *et al*. report chlorogenic acid and 1,3-diCQA in *Coreopsis tinctoria* Nutt.,*(709)* but have probably used non-IUPAC numbering, i.e. the reported compounds should be 5-CQA and 1,5-diCQA. However, the MS data presented are insufficient to distinguish 1,5-diCQA from 3,5-diCQA and this assignment is uncertain. In contrast, Ma *et al*. reported 5-CQA, 3,5-diCQA and 4,5-diCQA.*(710)*

Cosmos species: Shui *et al*. reported 3-CQA, 4-CQA and 5-CQA in *Cosmos caudatus*.*(711)*

4.4.36.1.4.5. Eupatorieae Tribe (2200 spp)

Ageratina species: Zhang *et al*. isolated and characterised by NMR the novel methyl 5-*o*-coumaroylquinate and methyl 5-CQ, methyl 3,4diCQ and *(702)* methyl 3,5diCQ.*(712)*

Brickellia species: Escandon-Rivera *et al*. have reported 3,5-diCQA in *Brickellia cavanillesii*.*(713)*

Eupatorium species: Clavin *et al*. reported 5-CQA in *Eupatorium arnottiana*,*(714)* and Maas *et al*. isolated from *E. perfoliatum* L. and characterized by NMR 3-CQA, 5-CQA, 3,5-diCQA and several dicaffeoylglucaric acids.*(715)*

Mikania species: Xu *et al*. have reported 3,5-diCQA and two uncharacterised *n*-butyl diCQ in the roots of *Mikania micrantha*.*(716)* Wei *et al*. identified these as the *n*-butyl esters of 3,5-diCQA and 4,5-diCQA,*(717)* but did not use IUPAC numbering. De Souza *et al*. using NMR identified 4,5-diCQA in an extract of *M. pseudohoffmaniana*,*(718)* but it is not clear whether or not these authors have used the IUPAC numbering system. De Melo *et al.* have reported '*chlorogenic acid*' as a significant component in the fresh leaves of *M. glomerata* but present below the LOQ in the leaves of some poorly defined but related species.*(650, 719)* Ferreira *et al*. identified methyl 3,5-diCQ in *M. laevigata*.*(720)*

Stevia species: Karaköse *et al*. using LC–ion trap-MS and commercial standards reported that *Stevia rebaudiana* contains 3-CQA (35 mg/kg), 4-CQA (70 mg/kg), 5-CQA (44 mg/kg), 5-*p*CoQA, 5-FQA, 3,4-diCQA (29 mg/kg), 3,5-diCQA (146 mg/kg), 4,5-diCQA (37 mg/kg), 3F-5CQA, 4C-5FQA, 5-CSA, 4-CSA, 3-CSA, 1,3,5-triCQA and 3,4,5-triCQA.*(721)* A subsequent statistical analysis of the data has demonstrated a clear correlation between the formation of cis-caffeoyl derivatives and sunshine hours prior to harvesting, effectively establishing a causal relationship at least in this species.*(587)* In a subsequent publication this group also reported *cis*-5-CQA and two *cis* isomers of 4,5-diCQA.*(722)*

Bender *et al.* reported 3-CQA, 4-CQA, 5-CQA, 5-*p*CoQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and an incompletely characterised CSA, and confirmed the dominance of 4-CQA in *S rebaudiana* Bertoni.*(723)* A similar qualitative profile was reported by Baroso *et al.* but with 5-CQA dominant.*(724)* Molina-Calle *et al*. reported 3-CQA, 4-CQA, 5-CQA, 1,5-diCQA, 3,4-diCQA and 4,5-diCQA based on the fragmentation obtained with LC–QTOF-MS^2, with 4-CQA eluting before 5-CQA and 3-CQA eluting last.*(725)* It is unclear whether or not IUPAC numbering was used, and these assignments at regio-isomeric level must be viewed as tentative.

4.4.36.1.4.6. Gnaphalieae Tribe (1240 spp)

Gnaphalium species: Shikov *et al*. detected 5-CQA and 1,5-diCQA in *Gnaphalium uliginosum*,*(726)* and Olennikov *et al*. reported 3-CQA, 4-CQA, 1,3-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA plus 1,3,5-triCQA and 3,4,5-triCQA,*(727)* but surprisingly made no reference to 5-CQA. However, it is probable that they did not use IUPAC numbering, and it is 3-CQA IUPAC which is not reported.

Rastrelli *et al*. reported 4-CQA, 3,5-diCQA, 4,5-diCQA and 3,4,5-triCQA in *G. stramineum*.*(728)* Cicek *et al.* using LC–MS reported 5-CQA, 3,5-diCQA and 4,5-diCQA in *G. hoppeanum*, *G. norvegicum*, *G. supinum*, *G. sylvaticum* and *G. uliginosum* accompanied by a series of caffeoylglucaric acids some of which have previously been reported only in *Leontopodium alpinum*.*(729)*

Helichrysum species: *Helichrysum* is used in traditional medicines and as flavouring agents. Several species have been analysed using modern procedures including ion trap-MS and it is clear that this species contains an extensive range of CGA, including 1-acyl homo and hetero-diacyl quinic acids, and tri-acyl quinic acids some of which contain a malonic acid residue. Although based on a limited number of samples it is clear that there are significant quantitative variations in CGA content with tissue and species.

Kulisic-Bilusic *et al*. reported 3-CQA, 5-CQA and 5-*p*CoQA in *Helichrysum arenarium*.*(730)* but did not use IUPAC numbering. Carini *et al.* reported 3-CQA, 4-CQA and 5-CQA plus two incompletely characterised diCQA in *H. stoechas*.*(731)* Gouveia and Castilho reported 5-CQA, 1,3-diCQA, 3,4-diCQA, 1,5-diCQA, 3,5-diCQA, 4,5-diCQA, 1C-5FQA, 3,4,5-triCQA and three malo-diCQAs in flowers, stems or leaves of *H. devium*.*(732)* In addition, in *H. melaleucum* they also characterised 5-*p*CoQA, 1,5-di*p*CoQA 4C-5*p*CoQA plus a significant number of CGA that were not fully characterised.*(733)* Examination of their ion trap-MS fragmentation data suggests the presence of a methyl CQ (M_r = 367), a hydroxy-dihydrocaffeoyl-CQA (M_r = 534), a diCQA glycoside (M_r = 678) and four incompletely characterised *p*Co-CQAs (M_r = 500).*(733)* Several other species of *Helichrysum* were found to have similar CGA profiles, but with significant additions, for example 3-CQA, *cis*-5-*p*CoQA, 3*p*Co-5CQA, 3C-5*p*CoQA, 3C-4*p*CoQA and a second incompletely characterised CFQA, either 1C or 5C-4FQA in *H. monizii*.*(621)* A similar LC–ion trap-MS study of *H. obconicum* detected 3-CQA, 5-CQA, 3,4,5-triCQA, 5-*p*CoQA, 3*p*Co-4CQA, 3*p*Co-5CQA, 3C-5*p*CoQA, 4*p*Co-5CQA and 3,4,5-triCSA. A Malo-C-*p*CoQA, an acetyl-diCQA and two diCSA were detected but could not be assigned to regio-isomeric level. Six diCQA were assigned but the fragmentation for the putative 1,4-diCQA did not include the characteristic fragments expected. A diCQA glycoside and four Malo-diCQA were partially assigned but these assignments should be treated as tentative.*(734)* DiCQAs derivatised with an aliphatic dicarboxylic acid are particularly difficult to assign, requiring targeted MS^3 and MS^4 fragmentation, and even then ions corresponding to 1,3-diCQA and 3,5-diCQA derivatives cannot be distinguished.*(488)* Heyman *et al*. using LC–ion trap-MS^4 and NMR examined 30 *Helichrysum* spp. of South African origin and reported 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 1,3,5-triCQA and either 5Malo-1,3,4-triCQA or 3Malo-1,4,5-triCQA in *H. populifolium*.*(735)* Martin *et al*. reported that *H. populifolium* produced 1,5-diCQA.*(736)*

A later study provides quantitative data for the major CGA in various tissues of these four species that can be summarised as follows: 5-CQA 0.35–3.76 g/kg, 1,3-diCQA below LOQ up to 0.04 g/kg, 3,4-diCQA below LOQ up to 0.19 g/kg, 1,5-diCQA 0.096–4.4 g/kg, 3,5-diCQA 0.04–3.0 g/kg, 4,5-diCQA **57** 0.17–0.5 g/kg and 3,4,5-triCQA below LOQ up to 0.05 g/kg.*(737)* Commercial standards were used for calibration, with response factors as follows: 5-CQA 0.54; 1,3-diCQA 1.44; 3,4-diCQA 1.17; 1,5-diCQA 0.90; 3,5-diCQA 1.35; 4,5-diCQA 1.21; and 3,4,5-triCQA 1.30. This suggests that all contained non-UV-absorbing impurities, and that the quantitative data, particularly for 3,4,5-triCQA, are not reliable.

Mari *et al*. analysed the flowers of *H. italicum* using LC–MS^2 and reported 5-CQA, 4M-5CQA, 3,4-diCQA, 4,5-diCQA and methyl 3,5-diCQ based on fragmentation and NMR spectroscopy of the isolates.*(738)* Note that the structure shown by these authors for methyl 3,5-diCQ is incorrect. Also note that the assignment of 4M-5CQA (M_r = 368) seems very unlikely because of an MS^2 fragment at *m/z* 193, suggesting that this component should be assigned as an FQA. Moreover, the original identification of 1M-5CQA in *Phyllostachys edulis(26)* is now known to be incorrect,*(25)* and that compound is more likely to be a methyl CQ.

According to the abstract Soliman *et al*. analysed the flowers and other aerial parts of *H. bracteatum* (Vent.) Andrews, *Gazania nivea* DC. and *Dimorphotheca ecklonis* DC. and reported 3-CQA, 1,5-diCQA, 3,5-diCQA, 1,4,5-triCQA, methyl 3,4-diCQ and methyl 3,5-diCQ,*(526)* but it is not known which numbering system was used or which compounds were in which species.

Leontopodium species: Schwaiger *et al*. using LC–MS and NMR reported 5-CQA, 3,5-diCQA and at least three, possibly five more incompletely characterised diCQA in *Leontopodium alpinum* (Edelweiss), but whether these are *cis* isomers and whether 1-acyl diCQA are present is unclear. Screening of eight other species (*L. campstre*, *L. leontopodioides*, *L. ochroleucum*, *L. francheti*, *L. palbinianum*, *l. sinense*, *L. soulei* and *L. subulatum*) showed variations in content of approximately one order of magnitude.*(739)* Cicek *et al.* using LC–MS reported 5-CQA, 3,5-diCQA and 4,5-diCQA in *L. alpinum* accompanied by a series of novel caffeoylglucaric acids some of which are also found in *Gnaphalium* species.*(729)*

Phagnalon species: Gongora *et al*. have made several studies of *Phagnalon rupestre*, reporting 3,5-diCQA and 4,5-diCQA, and their methyl esters.*(740-742)*

4.4.36.1.4.7. Heliantheae tribe (1461 spp)

Acmella species: Kasper *et al.* reported 3-CQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and 1,3-diCepiQA, in *Acmella ciliata* Kunth.*(743)* These were all identified by comparing their NMR data, which are not presented, with literature values,*(640)* but as discussed elsewhere the assignment of 1,3-diCepiQA remains uncertain and further evaluation of this assignment is not possible.

Ambrosia species: Tamuar *et al*. reported 5-CQA and 3,5-diCQA in *Ambrosia artemisiifolia*L after extraction and NMR characterisation.*(744)*

Arnica species: Petersen *et al*. reported 5-CQA in *A. chamissonis*.*(20)* Comparatively early studies located 5-CQA, 1,3-diCQA, 1,5-diCQA, and 1,4,5-triCQA in *Arnica montana*: these four compounds plus methyl 3,4,5-triCQ 334 were found in *A. chamissonis* ssp. *foliosa* var. *incana*.*(745)* Spitaler *et al*. demonstrated that the content of 1Mo-3,5diCQA in the flower heads of *A. montana* cv ARBO increased with the altitude of cultivation in the range 590 to 2230 m, with temperature rather than UVB irradiation being the key trigger. 5-CQA, 3,5-diCQA, a second diCQA (probably 4,5-

diCQA) and five other cinnamoylquinic acid derivatives were observed but not fully characterised.*(746-749)* Perry *et al*. reported that 3,5-diCQA was the dominant CGA in Spanish *A montana.(750)*

An extensive study by Lin *et al*. using LC–MS^2 with NMR-characterised in-house isolated standards and surrogate standards such as green coffee extract and artichoke extract made a thorough study of the CGA in arnica flowers (*A. montana*). In *A. montana* they reported 1-CQA, 3-CQA, 4-CQA, 5-CQA, 5-SiQA, 5-FQA, 1,3-diCQA, 1,4-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 1,4,5-triCQA, 3,4,5-triCQA, 3C-5FQA, 3Si-4CQA, 3Si-5CQA, plus a series of tri and tetra-acyl quinic acids, as follows: 1Mo-3Si-5CQA, 1,5diC-3MoQA, 1Mo-4Si-5CQA, 1Mo-3,5diCQA, 1Mo-4,5diCQA, 3Si-4Mo-5CQA, 1,5diC-3,4diMoQA, 1,4,5triC-3MoQA plus an incompletely characterised diC-SucQA.*(110)* This appears to be the first report of sinapic acid-containing CGA in Asterales.

Jaiswal *et al*. using LC-ion trap-MS found 1-CQA, 3-CQA, 4-CQA, 5-CQA and *cis*-5-CQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and two *cis*-3,5-diCQA, 1,3,5-triCQA, 3,4,5-triCQA, 5-FQA, 1C-3FQA, 1C-4FQA, 1C-5FQA, 1,3diC-4MoQA, 3,5diC-4MoQA, 1,5diC-3MoQA, 1Mo-4,5diCQA, 3C-4F-5MoQA, 3F-4Mo-5CQA, 1,5diC-4FumQA, 1,5diC-3FumQA, 3,5diC-1,4diMoQA, 1Mo-3,4,5triCQA and 1,3,4triC-5MoQA in *A. montana* leaves and flowers.*(501, 751)*

Clauser *et al*. using LC–ion trap-MS^3 and commercial 5-CQA as calibrant reported that the major CGA in *A. montana* flowers were 5-CQA (2–5 g/kg), 3,5-diCQA (5.0–11.3 g/kg) and 1Mo-4,5diCQA or 1Mo-3,5diCQA (3.4–8.6 g/kg).*(752)* Using 5-CQA as the calibrant for diCQA over-estimates the diCQA content by *ca* 40% because although the molar absorbance approximately doubles (see Part 3) the molecular mass only increases by 1.46.

These three sets of data are similar, and while some of the differences might reflect genuine difference in the material analysed, some might be explained by the difficulty of assigning the more complex CGA without the use of an ion trap-MS.

Echinacea species: Cheminat *et al.* reported 5-CQA, 3,5-diCQA and 4,5-diCQA after NMR characterisation of isolates prepared from *Echinacea pallida*.*(753)* Pellati *et al* reported 'chlorogenic acid' and 'cynarin' at a significant level in *E. angustifolia* var. *angustifolia* and *E. tennesseensis* but only 'chlorogenic acid' in *E. paradoxa* var. *paradoxa* and *E. atrorubens*. In all other species examined, *E. pallida, E. purpurea, simulate, E. paradoxa* var *neglecta, E. laevigata* and *E. sanguinea*, both these components were below the limit of detection,*(754)* but is uncertain which numbering system was used.

Eclipta species: Lee *et al.* isolated and characterised by LC–MS and NMR 5-CQA, 3,4-diCQA, 3,5-diCQ and 4,5-diCQA from the aerial parts of *Eclipta prostrata*.*(755)* In addition to the foregoing, Fang *et al* using LC–ion trap-MS reported 4-CQA,*(756)* but the fragments did not include *m/z* 173, which should be the MS^2 base peak, and the close similarity of the fragmentation to that he reports for 5-CQA suggests that this might be *cis* 5-CQA.

Helianthus species: Sunflower seeds (*Helianthus annuus* L.) were one of the first commodities to be analysed for their CGA content because of their role after oxidation in the discolouration and insolubilization of sunflower proteins,*(757-759)* and because undefined 'chlorogenic acid' the associated cinnamic acids (caffeic, ferulic and *p*-coumaric) appear in sunflower honeys and are important in monitoring authenticity.*(760, 761)*

A more detailed analysis of sunflower shells and kernels established that 5-CQA dominated and inspection of their ion trap-MS data suggests that a fourth uncharacterised CQA detected is probably *cis*-5-CQA. Quantitative data are presented for the CGA in several varieties of oil seed and non-oil seed sunflower kernels and shells but there are no major differences in profile. As an example, kernels contained 2.5–4.4 g/kg of 3-CQA, 0.6-0.9 g/kg of 4-CQA, 30.5 g/kg of 5-CQA, 0.1 g/kg of 5-*p*CoQA, 0.2–0.4 g/kg of 5-FQA, 0.3 g/kg of 3,4-diCQA, 2.1–3.3 g/kg of 3,5-diCQA and 1.2–1.7 g/kg of 4,5-diCQA while the shells contained 29–48 mg/kg of 3-CQA, 21–47 mg/kg of 4-CQA, 591 mg/kg of 5-CQA, 12–21 mg/kg of 5-*p*CoQA, 5–12 mg/kg of 5-FQA, 10–14 mg/kg of 3,4-diCQA, 44–81 mg/kg of 3,5-diCQA and 26–43 mg/kg of 4,5-diCQA.*(762)* These quantifications were made using the most appropriate commercial standard (5-CQA or 1,3-diCQA) with a correction for molecular mass, but the response factors were not reported. In addition to the CGA reported by Weisz *et al*., Karamac *et al*. also reported 3-*p*CoQA and 4-*p*CoQA. In addition they reported six uncharacterised diCQA (compared with three), five uncharacterised CDQA and one uncharacterised CFQA in sunflower kernels.*(763)*

A similar analysis of free (80% acetone-soluble) and bound (released by hydrolysis with 1.2 M HCl–MeOH) CGA in disc florets and ray florets has recorded some marked differences in CGA profiles. For example, 5-CQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA are found only in the free form, with 1,5-diCQA dominating, and always at greater concentration in the disc florets. In contrast, 3-FQA, 4-FQA, 5-FQA and three incompletely characterised CFQA were found only in the bound form, again at greater concentration in the disc florets.*(764)* It should be noted that mass fragmentation data were available for only one (3-FQA) of these six putative ferulic acid-containing CGA and this yielded an ion at *m/z* 179 strongly suggesting that this should have been assigned as methyl 3-CQ, and possibly this mis-assignment applies to the other five related components which would be expected to form from residual CQA and diCQA when the sample is heated in HCl–MeOH. 1,5-DiCQA has been reported also in sunflower sprouts.*(765)*

The tubers of Jerusalem artichokes, *H. tuberosus*, have been reported to contain '*chlorogenic acid*' that contributes to after-cooking blackening, but, surprisingly, no further information has been located.*(766, 767)* In contrast, Jaiswal *et al*. *(496)* analysed the leaves of *H. tuberosus* and *reported* 1-CQA, 3-CQA, 4-CQA, 5-CQA, 3-FQA, 4-FQA, 5-FQA, 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, 1,4-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA, 1C-3FQA, 1C-4FQA, 1C-5*p*CoQA, 3C-5*p*CoQA, 3*p*Co-5CQA and 4C-5*p*CoQA. An epimeric CQA was also present, identical to that found in *Carlina acaulis*, but different from that in *Rudbeckia hirta*. *(496)*

There are other papers reporting the CGA profile of in the leaves of *H. tuberosus*. Yuan *et al*. using LC and a 5-CQA commercial standard reported 5-CQA, 1,3-diCQA, 3,4-diCQA, 3,5-diCQA in the leaves of *H. tuberosus*,*(768)* but did not use IUPAC numbering. Note however that the retention time of the putative 1,3-diCQA is so late as to suggest that it might be 1,5-diCQA IUPAC. A 3,5-diCQA methyl ether was also reported, but the structure shown is methyl 3,5-diCQ. Chen *et al.,* using LC–triple quadrupole-MS, reported 5-CQA, two other CQAs, four diCQAs, one *p*CoQA and one FQA,*(769)* but the assignment to regio-isomer level is uncertain and should be viewed as tentative. By defining their primary standard as commercial 3-CQA in these two original papers it appears that they used the non-IUPAC numbering.

Rudbeckia species: Jaiswal *et al*. using LC–ion trap-MS reported 3-CQA, 4-CQA, 5-CQA, 3-FQA, 4-FQA, 3-*p*CoQA, 5-*p*CoQA, 1,4-diCQA, 1,5-diCQA, 3,5-diCQA, 3-CSA, 4-CSA and 5-CSA in the leaves of *Rudbeckia hirta*. An epimeric CQA was also present, but different from that found in *Helianthus tuberosus* and *Carlina acaulis*. *(496)* In contrast, *R. laciniata* has been reported by Lee *et al*. to contain 3-CQA, methyl 5CQ, 3,4-diCQA, 3,5-diCQA, methyl 3,4diCQ, methyl 3,5diCQ, methyl 4,5diCQ and 3,5-diCepiQA.*(770)* LC–ion trap-MS failed to detect 3,5-diCepiQA in *R. hirta*.*(496)* Note that Könczol *et al.* consider the original assignment of 3,5-diCepiQA as unproven,*(605)* thus placing some doubt on its occurrence in *R. laciniata*.

Sanvitalia species: Wang *et al*. reported 5-CQA in *Sanvitalia procumbens* var. *oblongifolia*.*(771)*

Sphagneticola species: Fucina *et al* using LC–ion trap MS^3 reported 3-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA, 4.5-diCQA, an incompletely assigned triCQA plus 3F-4CQA in *Sphagneticola trilobata*.*(772)* Although the fragmentations reported support the assignments given, the order of elution is unusual, with 5-CQA preceeding 3-CQA, and 4,5-diCQA preceding 3,5-diCQA followed by 3,4-diCQA.

Xanthium species: The fruits of the *Xanthium* spp. are used in traditional medicines and the seeds of *Xanthium strumarium* were shown by Agata *et al*. to contain 3,5-diCQA and 1,3,5-triCQA after isolation and NMR characterisation.*(773)* Yoon *et al*. reported 5-CQA, 1,3-diCQA, 1,5-diCQA, 3,5-diCQA, 1,3,5-triCQA, methyl 5-CQ and methyl 3,5-diCQ in *Xanthium strumarium*,*(774)* but did not use IUPAC numbering.

Han *et al*. using LC–ion trap-MS^2 identified and quantified the CGAs in the fruits of *Xanthium sibricum* var. *subinerme* (Winkl.) Widder and *X. mongolicum* Kitag.*(775)* These Xanthium species contain 0.3-1.2 g/kg of 1-CQA, 0.1–0.4 g/kg of 4-CQA, 0.7–2.2 g/kg of 5-CQA, 0.6–3.0 g/kg of 1,5-diCQA, 0.5–0.6 g/kg of 1,3-diCQA, 0.1–0.5 g/kg of 4,5-diCQA and 0.1 g/kg of 1,3,5-triCQA. 1,4-DiCQA was also reported. Quantification employed a combination of commercial standards and purified isolates with the following response factors: 5-CQA 13.75; 1-CQA 13.73; 4-CQA 14.04; 1,5-diCQA 32.29; 1,3-diCQA 32.21; 4,5-diCQA 31.88; 1,3,5-triCQA 45.32. With the exception of 1,3,5-triCQA, which appears to contain non-UV-absorbing impurities, these calibrants show the expected relative response factors.

Yang *et al*. using LC–MS^2 reported four incompletely characterised CQA and five incompletely characterised diCQA in *X. sibricum*.*(776)*

It has been reported that *X. occidentale* contains 5-CQA and 1,3-diCQA,*(777)* and that *X. strumarium* contains 3-CQA, 3,5-diCQA and 1,3,5-triCQA,*(778)* and plus 1,5-diCQA, 1,3-diCQA, methyl 3,5-diCQ and methyl 3-CQ.*(779)*

Zinnia species: Ranger *et al*. using LC–MS reported 5-CQA and a *p*CoQA in the leaves of *Zinnia elegans*.*(780)*

4.4.36.1.4.8. Inuleae tribe (687 spp)

Achyrocline species: Marques and Farah using LC–MS reported 3-CQA 66 mg/kg, 4-CQA 97 mg/kg, 5-CQA 336 mg/kg, 3,4-diCQA 571 mg/kg, 3,5-diCQA 309 mg/kg and 4,5-diCQA 242 mg/kg in *Achyrocline satureioides*,*(35)* but the

calibrants are not clearly stated. Toffoli-Kadri *et al*. reported 3,5-diCQA and 4,5-diCQA in *A. alata*,*(781)* but it is not clear which numbering system was used.

Geigeria species: Zheleva-Dimitrova *et al* have profiled extracts of *Geigeria alata* by LC–ion trap-MS^2 and reported 3-CQA, 4-CQA, 5-*p*CoQA, 3-FQA, 4-FQA, 5-FQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3,4,5-triCQA, 3C,5FQA and 3C,5SiQA.*(782)* Sinapoylquinic acids are rare in Asteraceae.

Inula species: Jaiswal *et al*. using LC–ion trap-MS reported 1-CQA, 3-CQA, 5-CQA, 5-FQA, 5-*p*CoQA and 3C-4FQA in the leaves of *Inula helenium*.*(501)* Stojakowska *et al*. analysed an extract of *I. helenium* L. callus culture and reported 3-CQA, 4-CQA, 5-CQA, 1,3-diCQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA, plus 3C-5FQA and 3C-5SiQA .*(783)*

Kinoshita *et* al. reported 5-CQA in the root of *I. linariaefolia*.*(784)* Stojakowska *et al*. reported 5-CQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in the roots of *I. ensifolia*.*(785)*

1,5-diCQA has been reported in the roots of *I. crithmoides,(786)* accompanied by 3,5-diC-1-methyl-QA and 4,5-diC-1-methyl-QA.*(787)* However, the *O*-methyl protons were recorded at δ 3.71–3.74 suggesting that they might be methyl esters rather than methyl ethers.

Mahmoudi *et al*. reported 5-CQA, 1,3-diCQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and one incompletely characterised *p*CoCQA in the leaves *I. vicosa* Aiton,*(788)* but did not use IUPAC numbering.

Perralderia species: Boussaha *et al*. have reported methyl 3,4-diCQ, methyl 3,5-diCQ and 1,5-diCQA in *Perralderia coronopifolia* Coss. subsp. *eu-coronopifolia* M. var. *typica* M.*(789)*

Schizogyne species: Venditti *et al*. reported 3-CQA, 4-CQA, 1,3-diCQA and 3,5-diCQA in *Schizogyne sericea*.*(790)* Note that the authors describe 3-CQA as '*chlorogenic acid*' but show all structures using IUPAC numbering and it is not possible to judge which numbering system has been used.

Telekia species: 5-CQA has been reported in the flowers of *Telekia speciose*.*(791)*.

Tessaria species: Ono *et al*. isolated from *Tessaria integrifolia* and characterised by NMR methyl 3,4-diCQ, methyl 3,5-diCQ, methyl 4,5-diCQ, 4,5-diCQA and 4,5-diCisoQA.*(792)* Note that these authors did not use the IUPAC numbering, and that the structure shown corresponds to the previously reported 4,5-diCepiQA.

4.4.36.1.4.9. Millerieae tribe (380 spp)

Smallanthus species: Takenaka *et al.* isolated and characterised by NMR 5-CQA and 3,5-diCQA, and several novel caffeic acid esters of altraric acid, from the roots of Yacon (*Smallanthus sonchifolius*),*(793)* Serra-Barcellona *et al*. isolated and characterised 5-CQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA from the leaves of *S. sonchifolius* and *S. macroscyphus*.*(794, 795)* Russo *et al*. reported 5-CQA, 1,3-diCQA, 1,5-diCQA, 3,5-diCQA and 4,5-diCQA in the leaves of 14 varieties of *S. sonchifolius*.*(796)*

4.4.36.1.4.10. Plucheae tribe

Pluchea species: Martino *et al*. reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *Pluchea symphytifolia*.*(797)* This was confirmed by Scholz *et al*.*(798)* who reported 3,4-diCQA (2.3 g/kg), 4,5-diCQA (1.6 g/kg), 3,5-diCQA (2.3 g/kg), 3,4,5-triCQA (0.4 g/kg), 1,3,4,5-tetraCQA (0.5 mg/kg) and two novel cyclobutane derivatives thereof (1 g/kg), in the aerial parts of *P. symphytifolia*, a medicinal plant from Oaxaca and Mexico. Exposure of the greenhouse grown plant to UV light significantly increased the contents of the cyclobutane derivatives.

Arsiningtyas *et al.* isolated 3,5-diCQA, 4,5-diCQA, 3,4,5-triCQA and 1,3,4,5-tetraCQA from the leaves of *P. indica*,*(799)* and Ali using LC–MS^2 also reported 3-CQA and 5-CQA but failed to detect the tetra-CQA. The diCQA, particularly 3,5-diCQA exceeded the CQA content.*(166)* Cordova *et al.* reported 5-CQA, 3,4-diCQA (dominant), 3,5-diCQA, 4,5-diCQA, 3,4,5-triCQA and 1,3,4,5-tetraCQA in *P. carolinensis* from Cuba,*(800)* but did not use IUPAC numbering.

The cyclobutane derivatives are photoproducts formed from 1,3-diCQA. It seems surprising that exclusively the 1- and 3-caffeoyl moieties react in a [2+2] photocycloaddition and not any pair of 1,2 dicaffeoyl moieties, which appear to be sterically closer. We would like to interpret this observation in terms of the Schmidt law, which states that in solid state photocycloadditons a critical distance must occur between the two reacting olefinic moieties. This critical distance appears to be present only in the case of the 1,3-diacyl regioisomers.

4.4.36.1.4.11. Senecioneae tribe (3500 spp)

Cacalia species: The nomenclature and classification of *Cacalia* is uncertain and confused. Park *et al*. analysed the leaves of *Cacalia firma* (Komarov) Nakai which elsewhere is described as *Parasenecio firmus* (Komarov) and according to the English abstract reported contents on a dry basis as 3-CQA (1.35 g/kg), 5-CQA (5.2 g/kg), 3-*p*CoQA (3.84 g/kg), 3,4-diCQA (1.44 g/kg), 3,5-diCQA (3.74 g/kg) and 3,5-diCmucoQA (2.47 g/kg). 4,5-DiCQA was not detected.*(801)* However, as commented elsewhere, the order of elution from the C_{18} column packing is not typical, and 3,5-diCmucoQA is described elsewhere in the text as 3,5-di*CepiQA*, and some uncertainty remains about the validity of this report.

Gynura species: Wan *et al.* have reported 3,5-diCQA in the leaves of *Gynura divaricata*.*(802)* Chen *et al*. extracted the following CGA from the aerial parts of *G. divaricata* and characterised them by NMR and MS: 5-CQA, 5-*p*CoQA, 5-FQA, methyl 5-CQ, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, methyl 3,4-diCQ, methyl 3,5-diCQ, methyl 4,5-diCQ and ethyl 4,5-diCQ.*(803)* A subsequent analysis of three samples from different locations revealed significant differences in profile with one out of three samples (from Guangzhou) lacking CQA whereas another (from Nanjing) lacked *p*CoQA. Only the sample from Nanjing contained 3,4-diCQA, 3,5-diCQA and 4,5-diCQA (but lacked a fourth diCQA reported in some *G. bicolor*), the sample from Nanping contained only 3,4-diCQA and the sample from sample Guangzhou contained none of them.*(804)*

Teoh *et al*. reported 5-CQA, 5-*p*CoQA and 3,5-diCQA in the leaves of *G. bicolor*.*(805)* As for *G. divaricata* Chen *et al*. reported considerable variation in the composition of *G. bicolor* with the sample from Nanjing containing *cis* and *trans* 3-CQA and 5-CQA, *trans* 4-CQA, the corresponding *p*CoQA except for *cis* 5-*p*CoQA, plus 4-FQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and a fourth incompletely characterised late eluting diCQA. The other four samples (from Nanping, Guangzhou, Haikou and Nanchang) lacked 3,4-diCQA, 4,5-diCQA and the late eluting isomer, and only one other (Haikou) contained 3,5-diCQA.*(804)*

The Thai medicinal plant *G. pseudochina* var. *hispida* contains 5-CQA, 3,5-diCQA and 4,5-diCQA, all extracted and characterised by NMR.*(806)*

Hubertia species: Some authorities consider *Hubertia* to be identical with *Senecio*. Three novel compounds have been characterised by LC–NMR, LC–MS and 600 MHz NMR after isolation in extracts of *H. tomentosa*. These are 3,5-di-*O*-caffeoyl-4-*O*-[(4-hydroxyphenyl) acetyl]quinic acid **366**, 3,5-di-*O*-caffeoyl-4-*O*-[(1-hydroxy-4-oxocyclohexa-2,5-dienyl)acetyl]quinic acid, and its 2-hydroxy-quinic acid analogue. This last is a tri-acyl derivative of the novel 2-hydroxy-quinic acid, in which the additional hydroxyl is disposed equatorially, and which was not found in *H. ambavilla*. Several CQA and diCQA, including 5-CQA, were also present but not fully characterised in this study.*(566)*

Jacobaea species: NMR analysis of tissue from *Jacobaea vulgaris*, *J. aquatic* and their crosses has detected 3-CQA, 5-CQA and 5-FQA.*(807)*

Ligularia species: Several species of *Ligularia* have been analysed and the somewhat inconsistent results are summarised below. Shang *et al*. using LC–ion trap-MS^3 analysed the leaves of *Ligularia fischeri*, an edible medicinal plant used in Korean folk medicines, and reported 26.7 g/kg of 5-CQA, 17.0 g/kg of 3,4-diCQA, 49.0 g/kg of 3,5-diCQA and 9.0 g/kg of 4,5-diCQA.*(808)* The reported fragmentations plus NMR data convincingly establish the identity of these CGA but the calibrant response factors were not reported.

In contrast, a contemporaneous study by Lee *et al*. of the leaves of *L. stenocephala*, *L. fischeri* var. *spiciformis* and *L. fischeri*, failed to locate 4,5-diCQA, and reported 5-CQA, 3,5-diCQA and 3,5-diCmucoQA as the major CGA *(809)* Lee's study used purified CGA isolated from *Lactuca indica* for identification,*(549)* and reported additionally that the leaves of *L. fischeri* var. *spiciformis*, but not *L. fischeri*, also contained 3-CQA, whereas the leaves of *L. stenocephala* contained 3-*p*CoQA, but not 3-CQA.*(809)* Confusingly, another study from the Lee's group of *L. stenocephala* leaves yielded 3-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and 3,5-diCmucoQA.*(810)*

There are, however as stated elsewhere, some peculiar features to this group's reversed phase (C_{18}) chromatograms: for example, the earliest eluting CGA (*ca* 2.5 min) is annotated as 3,4-diCQA, with 3-CQA (*ca* 9 min) eluting after 5-CQA (*ca* 5 min) and these assignments must be treated with caution. Nugroho *et al*. describe their standards as supplied by Professor Kang Ro Lee (see Kwon *et al.(661)*) and in this original account there is no reference to 3,4-diCQA.

A later study established that CGA contents were significantly higher in the leaves of *Ligularia fischeri* (Ledeb.) Turcz plants grown in sunlight than of those grown in shade and reported also 3,4,5-triCQA and 1,3,4-triCQA.*(811)* The CGA

identifications were made using LC–MS and NMR after isolation. Similarly, Park *et al*. reported 3-CQA, 5-CQA and 3,5-diCQA in the leaves of *L. fischeri* Turcz.*(812)*

Kim *et al*. reported 1,5-diCQA in *L. taquetii,(481)*, but in contrast Hussain *et al*. reported 3,5-diCQA in *L. thomsonii*,*(813)* and neither group referred in these studies to any other CGA.

Petasites species: Jaiswal *et al*. using LC–ion trap-MS reported 5-CQA, 5-FQA, 3,5-diCQA, 4,5-diCQA, 1C-3FQA and 1C-4FQA in the leaves of *Petasites hybridus*,*(501)* Kim *et al*. using LC–ion trap-MS^n and NMR have reported 5-CQA, 3,5-diCQA and 4,5-diCQA in *P. japonicas*,*(814)* and according to the Engliosh abstract Zhang *et al*. reported 5-CQA in *P. trichlobus*.*(815)*

Roldana species: Arciniegas *et al*. isolated 5-CQA and 4,5-diCQA from *Roldana aschenborniana*,*(816)* but did not use IUPAC numbering.

Senecio species: Tan *et al*. reported 3,5-diCQA in *Senecio scandens*.*(817)* Yang *et al*. reported in *S scandens* 5-CQA plus a *p*CoQA, an FQA, two diCQA and two CFQA that were incompletely characterised. In contrast, only 5-CQA and the two diCQA were found in *S. vulgaris*,*(818)* but note that IUPAC numbering was not used.

De Souza *et al*. using LC–quadrupole ion trap-MS reported 1,4-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in the flowers of *S. brasiliensis* (Spreng) Less.*(819)* These structural assignments should be treated with caution — the authors show the structucre of their putative 4,5-diCQA as having the C1 and C5 hydroxyls axial and the C3 and C4 hydroxyls equatorial suggesting that possibly they have used non-IUPAC numbering. Although an ion trap instrument is used the relevant fragmentation is not presented and the assignments cannot be confirmed.

See also *Hubertia* species which some authorities consider to be identical to *Senecio* spp.

Tussilago species: Gao *et al*. reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in the flower buds of *Tussilago farfara* L. and characterised all three by NMR and optical activity. All three diCQA had strong negative specific rotation.*(820)* Other investigators have reported the same profile of diCQA.*(821-823)* Kang *et al.* using 1D and 2D NMR reported methyl 4,5-diCQ, methyl 3,5-diCQ and 3,4-diCisoQA in the flower buds of *Tussilago farfara*.*(824)* It is unclear whether or not the IUPAC numbering system was used. Their data, particularly the positive specific rotation, for the acyl-*iso*-quinic acid match well with data from Ono *et al*.,*(792)* and Wang *et al*.*(695)* for isolates of 4,5-diCepiQA IUPAC from *Tessaria integrifolia* (Inuleae) and *Psiadia trinerva* (Astereae), respectively, and very different to the corresponding data for 3,4-diCQA, 3,5-diCQA and 4,5-diCQA.

4.4.36.1.4.12. Tageteae tribe (267 spp)

Tagetes species: Peteresen *et al*. failed to find 5-CQA in *Tagetes tenuifolia.(20)* Ranilla *et al*. reported a high content of hydroxycinnamic acids in the leaves of *T. minuta*, but did not report their precise identitiy.*(56)*

4.4.36.1.5. UNCLASSIFIED

Bellis species: Asteraceae Scognamiglio *et al*. reported 3-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA, 4.5-diCQA and methyl 3,4-diCQ in the leaves of *Bellis perennis*.*(825)*

Lapsana species: Asteraceae Fontanel *et al*. reported 5-CQA and 3,5-diCQA in *Lapsana communis*.*(826)*

ASTERALES SUMMARY

The Asteraceae, formerly Compositae, is considered to be the largest family of flowering plants and contains over 1600 genera and over 24,000 species,*(477)* some of which are used for food, as flavourings, or in traditional medicine. The classification is complex with seven subfamilies, *(477)* but data for the CGA content are available only for four, Asteroideae, Carduoideae, Cichorioideae and Mutisioideae.

Data for the Mutisioideae subfamily are limited to one genus in the tribe Mutisieae which has not been thoroughly profiled but appears to contain 1-acyl diCQA.

The Carduoideae subfamilly is better represented with 16 genera from the Cardueae (= Cynareae) tribe, and seven genera have been well profiled, six (*Arctium, Cynara, Echinops, Ononpordum, Rhaponticum, Saussurea*) showing 1-acyl diCQA but the seventh not. Good evidence of a caffeoyl ester of a quinic acid epimer in *Carlina* which also has been profiled but which does not have 1-acyl-diCQA.

Some genera seem to have a much narrower diCQA profile (*Centaurea*, *Cirsium*, *Dolomiaea*, *Silybum*) or even to lack diCQA (*Cnicus*) but thorough profiling is required to confirm this.

Data for the Cichorioideae subfamily encompasses only two tribes with sufficient data. For Tribe Cichorieae (= Lactuceae) 14 of the 21 genera studied have been profiled. Many profiled genera lack 1-acyl-diCQA (*Crepis, Hieracium, Hypochoeris, Lactuca, Leontodon, Picris, Prenanthes, Rhagadiolus, Robertia, Tragopogon* and *Urospermum*) whereas others clearly have 1-acyl-diCQA (*Cichorium, Podospermum* and *Scorzonera*).

Podospermum and *Scorzonera* stand out with the presence of dihydrocaffeoyl-quinic acid derivatives, which might have been overlooked elsewhere, and *Sonchus* stands out with *p*-hydroxyphenylacetyl-quinic acids otherwise found only in *Hubertia*, but again possibly overlooked.

Good evidence for a dicaffeoyl-*epi*-quinic acid in *Scorzonera*, and *Andryala* may contain a novel (*p*-coumaroyl-caffeoyl)-quinic acid depside.

For tribe Vernonieae data only for four genera, of which only two profiled. *Lychnophora* without 1-acyl-diCQA but *Vernonia* clearly with 1-acyl-diCQA, and evidence of a dicaffeoyl-*epi*-quinic acid. *Eremanthus* and *Elephantopus* on very limited data, no LC–MS profiling, appear to have no 1-acyl-diCQA.

There are more data for the Asteroideae subfamily, and 12 tribes are represented, but insufficient data for five of them, and even in the other seven not many genera fully profiled.

The Senecioneae tribe is represented by nine genera but only *Petasites* has LC–MS profile which suggests there is a 1-acyl CFQA, but no evidence of 1-acyl-diCQA. *Cacalia, Hubertia, Gynura, Jacobea, Ligularia, Roldana, Senecio* and *Tussilago* have not been profiled but appear not to contain 1-acyl diCQA

Hubertia, as also *Sonchus* above, has *p*-hydroxyphenylacetyl-quinic acids, but *Hubertia* also has esters of 2-hydroxyquinic acid. *Tussilago* a strong candidate for a dicaffeoyl-*epi*-quinic acid. *Ligularia* and *Cacallia* possibly also.

The Astereae tribe is represented by 13 genera of which only two have been profiled, *Aster* and *Erigeron*, both with 1-acyl-diCQA, but *Kalimeris, Heterotheca* and *Solidago* also have 1-acyl-diCQA. *Aster* extremely variable.

Many unprofiled genera (*Baccharis, Centipeda, Chrysothamnus, Dichrocephala, Grindelia, Happlopappus* and *Symphiotrichum*) show no evidence of 1-acyl-diCQA. *Psiadia* has only 3,5-diCQA and 4,5-diCQA but also a diacyl-*epi*-quinic acid.

Aster, Erigeron and *Symphiotrichum* have the less common diacyl-quinic acids (diFQA, CFQA, pCoCQA, pCoFQA) and *Aster* and *Erigeron* also have aliphatic derivatives. These and the *epi*-quinic acid derivative of *Psiadia* may have been overlooked in the non-profiled genera.

For Tribe Anthemidieae, five out of 11 genera have 1-acyl. *Achillea, Artemisia, Chrysanthemum* and *Matricaria* have been profiled and all have 1-acyl-diCQA but subject to ploidy in *Achillea* and *Matricaria*. *Artemisia* also has diFQA and CFQA, and *Chrysanthemum* also has aliphatic. A single report for *Inulanthera* records 1-acyl and possibly a diacyl-*epi*-quinic acid which might also be present in some but not all *Chrysanthemum* and *Artemisia*.

Single reports for *Anthemis, Calea, Eriocephalus, Laggera* and *Tanacetum* show no evidence for 1-acyl.

Tribe Inuleae has only two profiled genera, *Giegeria* lacking 1-acyl diCQA and *Inula* which has 1-acyl-diCQA, as also do *Perralderia* and *Schizogyne*. Others apparently do not, but *Tessaria* a good candidate for diacyl-*epi*-quinic acid. *Geigeria* has CFQA and CSiQA, the latter very rare in Asterales.

Tribe Heliantheae represented by 11 genera. LC–MS profiles of Arnica, *Helianthus* and *Rudbeckia* show 1-acyl diCQA. *Arnica* also has CFQA and CSiQA, sinapic acids very rare in Asterales. *Helianthus* has CFQA and *p*CoCQA and evidence for a mono-caffeoyl ester of an undefined quinic acid isomer, probably the same as in *Carlina*. A similar compound also in *Rudbeckia*

Xanthium, Echinacea and *Acmella* also have 1-acyl-diCQA, and *Acmella* might have a quinic acid epimer but data less good than for *Helianthus* and *Rudbeckia*.

Single reports for each of *Ambrosia* and *Sphagneticola* do not report 1-acyl diCQA, and single reports for *Sanvitalia* and *Zinnia* do not report any diCQA.

Tribe Eupatoreae represented by five genera but only *Stevia* profiled with clear evidence of 1-acyl triCQA and 1-acyl-diCQA. No other references to 1-acyl-diCQA in other genera studied. *Ageratina* reported to contain *o*-coumaroyl-quinic acids but not *p*-coumaroyl-quinic acids.

There are limited data for several genera of uncertain taxonomy. Of these *Pluchea* has not been profiled but reported to contain novel cyclobutanes that have been shown *in vitro* to form from 1,3-diCQA under UV light irradiation. No explicit report of 1,3-diCQA itself, or other 1-acyl quinic acid derivatives, but 3,4-diCQA, 3,5-diCQA and 4,5-diCQA are present.

Overall clear chemotaxonomic potential but further LC–MS profiling essential with specific searches for the rarer and possibly novel chlorogenic acids. Full characterisation required for putative quinic acid epimers.

4.4.37. ORDER ESCALLONIALES

4.4.37.1. Escalloniaceae

Simirgiotis *et al*. using LC–ion trap-MS examined an extract of *Escallonia illinita* and failed to obtain unequivocal evidence for the presence of CGA. Tentative assignment was made of an FQA and a CQA derivative,*(148)* but the λ_{max} and / or the MS^2 fragments were atypical and these assignments are doubtful.

ESCALLONIALES SUMMARY

Insufficient data.

4.4.38. ORDER APIALES

4.4.38.1. Apiaceae family

The Apiaceae, formerly Umbelliferae, is a large family of over 400 genera and over 3,700 species, some of which are used as staple foods and others for flavouring or decoration. The Apiaceae family has been investigated comparatively little with regard to the presence of CGA despite two studies of CGA biosynthesis utilizing carrot (*Daucus carota*)*(827)* and parsley (*Petroselinum crispum*).*(828)*

The majority of the studies of secondary metabolites in Apiaceae have focused on the diterpenes and terpene-derived phenols such as thymol, plus rosmarinic acid, lithospermic acid and associated derivatives. Rosmarinic acid is an ester of caffeic acid with 2*R*-hydroxy-dihydrocaffeic acid (2*R*,3',4'-trihydroxyphenylpropionic acid or 3',4'-dihydroxyphenyl-lactic acid) and there are other dihydrocaffeic acid and 2-hydroxy-dihydrocaffeic acid derivatives found in this family. These latter, as discussed below, include at least two compounds with M_r = 372 and described as trihydroxy-dihydrocinnamoylquinic acids, which could conceivably be quinic acid conjugates of 3',4'-dihydroxyphenyl-lactic acid.

Anthriscus species: Petersen *et al.* reported 5-CQA in *Anthriscus cerefolium* and *A. sylvestris.(20)*

Apium species: Petersen *et al.* reported 5-CQA in Celery (*Apium graveolens*),*(20)* which also contains 5-pCoQA, 5-CQA and 5-FQA, but apparently no other regio-isomers.*(829)*

Astrantia species: Petersen *et al.* reported 5-CQA in *Astrantia major*.*(20)*

Bupleurum species: Haghi *et al* reported 3-CQA, 4-CQA and 5-CQA in the aerial parts of *Bupleurum chinense*.*(830)* Nguyen *et al*. isolated from the aerial parts of *B. falcatum* L. and characterised 3F5CQA by NMR.*(831)*

Carum species: Petersen *et al.* reported 5-CQA in *Carum carvi*.*(20)* Dirks *et al.(832)* reported 3-CQA, 4-CQA, 5-CQA, 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, 3-FQA, 4-FQA and 5-FQA in caraway (*Carum carvi*).

Caucalis species: Burr parsley (*Caucalis platycarpos* L.) is used in folk medicines and is reported to contain 3-CQA (*ca* 1 g/kg dry matter), plus 1-CQA, 4-CQA, 5-CQA 3-FQA, 4-FQA, 5-FQA, 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, 1,3-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA that were not quantified.*(833)* Although Plazonic *et al.* clearly use the IUPAC numbering system, the authors describe the only CGA standard commercially available as 3-CQA, and this should be 5-CQA. Accordingly, it is possible that it is 5-CQA that has been quantified, not 3-CQA as stated. Plazonic *et al*. also reported several incompletely characterized CGA-like components. One which they designated as a '*quinic-quinic-caffeic acid ester*' (M_r = 528) yielded MS^2 and MS^3 base peaks at *m/z* 365 and *m/z* 203, respectively, almost certainly the uncharacterized component reported also in coriander *(834)* and reminiscent of caffeoyl-tryptophan as discussed below.

Cenolophium species: Petersen *et al.* reported 5-CQA in *Cenolophium denudatum.(20)*

Centella species: Antognoni *et al*. reported 5-CQA, 3,5-diCQA, and the novel 3,5diC-4MaloQA (Irbic acid) in *Centella asiatica* cell culture but commented that this novel CGA had not been found in the intact plant.*(835)* Long *et al.* analysed the leaves and stems of *C. asiatica* and *C. glabrata* using LC–quadrupole-MS and reported 5-CQA in both. They also recorded 1-CQA, 3-CQA, 4-CQA, 1,4-diCQA, 3,4-diCQA, 3,5-diCQA and 3,5diC-4MaloQA (Irbic acid),*(836)* but this was not found in *C. glabrata*. Note that the CQA apparently eluted in the sequence 4-CQA, 5-CQA, 1-CQA and finally 3-CQA, and this is unexpected on a C_{18} reversed phase column packing. Accordingly these assignments must be viewed as uncertain. Maulidiana *et al*. analysed *C. asiatica* using LC–ion trap-MS and reported 5-CQA, 1,3-diCQA, 3,4-diCQA, 3,5-diCQA, 3,5diC-4MaloQA (Irbic acid) and an incompletely characterized irbic acid isomer.*(837)* These authors did not use the IUPAC nomenclature. Ali using LC–MS^2 reported 3-CQA, 5-CQA, 5-FQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3F-5CQA and 3C-5FQA in *C. asiatica.* The composition was very variable, but using commercial 5-CQA as calibrant the two major CGA were 3,4-diCQA (126–408 mg/ kg fresh weight) and 3,5-diCQA (671–718 mg/kg fresh weight) accompanied by 3F-5CQA (41–129 mg/kg fresh weight) and 3C-5FQA (72–106 mg/kg fresh weight).*(166)*

Satake *et al*. isolated 5-CQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA from the aerial parts of *C. asiatica* and characterised them by NMR.*(838)*

Chaerophyllum species: Dall'Aqua *et al*. reported 5-CQA, 3,5-diCQA and methyl 3,5-diCQ in the roots of *Chaerophyllum hirsutum*.*(839)*

Coleus species: Petersen *et al*. reported that *Coleus blumei* aand *C. forskohlii* apparently lacks the enzymes to synthesise quinic acid conjugates.*(20)*

Coriandrum species: Dirks *et al.(832)* reported 3-CQA, 4-CQA, 5-CQA, 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, 3-FQA, 4-FQA and 5-FQA in coriander (*Coriandrum sativum*), and the presence of 3-CQA, 4-CQA and 5-CQA was confirmed by Martins *et al*. who also reported 3,5-diCQA and 4,5-diCQA in the seeds of *C. sativum*.*(840)* A further study of coriander by LC–ion trap-MS detected in leaves and fruit a caffeic acid glycoside and several imperfectly characterized CGA-like components.*(834)* From re-examination of the published fragmentation data it seems likely that *cis*-5-CQA and *cis*-5-FQA are present, but there was no clear evidence for the presence of 4-acyl quinic acids in contrast to the earlier report by Dirks *et al.(832)* and Martins *et al.(840)*

Kaiser *et al*. also suggested the possible presence of a hydroxylated CQA (M_r = 370), but the fragmentation is inconclusive. An incompletely characterised di-caffeic acid derivative (M_r = 528) yielded MS^2 and MS^3 base peaks at *m/z* 365 and *m/z* 203,*(834)* respectively, reminiscent of the MS^1 and MS^2 fragments of caffeoyl-tryptophan,*(841)* and it is tentatively suggested that this di-caffeic acid derivative might be either a previously unreported dicaffeoyl-tryptophan or a caffeoyl-tryptophan glycoside and the same as the incompletely characterised component seen also in *Caucalis*.

Crithmum speices: Siracusa *et al.*using LC–MS reported 3-CQA, 5-CQA (dominant). 4-CQA, 5-FQA, 5-*p*CoQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in an extract of samphire (*Crithmum maritnum* L.). 1-CQA was also reported but its

elution after 5-CQA is unexpected, and it might be *cis* 5-CQA. The other assignments, with the exception of 5-CQA for which an authentic standard was available, should be treated with caution.*(359)*

Cuminum species: 5-CQA (*ca* 4 mg/kg) and an uncharacterised diCQA have been reported in the spice cumin, *Cuminum cyminum*.*(53)*

Daucus species: Kammerer *et al*. reported 3-CQA, 5-CQA, 4-CQA, 5-*p*CoQA, 5-FQA, 3,5-diCQA, 4,5-diCQA, 4F-5CQA in black carrots (*Daucus carota* ssp. *sativus*). The amount of 5-CQA in roots was 0.66 g/kg.*(842)* Ma *et al*. analysed carrots grown in China for juice production using LC–MS^2 and reported *cis* and *trans* 5-CQA, two diCQA and a *p*CoQA.*(843)* *(178)* Analysis by LC–MS^2 of extracts prepared from the insoluble residue remaining after commercial juice extraction detected 3-CQA, 4-CQA, 5-CQA **(**dominant), 4-*p*CoQA and 5-*p*CoQA.*(179)*

Dorema species: Petersen *et al.* reported 5-CQA in *Doreema ammoniacum,(20)* and Delnavazi *et al*. extracted polyphenols from *Dorema glabrum* Fisch. & C.A. Mey and characterised 5-CQA, 4,5-diCQA and 1,5-diCQA by NMR.*(844, 845)*

Eryngium species: Petersen *et al.* reported 5-CQA in *Eryngium bourgatii*,*(20)* which in a more extensive analysis of the leaves and flowers by LC-QTOF-MS^2 was shown to contain five incompletely defined CQA with identical MS^2 fragmentation (*m/z* 191), strongly suggesting the presence of at least one *cis* isomer, but otherwise precluding assignment at regio-isomeric level.*(846)* In addition, Cadiz-Gurrea *et al*. reported 4-FQA, 5-FQA, 5-pCoQA, 3,4-diCQA, 3,5-diCQA and 3C-5FQA but the MS^2 fragments presented do not match perfectly with the original hierarchical keys *(122, 221)* and these assignments to regio-isomeric level must be viewed as tentative. Two putative trihydroxycinnamoylquinic acids (M_r = 372), actually trihydroxy-dihydrocinnamoylquinic acids, that produced only *m/z* 191 at MS^2, were also reported.*(846)* Although not assigned in the original publication, these are plausibly quinic acid esters of 3-hydroxy-dihydrocaffeic acid which have been reported in brewed coffee by Matei *et al*.,*(847)* brewed maté *(848)* and in *Lonicera henryi* by Jaiswal *et al*.,*(849)* but because *Eryngium* also contains rosmarinic acid (the caffeoyl ester of 2*R*-hydroxy-dihydrocaffeic acid (2*R*,3',4'-trihydroxyphenylpropionic acid)) it is not implausible that these might be quinic acid esters of 2*R*-hydroxy-dihydrocaffeic acid. A third possibility, baswed purely on mokecular mass, is the quinic acid–3,4-dihydroxyphenyl-lactic acid ether as reported in *Hymenocrater* (Lamiaceae, Lamiales) by Gohari *et al*.*(850)*

Ferula species: Znati *et al*. recorded 5-CQA, 3,5-diCQA and methyl 3,5-diCQ in the flowers of *ferula lutea*.*(851)*

Ferulago species: Alkhatib *et al*. reported 5-CQA and 3,5-diCQA *in* Ferulago *asparagifolia.(852)*

Foeniculum species: Fennel (*Foeniculum vulgare*) is an aromatic plant and the seeds are used in Asian and Mediterranean cuisines and folk medicines. The flowers are used in some German cuisine. Petersen *et al.* reported 5-CQA in *Foeniculum vulgare,(20)* and Krizman *et al*. using LC–ion trap-MS^2 reported 3-CQA, 4-CQA, 5-CQA, 1,3-diCQA, 1,4-diCQA, 1,5-diCQA and rosmarinic acid.*(853)* The 1,5-diCQA was characterised by NMR, and the early elution of 1,3-diCQA is as expected for this regio-isomer, but Krizman's assignment of 1,4-diCQA is questionable

because their data lacked the MS^2 fragment ions (*m/z* 317, *m/z* 299, *m/z* 255 and *m/z* 203) characteristic of this isomer.*(122)*

Parejo *et al*. using LC–quadrupole MS with NMR characterisation of isolates reported 3-CQA, 4-CQA, 5-CQA and 1,5-diCQA in commercial fennel processing waste,*(854)* and in a separate study additionally reported 1-CQA, 1-FQA, 3-FQA, 4-FQA, 4-pCoQA, 5-pCoQA and 1,3-diCQA,*(855)* and 1,4-diCQA,*(856)* this latter based only on the data of Krizman *et al*. as discussed above. Pacifico *et al*. using LC–ion trap-MS^2 reported four CQA including 1-CQA, one FQA and one diCQA in the leaves of *F. vulgare*.*(857)* Note that the retention times quoted for the 1-acyl quinic acids relative to the 5-acyl isomers are longer than normally expected on a reversed phase column and should be treated as tentative. Similarly the putative 1,3-diCQA elutes very close to the putative 1,5-diCQA again casting some doubt on this assignment.

Salami *et al*. using commercial standards reported 5-CQA and 1,5-diCQA in 23 samples of fennel (*F. vulgare* from various sources.*(858)*

Hymenocrater species: Nepetoideae Gohari *et al*. in 2010 extracted a novel compound (M_r = 372) from *Hymenocrater calycinus* and characterised it by ^{1}H and ^{13}C-NMR, defining it as 3-(3, 4-dihydroxyphenyl) lactic acid 2-*O*-quinic acid, i.e. the phenyl-lactic acid and quinic acid are joined by an ether linkage rather than an ester linkage as would occur in a true chlorogenic acid.

The two putative trihydroxycinnamoylquinic acids (M_r = 372), actually trihydroxy-dihydrocinnamoulquinic acids, that produced only *m/z* 191 at MS^2, reported in *Eryngium*,*(846)* might be related to this novel ether. An ether-linked compound has also been reported in *Convolvulus dorycnium* (Convolvulaceae, Solanales).*(859)*

Levisticum species: Petersen *et al.* reported 5-CQA in *Levisticum officinale*.*(20)*

Ligusticopsis species: Adhikari *et al*. report 5-CQA, 5-*p*CoQA and 3,5-diCQA in the roots of *Ligusticopsis wallichiana* with identification based on literature data.*(860)*

Ligusticum species: *Ligusticum mutellina* contains at least one uncharacterized '*chlorogenic acid*',*(861)* but Petersen *et al.* were unable to find 5-CQA in *L. scoticum*.*(20)*

Several CGA have been reported in Guan-Xin-Ning which is prepared from a mixture of *Salvia miltiorrhiza* Bge. and *Ligusticum chuangxiong* Hort, but from which of the two components was not stated.*(862)* However, analyses of Danshen prepared from the roots of *Salvia miltiorrhiza* Bge. did not report any CGA,*(863, 864)* suggesting that the CGA were present in *Ligusticum*.

Melissa species: Petersen *et* al. reported that *Melissa officinalis* lacks the enzymes to produce quinic acid conjugates.*(20)*

Meum species: Early studies established the presence in *Meum athamanticum* of an incompletely characterised CQA and FQA,*(865)* methyl-1-CQA and methyl 1-FQA,*(866, 867)* More recently 5-CQA has been reported in *Meum*

mutellina L. Gaert. (*Mutellina purpurea* L.).*(868)* Sieniawska *et al*. using positive ion LC–MS reported 5-CQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and an incompletely characterised CFQA in *Mutellina purpurea*.*(869)*

Melanoselinum species: Spinola *et al*. using LC–ion trap-MS^4 analysed one sample of *Melanoselinum decipiens*, a Madeira endemic, and reported 5-CQA, 1,5-diCQA, 3,5-diCQA and 4,5-diCQA plus one FQA, one *p*CoCQA, one CFQA and two diCSA that were incompletely characterised.*(870)* Examination of the reported fragmentation data suggests that one uncharcterised component might be *cis*-5-CQA and another described as a *p*CoQA which yielded an MS^2 fragment at *m/z* 179 might have been misidentified.

Monizia species: Spinola *et al*. using LC–ion trap-MS^4 analysed two samples of *Monizia edulis* a Madeira endemic, and reported a substantial range of acyl-quinic acids.*(870)* They presented strong evidence for the presence of 3-CQA, 5-CQA, methyl-5-CQA, 3,4-diCQA, 1,5-diCQA, 3,5-diCQA and 4,5-diCQA, plus one FQA, one *p*CoCQA, two CFQA and two diCSA that were not completely characterised. Examination of the reported fragmentation data suggests that one uncharcterised component might be *cis*-5-CQA and another described as a *p*CoQA which yielded an MS^2 fragment at *m/z* 179 might have been misidentified.

Ocimum species: Farag *et al*. examined *Ocimum basilicum* L.*, O. africanum* Lour.*, O. americanum* L. and *O. minimum* L. and found no acyl quinic acids.*(871)*

Origanum species: Kaiser *et al*. using LC–ion trap-MS detected in marjoram (*Origanum majorana*) at least three *p*-coumaric acid derivatives, including a glycoside (M_r = 326), and two uncharacterized compounds (M_r = 324), plus rosmarinic acid and lithospermic acid (caffeoyl-rosmarinic acid). Fotakis *et al*. reported that 3-CQA was a major component of *O. majorana* L.,*(872)* but it is unclear which numbering system was used.

Liu *et al* characterised three novel components each with a tetra-carboxy-cyclohexene skeleton,*(873)* but it sems unliley that these are closely associated biosynthetically with the better known acyl quinic acids.

Pastinaca species: Using HPLC and a commercial standard enabled Nikolic *et al.*to report 5-CSA in the roots of parsnip, *Pastinaca sativa*.*(874)*

Petroselinum species: Kaiser *et al*. using LC–ion trap-MS detected in parsley (*Petroselinum crispum*) a *p*-coumaric acid glycoside, two other sugar derivatives of *p*-coumaric acid, plus two uncharacterized compounds (M_r = 558) that possibly also contain *p*-coumaric acid **3**.*(875)*

Peucedanum species: Petersen *et al.* reported 5-CQA in *Peucedanum officinale*.*(20)*

Pimpinella species: Dirks *et al.(832)* reported 3-CQA, 4-CQA, 5-CQA, 3-*p*CoQA, 4-*p*CoQA, 5-*p*CoQA, 3-FQA, 4-FQA and 5-FQA in anise (*Pimpinella anisum*). Marques and Farah using LC–MS reported the same CQAs and FQAs plus 3,4-diCQA, 3,5-diCQA and 4,5-diCQA but did not detect the *p*CoQAs.*(35)* Lee *et al.* isolated and characterized by NMR 15 CGA in *P. brachycarpa* as follows: 1C-5*p*CoQA , 1C-5(3-methoxydhC)QA, 1(3-methoxydhC)-5-CQA, 1-trans-*p*Co-5-cis-*p*CoQA, 1,5-di-O-cis-*p*CoQA, 1,5-diCQA, methyl 3,4-diCQ, methyl 3,5-diCQ, methyl 4,5-diCQ, methyl 4-CQ, methyl 5-CQ, methyl *cis* 5-CQ, methyl 4-*p*CoQ, methyl 5-*p*CoQ and methyl *cis* 5-*p*CoQ.*(876)*

Pituranthos species: LC–MS analyses of an extract of *Pituranthus scoparius* have detected 5-CQA and 5-FQA.*(877)*

Plectrantus species: Petersen *et al*. reported that *Plectrantus fruticolus* lacks the enzymes to produce quinic acid conjugates.*(20)*

Salvia species: The calli and cell suspensions of sage (*Salvia officinalis* L.) contain 3-CQA **33** and 5-CQA,*(878)* and 3-CQA, 4-CQA, 5-CQA, 1,3-diCQA.and 1,4-diCQA have been reported in Guan-Xin-Ning, a Chinese preparation produced from a mixture of *Salvia miltiorrhiza* Bge. and *Liguticum chuangxiong* Hort.*(862)* However, the MS^2 and MS^3 fragmentation data presented for the putative 1,4-diCQA lack the MS^2 ions (*m/z* 317, *m/z* 299, *m/z* 255 and *m/z* 203) characteristic of this isomer,*(122)* and this assignment should be viewed as tentative. Rosmarinic acid, lithospermic acid and 2'-hydroxy-dihydrocaffeic acid were also present in *S. officinalis*, and *S. chinensis* contains ethyl dihydrocaffeate, ethyl rosmarinate, methyl rosmarinate and rosmarinic acid.*(879)*

Sanicula species: Petersen *et al.* reported 5-CQA in *Sanicula marilandica*.*(20)*

Sesseli species: Petersen *et al.* reported 5-CQA in *Sesseli hippomarathrum* and *S. libanotis*.*(20)*

Sphallerocarpus species: Gao *et al* reported 5-CQA and two incompletely characterised diCQA glycosides in *Sphallerocarpus gracilis* seeds,*(880)* but the comparatively late elution (30–35 min) suggests that these might be triCQA.

4.4.38.2. Araliaceae family

The taxonomy of the Araliaceae is under review, but is currently thought to include some 250 species including the true ivies (*Hedera* spp.) and Ginseng (*Panax* spp.)

Aralia species: Petersen *et al*. reported 5-CQA in *Aralia californicum*.*(20)* Hyun *et al*. reported 3-CQA, 4-CQA, 5-CQA and 3,5-diCQA in the roots of *Aralia cordata*.*(881)*

Cussonia species: Papajewski *et al.* isolated and characterised by NMR two novel esters in *Cussoni barteri* [Seeman] which they described as 1'-*O*-chlorogenoyl-chlorogenic acid and 1'-*O*-chlorogenoyl-neochlorogenic acid, along with 3-CQA, 5-CQA, 5-FQA, 3,5-diCQA, 4,5-diCQA and 3F-4CQA.*(882)*

Eleutherococcus species: *Acanthopanax senticosus,* a Chinese medicinal plant, is synonymous with *Eleutherococcus senticosus.* Petersen *et al*. reported that it contained 5-CQA.*(20)* A more extensive study reported 5-CQA (0.4–1.2 g/kg),*(883)* 1,5-diCQA, 3,5-diCQA and 4,5-diCQA *(884)* and 3-*O*-(4'-*O*-β-D-glucopyranosyl)-feruloylquinic acid.*(885)* It has been reported that the CQA and diCQA content of *A. trifoliatus* leaves is greatest in November and January.*(886)* Zhang *et al*. reported 4-CQA, 5-CQA, 1,5-diCQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA, characterised by NMR and MS, in the leaves of *A. henryi*.*(887)*

Hedera species: Petersen *et al*. reported 5-CQA in *Hedera colchica* and *H. helix,(20)* and a more extensive study reported 3-CQA, 5-CQA, 3,5-diCQA and 4,5-diCQA in *Hedera helix*, all characterized by NMR.*(888)*

Kalopanax species: 5-CQA and 5-FQA have been isolated from *Kalopanax septemlobus*,*(889)* whereas 3-FQA, 3,5-diCQA and methyl 3,5-diCQ were isolated from *K. pictus* leaves and characterized by NMR.

Oplopanax species: You *et al.* tentatively identified 4-FQA, 5-FQA and methyl 4-FQ in the roots of *Oplopanax horridus* (Sm.) Miq. using LC–MS without fragmentation,*(890)* but caffeic acid-containing CGA were not found.

Polyscias species: Buchanan *et al*. isolated novel 3,5-di-(dihydro-*p*-hydroxy-cinnamoyl)quinic acid and 4,5-di-(dihydro-*p*-hydroxy-cinnamoyl)quinic acid from *Polyscias murrayi* and charatcterised both by NMR.*(891)*

Schefflera species: *Schefflera heptaphylla* (L.) Frodin contains 5-CQA, 3,5-diCQA and 4,5-diCQA.*(892)* Nguyen *et al* reported 5-*p*CoQA in the leaves of *S. sessiliflora* de P.V.*(893)*

4.4.38.3. Pittosporaceae family

Pittosporum species: Bäcker *et al.*have isolated phenolic acids from *Pittosporum angustifolium* and characterised 3,4-diCQA and 4,5-diCQA by NMR.*(894)*

APIALES SUMMARY

Apiaceae:

Some species lack quinic acid conjugates: *Coleus, Melissa, Ocimum, Plectrantus, Ligusticum*? *Petroselinum*?

Otherwise CQA are widespread accompanied by pCoQA and FQA, diCQA sometimes including 1-acyl quinic acids and CFQA (*Daucus Centella, Eryngium, Mutellina* = *Meum*, *Melanoselinum, Monizia*).

Centella may stand out with irbic acids malo-diCQA and CFQA

Caucalis and *Coriandrum* may have a caffeoyl-tryptophan glycoside

Trihydroxy-dihydrocinnamoylquinic acids in *Eryngium*

Hymenocrater ether-linked compound

Origanum tetra-carboxy-cyclohexene

Pastinaca 5-CSA and *Monizia* diCSA

Pimpinella methoxydihydrocaffeoylquinic

Araliaceae

Cussonia CQA, FQA, diCQA, CFQA and unique chlorogenoyl-chlorogenic

Oplopanax FQA but not CQA

Polyscias p-hydroxy-dihydrocinnamoylquinic

Pittosporaceae

diCQA

The Apiaceae are a prime candidate for LC–MS profiling of the chlorogenic acids and associated compounds. This aspect of their secondary metabolites has been rather neglected with the emphasis on rosmarininc acid and associated derivatives. There is a range of unusual CGA or CGA-related compounds which provide an interesting basis for a systematic study.

4.4.39. ORDER DIPSACALES

4.4.39.1. Adoxaceae family

The Adoxaceae is a small family of flowering plant encompassing four genera and probably less than 200 species. Note that some authorities place *Viburnum* in Caprifoliaceae.

Sambucus species: Barros *et al*. using LC–ion trap MS^2 and UV-irradiation specifically to locate *cis* isomers reported *cis*-3CQA, 3-*p*CoQA, 5-CQA, *cis*- and *trans*-5-*p*CoQA, an incompletely characterised CQA and 3,5-diCQA in *Sambucus nigra*.*(163)* The presence of *cis*-3CQA in the absence of the trans isomer is unexpected. Mikulik-Petkovsek *et al*. using LC–MS analysed *Sambucus cerulea, S. ebula, S. nigra* and *S. racemose* var. *Miquella* plus several inter-specific hybrids and reported 3-CQA, *cis*- and *trans*-4-CQA, *cis*- and *trans*-5-CQA, 3-FQA, 3-*p*CoQA, *cis*- and *trans*-4-*p*CoQA and two incompletely characterised diCQA. There were significant variations in profile with only *trans*-5-CQA present in all samples.*(895)* In a seprate study ofElderflower extracts 5-FQA, a third diCQA and two *p*CoCQA were also detected, and it was suggested that the three diCQA wre 1,5-diCQA, 3,5-diCQA and 4,5-diCQA.*(896)* The mass fragmentation of the putative 1,5-diCQA had a prominent MS^3 fragment at *m/z* 173 which coupled with its comparatively early elution suggests that it might be 3,4-diCQA.

Lin and Harnly reported 3-CQA, 4-CQA, 5-CQA, a *p*CoQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in the flowers of *S. canadensis*.*(897)*

Scabiosa species: Hlila *et al*. using LC–quadrupole ion trap-MS reported 1,4-diCQA in the flowers of *Scabiosa arenaria*.*(898)* However, they used the hierarchical key developed for non-quadrupole instruments and relate their MS^1 fragments to the MS^2 fragments used in the hierarchical key, and show the structure as 1,5-diCQA. Accordingly the assignment to regio-isomer level must be viewed as unproven. Ma *et al.* reported 5-CQA, 3,4-diCQA, 3,5-diCQA (dominant) and 4,5-diCQA in *S. comosa and S. tschilliensis*,*(899)* but did not use IUPAC numbering.

Viburnum species: Petersen *et al*. reported 5-CQA in *Viburnum dilatatum, V. hupehense* and *V. lantana*.*(56)* Kikuchi *et al*. reported 5-CSA and 5-CQA in *Viburnum plicatum* Thunb., a plant used in Chinese herbal medicines,*(900, 901)* and Kraujalyte *et al*. reported 5-CQA and a second CQA, probably 3-CQA in *V opulus*,*(902)* but did not use IUPAC numbering. Karacelik *et al.* analysing *V. opulus* fruit using LC–ion trap-MS^2 reported a *p*CoQA (probably 3-*p*CoQA), and what appear to be three CQA Iincluding 5-CQA confirmed with a commercial standard). The authors decribed one of these as a 'CQA dimer, M_r = 708)*(903)* but the parent ion at *m/z* 707 (rather than *m/z* 705) clearly defines this as an adduct of a neutral molecule and an ion formed because the MS has been overloaded.

Iwai *et al*. reported 5-CQA and 4M-5CQA in *V. dilatatum* Thunb.,*(904)* but the NMR spectrum shows the methoxyl signal at δ_H = 3.70 *(905)* and this is not consistent with the value obtained by Zeller (δ_H = 3.31) for an authentic methyl ether of quinic acid (1M-5CQA),*(25)* and as discussed for *Phyllostachys edulis*,*(26)* this compound seems more likely to be a methyl CQ or possibly an FQA.

4.4.39.2. Caprifoliaceae family

Abelia species: Al Taweel *et al*. reported 4-FQA in *Abelia triflora* after isolation and NMR characterisation.*(906)*

Diervilla species: Peteresen *et al*. reported 5-CQA in *Diervilla lonicera* and *D. trifolia*.*(56)*

Knautia species: Note that some authorities place *Knautia* in the Dipsacaceae. Petersen *et al*. reported 5-CQA in *Knautia dipsacifolia*.*(20)* An extract of *Knautia arvensis* yielded 4-CQA, 5-CQA, 3,5-diCQA and 4,5-diCQA, all characterized by NMR and MS. The uncommon 2-caffeoyl-isocitric acid was also reported.*(907)* This latter compound is isobaric with CQA at unit mass resolution.

Lonicera species and Flos Lonicerae: *Lonicera* includes the well known Honeysuckles which are used for ornamentation, herbal medicines and animal grazing purposes. *Lonicera japonica* and *L. caerulea* L. and products such as Flos Lonicerae prepared from the dried flowers of *Lonicera* spp. contain a wide range of CGA, sometimes at significant concentrations.*(908, 909)*

According to Li *et al*. Flos Lonicerae is known as Jinyinhua in Chinese, and is currently defined as the dried flower buds of *L. japonica* Thunb. It is one of the most widely used Chinese herbal medicines. Previous definitions in the Chinese pharmacopoeia have permitted the use also of *L. hypoglauca* Mig., *L. confusa* DC. and *L. dasystyla* Rehd. other species of the genus *Lonicera* such as *L. fulvotomentosa* Hsu et S. C. Cheng and *L. nubium* Hand.-Mazz have been traded.*(910)* Li *et al*. reported a UHPLC–MS/MS method to discriminate between the dried flowers of seven species: *L. fulvotomentosa* Hsu et S. C. Cheng, *L. hypoglauca* Miq., *L. hypoglauca* Miq. subsp. nudiflora Hsu et H. J. Wang, *L. nubium* Hand.-Mazz., *L. confusa* (Sweet) DC., *L. pampaninii* Lévl. and *L. japonica* Thunb. The CGA characterized by LC–MS^2 in the flowerbuds of all seven species were 3-CQA, 4-CQA, 5-CQA, 3,5-diCQA and 4,5-diCQA.*(910)* Gao *et al*. have examined 51 samples of flowers from *Lonicera* spp focussing on six components (three iridoid glycosides plus 5-CQA, 3,5-diCQA and 4,5-diCQA) as an index of Flos Lonicerae authenticity. Note however that the structure shown for 4,5-diCQA is actually 3,4-diCQA IUPAC. The species examined included *L. japonica*, *L. confuse*, *l. macranthoides*, *L. fulvotomentosa* and *L. hypoglauca*, and there were significant differences in the profile of these three CGA. For example, 3,5-diCQA dominated in *L. fulvotomentosa* whereas 5-CQA dominated in the other four species.*(911)*

In addition Lin and Harnly also isolated 3,4-diCQA from the flowers of *L. japonica*,*(897)* and Peng *et al.* reported 5-CQA, methyl 5-CQ, methyl 3,5-diCQ and butyl 3,5-diCQ in the flowers and buds of *L. japonica*,*(912)* and Zhang *et al.* reported methyl 3,5-diCQ in the stem.*(913)* According to Ma *et al.* the leaves of *L. japonica* contain methyl 5-CQ, methyl 3,4-diCQ as well as 5-CQA, 1,3-diCQA and 3,4-diCQA,*(914)* but it is impossible to judge from the English abstract whether or not these authors used the IUPAC numbering system. In contrast Lee *et al.* reported 5-CQA, methyl 5-CQ, 3,5-diCQA, 4,5-diCQA, methyl 3,5-diCQ after isolation and characterization by NMR.*(915)* Park *et al.*using LC–quadrupole-MS^2 reported one CQA, one FQA, 5-*p*CoQA **52**, three diCQAs and two CFQAs in Korean *L. japonica* plants but could not define these to regio-isomeric level.*(916)* They also reported an early eluting CQA dimer (M_r = 708) but this is clearly an adduct of an ion (*m/z* 353) and a neutral molecule (M_r = 354) as a consequence of overloading the mass spectrometer, rather than a true dimer which would have M_r = 706 and base peak at *m/z* 705. This peak is also

clearly impure. The assignments of the FQA and 5-*p*CoQA are suspect because both give a prominent fragment ion at *m/z* 179 suggesting that they are caffeic acid derivatives. Quantitative data are provided but the calibrant is not defined and it is unclear whether these are on a dry basis or fresh weight basis. More recently the 4'-glycosides of 3-CQA, 4-CQA and 5-CQA have been reported in the buds of *L. japonica*.*(917)*

L. caerulea fruits contain 180 mg/kg of 5-CQA,*(909)* but no reference was made regarding the possible presence of other CGA. Chen *et al*. isolated two novel saponin chlorogenates from the flower buds of the Chinese herbal medicinal plant *L. macranthoides*. Lonimacranthoide I and Lonimacranthoide IV, and characterized them as esters in which a CGA is attached at C23 of hederagenin.*(918)* Liu *et al.*reported 5-*p*CoQA and 3-FQA in *L. macranthoides*.*(919)* Hu *et al*. using LC–QTOF-MS^2 reported *cis* and *trans* 3-CQA, *cis* and *trans* 4-CQA and 5-CQA, plus methyl-3-CQ, methyl-4-CQ and methyl-5-CQ, ethyl-3-CQ, ethyl-4-CQ and ethyl-5-CQ accompanied by 3,4-diCQA, 1,4-diCQA, 3,5-diCQA, 4,5-diCQA and 3,4,5-triCQA, and 3-CSA and 4-CSA in *L. macranthoides*. The *cis* isomers, ethyl and methyl esters were confirmed by synthesis,*(920)* but note that the peak assigned s 1,4-diCQA lacks the characteristic fragment ions for this compound and might be incorrect. The most recent study by Zhang *et al*. has greatly extended the range of CGA reported to include six CQA, six diCQA, one triCQA, three CSA, six diCSA, one triCSA, three *p*CoQA, four *p*CoCQA, four FQA, five methyl CQ, three ethyl CQ, three DQA, six CFQA, six methyl diCQ, four FQA glycosides, six methyl CQ glycosides, and three ethyl diCQ.*(921)* The *cis* isomers and the methyl and ethyl esters were all confirmed by comparison with synthetic material.

Barreira *et al*. using LC–MS^2 reported 4-CQA, *cis* and *trans* 5-CQA, a *cis* and *trans* 3,5-diCQA and 4,5-diCQA in the fruits of *L. pericyclamenum*.*(922)* However, note that the authors report the dominant *cis* 5-CQA eluting before *trans* 5-CQA, for which a standard was available, which would not be typical behaviour, and it seems likely that the tabulated data for these two isomers have been reversed.

Becerra-Herrera *et* al. using positive ion LC–MS reported that 3-CQA exceeded 5-CQA in the fruits of *L. oblongifolia*.*(197)* Although the structures shown follow IUPAC numbering, the chromatograms presented have the putative 5-CQA eluting before the putative 3-CQA strongly suggesting that the assignments have been reversed. Unfortunately, these authors did not use any commercial standards, and because in positive ion mode both compounds showed identical fragmentation, it is not possible to confirm their assignments.

Jaiswal *et al*. using LC–ion trap-MS^n analysed extracts from the leaves of *L. henryi* and reported *cis* and *trans* 3-CQA, *cis* and *trans* 5-CQA, *cis* and *trans* 3-pCoQA, *cis* and *trans* 5-pCoQA, *cis* and *trans* 5-FQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3,4,5-triCQA, 4F-5CQA, 4C-5FQA and 4C-5*p*CoQA. In addition they made the first report of a 3-O-(3-hydroxydihydrocaffeoyl)quinic acid and established that it was possible to discriminate between 3'-*O*-glycosides and 4'-*O*-glycosides. In total, 12 such glycosides were characterised: *Cis* and *trans*-5-O-(3'-O-caffeoyl glucosyl)quinic acid, *cis* and *trans* 5-O-(4'-O-caffeoyl glucosyl)quinic acid, 3-O-(4'-O-caffeoyl glucosyl)quinic acid, 5-O-(4'-O-*p*-coumaroyl glucosyl)quinic acid, 5-O-(4'-O-caffeoyl rhamnosyl)quinic acid, 5-O-(4'-O-feruloyl glucosyl)quinic acid, 4-O-(4'-O-caffeoyl diglucosyl)quinic acid, 3-O-(4'-O-caffeoyl glucosyl)-5-*O*-caffeoylquinic acid, 4-O-(4'-O-caffeoyl glucosyl)-5-*O*-caffeoylquinic acid and a *cis* isomer of 4-O-(4'-O-caffeoyl glucosyl)-5-*O*-caffeoylquinic acid.*(849)* It is interesting to

note that while the mono-substituted quinic acids in *L. henryi* were never acylated at C4, whereas one of the glycosides and several di-substituted quinic acids were.

Peteresen *et al.* reported 5-CQA in *L. demissa*, *L. emphyllocalyx, L. ferdinandi* and *L. kamtschatica*, but could not locate it in *L. syringantha*.*(56)*

Qian *et al*. quantified 5-CQA, 4,5-diCQA and 3,4-diCQA in Flos Lonicerae at 15.3–18.1, 9.8–14.1 and 2.1–5.6 g/kg.*(923)* Calibrants were purified from Flos Lonicerae extracts with the following response factors: 5-CQA 3693; 4,5-diCQA 3740; 3,4-diCQA 2912. These values suggest that at least the diCQA contained non-UV-absorbing impurities and that the quantitative data are unreliable.

Zhang *et al.* using LC–MS^n methodology have reported in Flos Lonicerae all four CQA and all six diCQA accompanied by 3,4,5-triCQA, all four pCoQA,3-FQA, 4-FQA and 5-FQA, plus six CFQA, seven CQA glycosides and ten diCQA glycosides that were not characterized fully.*(908)* Only one of the six putative CFQA reported by Zhang *et al.* shows an *m/z* 367→193 MS^3 transition consistent with this assignment. Note that the putative 1-CQA and 1-pCoQA elute appreciably later than 5-CQA and 5-*p*CoQA, respectively, strongly suggesting that these are *cis* 5-CQA and *cis* 5-*p*CoQA. The putative 1,4-diCQA does not yield the characteristic MS^2 fragments and might have been mis-assigned, in which case, it is possible that some *cis* diCQA are present, as previously reported by Barreira *et al*.*(922)* In a subsequent study Zhang *et al.* reported in excess of 100 CGA using LC–ion trap HRMS supported by estimates of CLogP and MM2 molecular modelling. In addition to many commoner CGA the profile included ten diCQA, eight *p*CoCQA, seven *p*CoQA glycosides, nine CFQA, 11 FQA glycosides, nine triCQA, 15 diCQA glycosides, four CQA diglycosides, 11 CQA glycosides, three CQA diglycosides, nine CFQA glycosides, two *p*CoSiQA, two CSiQA, one FSiQA, many of these categories including *cis*-isomers and 1-acyl quinic acid derivatives.*(924)*

Morina species: According to the abstract Teng *et al*. reported 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *Morina nepalensis* var. *alba* Hand. Mazz. (*Acanthocalyx nepalensis*).*(925)*

Nardostachys species: Paek *et al*. detected and characterized spectroscopically 5-CQA, methyl 5CQ and 1,5-diCQA in *Nardostachys chinensis*.

Sambucus species: Formerly *Sambucus* was placed in the Caprifoliaceae but more recently it has been assigned to the Adoxaceae, and is discussed in that section.

4.4.39.3. Dipsacaceae family

Cephalaria species: Petersen *et al*. reported that they could not locate 5-CQA in *Cephalaria gigantea*.*(20)*

Dipsacus species: Petersen *et al*. reported 5-CQA in *Dipsacus laciniatus.(20)* Hung *et al.* using NMR and comparison with previously published data reported 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and the corresponding methyl esters in the

roots of *Dipsacus asper* Wall.*(926, 927)* Ling *et al*. using LC–QTOF-MS^2 reported 5-CQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in Radix dipsaci.*(928)*

Succisella species: Petersen *et al*. reported 5-CQA in *Succisella inflexa*.*(20)*

DIPSACALES SUMMARY

Adoxaceae: CQA, *p*CoQA, FQA and diCQA possibly including 1-acyl-diCQA.

Caprifoliaceae: Lonicera extensively studied. Similar but more extensive range with methyl and ethyl CQ and methyl diCQ, triCQA and CSA, diCSA and triCSA, plus CFQA and pCoCQA and DQA and (3-hydroxydihydrocaffeoyl)quinic acid, CSiQA, pCoSiQA, FSiQA and extensive range of glycosides (including rhamnosides). Also including 1-acyl-quinic acids and unusual sterol esters.

However, 5-CQA not found in *Lonicera syringnantha*. Also acyl-isocitric acids in *Knautia*.

Dipsacaceae: Less studied but similar to Adoxaceae. 5-CQA not found in *Cephaloria gigantea*.

SUMMARY FOR CAMPANULIDS

The Campanulids embraces seven orders,*(9)* but there are no data for Bruniales, Escalloniales or Paracryphiales. The data for Aquifoliales, Apiales, Dipsacales and Asterales are summarised below. Overall, there is an impression of more complex profiles.

There are no reports of GQA or GSA, but there is a single report of a ProtQA in Aquifoliales (*Ilex*) and derivatives of a quinic acid epimer.

The Asterales have CQA, *p*CoQA and FQA but sinapic acid-containing CGA are scarce. DiCQA are generally present, some 40% of genera have 1-acyl-diCQA, but some have more restricted range, perhaps only two regio-isomers, and some have acyl derivatives of a quinic acid epimer. Asterales has a significant range of aliphatic acids, plus hydroxyphenylacetyl-quinic acids, derivatives of 2-hydroxy-quinic acid and a novel depside.

In the Apiales and Dipsacales several genera have been reported to lack CQA, but generally the CQA, *p*CoQA, FQA and diCQA are present accompanied by sinapic acid conjugates in Dipsacales and Aquifoliales, both showing some 1-acyl-quinic acids.

The Apiales also show 1-acyl-quinic acids, malonoyl-dicaffeoylquinic acids, plus CFQA and *p*CoCQA. Dihydrocinnamoylquinic acids occur in Apiales and Dipsacales. The Apiales also record several uncommon CGA or

CGA-like compounds, including an ether-linked, rather than ester-linked, conjugate, tetra-carboxy-cyclohexenes, and chlorogenoyl-chlorogenic acids.

The Dipsacales include single examples of acyl-quinic acids occurring alongside the acyl-isocitric acids, plus rhamnosides.

4.4.40. ORDER SOLANALES

4.4.40.1. Convolvulaceae family

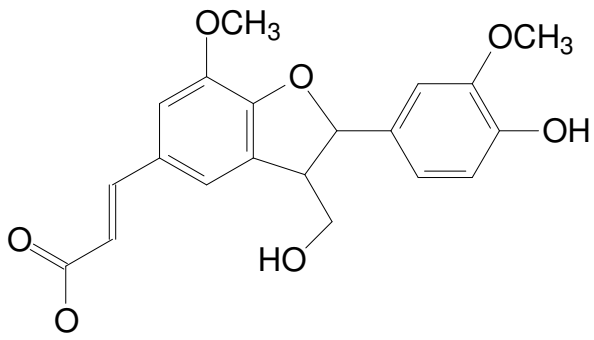
The Convolvulaceae are commonly referred to as the bindweed or morning glory family, and include 60 genera and over 1,600 species, many of them vines, including the Sweet Potatoes (*Ipomoea* spp.)

Convolvulus species: Petersen *et al*. reported 5-CQA in *Convolvulus tricolor*.*(20)* Kacem *et al*. reported 3,4-diCQA in *C. tricolor* seed husks,*(929)* but it is not clear which numbering system was used. Nacef *et al*. have reported in *C. dorycnium* a CGA-like compound in which the vanillic acid C4 is attached via an ether bond to C4 of methylquinate.*(859)* This is subtly different from the usual CGA ester structures of the SyQA reported in Ericybe *(930)* and the diVQA reported in *Fagara*,*(395)* but resembles the novel compound reported in *Hymenocrater calycinus* (Lamiaceae, Lamiales) in which 3'4'-dihydroxyphenyl-lactic acid is bound to quinic acid *via* an ether linkage formed from the lactic hydroxyl and the quinic acid C5 hydroxyl.*(850)*

Cuscuta species: Löffler *et al*. reported 5-CQA, 3,5-diCQA and 4,5-diCQA in *Cuscuta europea, C. gronovii, C. lupuliformis, C. reflexa, C. campestris, C. chinensis, C.odorata, C. pedicellata* and *C. platyloba* all grown on suitable host plants.*(931, 932)*

Li *et al*. reported novel acyl-quinic acid metabolites in rat plasma after feeding the seeds of *Cusucuta chinensis* and suggested that these arose from 5-CQA and 4C-5pCoQA,*(933)* but they did not explicitly identify the original substrates and these assignments should be treated as tentative.

Ericybe species: Liu *et al*. reported methyl 3Sy-5CQ in *Erycibe obtusifolia*, a plant used in Chinese herbal medicines.*(934)* In a susbsequent paper they reported methyl 4C-3SyQ, 3V-4CQA, methyl 3V-4CQ, 3V-5CQA, methyl 3V-5CQ, 3Si-5CQA, 4V-5CQA and two novel acyl quinic acid compounds substituted at C4 with a glycosmisoyl unit (below) plus the corresponding acyl methyl quinates in the stem of *E obtusifolia(935)*.



Fan *et al*. subsequently isolated several other CGA from the roots and stems of *E. obtusifolia* and characterised them by NMR. These include the novel methyl 3Sy-4CQ and methyl 4Sy-5CQ, plus methyl 3Si-4CQ, methyl 3Si-5CQ, methyl 4Si-5CQ, methyl 5CQ, methyl 3,4diCQ, methyl 3,5diCQ, methyl 4,5diCQ and 4,5-diCQA,*(930)* and in a separate study also methyl 3Sy-4FQA, 3Si-4CQA, 4Si-5CQA, 3Sy-4CQA, 4Sy-5CQA, 3,4-diCQA and 3,5-diCQA.*(936)* Song *et al*. reported *n*-butyl 3CQ, ethyl 3,4-diCQ, 4Sy-5CQA, 3Sy-5CQA, 3Sy-4CQA and methyl 4V-5CQ in the roots and stems of *E hainanensis*.*(937)* Feng *et* al. reported butyl 3,4-diCQA in *E. hainanensis*,*(938)* but do not define whether or not they

are using IUPAC numbering. Syringoyl-quinic acids have otherwise been found only in *Strychnos* (Loganiaceae),*(939)* and tobacco (*Nicotiana tabacum*),*(940)* and vanilloylquinic acids only in *Fagara* (Rutaceae).

Ipomoea species: The CGA profile of sweet potatoes varies with tissue and with source. Islam *et al*. who analysed numerous cultivars reported that 3,5-diCQA was the dominant CGA in the leaves of sweet potatoes grown in Japan and that 5-CQA, 3,4-diCQA, 4,5-diCQA and 3,4,5-triCQA were also present.*(941)* This was confirmed by Kurata *et al*.,*(942)* Yoshimoto *et al*.,*(943)* Sun *et al*.*(944)* and Sasaki *et al* reported also 3-CQA and 4-CQA.*(945)* In contrast Zhang *et al*. reported 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3,4,5-triCQA and 4F-5CQA in the leaves of *I. batatas* after isolation and NMR characterisation.*(946)*

Dini *et al*. reported 4-CQA, 1,3-diCQA, 3,5-diCQA and 4,5-diCQA in tubers grown in Peru.*(947)* In contrast, Wang and Clifford reported that only CQA could be found in the leaves of Chinese sweet potato (with 5-CQA **35** dominant) but 3-FQA, 4-FQA and 5-FQA, plus 3,4-diCQA and 4,5-diCQA and traces of at least four CFQA could be found in the stem. At least five CFQA were found in the peel of sweet potatoes cultivated in Tanzania.*(948, 949)* In contrast Luo *et al*. reported 3,5-diCQA was the most abundant CGA in sweet potato leaves of 20 cultivars grown in China (one of American origin), accompanied by 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 4,5-diCQA and 3,4,5-triCQA. Teramachi *et al*. reported 3,4-diCQA, 3,5-diCQA, 4,5-diCQA and their methyl esters plus the novel 3,5diC-4*p*CoQA and 1,3di*p*Co-4,5diCQA in the leaves of *I. pes-caprae*, characterised by high resolution FABMS and NMR.*(950)* Both Termachi *et al*. and Luo *et al*. cautioned against the risk of generating alkyl chlorogenates if hot aqueous alcohol were used for extraction.*(3)*

Truong *et al*. reported 5-CQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in the leaves, peel and roots of sweet potatoes grown in the USA, but did not find 3,4,5-triCQA.*(951)* Although the structures used by Truong *et al.* clearly follow the IUPAC numbering, the sequence of elution of the diCQA suggests that the assignments of the diCQA standards used for identification have been described using the non-IUPAC system. The same problem is found in the report of Jeng *et al*. who analysed individual fully expanded leaves, petioles and flowers of sweet potato and investigated the effect of different methods of drying on the tissue composition.*(952)* It appears from the chromatogram that 5-CQA, 3,5-diCQA and 4,5-diCQA are the dominant CGA.

Meira *et al*. reported methyl 3,5-diCQ, methyl 4F-5CQ and methyl 4-CQ in *I. subincana*.*(953)*

4.4.40.2. Menyanthaceae family

Petersen *et al*. have reported 5-CQA in *Menyanthes trifoliata*.*(20)*

4.4.40.3. Solanaceae family

The Solanaceae is a large and varied family, often called the nightshades, and rich in alkaloids many of which are potentially toxic. Well known members of the family include aubergines, potatoes, tomatoes, tobacco and many ornamental plants.

In the older literature CGAs were described as common constituents in many tomato and potato varieties adding significantly to the dietary burden of CGAs.

Atropa species: Petersen *et al.* reported 5-CQA in *Atropa belladonna*.*(20)*

Capsicum species: Uncharacterised chlorogenic acid has been reported in the fruits of *Capsicum annuum*,*(954)* and 5-CQA, its methyl ester and *n*-butyl ester have been reported in the leaves of some red pepper cultivars.*(955)* Mudric *et al*. reported 5-CQA and 5-*p*CoQA in the druits of *C. annuum* L., but with appreciable quantitative variation bettween cultivars.*(956)*

Datura species: Petersen *et al.* failed to find 5-CQA in *Datura stramonium*.*(20)*

Fabiana species. 5-CQA has been reported in *Fabiana imbricata*.*(957)*

Lycium species: Chinese wolfberry or Goji (*Lycium barbarum* L.) is used in traditional Chinese medicines and it contains 2.1–4.3 g/kg of 5-CQA,*(958)* a second incompletely charcterised CQA, and four incompletely characterised diCQA,*(959, 960)* but the fragmentations are not entirely convincing and these assignments should be treated as tentative. It has been demonstrated that supplementing with selenium leads to a greater content of chlorogenic acid in the leaves of *L. chinense*.*(961)* Abdennacer *et al.*using LC–MS reported two CQA including 5-CQA), two FQA, two diCQA and a *p*CoQA in *L. intricatum* fruites from Tunisia.*(962)* One of the putative diCQA eluted very early, and is likely to be a CQA glycoside.

Nicotiana species: 3-CQA, 4-CQA and 5-CQA have been reported in tobacco leaf,*(940, 963)* as have an FQA and a SyQA.*(964)* Madala *et al.*reported in cultured tobacco cells 5-CQA and 4-SyQA,*(940)* previously found only in *Strychnos*,(*371*) and *Erycibe*.*(930)*

Physalis species: Petersen *et al.* could not find 5-CQA in *Physalis alkakengi*,*(20)* but Chen *et al*. reported '*methyl 3-CQ*' and '*chlorogenic acid*' in the calyces of *P. alkekengi*.*(965)* The structure shown for methyl 3-CQ is methyl 5-CQ IUPAC.

Saracha species: Petersen *et al.* could not find 5-CQA in *Saracha edulis.(20)*

Solanum species: It is clear from recent studies that the fruit of *Solanum* species have complex and variable CGA profiles. Wu *et al*. examined 31 samples embracing 24 *Solanum* species, and including 16 accessions from the old world and 15 from the new world. Seventeen CGA were identified by LC–accurate mass-MS and NMR after isolation, or by comparison with 'in house' generated standards. This study established that the fruits of these 24 species varied extensively in CGA profile and are too complex to present succinctly in this review. Only 5-CQA was common

to all, but 3-CQA, 4-CQA, *cis* 5-CQA 5-*p*CoQA, 3-FQA, 5-FQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA were widespread. 3Malo-5CQA, 4C-5maloCQA and 3,4,5-triCQA were also present in many samples.

Stommel *et al.* analysed the fruit of ten *S. melongena* accessions (five F1 hybrid cultivars, three open-pollinated cultivars and two land race accessions), plus one *S. macrocarpon* and one *S. aethiopicum* accession. In addition to the CGA listed above they reported one SiQA, one CSA, two di-(hydroxycinnamoyl)quinic acid conjugates and a minor hydroxycinnamic acid conjugate that was unique to *S. aethiopicum*.*(966)*

Additionally Wu *et al*. have reported in *Solanum* spp. a range of novel and structurally complex CQA and methyl CQ glucosides, some of which where esterified at the glucose C6 with 5-CQA, caffeic, ferulic or sinapic acid, as follows:

5-(6-(5-CQA-glucopyranosyl)-CQA (Viarum acid A) *(967-969)*

3-Malonyl-5-(6-(5-CQA-glucopyranosyl)-CQA (Viarum acid B) *(967-969)*

5-(6-Sinapoyl-glucopyranosyl)-CQA *(968, 970)*

4-Malonyl-5-(6-sinapoyl-glucopyranosyl)-CQA *(968-970)*

3-Malonyl-5-(6-sinapoyl-glucopyranosyl)-CQA *(968-970)*

Methyl 5-(6-Sinapoyl-glucopyranosyl)-CQ *(968, 970)*

Methyl 5-(6-Feruloyl-glucopyranosyl)-CQ *(968)*

Methyl 5-(6-Caffeoyl-glucopyranosyl)-CQ *(968)*

The most recent studies have established the presence in some *Solanum* species also of 3,5-diFQA plus an FQA glycoside, but with considerable variation between species, and a lower content in the species and varieties selected for domestic consumption. The species studied were *S. aethiopicum*, *S. capsicoides*, *S. insanum*, *S. linnaeanum*, *S. macrocarpon*, *S. melongena* subsp. *ovigerum*, *S. melongena*, *S. richardii*, S. *viarum* and *S. violaceum*. With the exceptions of *S. viarum* and *S. richardii* the CQA dominated: in *S. richardii* hydroxycinnamic acid amides dominated and in *S. viarum* CQA and the group consisting of the viarum acids and structurally related sinapoyl-glucose derivatives were co-dominant.*(969)* Espin *et al*. reported 3-CQA and 5-CQA in *S. betaceum* Cav (Tamarillo).*(971)* Herraiz *et al* reported 3-CQA, 4-CQA, 5-CQA and a CSiQA in the fruit of *S. muricatum* (pepino) and *S. caripense*. One sample contained a diCQA and another what might be *cis*-5-CQA and a SiQA derivative. Numerous cinnamic acid glycosides were reported, two early eluting examples probably mis-assigned as diCQA when CQA glycosides are more likley.*(972)*

Im *et al*. analysed CGA in 25 varieties of potato on sale in the USA and in five Korean varieties of potato (*Solanum tuberosum*). They identified 3-CQA, 5-CQA and a third minor component thought to be 4-CQA. The content of 5-CQA in the varieties available in America ranged from 33 mg/kg to 1.1 g/kg fresh weight in 23 varities with two

outliers at 2 g/kg fresh weight (Fingerling French) and 6.3 g/kg fresh weight (Purple Peruvian). The Korean varities ranged from 3.5–340 mg/kg fresh weight.*(973)* Im *et al*. used commercial 5-CQA as calibrant. Narvaez-Cuenca *et al*. reported 3-CQA, 4-CQA and 5-CQA in the peel and flesh of 15 Colombian varieties, plus 5-FQA in the peel of two varieties and the flesh of 11, 3,5-diCQA in the peel of three and flesh of one, and an incompletely characterised CQA conjugate (M_r = 628) in the peel of one variety.*(974)* Andre *et al*. analysed 23 native Andean cultivars and quantified 3-CQA (6–204 mg/kg), 4-CQA (14–768) and 5-CQA (174–12746 mg/kg) with substantial variation in some cultivars (s.d. *ca* 50% of mean value). *Cis*-5-CQA and *cis* 5-FQA were also present.*(975)* Andre *et al*. used commercial 5-CQA as calibrant and expresed all data in 5-CQA-equivalents.

In a separate LC–ion trap-MS investigation they also reported a methylCQ and 1-CQA.*(976)*

Narvaez-Cuenca *et al*. reported 1-CQA, 3-CQA (2.4 g/kg), 4-CQA (7.3 g/kg), 5-CQA (25.4 g/kg) and 5-FQA (40 mg/kg) in Dutch potatoes,*(977)* but it is not clear whether the calibrant is 5-CQA or caffeic acid. The peel of Russet variety potatoes grown in Canada also contain 3-CQA and 5-CQA.*(978)* Lachman *et al*. analysed CGA in seven potato cultivars grown in the Czech Republic. The content of 3-CQA, 4-CQA and 5-CQA together, quantified using commercial 5-CQA, ranged from 315 mg/kg dry matter to 2400 mg/kg, averaging 1700 mg/kg.*(979)* Zhu *et al.*analysed 16 varieties of potato from eight countries on sale in Hong Kong and quantified the CGA, using 5-CQA as calibrant, reporting 1-CQA (79–290 mg/kg dry basis), 3-CQA (160–834 mg/kg dry basis), and 5-CQA (421–2185 mg/kg dry basis), using LC–APCI-MS.*(980)* The assignment of 5-CQA is supported by the use of a commercial standard, but 1-CQA is unexpected and might be in error, raising doubts also about the assignment of 3-CQA. Lopez-Cobo *et al*. also report 1-CQA, 4-CQA and 5-CQA, plus three diCQA and 3-FQA. Note that these authors did not use the IUPAC numbering, and the assignment of I-CQA should be treated with caution.*(981)*

In contrast, a large selection of tomato and potato varieties currently available in German supermarkets were screened for their CGA content using LC–ion trap-MS and it was found that most varieties did not contain any CGAs in either fruits or tubers.*(982)* It appears that the breeding of novel varieties has led to a loss of CGA biosynthesis in some modern cultivars but it should be noted that Navarre *et al*. reported that whether measured on a fresh weight or dey weight basis 5-CQA and *cis* 5-CQA content in tubers declined during maturation, whereas 3-CQA and 4-CQA both increased,*(983)* but 5-CQA was always dominant.*(984)* Torres-Contreras *et al*. reported that wounding of potato tubers could increase the contents of 3-CQA, 4-CQA and 5-CQA significantly, in some cases doubling the original content, but with little or no effect on the diCQAs.*(985)* Despite there being many factors that clearly influence the CGA profile and content, the absence of CGA in products currently sold in German supermarkets is surprising. One might speculate that in the breeding and selection process CGAs were considered as undesirable since they add unfavourable sensory properties to the products such as bitterness and astringency as well as undesirable plant browning capabilities which negatively influence their shelf life. A similar observation has been made by Meyer *et al*. the fruit of domesticated *Solanum* spp.*(969)*

There have been extensive studies of eggplant *S. melongena* L. Whitaker *et al*. reported 3-CQA, 4-CQA, 5-CQA dominant, 3,5-diCQA, 4,5-diCQA plus two minor components tentatively identified as 3Ac-5CQA and 3Ac-4CQA.*(986)* Ma *et al*. reported subsequently that these two minor components occurred in greater concentration (15–25% of

total CGA) in the fruits of *S. anguivi* and *S. viarum* and their isolation in greater quantity led to their identification as 3Malo-5CQA and 4Malo-5CQA.*(987)* *S. melongena* cv Black Beauty also contains methyl 5-(6-caffeoyl-glucopyranosyl)-CQ and methyl 5-(6-feruloyl-glucopyranosyl)-CQ,*(968)* similar to compounds observed previously in *S. viarum*.

The aerial parts of *S. palinacanthum* contain 3,5-diCQA,*(988)* and the fruit of *S. sessiliflorum* contains 5-CQA.*(989)* Garcia-Salas *et al*. using LC–quadrapole-MS reported 3-CQA, 4-CQA, 5-CQA, an uncharacterised FQA and CSA, plus a diCQA that eluted before 3-CQA. There were also four CQA-dehydrodimers.*(990)* These authors did not use the IUPAC numbering, and it is also clear from the early elution and the fragment ion at *m/z* 323 that the compound assigned as a diCQA is actually a CQA-glycoside. Some quantitative data are presented as mg/g but, presumably, should be mg/kg. 5-CSA has been isolated from the leaves of *S. somalense*.*(991)*

S. lycopersicon, formerly *Lycopersicon esculentum* (but also described as *S. lycopersicum* formerly *Lycopersicum esculentum*) the well-known tomato, contains 3-CQA (0.08–1.29 g/kg), 5-CQA (0.16–0.64 g/kg) and an incompletely characterised diCQA (0.13–0.35 g/kg) when produced on well-watered plants. The content rose in some varieties as a consequence of water stress, but declined in others.*(992)* 5-CQA was used as calibrant but, it is not clear whether any correction was applied for molecular weight. Two uncharacterised diCQA, a triCQA plus 4-CQA and 5-CQA (dominant) have been reported in some tomato fruits but not stems or leaves.*(993, 994)* In contrast Ferreres *et al*. reported 3-CQA, 5-CQA, two FQAs and two *p*CoQAs in tomato leaves,*(995)* but note that these authors did not use the IUPAC numbering. Sanchez-Rodriguez *et al*. reported 4-CQA, 5-CQA and a third incompletely characterised CQA (probably *cis*-5-CQA), plus 5-*p*CoQA, 4,5-diCQA and two triCQA in the fruite of cherry tomatoes.*(996)*

Chanforan *et al*. analysed three cultivars used for tomato paste manufacture and reported 3-CQA, 4-CQA, 5-CQA (in total 32 mg/kg dry basis with 5-CQA dominant), 3,4-diCQA, 3,5-diCQA, 4,5-diCQA (in total 24 mg/kg), 3,4,5-triCQA (11 mg/kg) and a glucoside thereof plus an incompletely characterized *p*CoQA.*(997)* Unusually, quantification was made at 280 nm with a commercial 5-CQA calibrant, thus over-estimating the diacyl quinic acids by *ca* 40% and the triacyl quinic acids by *ca* 60%. Siracusa *et al.* using LC–MS reported 5-CQA, two FQA, two *p*CoQA, three diCQA, three CFQA and two diFQA in the fruit of 11 tomato 'long-storage' genotypes grown in Italy.*(998)* Vallverdu-Queralt *et al*. using LC–MS^2 and accurate mass LC–MS reported 3-CQA, 4-CQA and 5-CQA plus a *p*CoQA, an FQA-glycoside, and two diCQA,*(999)* and with the exception of the FQA-glycoside reported these same CGA plus a fourth CQA in sofritos, described as a Mediterranean product consisting of tomatoes, onions and garlic. The content of 5-CQA (4.4–5.5 mg/kg fresh weight) was considerably higher than previously reported by these authors for fresh tomatoes (0.36–0.46 mg/kg) and presumed to have originated in the onions and / or garlic.*(999)* This group also reported two uncharacterized triCQA in another study.*(1000)*

Withania species: Petersen *et al.* reported 5-CQA in *Withania somnifera*.*(20)*

SOLANALES SUMMARY

Convolvulaceae: A considerable range with CQA, diCQA, CFQA, CSiQA, pCoCQA, triCQA and methyl esters plus the less common SyQA, VQA plus the unique glycosmisoyl-QA and an ether-linked compound.

Solanaceae: *Solanum* is complex and variable, with distinctive viarum acids and associated SiQA and FQA-glycosides, CSiQA, triCQA and CSA, perhaps again a reflection of selective breeding for culinary purposes.

In contrast, *Datura* and *Saracha* lacking 5-CQA

Capsicum has n-butyl esters

Nicotiana has the scarce SyQA

As for the Asterales, the profiles are complex.

4.4.41. ORDER LAMIALES

The Lamiales embraces some 20 families and some 24,000 species and the taxonomy is in a state iof flux. A screening of 48 species for chlorogenic acid (= 5-CQA) by TLC and HPLC revealed 5-CQA in only 11 species with many of those species negative for 5-CQA being positive for rosmarinic acid. *Dracocephalum* and *Glechoma* were positive for both test substances, and *Leonurus, Phlomis, Plantago, Calceolaria, Chelone* and some *Penstemon* were positive only for 5-CQA.*(20)* It should be noted that screening by HPLC with UV detection, and especially by TLC, will not be as sensitive as profling by LC–MS, and as noted earlier the absence of 5-CQA is not categorically indicative of the absence of other CGA.

Rosmarinic acid is a conjugate of caffeic acid with the side chain hydroxyl of 3',4'-dihydroxyphenyl-lactic acid (2*R*-hydroxy-dihydrocaffeic acid = 2*R*,3',4'-trihydroxyphenylpropionic acid). It is interesting to note that Gohari *et al.* have reported a novel 3'4'-dihydroxyphenyl-lactic acid–quinic acid derivative in *Hymenocrater calycinus* (Lamiaceae, ?Nepetoideae) in which 3'4'-dihydroxyphenyl-lactic acid is bound to quinic acid *via* an ether linkage formed from the lactic hydroxyl and the quinic acid C5 hydroxyl.*(850)* This observation raises the possibility that suche conjugates might be more widely distributed, or even, that 3'4'-dihydroxyphenyl-lactoyl-quinic acids might also occur.

This ether-linked conjugate resembles the novel compound isolated from *Convolvulus dorycnium* (Convolvulaceae, Solanales) in which the vanillic acid C4 is attached via an ether bond to C4 of methylquinate.*(859)*

4.4.41.1. Acanthaceae family

Peteresen *et al*. reported 5-CQA in *Barteria micans* but not in *Acanthus hungaricus* and *A. longifolius, Jacobinia zelandia,* or *Odontonemia schomburgkianum*.*(20)*

4.4.41.2. Gesneriaceae family

Petersen *et al*. did not locate 5-CQA in *Phineas multiflora*, *Streptocarpus caulescens* or *S. rexii*.*(20)*

4.4.41.3. Lamiaceae family

The Lamiaceae, formerly Labiatae, includes over 200 genera and some 7,000 species and its classification has changed markedly over the years making early analytical data difficult to relate to more modern. Many Lamiaceae are used as herbs and seasonings, or as herbal teas or tisanes, for example the mints (*Mentha* spp).

The account which follows is based on the belief that there are are currently seven subfamilies[2] — Viticoideae, Symphorematoideae, Ajugoideae, Prostantheroideae, Nepetoideae, Scutellarioideae and Lamioideae. The Prostantheroideae and Nepetedoideae are subdivided into tribes.

Data have not been found for Symphorematoideae, Prostantheroideae and Scutellarioideae, but there are many unplaced genera for which some relevant information is available.

4.4.41.3.1. Viticoideae subfamily

The Viticoideae are thought not to be monophyletic, and *Premna* and *Vitex* are thought not to be closely related.

Premna species: According to the abstract Ali found no CGA in *Premna cordifolia*.*(166)*

Vitex species: Note, some authorities place *Vitex* in the Verbenaceae. Kirmizibekmez and Demir reported the novel 4-*p*-hydroxybenzoyl-5-caffeoylquinic acid in *Vitex agnus-castus* after isolation and NMR characterisation and gave it the trivial name castusic acid.*(1001)* Leitao *et al*. isolated methyl 3,4-diCQ and methyl 3,4-diCQ from the leaves of *V. polygama* and 3,5-diCQA from the fruits of *V. cymosa* Bertero.*(1002)* 3,5-DiCQA has been reported in the leaves of *Vitex quinate*.*(1003)*

4.4.41.3.2. Ajugoideae subfamily

Ajuga species: Boudjelal *et al*. using LC–MS profiling detected 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA and 4,5-diCQA in *Ajuga iva* and *A. herba-alba* (Ajugoideae*).(611)*

4.4.41.3.3. Nepetoideae subfamily

4.4.41.3.3.1. Ocimeae Tribe

Hyptis species: 3,4-DiCQA has been reported in *Hyptis marrubioides* Eppling,*(1004)* but note that IUPAC numbering was not used.

Lavandula species: Petersen *et al*. sought but failed to find 5-CQA in *Lavandula angustifolia* and *L. multifidi*.*(20)* In contrast, 3-CQA, 4-CQA and 5-CQA (dominant) have been reported in *Lavandula pedunculata*,*(1005)* but only 5-CQA was detected in the associated waste after essential oil distillation.*(1006)* Note that these authors use the non-IUPAC numbering.

[2] see https://en.wikipedia.org/wiki/Lamiaceae

Ocimum species: Farag *et al*. profiled extracts of *Ocimum basilicum* L.*, O. africanum* Lour.*, O. americanum* L. and *O. minimum* L. by UHPLC–MS and found no acyl quinic acids,*(871)*

Plectranthus species: Petersen *et al*. failed to find 5-CQA in *Plectranthus ciliata*.*(20)*

4.4.41.3.3.2. Mentheae Tribe

Dracocephalum species: Kakasy *et al*. using GC–MS and a commercial standard reported 5-CQA in *Dracocephalum moldavica* and *D. rayschiana* flowers,*(1007)* consistent with the report of Dai *et al*. who examined *D. peregrinum*.*(1008)*

Mentha species: 3-CQA, dominant, 5-CQA and an incompletely characterised FQA have been reported in *Mentha spicata* L.*(1009)*

Origanum species: 3-CQA, 5-CQA and an incompletely characterised diCQA have been reported in in *Origanum vulgare* L.*(1010, 1011)*

Rosmarinus species: Vallverdu-Queralt *et al*. reported 5-CQA and an incompletely characteriswed diCQA in *Rosmarinus officinalis*.*(1011)*

Salvia species: Petersen *et al*. sought but failed to find 5-CQA in *Salvia officinalis* and *S. splendens*.*(20)*

Satureja species: Petersen *et al*. sought but failed to find 5-CQA in *Satureja montana*.*(20)* In contrast three CQAs (3-CQA, 4-CQA and 5-CQA) have been located in extracts of *S. parviflora* (Phil.) Eppling (= *Clinopodium gilliesii* (Benth.) Kuntze),*(1012)* albeit, extracted under conditions likely to favour acyl migration.

Thymus species: Boros *et al*. reported 5-CQA in *Thymus glabrescens* Willd, *T. pannonicus* All., *T. praecox* Opiz, *T. pulegioides* L. and *T. serpyllum* L,*(1013)* and Vallverdu-Querault *et al.* reported it and an incompletely characterised diCQA in *T. vulgare*.*(1011)*

4.4.41.3.4. Lamioideae subfamily

Lamium species: An uncharacterised chlorogenic acid has been reported in *Lamium album*.*(1014)*

Leonurus species: An uncharacterised chlorogenic acid has been reported in *Leonurus cardiaca*.*(1015)*

Marrubium species: An uncharacterised chlorogenic acid has been reported in *Marrubium vulgare L.(1016)* but Petersen *et al*. failed to locate 5-CQA in this species.*(20)*

Phlomis species: *Phlomis umbrosa*, *P. brunneogaleata, P. oliveri* Benth, *P. armeniaca* and *P. megalantha* contain 5-CQA,*(1017-1019)* and *P. brunneogaleata* additionally contains methyl 3-CQ and 5-CSA, which were characterised by NMR.*(1020)* 3-*p*CoSA has been isolated from *P. cashmeriana* and charcaterised by NMR.*(326)*

Stachys species: A detailed investigation of *Stachys recta* detected 1-CQA, 3-CQA, 4-CQA and 5-CQA, which dominated this fraction, and 3,4-diCQA, 3,5-diCQA and 4,5-diCQA,*(1021)* but only 5-CQA was reported in *S. tymphaea*.*(1022)* Leporini *et al*. reported 1-CQA, 3-CQA and 5-CQA in *S. glutinosa*.*(1023)* Venditti *et al*. reported 5-CQA in *S. palustris*,*(1024)* but did not refer to any other CGA, and did not use IUPAC numbering.

Sideritis species: Petreska *et al*. using LC–ion trap-MS^2 reported 5-CQA and an incompletely characterised FQA (or possibly methyl CQ) in the aerial parts of *Sideritis scardica*, *S. raeseri*, *S. taurica*, *S. syriaca* and *S. perfoliata which* are used as an herbal tea and folk medicine in the Balkans. 5-CQA content ranged from 30 to 70 g/kg.*(1025)* 5-CQA has also been reported in *S. syriaca*,*(1026)* and the content is considered to be of taxonomic significance.*(1027)* Two novel acyl-quinic acids have been isoalated from *S. syriaca* ssp *syriaca* and characterised by NMR and MS as 1-*p*-coumaroyl-3-protocatechuoyl-5-dihydrocaffeoylquinic acid and 1-*p*-coumaroyl-3-dihydrocaffeoyl-5-protocatechuoylquinic acid with the qunic acid esterified to rhamnose, and accompanied by 5-CQA.*(1028)*

4.4.41.3.5. Unclassified

Bostrychanthera species: See *Gomphostemma* species.*(1029)*

Calamintha species: Petersen *et al* failed to find 5-CQA in *Calamintha nepeta*.*(20)*

Chelanopsis species: See *Gomphostemma* species.*(1029)*

Collinsonia species: Petersen *et al* failed to find 5-CQA in *Collinsonia canadensis*.*(20)*

Glechoma species: Varga *et al*. confirmed the presence of 5-CQA in the aerial parts of *Glechoma hederacea* using LC–QTOF-MS,*(1030)* but Döring and Petersen reported that *G. hederacea* contains '*chlorogenic* acid' in the leaves (*ca* 20 g/kg), flowers (*ca* 16 g/kg) and stems (*ca* 13 g/kg), but not the roots,*(1031)* and some negative reports might reflect the tissue analysed.

Gomphostemma species: A substantial chemotaxonomic investigation by Bongcheewin *et al*.*(1029)* established that an incompletely characterised diCQA was found in *Chelanopsis* subgen. *Chelanopsis*, specifically *Ch. moschata* Miq. and *Ch. longipes* Makino, but not in *Chelanopsis* subgen. *Aequidens.* The majority of *Chelanopsis* spp. examined also contained 5-CQA

The majority of *Gomphostemma* subgenus *Pogosiphon* examined contained 5-CQA but only *G. microdon* and *G. nutans* contained the diCQA. Relatively few species in *Gomphostemma* subgenus *Stenostoma* contained 5-CQA and only two samples of *G. microcalyx* contained the diCQA. Approximately half of the samples from *Gomphostemma* subgenus *Gomphostemma* contained 5-CQA but none contained the diCQA.*(1029)*

This diCQA was also found in one of two samples *Bostrychanthera deflexa* and a few species of *Gomphostemma*. *(1029)*

Hedeoma species: Leyva-Lopez *et al*. reported 3-CQA in *Hedeoma patens*, known locally as oregano but did not locate any CGA in two other plants (*Lippia* spp. Verbenaceae) also known locally as oregano.*(1032)*

Hymenocrater species: As mentioned above a novel 3'4'-dihydroxyphenyl-lactic acid–quinic acid has been reported in *Hymenocrater calycinus* in which 3'4'-dihydroxyphenyl-lactic acid is bound to quinic acid *via* an ether linkage formed from the lactic hydroxyl and the quinic acid C5 hydroxyl.*(850)* No other quinic acid derivatives were reported.

Hyssopus species: Dzamic *et al*. analysed extracts of the aerial parts of wild *Hyssopus officinalis* L. Subsp *pilifer* (Pant.) Murb. and identified 3-CQA, 4-CQA, 5-CQA (dominant), 3-FQA, 4-FQA and tentatively, the novel 5-*p*-hydroxybenzoylQA by accurate mass LC–MS. This novel compound had an accurate mass of 312.0845 and produced a fragment at *m/z* 191 consistent with this assignment,*(1033)* but is recorded as having 328 nm λ_{max}, suggestive of a more conjugated structure. The same profile, including the novel 5-*p*-hydroxybenzoylQA was reported by Venditti *et al*. but no further characterisation was presented.*(1034)*

Melissa species: In distinct contrast, Marques and Farah reported 3-CQA 106 mg/kg, 4-CQA 35 mg/kg, 5-CQA 170 mg/kg, 3,4-diCQA 168 mg/kg and 4,5-diCQA 455 mg/kg dry basis in *Melissa officinalis.* FQA were not detected and only a trace of 3,5-diCQA was present.*(35)* The calibrants were not clearly stated.

Melittis species: An uncharacterised chlorogenic acid hs been reported in *Melittis melissophyllum* L.*(1035)*

Mesona species: An uncharacterised chlorogenic acid has been reported in *Mesona procumbens.(1036)*

Micromeria species: Petersen *et al.* failed to find 5-CQA in *Micromeria thymifolia*.*(20)*

Prunella species: Sahin *et al*. reported 5-CQA in *Prunella vulgaris* L.*, P. laciniata* L. and *P. grandiflora* L. but not in *P. orientailis* Bornm.*(1037)*

4.4.41.4. Orobanchaceae family

The majority of the Orobanchaceae, commonly called Broomrapes, are parasitic on the roots of other plants. *Siphononstegia chinensis*, one of only four species in the family and formerly placed in the Scrophulariaceae, is now placed in the Orobanchaceae. According to the English abstract Zhang *et al*. reported that it contains 4,5-diCQA, macranthoin F = methyl 4,5-diCQ and methyl 3,4,5-triCQ.*(1038)* The authors' abstract describes macranthoin F as 3,4-diCQA suggesting that they did not use the IUPAC numbering system**.** Lee *et al*. have characterised by NMR 5-CSA isolated from extracts of *Castilleja rubra*.*(1039)*

4.4.41.5. Plantaginaceae family

The Plantaginaceae are commonly known as plantains, but should not be confused with the plantains of *Musa* spp, related to the bananas.

Digitalis species: Petersen *et al*. failed to locate 5-CQA in *Digitalis lanata* or *D. lutea*.*(20)*

Plantago species: Petersen *et al*. located 5-CQA in *Plantago media* but not in *P. nivalis, P. schwarzenbergiana* or *P. sempervirens*.*(20)*

Veronica species: Barreira *et al*. using LC–MS^2 demonstrated significant differences in CGA profile with *Veronica montana* containing 3-CQA, 5-CQA and 3,5-diCQA, *V. polita* containing only 5-CQA, and *V. spuria* not containing any.*(1040)*

4.4.41.6. Oleaceae family

The Oleaceae include 29 genera and at least 600 species, of which the best known is the olive.

Jasminium species: Ferreres *et al*. using LC–MS^2 and 5-CQA as calibrant located in *Jasminum grandiflorum* flowers 4-*p*CoQA, 5-dhCQA (6.7 g/kg) and 5-(3-methoxy-dihydrocaffeoy)lquinic acid (M_r = 386; 0.8 g/kg).*(1041)* Note that a dihydrocaffeic acid derivative will have a weaker absorbance at 325 nm than a caffeic acid derivative and the content of 5-dhCQA might have been underestimated.

Jaiswal *et al*. have reported 3-O-(3-hydroxy-dihydrocaffeoyl)quinic acid (M_r = 372) in *Lonicera henryi* and observed that it produces by loss of water an MS^2 base peak at *m/z* 353.*(849)* This behaviour is identical to that reported for the fragmentation of the putative 5-dhCQA and putative 5-(3-methoxy-dihydrocaffeoy)lquinic acid which yield MS^2 fragment ions at *m/z* 337 and *m/z* 367, respectively, suggesting that they might be 5-(3-hydroxy-dihydrocoumaroyl)-QA and 5-(3-hydroxy-dihydroferuloyl)-QA.

Olea species: *Olea europaea* has been reported to contain 5-CQA,*(1042)* but it was not found by Llorent-Martinez *et al*.,*(433)* or Petersen *et al*.*(20)*

Osmanthus species: Wu *et al*. isolated methyl 5-CQ, *n*-butyl 5-CQ, *n*-butyl 5-FQ and *n*-butyl 4,5-diCQ from *Osmanthus yunnanensis*.*(1043)*

4.4.41.7. Scrophulariaceae family

Petersen *et al*. reported 5-CQA in *Calceolaria scabiosifolia, Chelone lyonii* and *Penstemon digitailis*, but absent from *P. hirsutus* and *P. serrulatus*, *Linaria triornithophora, Nemesia strumosa, Schrophularia nodosa, Verbascum phlomoides* and *V. undulatum*, and *Veronica longifolia*.*(20)*

4.4.41.8. Verbenaceae family

Petersen *et al*. failed to locate 5-CQA in *Lantana camara, Verbena spec., V. officinalis, V. rigida* or *V. urticifolia*.*(20)*
Leyva-Lopez *et al*. failed to locate any CGA in *Lippia graveolens* and *L. palmeri*.*(1032)*

Vitex species: Note, some authorities place *Vitex* in the Lamiaceae, see above.

LAMIALES SUMMARY

As the Apiales, the Lamiales has been rather overlooked with the emphasis having been on other classes of phytochemicals. There are very few reports other than for Lamiaceae, but there is ample evidence that some scarce hydroxybenzoyl-containing chlorogenic acids are present in some genera, and more limited evidence for the presence of the scarce dihydrocinnamoylquinic acids in the Oleaceae.

Frequently families seem to have both members lacking 5-CQA and members producing it, and the presence or otherwise of an incompletely characterised diCQA has been suggested as a potentially useful taxonomic marker in *Gomphostemma* and related species. The negative reports might reflect the tissue analysed, and sometimes lack of sensitivity when only TLC or LC–UV has been used, and there is a clear requirement for more LC–MS profiling.

Acanthaceae: Few data, some without 5-CQA

Gesneriaceae: No reports of 5-CQA but few data

Lamiaceae: For seven species there is only a single report, and that negative for 5-CQA.

Hyssopus has FQA and the scarce *p*-hydroxybenzoylquinic acid.

Mentha has FQA

Phlomis has *p*CoSA

Stachys has a fourth and early eluting CQA, possibly 1-CQA

Sideritis has 1-*p*-coumaroyl-3-protocatechuoyl-5-dihydrocaffeoylquinic acid

Vitex has the novel 4-*p*-hydroxybenzoyl-5-caffeoylquinic acid = castusic acid

Oleaceae family

Jasminium has the scarce 5-dhCQA and 5-(3-methoxy-dihydrocaffeoy)lquinic acid

In contrast to the Asterales and Solanales the impression is of simpler profiles.

4.4.42. ORDER GENTIANALES

4.4.42.1. Apocynaceae family

The Apocynaceae contain over 400 genera and 1500 species, but have been little studied. *Parabarium huaitingii* contains 5-CQA, 5-CSA and 3,4-diCQA.*(1044)* *Apocynum venetum* leaves contain 3-CQA, 4-CQA and 5-CQA.*(1045)* *Catharanthus roseus* stems and leaves contain the same three CQA but petals contained only 4-CQA.*(547)* 5-CQA has been reported in *Hancornia speciosa* Gomes.*(1046)* An unusual quinic acid derivative, 3,4-epoxy-1,5-γ-quinide (winepoxide), has been reported in *Winchia calophylla*,*(1047)* but it is not known whether any acylated derivatives are present. The stringy seed pulp of *Landolphia owariensis* P. Beauv contains 5-CQA and methyl-5CQ.*(1048)* Surveswaran *et al*. reported 5-CQA and incompletely characterised diCQA in *Decalepsis hamiltonii*, *Hemidesmus indicus*, *Tylophora ovata* and *T. indica* and *Wattakaka volubilis.(1049)*

4.4.42.2. Loganiaceae family

The Loganiaceae are a tropical family of 13 genera that have been little investigated with regard to their CGA content. However, Itoh *et al*. reported a new quinic acid derivative, 4-SyQA, from the bark and wood of *Strychnos lucida*,*(939)* subsequently found in *Erycibe* (Convolulaceae) *(930, 934)* and *Nicotiana* (Solanaceae).*(940)*

4.4.42.3. Rubiaceae family

The Rubiaceae embraces over 600 genera and over 13,000 species, this latter statistic making it the fourth largest family of plants. Over 200 individual *trans* CGA plus a significant number of cinnamoyl amides have been recorded in the Rubiaceae, including some 1-acyl diCQA, methyl esters and CGA containing aliphatic substituents.

4.4.42.3.1. Subfamily CINCHONOIDEAE

4.4.41.3.1.1. Tribe Guettardeae

Guettarda species: 5-CQA and 4,5-diCQA have been isolated from the leaves of *Guettarda acreana* DC and characterized by NMR.*(291)*

4.4.42.3.1.2. Tribe Isertieae

Isertia species: *Isertia pitteri* contains butyl 4,5-diCQ, 1,5-diCQA, 3,4-diCQA and 4,5-diCQA.*(464, 1050)*

Sabicea species: The roots of *Sabicea brasiliensis* contain 5-CQA, 3,5-diCQA and 4,5-diCQA.*(1051)*

4.4.42.3.1.3. Tribe Naucleeae

Neolamarckia species: According to the abstract *Neolamarckia cadamba*, formerly *Anthocephalus cadamba*, contains 5-CQA.*(1052)*

4.4.42.3.2. Subfamily GOCHNATIOIDEAE

4.4.42.3.2.1. Tribe Gochnatieae

Gochnatia species: Lucarini *et al*. isolated 3,5-diCQA from the aerial parts of *Gochnatia pulchra*.*(1053)*

Moquiniastrum species: According to the abstract, Strapasson *et al*. reported methyl 5-CQ, ethyl 5-CQ, methyl 3,5-diCQ, ethyl 3,4-diCQ, ethyl 3,5-diCQ, methyl 4,5-diCQ, ethyl 4,5-diCQ, methyl 4,5-diCQ, ethyl 4,5-diCQ, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA in the trunk bark of *Moquiniastrum polymorphum* subsp *floccosum*,*(1054)* but it is not known which numbering system was used.

4.4.42.3.3. Subfamily IXOROIDEAE

4.4.42.3.2.1. Tribe Coffeeae

Coffea species: As discussed in Part 1 the coffee bean is the original source of 5-CQA and its potential importance in the taxonomy of this genus has long been recognized,*(1055-1058)* with many of the non-commercial 'wild' species, for example *C. pseudozanguebariae*,*(1059)* having significantly smaller CGA contents than the commercially exploited *C. arabica* (arabica coffee) and *C. canephora* (robusta coffee). The most comprehensive of these chemo-

taxonomic studies, one embracing 20 species, a second embracing 25 species and including seven some from Madagascar, and the most recent investigating 21 African species, were performed before LC–MS methods became available,*(1056, 1057, 1060)* and a reinvestigation that could examine the quantitatively minor CGA would be useful. These 'wild' species frequently have lower caffeine contents than the commercially exploited species and some have components absent from commercial arabicas and robustas, but these features fall outside the scope of the present review. High caffeine is always associated with high CGA, and *vice versa*, with no exceptions identified to date, but the molar ratio varies extensively. Nevertheless there is always a significant amount of CGA that cannot be complexed to caffeine.*(1060)* Anthony *et al.* concluded that there are two distinct metabolic pathways, one producing low CGA (below *ca* 25 g/kg accompanied by low caffeine) and the other leading to more than 45 g/kg CGA,*(1057)* but Campa *et al*. concluded that there were three groups for CGA content (not exceeding 25 g/kg; 50–65 g/kg; and 75–120 g/kg).*(1060)*

There are marked differences in CGA and cinnamoyl-amino acid profile and content between these two commercial species. The seeds, or more accurately the commercial green beans, of *C. arabica* contain 3-CQA, 4-CQA and 5-CQA, 3-FQA, 4-FQA and 5-FQA at least two pCoQA (4-*p*CoQA and 5-*p*CoQA) and three diCQA (3,4-diCQA, 3,5-diCQA and 4,5-diCQA), plus in some samples traces of several CFQA,*(1061, 1062)* *p*CoCQA, CSiQA, DQA, TSA, CSA and possibly diFQA.*(1062)* These CGA are found also in the seeds of *C. canephora* at a greater concentration with the possible exception of the *p*CoQA.*(1061, 1063-1065)* Some illustrative quantitative data are presented in Tables 4.1. and 4.2.

Table 4.1. CGA content in arabica and robusta coffee beans of African origin. Data from Ky *et al.*2001.*(1065)*

	C. arabica content green beans in g/kg dry basis *N* = 38	*C. canephora* content green beans in g/kg dry basis *N* = 38
3-CQA	1.6–2.5	4.3–13.3
4-CQA and 5-CQA	24.3–37.2	46.8–89.6
5-FQA	0.8–2.2	6.2–20.4
3,4-diCQA	0.8–1.7	5.4–9.5
3,5-diCQA	1.7–3.6	3.8–11.3
4,5-diCQA	1.8–3.8	4.1–12.4
Total of the above	32.0–46.0	68.1–122.1

C. canephora also contains DQA, SiQA, diFQA, di*p*CoQA, C-FQA, C-*p*CoQA, C-DQA, C-SiQA, *p*Co-FQA, *p*Co-DQA, F-DQA, F-SiQA, T-CQA, T-FQA plus the following tri-acyl quinic acids: tri-CQA, diC-FQA, diF-CQA and diC-SiQA.*(122, 221, 355, 1066-1070)*

Table 4.2. CGA content of arabica coffee beans. Data are the range in mean contents (g/kg dry matter) reported by Baeza *et al*. for arabicas from Colombia, Brazil, Ethiopia and Kenya.*(1062)*

	g / kg dry matter
*p*CoQA	0.50–0.61
CQA	49.8–61.0
FQA	3.80–4.60
DQA	0.05–0.07
*p*CoCQA	0.04–0.09
diCQA	3.74–5.32
CFQA	0.19–0.36
diFQA	0.013–0.024
CSiQA	0.006–0.011
TSA	0.020–0.032
CSA	0.038–0.053
Total of the above	59.67–69.42

It has been estimated crudely that the summed content of the minor CGA (DQA, *p*CoCQA, *p*CoFQA, diFQA, *p*CoDQA, CDQA, FDQA) in a robusta coffee are unlikely to exceed some 7 g/kg,*(221, 1066, 1067)* but that is appreciably more than in the arabicas reported by Baeza *et al*.***(1062)***

Principal component analysis allowed the most discriminating compounds to be identified. Based on their concentrations, 3-O-caffeoylquinic and 4,5-O-dicaffeoylquinic acids were found to be characteristic markers for Northwest and East (Harar) region coffees, respectively. Sub-regional coffee types from West, except Jimma B, could be distinguished by their 3,5-O-dicaffeoylquinic to 4,5-O-dicaffeoylquinic acid concentration ratios, while Yirgachefe coffees from South could be distinguished by their 4,5-O-dicaffeoylquinic to 3,4-O-dicaffeoylquinic acid concentration ratios

For both arabica and robusta coffees there is evidence of significant differences in CGA profile with geographical origin,*(355, 1061, 1065, 1068, 1071-1075)* but whether this is a reflection only of genotype is unclear.*(1076, 1077)* Mehari *et al* investigated Ethiopian *C. arabica* cultivars and in addition to the three regular CQA and three regular diCQA noted also small amounts of *cis*-5-CQA and a *cis*-3,5-diCQA, plus an additonal late-eluting CQA-like component,*(1075)* and Baeza *et al*. have also noted some *cis* isomers.*(1062)*

Not surprisingly some studies on CGA biosynthesis have utilised *Coffea*.*(1078-1080)* These differences in CGA profile are sufficient to discriminate between these two species even after the beans have been roasted,*(1081)* but the changes on roasting and brewing of coffee are not dealt with here. Coffee pulp, i.e. the flesh of the fruit (cherry) from arabicas and robustas contains CQA, FQA and diCQA,*(1082)* arabica pulp contains pCoQA,*(1083)* but CFQA were not detected even in the pulp of robustas.*(1082)*

The CGA content of the leaves of *Coffea* spp. have also been investigated. Mondolot *et al*. established that 5-CQA is the dominant CGA in leaves of *C. canephora* but FQAs are also present, and diCQAs particularly in juvenile leaves, but it is important to note that the content and profile varies significantly with leaf age.*(1084)*

In a subsequent study this group investigated the CGA in leaves of 23 *Coffea* spp. From Africa and Madagascar. The three CQA (3-CQA, 4-CQA and 5-CQA) accumulated in the leaves of all 23 species and accounted for >80% of CGAs in 21 species, *C. stenophylla* and *C. andrambovatensis* being the exceptions with a higher FQAs content. 5-CQA usually dominated the CQAs, but in *C. augagneuri* 4-CQA was dominant. DiCQAs were not detected in *C. stenophylla* or *C millotii*. 3,5-DiCQA dominates this fraction in all species except *C. augagneuri* where 3,4-diCQA was dominant, but was the minor diCQA in all other species examined.*(1085)*

Psilanthus and *Psilanthopsis* species: Early taxonomic studies *(1056)* established that the seeds of *Psilanthopsis kapkata* from Tanzania contained CQA (*ca* 41 g/kg), FQA (*ca* 3.4 g/kg) and diCQA (*ca* 6 g/kg). The seeds of *Psilanthus ebracteolatus* from the Ivory Coast contained CQA (*ca* 1.8 g/kg), FQA (*ca* 0.6 g/kg) and diCQA (*ca* 0.3 g/kg) whereas the seeds of *Psilanthus manni* from the Ivory Coast contained CQA (*ca* 3.5 g/kg) and FQA (*ca* 0.3 g/kg) with the diCQA undetectable. Recently *Psilanthus* has been incorporated into *Coffea* on morphological grounds*(1086)* but this is not supported by the significant differences in chromatographic profile obvious at 276 nm.*(1056)*

4.4.42.3.2.2. Tribe Gardenieae

Gardenia species: Although data are limited, *Gardenia* not only utilises sinapic acid to a much greater extent than *Coffea*, but also 3-hydroxy-3-methyl-glutaric acid that to date has not been reported in *Coffea*.*(1087-1089)* When 3-hydroxy-3-methyl-glutaric acid is esterified with any of the quinic acid hydroxyls, it is desymmetrised and two pairs of diastereomeric CGAs result with the C-3 of glutaric acid becoming a stereogenic center. On some occasions the resulting pair of diastereomers can be resolved, but not in all cases. The gluQA are the only example of CGA so far observed which lacks an aromatic substiuent, but such compounds may well have been overlooked, especially as they lack the typical UV absorbance in the 280–330 nm range.

According to the English abstract Fu *et al*. reported chlorogenic acid, 3,4-diCQA,3C-4SiQA, methyl-3C-4SiQ, methyl-3C-5SiQ, 3,4diC-3glutQA and 3,5diC-4-glutQA in *Gardenia jasminoides* Ellis,*(1090)* but it is unclear whether or not IUPAC numbering was used.

Gardenia jasminoides Fructus (fruit extract) is used in the traditional Chinese herbal medicine, Zhizi, and as a source of pigments for colouring food, the composition varying with geographic origin.*(1091)* Along with Herba Artemisiae (Yinchen) it is a component of Yinchen-Zhizi,*(1092)* and along with fermented soybean (Dan dou chi) it is a component of Zhi-zi-chi.

Clifford *et al*.*(1087)* reported 3-CQA, 4-CQA, 5-CQA, 3-SiQA, 4-SiQA, 5-SiQA, 3-GluQA, 4-GluQA, 5-GluQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 3Si-5CQA, 3Si-4CQA, 3C-4SiQA, 4Si-5CQA, 3Si-5FQA, 4Si- 5FQA, 4Si-5*p*CoQA, 3C-4gluQA, 3glu-5CQA, 3C-5gluQA, 4glu-5CQA, 4C-5gluQA, 3glu-5FQA, 4glu-5FQA, 3,5diC-4gluQA and 3F-4Glu-5CQA from Gardeniae

Fructus. Kim *et al.(1088)* identified methyl 3Si-5CQ, ethyl 3Si-5CQ, methyl 4Si-5CQ, ethyl 4Si-5CQ, methyl 3,5diC-4gluQ in Gardeniae Fructus. Zhou *et al*. using LC–triple quadrupole-MS and TOF-MS with careful tuning of the collision energy reported 3-CQA, 4-CQA, 5-CQA, 3Si-5CQA and 3C-4SiQA.*(1093)* Yang *et al*. isolated 3,5-diCQA, 3Si-5CQA, 3,5diC-4gluQA and 4Si-5CQA from *G. jasminoides* fruit*(1094)* Bergonzi *et al*. using LC–MS and 5-CQA as calibrant reported an uncharacterized SiCQA 7-20 g/kg, 3,4diC-5gluQA 3.8-6.0 g/kg and six other uncharacterized CGA together in the range 10.2-19.1 g/kg in five samples of Gardeniae Fructus but,*(1095)* it is not clear whether or not the IUPAC numbering system has been used. Note that using 5-CQA as calibrant will over-estimate diacyl quinic acids by *ca* 40%. Yu *et al.* reported 3,5-diCQA, methyl 3,4-diCQ, methyl 4,5-diCQ, 4Si-5CQA and 3,5diC-4-gluQA by comparison with previously published data.*(901)* Fu *et al*. using LC–QTOF-MS tentatively identified 3-CQA, 4-CQA, 5-CQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 5C-4SiQA and 3,5diC-4gluQA in Yinchen-Zhizi.*(1092)* Zhao *et al*. using LC–QTOF-MS reported 5-CQA, 3,4-diCQA, 3,5-diCQA, 4,5-diCQA, 5C-4SiQA, 5C-3SiQA and 3,5diC-4gluQA in Zhi-zi-chi.*(1096)*

Although there may be genuine differences in profile between different samples of Zhizi and related herbal preparations, it is likely that some of the discrepancies in the compounds detected might result from using non-ion trap-MS instruments to characterize the more complex CGA for which authentic standards are not available.

4.4.42.3.2.3. Tribe Ixoreae

Ixora species: Versiani *et al*. reported 5-CQA in the flower of *Ixora coccinea*,*(1097)* whereas Jaiswal *et al*. using LC–ion trap-MS^n have reported 3-CQA, *cis* and *trans* 5-CQA, 5-*p*CoQA, methyl 3-CQ, methyl 5-CQ, 3,5-diCQA, 4,5-diCQA and two incompletely characterized CSA in the leaves and stem.*(1098)* The two CSA were distinct from those previously reported in maté (*Ilex paraguariensis*). *(465)*

4.4.42.3.2.4. Tribe Vanguerieae

Vangueria species: According to the abstract Bisshay *et al.* have isolated ethyl 1-glucosyl-4-caffeoyl quinate from the leaves and stembark of *Vangueria edulis*.*(1099)*

4.4.42.3.3. Subfamily RUBIOIDEAE

4.4.43.3.3.1. Tribe Psychotrieae

Psychotria alliance: Berger *et al*. reported 5-CQA, 5-*p*CoQA and 3,5-diCQA in all samples studied.*(1100)*

4.4.42.3.3.2. Tribe Rubieae

Galium species: Methyl 3CQ and methyl 5-CQ have been reported in *Galium odoratum* leaves.*(1101)* Jaiswal *et al*. using LC–MS^n reported 39 hydroxycinnamates in the leaves of *G. odoratum* L. Scop., *G. verum* L., *G. glaucum* L., *G. mollugo* L., *G. boreale* L., and *G. harcynicum* L. (syn. *G. saxatile* L.) of which 25 were identified to regio-isomer level.*(1102) G. odoratum* contained *cis* and *trans* 3-CQA, 4-CQA and 5-CQA, *trans* 3-FQA, *cis* and *trans* 4-FQA and 5-FQA, *trans* 3-*p*CoQA, *cis* and *trans* 4-*p*CoQA and 5-*p*CoQA, plus 1,5-diCQA, 3,5-ciCQA and 4,5-diCQA plus two incompletely characterised CQA epimers. *G. verum* did not contain the CQA epimers, but and FQA epimer was noted along with 1,3-diCQA and several diCQA *cis* isomers not seen in *G. odoratum*. In contrast, *G. harcynicum* presented a much simpler profile with only *cis* and *trans* 3-CQA, 4-CQA and 5-CQA plus 3,5-diCQA, a *cis* isomer thereof and 4,5-diCQA. *G. mollugo*, *G. boreale* and *G. glaucum* also had quite simple profiles. *G. mollugo* presented *cis* and *trans* 3-CQA, but only *trans* 4-CQA and 5-CQA, 3-FQA, 3-*p*CoQA and 5-*p*CoQA. *G. boreale* contained 5-CQA, 3-FQA plus *cis* and *trans* 4-FQA and 5-FQA whereas *G. glaucum* presented 5-CQA, *cis* and *trans* 4-FQA, 3-*p*CoQA plus *cis* and *trans* 4-*p*CoQA and 5-*p*CoQA.*(1102)* Petersen *et al*. reported 5-CQA in *G. boreale* and *G. rubioides*.*(20)*

Phuopsis species: Petersen *et al*. did not find 5-CQA in *Phuopsis stylosa*.*(20)*

Rubia species: Petersen *et al*. reported 5-CQA in *Rubia tinctoria*.*(20)*

4.4.42.3.3.3. Tribe Spermacoceae

Hedyotis species: Li *et al*. using LC–quadrupole-MS reported 3-CQA, 4-CQA, 5-CQA and the equivalent *p*CoQA and FQA in the aerial parts of *Hedyotis diffusa* Willd.*(1103)*

GENTIANALES SUMMARY

Coffea and *Gardenia* have been extensively profiled and have extensive but disitinctive ranges of chlorogenic acids, both ranges incorporating scarce if not unique components. *Galium* clearly has variable and disitinctive profiles, but data for the other families are limited by comparison and preclude generalisations being made, but with similar LC–MS profiling there is a good chance of further distinctive patterns being identified. There is an impression that

Gentianales erturn to the more complex profiles similar to the Asterales and Solanales, contrasting with the Lamiales.

Apocynaceae: CQA present

Loganiaceae: SyQA are distinctive, otherwise known only in Convolvulaceae and Solanaceae, but continues the trend for hydroxybenzoylquinic acids hinted at also in the Lamiales.

Rubiaceae:

Rubioideae

Galium have variable and distinctive profiles including some acyl-*epi*-quinic acids

Cinchonoideae:

Guttarideae: CQA and diCQA present but only one sample

Iserteae: CQA and diCQA present, including 1-acyl-diCQA, but only two samples

Naucleae: Data only from one abstract records the presence of 5-CQA

Gochnatioideae:

Gochnateae: Two species reported to contain diCQA

Ixoroideae:

Coffeae:

Coffea particularly rich with wide spectrum of mixed diacyl and mixed triacyl quinic acids but no aliphatic or hydroxybenzoyl substituentsand no 1-acyl derivatives. Commercial well profiled but wild spp are known to be very different different but have not been extensively profiled by modern methods.

Psilanthus and *Psilanthopsis*: No LC–MS profiling, but CQA, FQA and sometimes diCQA are present, but much simpler profile than commercial *Coffea*. The incorporation of *Psilanthus* into *Coffea* seems unjustified on the basis of the remarkably different λ_{276} profile. A distinct requirement for LC–MS profiling of these genera and the non-commercial *Coffea* which might then suggest that it is the commercial *Coffea* that do not fit well.

Gardenieae:

*Gardenia w*ell profiled. Complex profile with scarce, but possibly overlooked, glutQA and SiQA. Many mixed diacyl and triacyl-QA are present but no 1-acyl. Unexpectedly, *p*-coumaric acid and ferulic acid do not occur as mono-acyl-quinic acids, but are found in the pCo and F in mixed diacyl-quinic acids, in contrast to sinapic acid.

Ixoreae: Limited data but a simpler profile with CQA, *p*CoQA, diCQA and CSA

Vanguereae: Data for only one sample but novel glucosyl derivatives

Rubioideae:

Psychotrieae: Data for only one sample, but a relatively simple profile with CQA, pCoQA and diCQA.

Rubieae: *Galium* has been well profiled and apparently has a complex profile, but the data not readily accessible

Spermacoceae: Another simple profile with CQA, pCoQA, FQA

4.4.43. ORDER BORAGINALES

4.4.43.1. Boraginaceae family

Note that the classification of the Boraginales appears to be uncertain, and some authorities associate the Boraginaceae and the Hydrophyllaceae. There have been few studies of these species with regard to their content of CGA. Petersen *et al*. reported 5-CQA in *Echium italicum*, *Nonium lutea* and *Hydrophyllum candense*, but absent from *H. virginicum* and, *Cerinthe major, Heliotropium amplexicaule, Lindelophia longifolia, Lithospermum arvense, Symphytum asperum* and *S. officinale,* and *Nemophylla menziesii.(20)*

BORAGINALES SUMMARY

Insufficient data with no LC–MS profiling.

Boraginaceae: Some with CQA, some without

4.4.44. ORDER GARRYALES

4.4.44.1. Eucommiaceae family

The Eucommiaceae contain only one species, *Eucommia ulmoides*, a tree found only in China and at risk of extinction. Its bark is prized in traditional Chinese medicine and contains 3-CQA, 4-CQA and 5-CQA and several CQA glycosides.*(58)*

GARRYALES SUMMARY

Eucommia has CQA

SUMMARY FOR LAMIIDS

The Lamiids encompasses eight orders, four of which were newly recognised in APG IV,*(9)* and for three of those four there are no data. The data for Solanales, Lamiales, Gentianales, Boraginales and Garryales are summarised below.

Vanolloyl- and glycosimisoyl-QA are found in the Solanales, *p*-hydroxybenzoyl- and protocatechuoyl-QA in Lamiales, and syringoyl-QA in both Solanales and Gentianales suggesting a possibly useful taxonomic characteristic, because there are no reports of (hydroxy)benzoyl-QA in the two most thoroughly profiled genera within the Gentianales (*Coffea* and *Gardenia*).

There are reports of samples from the Solanales, Lamiales and Boraginales lacking 5-CQA, although based on extremely limited data for the Boraginales. Otherwise CQA are generally found but other subgroups rarely if ever reported in Lamiales (one report of FQA), but dihydrocaffeoyl-quinic acids have been reported. Solanales have diCQA, CFQA, CSiQA plus malonoyl derivatives and complex glycosides.

Gentianales, or at least the well-profiled *Coffea* and *Gardenia*, have complex profiles, but with some distinct differences. Glutaroyl and substantial sinapoyl derivatives are restricted to Gardenia, whereas some very rare hydroxycinnamoyl derivatives (such as DQA, TQA) are found only in *Coffea*. The character of non-commercial *Coffea* however is not well known and there is a need for LC–MS profiling

Data for Garryales and Boraginales are too limited to permit generalisations.

4.5. Concluding remarks

A primary objective of this chapter was to summarise the modern data for the botanical distribution of CGA and thereafter to assess whether or not these data identified taxonomically significant differences. At the present state of knowledge this is not possible, but such a potential probably does exist if more high quality data can be acquired. Some suggestions are made regarding areas deserving more attention, particularly further investigation of the novel compounds that have only recently been identified.

This summary presented in this chapter is no more than a snapshot as of December 2016, and while the literature has been diligently searched some material will have been overlooked.

Well over 400 different CGA collected from approximately 1100 publications covering over 400 genera are mentioned in this account, a mere fraction of the known species. Comparatively few of these 400 genera have been thoroughly profiled by LC–MS and for many genera there is only a single report, not even an LC–MS profiling, severely limiting the inferences that can be drawn.

The ideal source of compositional data for this review are studies where plant extracts have been profiled by LC–MS^n. These are still comparatively rare and many analytical studies have focused on a single CGA, usually 5-CQA, or a small group of CGA that for some reason is of particular interest to those investigators, possibly the only CGA of which they were aware or for which they could obtain standards, and the failure to report other CGA in that species cannot be taken as establishing their absence unequivocally.

Although some 1100 references have been examined, and these have generated data for over 400 CGA in over 400 genera that fall within 44 Orders, this only represents a tiny fraction of the plant kingdom, and severely limits the inferences that can be drawn. Never the less, it is hoped that the following will be of interest.

One item that is clear, is that contrary to the generally held belief, there is good evidence for the occurrence of CQA in Bryophytes which lack vascular tissue. In the Pteridophyta there are reports also of *p*CoQA and diCQA, but reports of CSA are more numerous. Data for Gymnosperms are, surprisingly, more limited than for the Pteridophyta, but even here CQA have occasionally been reported along with *p*-coumaroyl esters of 2-hydroxy-quinic acid and *myo*-inositol.

For the Angiospermae, the general impression that forms from the comparatively limited data available is that the Magnolids have a fairly simple acyl-quinic acid acid profile. In the Commelinids, acyl-shikimic acids become more prominent. Galloylquinic acids appear first in the Eudicots and are more prominent in the Fabids. Profiles become more complex in the Malvids and galloyl-quinic acids remain prominent. Campanulids tend to have complex profiles with a noticeable increase in quinic acids having two or more different substituents. Several aliphatic acids become obvious, whether or not 1-substituted dicaffeoylquinic acids are present seems to become taxonomically interesting, and the presence occasionally of acyl derivatives of one or more quinic acid epimers becomes another interesting feature. Hydroxyphenylacetyl-quinic acids also appear. The GQA decline in prominence and may be absent. In the Lamiids hydroxybenzoylquinic acids other than gallic acid become more obvious.

Are CGA universally distributed?

It is sometimes assumed that CGA are universal, at least in higher plants, but negative observations might not have been published. However, there are at least three LC–MS profiling studies which have failed to locate any chlorogenic acids in several species, five from the Lamiaceae (*Ocimum basilicum* L.*, O. africanum* Lour.*, O. americanum* L., *O. minimum* L. and *Premna cordifolia)(166, 871)* plus one from the Brassicaceae (*Cakile maritima*),*(358)* and these are sufficient to suggest that CGA are not universal even in higher plants. Indeed it has been reported explicitly that some Lamiaceae lack the enzymes to synthesise CQA, for example *Coleus blumei = Plectranthus scutellarioides, C. forskohlii, Melissa officinalis* and *Plectranthus fruticolus*.*(20)*

Contrary to the generally held belief, it is interesting to note that there is good evidence for the occurrence of CQA in Bryophytes which lack vascular tissue. In the Pteridophyta there are reports also of *p*CoQA and diCQA, but reports of CSA are more numerous. Data for Gymnosperms are, surprisingly, more limited than for the Pteridophyta, but even here CQA have occasionally been reported along with *p*-coumaroyl esters of 2-hydroxy-quinic acid and *myo*-inositol. LC–MS profiling of a representative range of species is required in order to reassess the situation.

Is 5-CQA always present in species that contain CGA?

With reference to CGA-containing species, it is easy to think that 5-CQA, the archetypal CGA, is certain to be present, but there are a few cases reported where it has been sought and not found despite other CGA being present, for example Barnyard Millet, *Echinochloa frumentacea* link,*(88)* rice (*Oryza sativa*),*(96) Asimina triloba*,*(49)* Agrimonia eupatoriae herba, a pharmaceutical material prepared from *Agrimonia eupatoria (238)* and red-fruited *Prunus tomentosa*.*(200)*

There is a more extensive study by Petersen *et al*. where 5-CQA was sought and frequently not found, but it is unclear whether or not other acyl-quinic acids were present.*(20)*

In some *Galium* spp. 3-FQA is present, but 5-FQA was not detected.*(1102)*

Do all regio-isomers occur naturally?

Following on from the conclusion that some CGA-containing species do not necessarily contain 5-CQA, it is interesting to consider whether or not all possible regio-isomers are known for each CGA subgroup. Before attempting to answer this question, it is important to point out that acyl migration is an ever-present risk during sample work-up, well-illustrated by the facile conversion of 1,5-diCQA *via* the unstable 1,4-diCQA to the comparatively stable 1,3-diCQA. Observation of a regio-isomer does not categorically prove biosynthesis.

All four triCQA and triGQA, plus all six diCQA have been reported, but only five of the six diFQA, four of the six di*p*CoQA, ten of the 12 CFQA, ten of the 12 *p*CoCQA, six of the 12 CDQA and DFQA (no 1-acyl in either case), and just

three of the 12 SiCQA and *p*CoDQA (again no 1-acyl). In contrast seven of the 12 *p*CoFQA have been reported. All four GQA, all six diGQA and all four triGQA also have been reported. The shikimic acid conjugates have been rather less investigated, but all three CSA and all three diCSA have been observed.

There seems no good reason to assume that the missing isomers won't be found somewhere, but LC–MS^n profiling of *Coffea canephora (1066)* and *Artemisia annua*,*(8)* two species which do not esterify C1 of the quinic acid moiety, using the same equipment and method has produced unexpected and interesting data. Allowing for this constraint on which quinic acid hydroxyls are esterified, *A. annua* produces the theoretical maximum of three diCQA, three diFQA, six CFQA, six *p*CoCQA and six *p*CoFQA. In contrast, although *C. canephora* produces the theoretical maximum of three diCQA, three di*p*CoQA and three diFQA, plus the theoretical maximum of six CFQA and six *p*CoCQA, it produces only three of the six possible CDQA, FDQA, *p*CoFQA and *p*CoDQA.

It is thus clear, that for *C. canephora*, there is some constraint on its ability to synthesise the expected range of regio-isomers for certain CGA subgroups, which at least for the *p*CoFQA is not operating in *A. annua*.

It is also clear that while all six diCQA have been found in some Asteraceae, some only produce four (no 1,3-diCQA, no 1,4-diCQA), some three (no 1-acyl-quinic acids), and others produce only two (either 3,4-diCQA and 3,5-diCQA, or 3,5-diCQA and 4,5-diCQA). At least in the *Achillea millefolium* L. aggregate, diploid species lack the ability to produce 1,5-diCQA,*(582)* and this might be an important feature in other species. The occurrence of 1-acyl diCQA is further discussed below.

Accordingly, while all regio-isomers in a given CGA subgroup might occur in some species, certain other species do not necessarily produce the whole set.

Do 5-acyl regio-isomers always dominate the profile?

In many species the 5-acyl regio-isomer dominates its subgroup, but this is not inevitably the case. In some Brassicales, some Aquifoliales and some Rosales 3-CQA clearly dominates. In at least some samples of *Malus* and *Cratageus* 5-CQA dominates the CQA subgroup but 4-*p*CoQA dominates the *p*CoQA subgroup. In *Hemerocallis* the 4-acyl regio-isomer dominates the CQA, *p*CoQA and FQA subgroups and the 5-acyl regio-isomer makes the least contribution.*(106)* Note that while acyl migration during sample workup is always a risk, this phenomenon cannot explain the dominance of 3-CQA in some species because 3-CQA is the regio-isomer most easily hydrolysed during sample workup, and it would never accumulate sufficiently to dominate.*(1104)*

Do CQA and diCQA subgroups always dominate the profile?

In many species the CQA and diCQA subgroups dominate the mono-acyl- and di-acyl-quinic acid subgroups, respectively, but this is not inevitably the case. In *Hemerocallis* the *p*CoQA subgroup dominates the mono-acyl-

quinic acids and diacyl-quinic acids were not detected.*(106)* The FQA and diFQA dominated the profile of *Aster ageratoides*.*(8)*

Caveats

Many of the 400-plus CGA mentioned in this review have been identified comparatively recently, and having been rarely sought, there are comparatively few data for their occurrence and it is impossible to judge their true distribution. This factor, coupled with clear variations in tissue distribution within a species, and variations with maturity, make it likely that the compounds dominating the profile may be variable. Also note, as discussed above and in Part 2 of these notes, that quantifications reported using impure standards may distort which isomer dominates.

Among the more recently reported CGA where taxonomic significance might be found, are (hydroxy)benzoylquinic acids other than gallic acid, the hydroxyphenylacetyl-quinic acids, the dihydrocinnamoylquinic acids, the quinic acid conjugates with only an aliphatic acid substituent, conjugates of 2-hydroxy-quinic acid, and conjugates of quinic acid enantiomers and stereo-isomers.

Distribution of (hydroxy)benzoyl and hydroxyphenylacetyl-quinic and shikimic acids

On present evidence the galloylquinic acids have a comparatively restricted distribution, not being found above the Eudicots or in the Campanulids or Lamiids. They have been found in the Gunnerales, Fabales, Rosales, Fagales, Oxalidales, Malpighiales, Celastrales, Geraniales, Myrtales, Sapindales, Saxifragales and Ericales. Depsidic galloyl derivatives have been reported only in Gunnerales, Fabales and Sapindales. Derivatives of a gallic acid-*O*-methyl ether and of a gallic acid-derived purpurogallin have been reported only in Fabales and Fagales, respectively. Note, however, that the present evidence suggests that GQA occur only in some genera within a family, and this feature might prove of taxonomic significance.

Although the other benzoyl-quinic acids have been much less studied, only the eudesmoylquinic acids in the Oxalidales and vanilloylquinic acids in the Sapindales definitely occur alongside the galloylquinic acids. The benzoylquinic acids have been reported in the Rosales, but only in *Prunus* a genus that does not have galloylquinic acids.

p-Hydroxybenzoyl-, protocatechuoyl-, vanilloyl- and syringoyl-quinic acids have all been reported in the Lamiids, and while, as yet there are no reports of these in the Campanulids there have been two reports of *p*-hydroxyphenylacetyl-quinic acids therein.

Galloylshikimic acids have a distribution similar to but more restricted than the galloylquinic acids, and have not been reported in the Gunnerales, Fabales Rosales, Oxalidales or Celastrales.

Distribution of aliphatic acid derivatives of quinic acid

Chlorogenic acids which incorporate an aliphatic acid substituent have been reported only in 23 genera, of which 13 are in the Campanulids and two in the Lamiids. Two, *Linum* and *Quinchamalium*, must be treated as tentative and in need of confirmation.

Of the 13 genera in the Campanulids, twelve fall within the Asterales, six in the Asteroideae subfamily, five in the Carduoideae subfamily, and one in the Cichorioideae subfamily. The thirteenth falls within the Apiales, but there have been no reports of aliphatic acid-containing CGA in the well-profiled Aquifoliales or Dipsacales, suggesting that there may be a restricted distribution.

There are three reports from the Monocots, two from the Fabids (hydroxymethylglutaric acid plus a tentative succinic acid), one from the Malvids (succinic acid) plus single reports from the Ericales (malonic acid) and Santalales (methyl oxalic), this latter tentative and requiring confirmation.

Of the nine aliphatic acids found so far, seven are found in the Asterales, the exceptions being hydroxymethylglutaric acid which has been found as a quinic acid conjugate only in the Lamiids and as a shikimic acid conjugate only in the Fabids, plus formic acid found only as a shikimic acid conjugate in Monocots. Succinic acid is the most often encountered but malonic acid the most widely distributed (Solanales, Ericales and Asterales). Within the Asterales, *Arctium* is currently the most prolific and boasts quinic acid conjugates with five different aliphatic acids. *Saussurea* (Asteraceae, Carduoideae) has been reported to contain an acyl-quinic acid in which the esterifying malic acid residue is itself substituted with caffeic acid.*(523)*

Acetic acid conjugates of quinic acid have been reported three times, once in Monocots, once in Campanulids and once in the Lamiids (Solanales) where it is the only aliphatic acid encountered.

Only hydroxymethylglutaric acid has been reported in the Gentianales, apparently restricted to *Gardenia* and seemingly absent from other well-studied genera such as *Coffea*.

Note that the aliphatic acid residue usually accompanies one or more cinnamic acid residues, but hydroxymethylglutaroyl-quinic acids and hydroxymethylglutaroyl-shikimic acids have been reported in the Gentianales and Malpighiales, respectively, and might very well have been overlooked because they lack the distinctive UV absorption in the range 280 to 320 nm.

Distribution of dihydrocinnamoylquinic acids

Dihydrocinnamoylquinic acids have been reported only in 11 genera, predominantly in the Campanulids and Lamiids, with single reports from the Monocots (Alismatales) and Superasterids (Caryophyllales).

Dihydrocaffeoylquinic acids are the most widely distributed, having been reported in all four sections. All other reports are of dihydrocinnamic acids with either a sidechain hydroxyl or methoxyl, reported in Campanulids and Lamiids, but in several cases confirmation is required with clarification of where exactly the sidechain substituent is placed.

The dihydrocinnamoylquinic acids will have a strong UV absorption at 280 nm, but will not absorb at 320 nm unless present in a diacyl-quinic acid with one of the commoner cinnamic acids also present.

Distribution of CGA containing the rarer cinnamic acids

Chlorogenic acids containing caffeic, *p*-coumaric or ferulic acid are widespread, but chlorogenic acids containing other cinnamic acids have been reported far less frequently, in only 16 genera. These are predominantly in the Campanulids and Lamiids, but the Fabids has the only reports of 3,4,5-trihydroxycinnamoyl-quinic acid (Fabales and Rosales) and 4-methoxycinnamoyl-quinic acid (Rosales).

Sinapoylquinic acids are the most widely distributed of these less common cinnamic acids, being reported in nine genera across the Aquifoliales, Asterales, Caprifoliales, Gentianales and Solanales. The Gentianales is the order with the greatest range, boasting dimethoxycinnamoyl-, 5-hydroxyferuloyl-, sinapoyl, 3,5-dihydroxy-4-methoxycinnamoyl and trimethoxycinnamoyl-quinic acids, all of which have been found together in *Coffea canephora*. 2-Hydroxy-cinnamoyl-quinic acid (*o*-coumaroyl-quinic acid) and 3-hydroxy-4-methoxycinnamoyl-quinic acid (isoferuloyl-quinic acid) have been reported only in the Asterales, and this order has the only example of a cinnamic acid depside, a (*p*-coumaroyl-caffeoyl)-quinic acid.

Note that these less common cinnamic acids often occur in diacyl- or triacyl-quinic acids along with one or more of the more common cinnamic acids.

Distribution of 1-acyl diCQA

The diCQA are well known but in a surprisingly large number of studies receive no mention. While on some occasions they might simply have been overlooked, it seems probable that they are not universal in CGA containing species. The diCQA are, however, the most extensively reported subgroup within the diacyl-quinic acids, and at least in *Pluchea indica* the diCQA content exceeds the CQA content.*(166)*

There can be no doubt that 1-acyl-diCQA are less widely distributed than those without esterification at C1 of the quinic acid. There are no certain reports of the 1-acyl-diCQA above the Fabids, and only one of the four reports for the Fabids is actually for a 1-acyl diCQA. The other three are for a 1-acyl triCQA or a tetra-acyl-quinic acid.

There are few reports for diCQA in the Malvids, and none for 1-acyl diCQA. There are no reports for diCQA in Rosids or Superrosids, and only a few for Superasterids and Asterids and none for the 1-acyl diCQA.

The diCQA become much more prominent in the Campanulids, and especially the Asteraceae, where diCQA have been reported for 99 out of 107 genera studied, and of these just under half have 1-acyl-diCQA. 1-Acyl diCQA are less frequent in the Cichorioideae (9 out of 25 genera) compared with the Asteroideae (28 out of 60 genera) and the Carduoideae (8 out of 12 genera).

Within the Apiales there are many CGA-containing genera for which diCQA have not been reported. Of 19 genera in the Apiaceae reported to contain diCQA, eight also have 1-acyl-diCQA, a similar percentage to that recorded for the Asteraceae overall, but this falls to one out of six in the Araliaceae. There are comparatively few data for the remaining Campanulids but such reports as do exist sometimes include 1-acyl diCQA.

There are few reports of diCQA for the Lamiids, but it is interesting to observe that there is a report of 1-acyl-diCQA in some *Galium* spp. (Rubiaceae) plus one unequivocal report of 1-acyl diCQA (*Ipomoea*, Convolvulaceae) out of 27 genera where diCQA have been found.

The distribution of CGA in which (–)-quinic acid does not occur

There are comparatively few reports of chlorogenic acids where (–)-quinic acid is not present. As discussed in Parts 1 to 3 and above, several early claims for such chlorogenic acids are not convincing and are not included here.

A 1-caffeoyl-4-deoxyquinic acid has been reported in *Arachis*.*(149)* Dicaffeoyl-*epi*-quinic acids have been reported in *Psiadia*, *Scorzonera*, *Tessaria* and *Tussilago*.*(562, 695, 792, 1105)*

A total of at least two epimers of CQA have been reported in *Ilex*, *Carlina*, *Helianthus*, *Rudbeckia* and *Galium*,*(465, 496, 1102)* an epimer of FQA has been reported in *Galium,(1102)* and an epimer of CFQA has been reported in *Ilex*,*(465)* but the quinic acid moiety has not been fully characterised.

Acyl derivatives of 2-hydroxy-quinic acid have been reported in *Cedrus* and *Hubertia*,*(43, 566)* and tentatively in *Bauhinia* and *Aesculus*.*(152, 399)*

An epimer of CSA has been reported in *Rudbeckia* but the shikimic acid moiety was not fully characterised,*(496)* and 3-*epi*-(–)-shikimic acid has been isolated from *Sequoiadendron*.*(38)*

Since there is good evidence for the presence of CGA containing quinic acids other than (–)-quinic acid, there must be occasions when more than one free quinic acid also is present in plant extracts. A single free quinic acid,

presumably (–)-quinic acid, is quite often reported,*(237, 433, 614, 620, 621, 732-734)* but, interestingly there are a few reports of extracts apparently containing more than one free quinic acid. The use of accurate mass MS, or authentic standards, is essential because citric and isocitric acid are not easily resolved, *m/z* 191.01918 compared with 191.05556 for quinic acids.

Two putative free quinic acids detected by accurate mass LC–MS have been reported in in extracts of *Moringa oleifera* with *m/z* 191.0578 and 191.0556,*(366)* which both seem convincing. Two putative quinic acids have also been reported in *Rhus coriaria* L.,*(380)* (*m/z* 191.0566 and 191.0365) but the second of these falls midway between a quinic acid and an (iso)citric acid and requires confirmation. Similarly, two putative isomers have been reported in *Myrtus communis* with parent ions at *m/z* 191 0570 and 191.0207,*(341)* but the second of these is almost certainly either citric acid or isocitric acid.

Three putative isomers have been reported in the leaf of *Quercus pubescens*,*(1106)* and in *Ilex paraguariensis*, but accurate mass MS data were not provided in either report, and in the latter case these were reported as three different conformers of (–)-quinic acid,*(1107)* which seems implausible because chromatographic resolution of conformers is unlikely. This report is of interest, however, because two epimeric CQA and one epimeric CFQA have been reported in *Ilex*..*(465)*

4.7. References

1. Dawidowicz, A. L.; Typek, R. Thermal transformation of *trans*-5-*O*-caffeoylquinic acid (trans-5-CQA) in alcoholic solutions. *Food Chem.* **2015,** *167* (0), 52-60.

2. Lech, K.; Witkos, K.; Jarosz, M. HPLC-UV-ESI MS/MS identification of the color constituents of sawwort (*Serratula tinctoria* L.). *Anal. Bioanal. Chem.* **2014,** *406* (15), 3703-3708.

3. Luo, C.; Wang, X.; Gao, G.; Wang, L.; Li, Y.; Sun, C. Identification and quantification of free, conjugate and total phenolic compounds in leaves of 20 sweetpotato cultivars by HPLC-DAD and HPLC-ESI-MS/MS. *Food Chem.* **2013,** *141* (3), 2697-2706.

4. Clifford, M. N.; Kazi, T. The influence of coffee bean maturity on the content of chlorogenic acids, caffeine and trigonelline. *Food Chem.* **1987,** *26*, 59-69.

5. Bertrand, C.; Noirot, M.; Doulbeau, S.; De Kochko, A.; Hamon, S.; Campa, C. Chlorogenic acid content swap during fruit maturation in *Coffea pseudozanguebariae*: Qualitative comparison with leaves. *Plant Science* **2003,** *165* (6), 1355-1361.

6. Lattanzio, V.; Morone, I. Variations of the orthodiphenol content of *Cynara scolymus* L. during the plant growing season. *Experientia* **1979,** *35*, 993-994.

7. Pandino, G.; Lombardo, S.; Lo Monaco, A.; Mauromicale, G. Choice of time of harvest influences the polyphenol profile of globe artichoke. *Journal of Functional Foods* **2013,** *5* (4), 1822-1828.

8. Clifford, M. N.; Zheng, W.; Kuhnert, N. Profiling the chlorogenic acids of Aster by HPLC-MS^n. *Phytochemical Analysis* **2006,** *17*, 384-393.

9. Byng, J. W.; Chase, M. W.; Christenhusz, M. J. M.; Fay, M. F.; Judd, W. S.; Mabberley, D. J.; Sennikov, A. N.; Soltis, D. E.; Soltis, P. S.; Stevens, P. F.; Briggs, B.; Brockington, S.; Chautems, A.; Clark, J. C.; Conran, J.; Haston, E.; Moller, M.; Moore, M.; Olmstead, R.; Perret, M.; Skog, L.; Smith, J.; Tank, D.; Vorontsova, M.; Weber, A. An update of the Angiosperm Phylogeny Group classification for the orders and families of flowering plants: APG IV. *Botanical Journal of the Linnean Society* **2016,** *181* (1), 1-20.

10. Nam, J. H.; Cho, I. S.; Kim, S. J.; Nam, C. W.; Seo, J. T.; Yoo, D. L.; Kim, W. B.; Ryu, S. Y.; Lee, E. H.; Kim, M. Y.; Yoo, Y. M.; Park, H. J.; Jung, H. J. Phytochemical constituents of *Climacium dendroides*. *Journal of the Korean Society for Applied Biological Chemistry* **2008,** *51* (2), 136-141.

11. Erxleben, A.; Gessler, A.; Vervliet-Scheebaum, M.; Reski, R. Metabolite profiling of the moss *Physcomitrella patens* reveals evolutionary conservation of osmoprotective substances. *Plant Cell Rep.* **2012,** *31* (2), 427-436.

12. Jockovic, N.; Andrade, P. B.; Valentao, P.; Sabovljevic, M. HPLC-DAD of phenolics in bryophytes *Lunularia cruciata*, *Brachytheciastrum velutinum* and *Kindbergia praelonga*. *Journal of the Serbian Chemical Society* **2008,** *73* (12), 1161-1167.

13. Montenegro, G.; Portaluppi, M. C.; Salas, F. A.; Diaz, M. F. Biological properties of the Chilean native moss *Sphagnum magellanicum*. *Biol. Res* **2009,** *42* (2), 233-237.

14. Chase, M. W.; Reveal, J. L. A phylogenetic classification of the land plants to accompany APG III. *Botanical Journal of the Linnean Society* **2009,** *161* (2), 122-127.

15. Adam, K. P. Phenolic constituents of the fern *Phegopteris connectilis*. *Phytochem.* **1999,** *52* (5), 929-934.

16. Wada, H.; Tanaka, N.; Murakami, T.; Uchida, T.; Kozawa, K.; Saiki, Y.; Chen, C. M. Chemical and chemotaxonomical studies of *Filices* .76. An unusual flavanone derivative from *Wagneriopteris japonica* Loeve et Loeve. *Yakugaku Zasshi-Journal of the Pharmaceutical Society of Japan* **1988,** *108* (8), 740-744.

17. Veit, M.; Weidner, C.; Strack, D.; Wray, V.; Witte, L.; Czygan, F. C. The distribution of caffeic acid conjugates in the Equisetaceae and some ferns. *Phytochem.* **1992,** *31* (10), 3483-3485.

18. Saito, T.; Yamane, H.; Muropushi, N.; Takahashi, N.; Phinney, B. O. 4-*O*-caffeoylshikimic and 4-*O*-(*p*-coumaroyl)shikimic acids from the dwarf tree Fern, *Dicksonia antarctica*. *Biosci. Biotechnol. Biochem.* **1997,** *61*, 1397-1399.

19. Hohlfeld, M.; Veit, M.; Strack, D. Hydroxycinnamoyltransferases involved in the accumulation of caffeic acid esters in gametophytes and sporophytes of *Equisetum arvense*. *Plant Physiol.* **1996,** *111* (4), 1153-1159.

20. Petersen, M.; Abdullah, Y.; Benner, J.; Eberle, D.; Gehlen, K.; Hücherig, S.; Janiak, V.; Kim, K. H.; Sander, M.; Weitzel, C.; Wolters, S. Evolution of rosmarinic acid biosynthesis. *Phytochem.* **2009,** *70* (15ΓÇô16), 1663-1679.

21. Adam, K. P. Caffeic acid-derivatives in fronds of the lady fern (*Athyrium filix-femina*). *Phytochem.* **1995,** *40*, 1577-1578.

22. Fukuoka, M. Chemical and toxicological studies on bracken fern, *Pteridium aquilinum* var. *latiusculum*. VI. Isolation of 5-O-caffeoylshikimic acid as an antithiamine factor. *Chem. Pharm. Bull. (Tokyo)* **1982,** *30* (9), 3219-3224.

23. Chen, Y.-H.; Chang, F.-R.; Lin, Y.-J.; Wang, L.; Chen, J.-F. Identification of phenolic antioxidants from Sword Brake fern (*Pteris ensiformis* Burm.). *Food Chem.* **2008,** *105*, 48-56.

24. Harinantenaina, L.; Matsunami, K.; Otsuka, H. Chemical and biologically active constituents of *Pteris multifida*. *J Nat. Med* **2008,** *62* (4), 452-455.

25. Zeller, W. E. Synthesis of 1-O-methylchlorogenic acid: reassignment of structure for MCGA3 isolated from bamboo (*Phyllostachys edulis*) leaves. *J. Agric. Food Chem.* **2014,** *62* (8), 1860-1865.

26. Kweon, M. H.; Hwang, H. J.; Sung, H. C. Identification and antioxidant activity of novel chlorogenic acid derivatives from bamboo (*Phyllostachys edulis*). *J. Agric. Food Chem.* **2001,** *49* (10), 4646-4655.

27. Yonathan, M.; Asres, K.; Assefa, A.; Bucar, F. *In vivo* anti-inflammatory and anti-nociceptive activities of *Cheilanthes farinosa*. *J. Ethnopharmacol.* **2006,** *108* (3), 462-470.

28. Ma, C.; Zhou, Y.; Liu, A. R. [Determination of chlorogenic acid and eriodictyol-7-O-beta-D-glucuronide in *Pyrrosia* by RP-HPLC]. *Yao Xue. Xue. Bao.* **2003,** *38* (4), 286-289.

29. Cheng, D.; Zhang, Y.; Xin, X.; Gao, D. Comparative pharmacognosy of *Pyrrosia petiolosa* and *Pyrrosia davidii*. *Revista Brasileira de Farmacognosia* **2014,** *24* (4), 368-380.

30. Chen, Y. J.; Xie, G. Y.; Xu, G. K.; Dai, Y. Q.; Shi, L.; Qin, M. J. Chemical Constituents of *Pyrrosia calvata*. *Natural Product Communications* **2015,** *10* (7), 1191-1193.

31. Garcia, F.; Pivel, J. P.; Guerrero, A.; Brieva, A.; Martinez-Alcazar, M. P.; Caamano-Somoza, M.; Gonzalez, S. Phenolic components and antioxidant activity of Fernblock, an aqueous extract of the aerial parts of the fern *Polypodium leucotomos*. *Methods Find. Exp. Clin. Pharmacol.* **2006,** *28* (3), 157-160.

32. Virtbauer, J.; Krenn, L.; Kahlig, H.; Hufner, A.; Donath, O.; Marian, B. Chemical and pharmacological investigations of *Metaxya rostrata*. *Z. Naturforsch. C.* **2008,** *63* (7-8), 469-475.

33. Ivanova, A.; Marinova, E.; Toneva, A.; Kostova, I.; Yanishlieva, N. Antioxidant properties of *Smilax excelsa*. *Rivista Italiana Delle Sostanze Grasse* **2006,** *83* (3), 124-128.

34. Lin, L. C.; Kuo, Y. C.; Chou, C. J. Cytotoxic biflavonoids from *Selaginella delicatula*. *J. Nat Prod.* **2000,** *63* (5), 627-630.

35. Marques, V.; Farah, A. Chlorogenic acids and related compounds in medicinal plants and infusions. *Food Chem.* **2009,** *113* (4), 1370-1376.

36. Szwajgier, D.; Wydrych, M.; Wieclaw, E.; Targonski, Z. Anticholinesterase and antioxidant activities of commercial preparations from *Ginkgo biloba* leaves. *Acta Scientiarum Polonorum-Hortorum Cultus* **2013,** *12* (5), 111-125.

37. Lesjak, M. M.; Beara, I. N.; Orcic, D. Z.; Ristic, J. D.; Anackov, G. T.; Bozn, B. N.; Mimica-Dukic, N. M. Chemical characterisation and biological effects of *Juniperus foetidissima* Willd. 1806. *LWT - Food Science and Technology* **2013,** *53* (2), 530-539.

38. Geiger, H.; El-Dessouki, S.; Seeger, T. (3S,4S,5R)-3,4,5-trihydroxy-1-cyclohexene-carboxylic acid from *Sequoiadendron giganteum*. *Phytochem.* **1995,** *40* (6), 1705-1707.

39. Yan, J. X.; Lu, Y. F.; Yan, S. C. The effects of irradiance on the production of phenolic compounds and condensed tannins in *Larix gmelinii* needles. *Biologia Plantarum* **2014,** *58*, 159-163.

40. Zou, J. P.; Cates, R. G. Foliage constituents of Douglas Fir (*Pseudotsuga menziesii* (Mirb) Franco (Pinaceae)) - their seasonal variation and potential role in Douglas Fir resistance and silviculture management. *J. Chem. Ecol.* **1995,** *21* (4), 387-402.

41. Slimestad, R.; Hostettmann, K. Characterisation of phenolic constituents from juvenile and mature needles of Norway spruce by means of high performance liquid chromatography mass spectrometry. *Phytochemical Analysis* **1996,** *7* (1), 42-48.

42. Azevedo, H.; Dias, A.; Tavares, R. M. Analysis on the role of phenylpropanoid metabolism in the *Pinus pinaster-Botrytis cinerea* interaction. *Journal of Phytopathology* **2010,** *158* (9), 641-646.

43. Wu, Y. P.; Liang, X.; Liu, X. Y.; Zhong, K.; Gao, B.; Huang, Y. N.; Gao, H. *Cedrus deodara* pine needle as a potential source of natural antioxidants: Bioactive constituents and antioxidant activities. *Journal of Functional Foods* **2015,** *14*, 605-612.

44. Heilemann, J.; Wray, V.; Strack, D. Synthesis of 2-O-(4-coumaroyl)-myo-inositol by a protein preparation from needles of *Taxus baccata*. *Phytochem.* **1990,** *29* (11), 3487-3489.

45. Wu, d.; Li, Y. N.; Wu, L. J.; Gao, H. Y. [Isolation and identification of chemical constituents from *Taxus cuspidata* Sibe et Zucc]. *Yao xue xue bao = Acta pharmaceutica Sinica* **2010,** *45* (11), 1398-1401.

46. Mocan, A.; Schafberg, M.; Crisan, G.; Rohn, S. Determination of lignans and phenolic components of *Schisandra chinensis* (Turcz.) Baill. using HPLC-ESI-ToF-MS and HPLC-online TEAC: Contribution of individual components to overall antioxidant activity and comparison with traditional antioxidant assays. *Journal of Functional Foods* **2016,** *24*, 579-594.

47. Jimenez, V. M.; Gruschwitz, M.; Schweiggert, R. M.; Carle, R.; Esquivel, P. Identification of phenolic compounds in soursop (*Annona muricata*) pulp by high-performance liquid chromatography with diode array and electrospray ionization mass spectrometric detection. *Food Research International* **2014,** (0), DOI: 10.1016/j.foodres.2014.05.051.

48. Brannan, R. G.; Peters, T.; Talcott, S. T. Phytochemical analysis of ten varieties of Pawpaw (*Asimina triloba* [L.] Dunal) fruit pulp. *Food Chem.* **2015,** *168*, 656-661.

49. Haribal, M.; Feeny, P.; Lester, C. C. Caffeoylcyclohexane-1-carboxylic acid derivative from *Asimina triloba*. *Phytochem.* **1998,** *49*, 103-108.

50. Haribal, M.; Feeny, P. Combined roles of contact stimulant and deterrents in assessment of host-plant quality by ovipositing zebra swallowtail butterflies. *J. Chem. Ecol.* **2003,** *29* (3), 653-670.

51. Haribal, M.; Feeny, P. Oviposition stimulant for the zebra swallowtail butterfly, *Eurytides marcellus*, from the foliage of pawpaw, *Asimina triloba*. *Chemoecology* **1998,** *8* (3), 99-110.

52. Simirgiotis, M. J.; Ramirez, J. E.; Schmeda Hirschmann, G.; Kennelly, E. J. Bioactive coumarins and HPLC-PDA-ESI-ToF-MS metabolic profiling of edible queule fruits (*Gomortega keule*), an endangered endemic Chilean species. *Food Research International* **2013,** *54* (1), 532-543.

53. Vallverdu-Queralt, A.; Regueiro, J.; Rinaldi de Alvarenga, J. F.; Torrado, X.; Lamuela-Raventos, R. M. Home cooking and phenolics: effect of thermal treatment and addition of extra virgin olive oil on the phenolic profile of tomato sauces. *J. Agric. Food Chem.* **2014,** *62* (14), 3314-3320.

54. Mao, Y. W.; Tseng, H. W.; Liang, W. L.; Chen, I. S.; Chen, S. T.; Lee, M. H. Anti-inflammatory and free radial scavenging activities of the constituents isolated from *Machilus zuihoensis*. *Molecules* **2011,** *16* (11), 9451-9466.

55. Carter, M.; Feeny, P.; Haribal, M. An oviposition stimulant for Spicebush Swallowtail Butterfly, *Papilio troilus*, from leaves of *Sassafras albidum*. *J. Chem. Ecol.* **1999,** *25* (6), 1233-1245.

56. Ranilla, L. G.; Kwon, Y. I.; Apostolidis, E.; Shetty, K. Phenolic compounds, antioxidant activity and in vitro inhibitory potential against key enzymes relevant for hyperglycemia and hypertension of commonly used medicinal plants, herbs and spices in Latin America. *Bioresource Technology* **2010,** *101* (12), 4676-4689.

57. Kamto, E. L. D.; Ngono, D. S. B.; Mbing, J. N.; Atchade, A. d. T.; Pegnyemb, D. E.; van der Westhuizen, J. H. An aromatic amide *C*-glycoside and a cyclitol derivative from stem barks of *Piper guineense* Schum and Thonn (Piperaceae). *Phytochemistry Letters* **2014,** *10*, LXXVI-lxxxi.

58. Wang, Z.; Clifford, M. N. Comparison of the profiles of chlorogenic acids and their derivatives from three Chinese traditional herbs by LC–MS^n. *Yao Xue. Xue. Bao.* **2008,** *43* (2), 185-190.

59. Wu, H.; Hu, X.; Zhang, X.; Chen, S.; Yang, J.; Xu, X. Benzyl 2-beta-glucopyranosyloxybenzoate, a new phenolic acid glycoside from *Sarcandra glabra*. *Molecules* **2012,** *17* (5), 5212-5218.

60. Zhou, H.; Liang, J.; Lv, D.; Hu, Y.; Zhu, Y.; Si, J.; Wu, S. Characterization of phenolics of *Sarcandra glabra* by non-targeted high-performance liquid chromatography fingerprinting and following targeted electrospray ionisation tandem mass spectrometry/time-of-flight mass spectrometry analyses. *Food Chem.* **2013,** *138* (4), 2390-2398.

61. Garzon, G. A.; Narvaez-Cuenca, C. E.; Vincken, J. P.; Gruppen, H. Polyphenolic composition and antioxidant activity of Açai (*Euterpe oleracea* Mart.) from Colombia. *Food Chem.* **2016,** *217*, 364-372.

62. Brunschwig, C.; Leba, L.-J.; Saout, M.; Martial, K.; Bereau, D.; Robinson, J. C. Chemical composition and antioxidant activity of *Euterpe oleracea* roots and leaflets. *International Journal of Molecular Sciences* **2017,** *18* (1), 61- doi:10.3390/ijms18010061.

63. Leba, L. J.; Bruschwig, C.; Saout, M.; Martial, K.; Bereau, D.; Robinson, J.-C. *Oenocarpus bacaba* and *Oenocarpus bataua* leaflets and roots: a new source of antioxidant compounds. *Int,J. Mol. Sci* **2016,** *17*, doi:10.3390/ijms17071014.

64. Maier, V. P.; Metzler, D. M.; Huber, A. F. 3-*O*-caffeoylshikimic acid (dactylifric acid) and its isomers, a new class of enzymic browning substrates. *Biochem. Biophys. Res. Commun.* **1964,** *14*, 124-128.

65. Harborne, J. B.; Williams, C. A.; Greenham, J. Distribution of charged flavones and caffeoylshikimic acid in Palmae. *Phytochem.* **1974,** *13*, 1557-1559.

66. Dihazi, A.; Jaiti, F.; Wafataktak; Kilani-Feki, O.; Jaoua, S.; Driouich, A.; Baaziz, M.; Daayf, F.; Serghini, M. A. Use of two bacteria for biological control of bayoud disease caused by *Fusarium oxysporum* in date palm (*Phoenix dactylifera* L) seedlings. *Plant Physiol. Biochem.* **2012,** *55*, 7-15.

67. Ziouti, A.; ElModafar, C.; Fleuriet, A.; El Boustani, S.; Macheix, J. J. Phenolic compounds in date palm cultivars sensitive and resistant to *Fusarium oxysporum*. *Biologia Plantarum* **1996,** *38* (3), 451-457.

68. Hammouda, H.; Cherif, J. K.; Trabelsi-Ayadi, M.; Baron, A.; Guyot, S. Detailed polyphenol and tannin composition and its variability in Tunisian dates (*Phoenix dactylifera* L.) at different maturity stages. *J. Agric. Food Chem.* **2013,** *61* (13), 3252-3263.

69. Mansouri, A.; Embarek, G.; Kokkalou, E.; Kefalas, P. Phenolic profile and antioxidant activity of the Algerian ripe date palm fruit (*Phoenix dactylifera*). *Food Chem.* **2005,** *89* (3), 411-420.

70. Dhaouadi, K.; Raboudi, F.; Estevan, C.; Barrajon, E.; Vilanova, E.; Hamdaoui, M.; Fattouch, S. Cell viability effects and antioxidant and antimicrobial activities of Tunisian date syrup (Rub El Tamer) polyphenolic extracts. *J. Agric. Food Chem.* **2011,** *59* (1), 402-406.

71. Farag, M. A.; Mohsen, M.; Heinke, R.; Wessjohann, L. A. Metabolomic fingerprints of 21 date palm fruit varieties from Egypt using UPLC/PDA/ESI-qTOF-MS and GC-MS analyzed by chemometrics. *Food Research International* **2014,** *64* (0), 218-226.

72. Farag, M. A.; Handoussa, H.; Fekry, M. I.; Wessjohann, L. A. Metabolite profiling in 18 Saudi date palm fruit cultivars and their antioxidant potential via UPLC-qTOF-MS and multivariate data analyses. *Food & Funct.* **2016,** *7* (2), 1077-1086.

73. Bankar, G. R.; Nayak, P. G.; Bansal, P.; Paul, P.; Pai, K. S. R.; Singla, R. K.; Bhat, V. G. Vasorelaxant and antihypertensive effect of *Cocos nucifera* Linn. endocarp on isolated rat thoracic aorta and DOCA salt-induced hypertensive rats. *J. Ethnopharmacol.* **2011,** *134* (1), 50-54.

74. Lima, E. B. C.; de Sousa, C. N. S.; Vasconcelos, G. S.; Meneses, L. N.; Pereira, Y. F. E. S.; Ximenes, N. C.; Santos, M. A.; Matos, N. C. B.; Brito, R.; Miron, D.; Leal, L. K. A. M.; Macedo, D.; Vasconcelos, S. M. M. Antidepressant, antioxidant and neurotrophic properties of the standardized extract of Cocos nucifera husk fiber in mice. *Journal of Natural Medicines* **2016,** *70* (3), 510-521.

75. Jiang, Y. M.; Liu, S. X.; Zhang, D. L.; Chang, F.; Li, Y. B. Studies on antibrowning of coconut (Cocos nucifera L) fruit. *Tropical Agriculture* **1995,** *72* (3), 254-256.

76. Chakraborty, M.; Mitra, A. The antioxidant and antimicrobial properties of the methanolic extract from *Cocos nucifera* mesocarp. *Food Chem.* **2008,** *107* (3), 994-999.

77. Zeng, X.; Wang, Y.; Qiu, Q.; Jiang, C.; Jing, Y.; Qiu, G.; He, X. Bioactive phenolics from the fruits of *Livistona chinensis*. *Fitoterapia* **2012,** *83* (1), 104-109.

78. Shui, G.; Leong, L. P. Screening and identification of antioxidants in biological samples using high-performance liquid chromatography-mass spectrometry and its application on *Salacca edulis* Reinw. *J. Agric. Food Chem.* **2005,** *53* (4), 880-886.

79. Steingass, C. B.; Glock, M. P.; Schweiggert, R. M.; Carle, R. Studies into the phenolic patterns of different tissues of pineapple (*Ananas comosus* [L.] Merr.) infructescence by HPLC-DAD-ESI-MS n and GC-MS analysis. *Anal Bioanal Chem* **2015,** 1-17.

80. Ma, C.; Xiao, S. Y.; Li, Z. G.; Wang, W.; Du, L. J. Characterization of active phenolic components in the ethanolic extract of *Ananas comosus* L. leaves using high-performance liquid chromatography with diode array detection and tandem mass spectrometry. *J. Chromatogr. A* **2007,** *1165* (1-2), 39-44.

81. Strack, D.; Leicht, P.; Bokern, M.; Wray, V.; Grotjahn, L. Hydroxycinnamic acid esters of isocitric acid: Accumulation and enzymatic synthesis in *Amaranthus cruentus*. *Phytochem.* **1987,** *26* (11), 2919-2922.

82. Deshpande, S. Mass spectrometry-based investigation of chlorogenic acid reactivity and profile in model systems and coffee processing. Ph.D. Jacobs University Bremen, Germany, 2014.

83. Kim, D. K.; ë „ì´^; ë°°ì¢…ì§„; ë°•ì •ì˜™; ì ´ìž¬í˜ ; ê¹€ë°˜ì§€; ì ´ì†Œì-°; ì ´ì €ë³„; ì•^ë‹¬ëž˜; í˜•ëª…ëª… Phenolic Constituents from *Juncus diastrophanthus*. *Korean Journal of Pharmacognosy* **2013,** *44* (4), 368-371.

84. Wenzl, P.; Chaves, A. L.; Mayer, J. E.; Rao, I. M.; Nair, M. G. Roots of nutrient-deprived *Brachiaria* species accumulate 1,3-di-*O-trans*-feruloylquinic acid. *Phytochem.* **2000,** *55*, 389-395.

85. Perez, A. J.; Hussain, S. M.; Pecio, +.; Kowalczyk, M.; Rodrigues, V.; Stochmal, A. UHPLC-HR-QTOF-MS based metabolomics reveals key differences between *Brachiaria decumbens* and *B. brizantha*, two similar pastures with different toxicity. *J. Agric. Food Chem.* **2016,** *64*, 4686-4694.

86. Roriz, C. L.; Barros, L.; Carvalho, A. M.; Santos-Buelga, C.; Ferreira, I. C. F. R. *Pterospartum tridentatum*, *Gomphrena globosa* and *Cymbopogon citratus*: A phytochemical study focused on antioxidant compounds. *Food Research International* **2014,** *62* (0), 684-693.

87. Parveen, I.; Winters, A.; Threadgill, M. D.; Hauck, B.; Morris, P. Extraction, structural characterisation and evaluation of hydroxycinnamate esters of orchard grass (*Dactylis glomerata*) as substrates for polyphenol oxidase. *Phytochem.* **2008,** *69* (16), 2799-2806.

88. Kim, C. S.; Alamgir, K. M.; Matsumoto, S.; Tebayashi, S.; Koh, H. S. Antifeedants of Indian barnyard millet, *Echinochloa frumentacea* link, against brown planthopper, Nilaparvata lugens (Stal). *Z. Naturforsch. C.* **2008,** *63* (9-10), 755-760.

89. Keski-Saari, S.; Ossipov, V.; Julkunen-Tiitto, R.; Jia, J.; Danell, K.; Veteli, T.; Guiquan, Z.; Yaowu, X.; Niemela, P. Phenolics from the culms of five bamboo species in the Tangjiahe and Wolong Giant Panda Reserves, Sichuan, China. *Biochem. Syst. Ecol.* **2008,** *36* (10), 758-765.

90. Piasecka, A.; Sawikowska, A.; Krajewski, P.; Kachlicki, P. Combined mass spectrometric and chromatographic methods for in-depth analysis of phenolic secondary metabolites in barley leaves. *Journal of Mass Spectrometry* **2015,** *50* (3), 513-532.

91. Ni, Q.; Wang, Z.; Xu, G.; Gao, Q.; Yang, D.; Morimatsu, F.; Zhang, Y. Altitudinal variation of antioxidant components and capability in *Indocalamus latifolius* (Keng) McClure leaf. *J. Nutr. Sci. Vitaminol. (Tokyo)* **2013,** *59* (4), 336-342.

92. Qawasmeh, A.; Obied, H. K.; Raman, A.; Wheatley, W. Influence of fungal endophyte infection on phenolic content and antioxidant activity in grasses: Interaction between *Lolium perenne* and different strains of *Neotyphodium lolii*. *J. Agric. Food Chem.* **2012,** *60* (13), 3381-3388.

93. Tang, Q.; Shao, M.; Wang, Y.; Zhao, H.; Fan, C.; Huang, X.; Li, Y.; Ye, W. Simultaneous determination of 10 bioactive components of *Lophatherum gracile* Brongn by HPLC-DAD. *Journal of Chromatographic Science* **2015,** *53* (6), 963-967.

94. Parveen, I.; Threadgill, M. D.; Hauck, B.; Donnison, I.; Winters, A. Isolation, identification and quantitation of hydroxycinnamic acid conjugates, potential platform chemicals, in the leaves and stems of *Miscanthus x giganteus* using LC–ESI–MS^n. *Phytochem.* **2011,** *72* (18), 2376-2384.

95. Parveen, I.; Wilson, T.; Threadgill, M. D.; Luyten, J.; Roberts, R. E.; Robson, P. R. H.; Donnison, I. S.; Hauck, B.; Winters, A. L. Screening for potential co-products in a *Miscanthus sinensis* mapping family by liquid chromatography with mass spectrometry detection. *Phytochem.* **2014,** (0).

96. Tian, S.; Nakamura, K.; Cui, T.; Kayahara, H. High-performance liquid chromatographic determination of phenolic compounds in rice. *J Chromatogr. A* **2005,** *1063* (1-2), 121-128.

97. Pinto, L. d. S.; Duebbern de Souza, F. H.; Nascimento, I. R.; Xavier Lopes, L. M. Phenylpropanoids from *Paspalum atratum* (Poaceae). *Biochem. Syst. Ecol.* **2015,** *63*, 68-71.

98. Smarrito, C. M.; Munari, C.; Robert, F.; Barron, D. A novel efficient and versatile route to the synthesis of 5-*O*-feruloylquinic acids. *Org. Biomol. Chem.* **2008,** *6* (6), 986-987.

99. Abdullah, Y.; Schneider, B.; Petersen, M. Occurrence of rosmarinic acid, chlorogenic acid and rutin in *Marantaceae* species. *Phytochemistry Letters* **2008,** *1* (4), 199-203.

100. Elguindy, N. M.; Yacout, G. A.; El Azab, E. F.; Maghraby, H. K. Chemoprotective effect of *Elettaria cardamomum* against chemically induced hepatocellular carcinoma in rats by Inhibiting NF-kappa B, oxidative stress, and activity of ornithine decarboxylase. *South African Journal of Botany* **2016,** *105*, 251-258.

101. Chan, E. W. C.; Lim, Y. Y.; Ling, S. K.; Tan, S. P.; Lim, K. K.; Khoo, M. G. H. Caffeoylquinic acids from leaves of *Etlingera* species (Zingiberaceae). *LWT - Food Science and Technology* **2009,** *42* (5), 1026-1030.

102. Chan, E. W.; Lim, Y. Y.; Tan, S. P. Standardised herbal extract of chlorogenic acid from leaves of *Etlingera elatior* (Zingiberaceae). *Pharmacognosy Res.* **2011,** *3* (3), 178-184.

103. Knittel, D. N.; Stintzing, F. C.; Kammerer, D. R. Simultaneous determination of bufadienolides and phenolic compounds in sea squill (*Drimia maritima* (L.) Stearn) by HPLC-DAD-MS as a means to differentiate individual plant parts and developmental stages. *Anal. Bioanal. Chem.* **2014**.

104. Di Petrillo, A.; Gonz+ílez-Param+ís, A. M.; Era, B.; Medda, R.; Pintus, F.; Santos-Buelga, C.; Fais, A. Tyrosinase inhibition and antioxidant properties of *Asphodelus microcarpus* extracts. *Bmc Complementary and Alternative Medicine* **2016,** *16* (1), 453.

105. Cai, W.; Zhang, Q. S.; Liu, P. P.; Zhang, H. G. Isolation and characterization of chemical constituents from *Dendrobium nobil* Lindl. *Asian Journal of Chemistry* **2014,** *26* (16), 5315-5316.

106. Clifford, M. N.; Wu, W.; Kuhnert, N. The chlorogenic acids of *Hemerocallis*. *Food Chem.* **2006,** *95*, 574-578.

107. Lin, Y. L.; Lu, C. K.; Huang, Y. J.; Chen, H. J. Antioxidative caffeoylquinic acids and flavonoids from *Hemerocallis fulva* flowers. *J Agric. Food Chem.* **2011,** *59* (16), 8789-8795.

108. Keyhanian, S.; Stahl-Biskup, E. Phenolic constituents in dried flowers of aloe vera (*Aloe barbadensis*) and their in vitro antioxidative capacity. *Planta Med.* **2007,** *73* (6), 599-602.

109. El Sayed, A. M.; Ezzat, S. M.; El Naggar, M. M.; El Hawary, S. S. In vivo diabetic wound healing effect and HPLC-DAD-ESI-MS/MS profiling of the methanol extracts of eight Aloe species. *Revista Brasileira de Farmacognosia-Brazilian Journal of Pharmacognosy* **2016,** *26* (3), 352-362.

110. Lin, L. Z.; Harnly, J. M. Identification of hydroxycinnamoylquinic acids of arnica flowers and burdock roots using a standardized LC-DAD-ESI/MS profiling method. *J. Agric. Food Chem.* **2008,** *56* (21), 10105-10114.

111. Jimenez-Sanchez, C.; Lozano-Sanchez, J.; Rodrigez-Perez, C.; Segura-Carretero, A.; Fernandez-Gutierrez, A. Comprehensive, untargeted, and qualitative RP-HPLC-ESI-QTOF/MS2 metabolite profiling of green asparagus (*Asparagus officinalis*). *Journal of Food Composition and Analysis* **2015,** *46*, 78-87.

112. Ivanova, A.; Serly, J.; Dinchev, D.; Ocsovszki, I.; Kostova, I.; Molnar, J. Screening of some saponins and phenolic components of *Tribulus terrestris* and *Smilax excelsa* as MDR modulators. *In Vivo* **2009,** *23* (4), 545-550.

113. Khaligh, P.; Salehi, P.; Farimani, M. M.; Ali-Asgari, S.; Esmaeili, M. A.; Ebrahimi, S. N. Bioactive compounds from *Smilax excelsa* L. *Journal of the Iranian Chemical Society* **2016,** *13* (6), 1055-1059.

114. Zhang, Q. F.; Guo, Y. X.; Zheng, G.; Wang, W. J. Chemical constituents comparison between Rhizoma Smilacis Glabrae and Rhizoma Smilacis Chinae by HPLC-DAD-MS/MS. *Nat. Prod. Res.* **2013,** *27* (3), 277-281.

115. Zheng, Z. G.; Duan, T. T.; He, B.; Tang, D.; Jia, X. B.; Wang, R. S.; Zhu, J. X.; Xu, Y. H.; Zhu, Q.; Feng, L. Macrophage biospecific extraction and HPLC-ESI-MS^{nn} analysis for screening immunological active components in Smilacis Glabrae Rhizoma. *J. Pharm. Biomed. Anal.* **2013,** *77*, 44-48.

116. Zhang, Q. F.; Cheung, H. Y.; Zeng, L. B. Development of HPLC fingerprint for species differentiation and quality assessment of Rhizoma Smilacis Glabrae. *Journal of Natural Medicines* **2013,** *67* (1), 207-211.

117. Zhang, Q. F.; Guo, Y. X.; Shangguan, X.; Zheng, G.; Wang, W. J. Identification and quantification of polyphenols in Rhizoma Smilacis Chinae by Hplc/Dad/Esi-Ms/Ms. *Journal of Liquid Chromatography & Related Technologies* **2013,** *36* (16), 2251-2260.

118. Gu, W. Y.; Li, N.; Leung, E. L. H.; Zhou, H.; Yao, X. J.; Liu, L.; Wu, J. L. Rapid identification of new minor chemical constituents from Smilacis Glabrae Rhizoma by combined use of UHPLC-Q-TOF-MS, preparative HPLC and UHPLC-SPE-NMR-MS techniques. *Phytochemical Analysis* **2015,** *26* (6), 428-435.

119. Jamaludin, F. L.; Mohamad, J. Antihypertension activity of water extract of *Tacca integrifolia* (Aktiviti Antihipertensi Ekstrak Air *Tacca integrifolia*). *Sains Malaysiana* **2016,** *45* (3), 425-433.

120. Zhang, X.; Wu, C.; Wu, H.; Sheng, L.; Su, Y.; Zhang, X.; Luan, H.; Sun, G.; Sun, X.; Tian, Y.; Ji, Y.; Guo, P.; Xu, X. Anti-hyperlipidemic effects and potential mechanisms of action of the caffeoylquinic acid-rich *Pandanus tectorius* fruit extract in hamsters fed a high fat-diet. *PLoS ONE* **2013,** *8* (4), e61922.

121. Wu, C.; Zhang, X.; Zhang, X.; Luan, H.; Sun, G.; Sun, X.; Wang, X.; Guo, P.; Xu, X. The caffeoylquinic acid-rich *Pandanus tectorius* fruit extract increases insulin sensitivity and regulates hepatic glucose and lipid metabolism in diabetic db/db mice. *The Journal of Nutritional Biochemistry* **2014,** *25* (4), 412-419.

122. Clifford, M. N.; Knight, S.; Kuhnert, N. Discriminating between the six isomers of dicaffeoylquinic acid by LC–MS^n. *J. Agric. Food Chem.* **2005,** *53*, 3821-3832.

123. Liu, H.; Zhang, X.; Wu, C.; Wu, H.; Guo, P.; Xu, X. Anti-hyperlipidemic caffeoylquinic acids from the fruits of *Pandanus tectorius* Soland. *J. Appl. Pharm. Sci.* **2013,** *3*, 16-19.

124. Ge, F.; Ke, C.; Tang, W.; Yang, X.; Tang, C.; Qin, G.; Xu, R.; Li, T.; Chen, X.; Zuo, J.; Ye, Y. Isolation of chlorogenic acids and their derivatives from *Stemona japonica* by preparative HPLC and evaluation of their anti-AIV (H5N1) activity *in vitro*. *Phytochemical Analysis* **2007,** *18* (3), 213-218.

125. Fan, L.-L.; Xu, F.; Hu, J.-P.; Yang, D.-H.; Chen, H.-B.; Komatsu, K.; Zhu, S.; Shang, M.-Y.; Wang, X.; Cai, S.-Q. Binary chromatographic fingerprint analysis of Stemonae Radix from three *Stemona* plants and its applications. *J. Natural Med.* **2015,** *69*, 402-410.

126. Pinto, M. E. F.; da Silva, M. S.; Schindler, E.; Barbosa, J. M.; El-Bacha, R. D.; Castello-Branco, M. V. S.; Agra, M. D.; Tavares, J. F. 3 ',8 ''-Biisokaempferide, a cytotoxic biflavonoid and other chemical constituents of *Nanuza plicata* (Velloziaceae). *Journal of the Brazilian Chemical Society* **2010,** *21* (10), 1819-1824.

127. Suguiyama, V. F.; Silva, E. A.; Meirelles, S. T.; Centeno, D. C.; Braga, M. R. Leaf metabolite profile of the Brazilian resurrection plant *Barbacenia purpurea* Hook. (Velloziaceae) shows two time-dependent responses during desiccation and recovering. *Frontiers in Plant Science* **2014,** *5*.

128. Champagne, A.; Hilbert, G.; Legendre, L.; Lebot, V. Diversity of anthocyanins and other phenolic compounds among tropical root crops from Vanuatu, South Pacific. *Journal of Food Composition and Analysis* **2011,** *24* (3), 315-325.

129. Ferreres, F.; Goncalves, R. F.; Gil-Izquierdo, A.; Valentao, P.; Silva, A. M.; Silva, J. B.; Santos, D.; Andrade, P. B. Further knowledge on the phenolic profile of *Colocasia esculenta* (L.) Shott. *J. Agric. Food Chem.* **2012,** *60* (28), 7005-7015.

130. Ruiz, A.; Mardones, C.; Rodriguez, R.; Arrabillaga, D.; Dominguez, E. Analysis of hydroxycinnamic acids derivatives in calafate (*Berberis microphylla* G. Forst) berries by liquid chromatography with photodiode array and mass spectrometry detection. *J. Chromatogr. A* **2013,** *1281*, 38-45.

131. Engprasert, S.; Shaojie, S.; Tanaka, H.; Morimoto, S.; Shoyama, Y. Phenolics from *Epimedium diphyllum*. *Natural Medicines* **1998,** *52* (6), 542.

132. Grace, S. C.; Logan, B. A.; Adams, W. W. Seasonal differrences in foliar content of chlorogenic acid, a phenylpropanoid antioxidant, in *Mahonia repens*. *Plant Cell and Environment* **1998,** *21* (5), 513-521.

133. Jin, H. G.; Kim, A. R.; Ko, H. J.; Woo, E. R. A new megastigmane glycoside from *Akebia quinata*. *Arch. Pharm. Res.* **2015,** *38*, 591-597.

134. Nguyen, T. Y.; Nguyen, V. T.; Zhao, B. T.; Lee, J. H.; Kim, J. A.; Son, J. K.; Choi, J. S.; Woo, E. R.; Woo, M. H.; Min, B. S. Quantitative determination of compounds from *Akebia quinata* by high-performance liquid chromatography. *Bulletin of the Korean Chemical Society* **2014,** *35* (7), 1956-1964.

135. Wang, J.; Xu, Q. L.; Zhou, Z. Y.; Tan, J. W. [Caffeoylquinic acid derivatives from stems of *Akebia trifoliata*]. *Zhong yao cai = Zhongyaocai = Journal of Chinese medicinal materials* **2014,** *37* (7), 1190-1193.

136. Pauli, G. F.; Poetsch, F.; Nahrstedt, A. Structure assignment of natural quinic acid derivatives using proton nuclear magnetic resonance techniques. *Phytochemical Analysis* **1998,** *9*, 177-185.

137. Bögge, S. C. Hydroxyzimtsäuren in Papaveraceae und Fumariaceae. Ph.D. Westfälische Wilhelms-Universität, Münster, 1996.

138. Liu, Y.; Deng, A. J.; Ma, L.; Zhang, H. J.; Zhang, Z. H.; Wu, L. Q.; Shen, Z. F.; Wang, W. J.; Qin, H. L. [Chemical constituents of the roots of *Macleaya microcarpa* and activation efficacy of benzophenanthridine alkaloids for the transcription of xbp1 gene]. *Yao xue xue bao = Acta pharmaceutica Sinica* **2015,** *50* (2), 207-210.

139. Lee, C. S.; Lee, S. A.; Kim, Y. J.; Seo, S. J.; Lee, M. W. 3,4,5-Tricaffeoylquinic acid inhibits tumor necrosis factor-alpha-stimulated production of inflammatory mediators in keratinocytes via suppression of Akt- and NF-kappaB-pathways. *Int Immunopharmacol.* **2011,** *11* (11), 1715-1723.

140. Park, K. H.; Park, M.; Choi, S. E.; Jeong, M. S.; Kwon, J. H.; Oh, M. H.; Choi, H. K.; Seo, S. J.; Lee, M. W. The anti-oxidative and anti-inflammatory effects of caffeoyl derivatives from the roots of Aconitum koreanum R. RAYMOND. *Biol. Pharm. Bull.* **2009,** *32* (12), 2029-2033.

141. Yoshikawa, K.; Kinoshita, H.; Arihara, S. Non-basic components of Coptis rhizoma. II. Four new hemiterpenoid glucosides, two new phenylpropanoid glucosides and a new flavonoid glycoside from *Coptis japonica* var. *dissecta*. *Natural Medicines* **1997,** *51* (3), 244-248.

142. Li, Z. F.; Wang, Q.; Feng, Y. L.; Luo, X. J.; Fan, M. M.; Yang, S. L. [Chemical constituents from *Coptis chinensis*]. *Zhong yao cai = Zhongyaocai = Journal of Chinese medicinal materials* **2012,** *35* (9), 1438-1441.

143. McNamara, C. E.; Perry, N. B.; Follett, J. M.; Parmenter, G. A.; Douglas, J. A. A new glucosyl feruloyl quinic acid as a potential marker for roots and rhizomes of goldenseal, *Hydrastis canadensis*. *J Nat. Prod.* **2004,** *67* (11), 1818-1822.

144. Gentry, E. J.; Jampani, H. B.; Keshavarz-Shokri, A.; Morton, M. D.; Velde, D. V.; Telikepalli, H.; Mitscher, L. A.; Shawar, R.; Humble, D.; Baker, W. Antitubercular natural products: berberine from the roots of commercial *Hydrastis canadensis* powder. Isolation of inactive 8-oxotetrahydrothalifendine, canadine, beta-hydrastine, and two new quinic acid esters, hycandinic acid esters-1 and -2. *J. Nat Prod.* **1998,** *61* (10), 1187-1193.

145. Farag, M. A.; El Sayed, A. M.; El Banna, A.; Ruehmann, S. Metabolomics reveals distinct methylation reaction in MeJA elicited *Nigella sativa* callus via UPLC-MS and chemometrics. *Plant Cell Tissue and Organ Culture* **2015,** *122* (2), 453-463.

146. Moore, J. P.; Westall, K. L.; Ravenscroft, N.; Farrant, J. M.; Lindsey, G. G.; Brandt, W. F. The predominant polyphenol in the leaves of the resurrection plant *Myrothamnus flabellifolius*, 3,4,5 tri-O-galloylquinic acid, protects membranes against desiccation and free radical-induced oxidation. *Biochem. J* **2005,** *385* (Pt 1), 301-308.

147. Mariotti, K. d. C.; Schuh, R. S.; Nunes, J. d. M.; Salamoni, S. P.; Meirelles, G.; Barreto, F.; Von Poser, G. L.; Singer, R. B.; Dallegrave, E.; Van der Sand, S. T.; Limberger, R. P. Chemical constituents and pharmacological profile of *Gunnera manicata* L. extracts. *Braz. J. Pharm. Sci.* **2014,** *50*, 147-154.

148. Simirgiotis, M. J.; Silva, M.; Becerra, J.; Schmeda-Hirschmann, G. Direct characterisation of phenolic antioxidants in infusions from four Mapuche medicinal plants by liquid chromatography with diode array detection (HPLC-DAD) and electrospray ionisation tandem mass spectrometry (HPLC-ESI-MS). *Food Chem.* **2012,** *131* (1), 318-327.

149. Stevenson, P. C.; Anderson, J. C.; Blaney, M.; Simmonds, M. S. J. Developmental inhibition of *Spodoptera litura* (Fab.) larvae by a novel caffeoylquinic acid from wild groundnut *Arachis paraguariensis* (Chod et Hassl.). *J. Chem. Ecol.* **1993,** *19*, 2917-2933.

150. Kimmins, F.; Padgham, D.; Stevenson, P. Growth inhibition of the cotton bollworm (*Helicoverpa armigera*) larvae by caffeoylquinic acids from the wild groundnut, *Arachis paraguariensis*. *Insect Science and its Application* **1995,** *16* (3-4), 363-368.

151. Ma, Y.; Kosinska-Cagnazzo, A.; Kerr, W. L.; Amarowicz, R.; Swanson, R. B.; Pegg, R. B. Separation and characterization of phenolic compounds from dry-blanched peanut skins by liquid chromatography-electrospray ionization mass spectrometry. *J. Chromatogr. A* **2014,** (0).

152. Liu, M.; Dong, J.; Lin, Z.; Niu, Y.; Zhang, X.; Jiang, H.; Guo, N.; Li, W.; Wang, H.; Chen, S. Rapid screening of transferrin-binders in the flowers of *Bauhinia blakeana* Dunn by on-line high-performance liquid chromatography–diode-array detector–electrospray ionization–ion-trap–time-of-flight–mass spectrometry–transferrin–fluorescence detection system. *J. Chromatogr. A* **2016,** *1450*, 17-28.

153. Tibe, O.; Meagher, L. P.; Fraser, K.; Harding, D. R. Condensed tannins and flavonoids from the forage legume sulla (*Hedysarum coronarium*). *J Agric. Food Chem.* **2011,** *59* (17), 9402-9409.

154. Armitage, R.; Bayliss, G. S.; Gramshaw, J. W.; Haslam, E.; Haworth, R. D.; Jones, K.; Rogers, H. J.; Searle, T. Gallotannins. Part III. The constitution of Chinese, Turkish, Sumach and Tara tannins. *J. Chem. Soc. Perkin Trans. 2* **1961,** 1842-1853.

155. Haslam, E.; Haworth, R. D.; Keen, P. C. Gallotannins. Part VII. Tara gallotannin. *J. Chem. Soc. Perkin Trans. 2* **1962,** 3814-3819.

156. Haslam, E.; Haworth, R. D.; Lawton, D. A. Gallotannins. Part VIII. The preparation and properties of some galloyl esters of quinic acid. *J. Chem. Soc. Perkin Trans. 2* **1963,** 2173-2181.

157. Clifford, M. N.; Stoupi, S.; Kuhnert, N. Profiling and characterization by LC–MS^n of the galloylquinic acids of green tea, Tara tannin and tannic acid. *J. Agric. Food Chem.* **2007,** *55*, 2797-2807.

158. Kondo, K.; Takaishi, Y.; Shibata, H.; Higuti, T. ILSMRs (intensifier of beta-lactam-susceptibility in methicillin-resistant *Staphylococcus aureus*) from Tara [*Caesalpinia spinosa* (Molina) Kuntze]. *Phytomed.* **2006,** *13* (3), 209-212.

159. Olennikov, D. N.; Tankhaeva, L. M.; Partilkhaev, V. V. Chemical Investigation of *Caragana arborescens* shoots. *Natural Product Communications* **2013,** *8* (5), 585-586.

160. Simmonds, M. S.; Stevenson, P. C. Effects of isoflavonoids from *Cicer* on larvae of *Heliocoverpa armigera*. *J. Chem. Ecol.* **2001,** *27* (5), 965-977.

161. Costa, A. R.; Freitas, L. A.; Mendiola, J.; Ibanez, E. *Copaifera langsdorffii* supercritical fluid extraction: Chemical and functional characterization by LC/MS and *in vitro* assays. *Journal of Supercritical Fluids* **2015,** *100*, 86-96.

162. Nogueira, M. S.; Furtado, R. A.; Bastos, J. K. Flavonoids and methoxy-galloyiquinic acid derivatives from the leaf extract of *Copaifera langsdorffii* Desf. *J. Agric. Food Chem.* **2015,** *63* (31), 6939-6945.

163. Barros, L.; Duenas, M.; Carvalho, A. M.; Ferreira, I. C. F. R.; Santos-Buelga, C. Characterization of phenolic compounds in flowers of wild medicinal plants from Northeastern Portugal. *Food Chem. Toxicol.* **2012,** *50* (5), 1576-1582.

164. Regos, I.; Urbanella, A.; Treutter, D. Identification and quantification of phenolic compounds from the forage legume sainfoin (*Onobrychis viciifolia*). *J Agric. Food Chem.* **2009,** *57* (13), 5843-5852.

165. Pontes, P. V.; Moreira, R. F. A.; Trugo, L. C.; de Maria, C. A. B. The content of chlorogenic acids in tropical fruits. *J. Sci. Food Agric.* **2002,** *82*, 1177-1181.

166. Ali, M. S. M. Analysis of phenolics and other phytochemicals in selected Malaysian traditional vegetables and their activities *in vitro*. University of Glasgow, 2008.

167. Zhang, H.; Jiang, L.; Ye, S.; Ye, Y.; Ren, F. Systematic evaluation of antioxidant capacities of the ethanolic extract of different tissues of jujube (*Ziziphus jujuba* Mill.) from China. *Food Chem. Toxicol.* **2010,** *48* (6), 1461-1465.

168. Singh, D. P.; Maurya, S.; Singh, S. P.; Singh, M.; Singh, U. P. Chemotaxonomic variability in *Zizyphus mouritiana* varieties and its pharmacological properties in relation to human health. *J Herb. Pharmacother.* **2007,** *7* (3-4), 229-237.

169. San, B.; Yildirim, A. N. Phenolic, alpha-tocopherol, beta-carotene and fatty acid composition of four promising jujube (*Ziziphus jujuba* Miller) selections. *Journal of Food Composition and Analysis* **2010,** *23* (7), 706-710.

170. Herrmann, K. Occurrence and content of hydroxycinnamic and hydroxybenzoic acid compounds in foods. *CRC Crit. Rev. Food Sci. Nutr.* **1989,** *28*, 315-347.

171. Möller, B.; Herrmann, K. Quinic acid esters of hydroxycinnamic acids in stone and pome fruit. *Phytochem.* **1983,** *22*, 477-481.

172. Donovan, J. L.; Meyer, A. S.; Waterhouse, A. L. Phenolic composition and antioxidant activity of prunes and prune juice (*Prunus domestica*). *J. Agric. Food Chem.* **1998,** *46* (4), 1247-1252.

173. Takeoka, G. R.; Dao, L. T. Antioxidant constituents of almond [*Prunus dulcis* (Mill.) D.A. Webb] hulls. *J. Agric. Food Chem.* **2003,** *51* (2), 496-501.

174. Ruiz, D.; Egea, J.; Gil, M. I.; Tomas-Barberan, F. A. Characterization and quantitation of phenolic compounds in New Apricot (*Prunus armeniaca* L.) varieties. *J Agric. Food Chem.* **2005,** *53* (24), 9544-9552.

175. Schmitzer, V.; Slatnar, A.; Mikulic-Petkovsek, M.; Veberic, R.; Krska, B.; Stampar, F. Comparative study of primary and secondary metabolites in apricot (*Prunus armeniaca* L.) cultivars. *J. Sci. Food Agric.* **2011,** *91* (5), 860-866.

176. Tomas-Barberan, F. A.; Gil, M. I.; Cremin, P.; Waterhouse, A. L.; Hess-Pierce, B.; Kader, A. A. HPLC-DAD-ESIMS analysis of phenolic compounds in nectarines, peaches, and plums. *J. Agric. Food Chem.* **2001,** *49*, 4748-4760.

177. Scattino, C.; Castagna, A.; Neugart, S.; Chan, H. M.; Schreiner, M.; Crisosto, C. H.; Tonutti, P.; Ranieri, A. Post-harvest UV-B irradiation induces changes of phenol contents and corresponding biosynthetic gene expression in peaches and nectarines. *Food Chem.* **2014,** *163* (0), 51-60.

178. Lin, L. Z.; Harnly, J. M. Phenolic compounds and chromatographic profiles of pear skins (*Pyrus* spp.). *J Agric. Food Chem.* **2008,** *56* (19), 9094-9101.

179. Delpino-Rius, A.; Eras, J.; Vilaro, F.; Cubero, M. A.; Balcells, M.; Canela-Garayoa, R. Characterization of phenolic compounds in processed fibers from the juice industry. *Food Chem.* **2014,** (0).

180. Vasco, C.; Riihinen, K.; Ruales, J.; Kamal-Eldin, A. Phenolic compounds in Rosaceae fruits from Ecuador. *J Agric. Food Chem.* **2009,** *57* (4), 1204-1212.

181. Guimaraes, R.; Barros, L.; Duenas, M.; Carvalho, A. M.; Queiroz, M. J.; Santos-Buelga, C.; Ferreira, I. C. Characterisation of phenolic compounds in wild fruits from Northeastern Portugal. *Food Chem.* **2013,** *141* (4), 3721-3730.

182. Fang, N.; Yu, S.; Prior, R. L. LC/MS/MS characterization of phenolic constituents in dried plums. *J. Agric. Food Chem.* **2002,** *50* (12), 3579-3585.

183. Nakatani, N.; Kayano, S.; Kikuzaki, H.; Sumino, K.; Katagiri, K.; Mitani, T. Identification, quantitative determination, and antioxidative activities of chlorogenic acid isomers in prune (*Prunus domestica* L.). *J. Agric. Food Chem.* **2000,** *48*, 5512-5516.

184. Olszewska, M. A.; Kwapisz, A. Metabolite profiling and antioxidant activity of *Prunus padus* L. flowers and leaves. *Nat. Prod. Res* **2011,** *25* (12), 1115-1131.

185. Pacifico, S.; Di Maro, A.; Petriccione, M.; Galasso, S.; Piccolella, S.; Di Giuseppe, A. M. A.; Scortichini, M.; Monaco, P. Chemical composition, nutritional value and antioxidant properties of autochthonous *Prunus avium* cultivars from Campania Region. *Food Research International* **2014,** *64* (0), 188-199.

186. Mozetic, B.; Trebse, P.; Hribar, J. Determination and quantitation of anthocyanins and hydroxycinnamic acids in different cultivars of sweet cherries (Prunus avium L.) from Nova Gorica region (Slovenia). *Food Technology and Biotechnology* **2002,** *40* (3), 207-212.

187. Mozetic, B.; Trebse, P.; Simcic, M.; Hribar, J. Changes of anthocyanins and hydroxycinnamic acids affecting the skin colour during maturation of sweet cherries (*Prunus avium* L.). *Lebensmittel-Wissenschaft Und-Technologie-Food Science and Technology* **2004,** *37* (1), 123-128.

188. Mozetic, B.; Trebse, P. Identification of sweet cherry anthocyanins and hydroxycinnamic acids using HPLC coupled with DAD and MS detector. *Acta Chimica Slovenica* **2004,** *51* (1), 151-158.

189. Usenik, V.; Stampar, F.; Petkovsek, M. M.; Kastelec, D. The effect of fruit size and fruit colour on chemical composition in 'Kordia' sweet cherry (*Prunus avium* L.). *Journal of Food Composition and Analysis* **2015,** *38*, 121-130.

190. Mitani, T.; Horinishi, A.; Kishida, K.; Kawabata, T.; Yano, F.; Mimura, H.; Inaba, N.; Yamanishi, H.; Oe, T.; Negoro, K.; Mori, H.; Miyake, Y.; Hosoda, A.; Tanaka, Y.; Mori, M.; Ozaki, Y. Phenolics profile of mume, Japanese apricot (*Prunus mume* Sieb. et Zucc.) fruit. *Biosci. Biotechnol. Biochem.* **2013,** *77* (8), 1623-1627.

191. Fujimoto, K.; Nakamura, S.; Matsumoto, T.; Ohta, T.; Ogawa, K.; Tamura, H.; Matsuda, H.; Yoshikawa, M. Medicinal flowers. XXXVIII. structures of acylated sucroses and inhibitory effects of constituents on aldose reducatase from the flower buds of *Prunus mume*. *Chem. Pharm. Bull. (Tokyo)* **2013,** *61* (4), 445-451.

192. Nakamura, S.; Fujimoto, K.; Matsumoto, T.; Nakashima, S.; Ohta, T.; Ogawa, K.; Matsuda, H.; Yoshikawa, M. Acylated sucroses and acylated quinic acids analogs from the flower buds of *Prunus mume* and their inhibitory effect on melanogenesis. *Phytochem.* **2013,** *92*, 128-136.

193. Zhang, X.; Lin, Z.; Fang, J.; Liu, M.; Niu, Y.; Chen, S.; Wang, H. An on-line high-performance liquid chromatography–diode-array detector-electrospray ionization–ion-trap–time-of-flight–mass spectrometry-total antioxidant capacity detection system applying two antioxidant methods for activity evaluation of the edible flowers from *Prunus mume*. *J. Chromatogr. A* **2015,** *1414*, 88-102.

194. Olszewska, M. A.; Michel, P. Activity-guided isolation and identification of free radical-scavenging components from various leaf extracts of *Sorbus aria* (L.) Crantz. *Nat. Prod. Res* **2012,** *26* (3), 243-254.

195. Hukkanen, A. T.; Polonen, S. S.; Karenlampi, S. O.; Kokko, H. I. Antioxidant capacity and phenolic content of sweet rowanberries. *J. Agric. Food Chem.* **2006,** *54* (1), 112-119.

196. Gaivelyte, K.; Jakstas, V.; Razukas, A.; Janulis, V. Variation in the contents of neochlorogenic acid, chlorogenic acid and three quercetin glycosides in leaves and fruits of Rowan (*Sorbus*) species and varieties from collections in Lithuania. *Nat. Prod. Commun.* **2013,** *8* (8), 1105-1110.

197. Becerra-Herrera, M.; Lazzoi, M. R.; Sayago, A.; Beltr+ín, R.; Del Sole, R.; Vasapollo, G. Extraction and determination of phenolic compounds in the berries of *Sorbus americana* Marsh and *Lonicera oblongifolia* (Goldie) Hook. *Food Anal. Methods* **2015,** 1-6.

198. Termentzi, A.; Kefalas, P.; Kokkalou, E. LC-DAD-MS (ESI+) analysis of the phenolic content of *Sorbus domestica* fruits in relation to their maturity stage. *Food Chem.* **2008,** *106* (3), 1234-1245.

199. Forino, M.; Tenore, G. C.; Tartaglione, L.; Carmela, D.; Novellino, E.; Ciminiello, P. (1*S*,3*R*,4*S*,5*R*)5-*O*-Caffeoylquinic acid: Isolation, stereo-structure characterization and biological activity. *Food Chem.* **2015,** *178*, 306-310.

200. Cao, J.; Jiang, Q.; Lin, J.; Li, X.; Sun, C.; Chen, K. Physicochemical characterisation of four cherry species (*Prunus* spp.) grown in China. *Food Chem.* **2015,** *173*, 855-863.

201. Ozga, J. A.; Saeed, A.; Wismer, W.; Reinecke, D. M. Characterization of cyanidin- and quercetin-derived flavonoids and other phenolics in mature saskatoon fruits (*Amelanchier alnifolia* Nutt.). *J. Agric. Food Chem.* **2007,** *55* (25), 10414-10424.

202. Slimestad, R.; Torskangerpoll, K.; Nateland, H. S.; Johannessen, T.; Giske, N. H. Flavonoids from black chokeberries, *Aronia melanocarpa*. *Journal of Food Composition and Analysis* **2005,** *18* (1), 61-68.

203. Lee, J. E.; Kim, G. S.; Park, S.; Kim, Y. H.; Kim, M. B.; Lee, W. S.; Jeong, S. W.; Lee, S. J.; Jin, J. S.; Shin, S. C. Determination of chokeberry (*Aronia melanocarpa*) polyphenol components using liquid chromatography-tandem mass spectrometry: Overall contribution to antioxidant activity. *Food Chem.* **2014,** *146*, 1-5.

204. McDougall, G. J.; Austin, C.; Van Schayk, E.; Martin, P. Salal (*Gaultheria shallon*) and aronia (*Aronia melanocarpa*) fruits from Orkney: Phenolic content, composition and effect of wine-making. *Food Chem.* **2016,** *205*, 239-247.

205. Romani, A.; Vignolini, P.; Ieri, F.; Heimler, D. Polyphenols and volatile compounds in commercial Chokeberry (*Aronia melanocarpa*) products. *Natural Product Communications* **2016,** *11* (1), 99-102.

206. Grunovaite, L.; Pukalskiene, M.; Pukalskas, A.; Venskutonis, P. R. Fractionation of black chokeberry pomace into functional ingredients using high pressure extraction methods and evaluation of their antioxidant capacity and chemical composition. *Journal of Functional Foods* **2016,** *24*, 85-96.

207. Esatbeyoglu, T.; Rodriguez-Werner, M.; Winterhalter, P. Fractionation and isolation of polyphenols from *Aronia melanocarpa* by countercurrent and membrane chromatography. *European Food Research and Technology* **2017,** 1-15 DOI: 10.1007/s00217-016-2837-3.

208. Du, H.; Wu, J.; Li, H.; Zhong, P. X.; Xu, Y. J.; Li, C. H.; Ji, K. X.; Wang, L. S. Polyphenols and triterpenes from *Chaenomeles* fruits: Chemical analysis and antioxidant activities assessment. *Food Chem.* **2013,** *141* (4), 4260-4268.

209. Kicel, A.; Micchel, P.; Owczarek, A.; Marchelak, A.; Zyzelewicz, D.; Budryn, G.; Oracz, J.; Olszewska, M. A. Phenolic profile and antioxidant potential of leaves from selected *Cotoneaster* Medik. species. *Molecules* **2016,** *21*, 688.

210. Liu, P.; Kallio, H.; Yang, B. Phenolic compounds in hawthorn (*Crataegus grayana*) fruits and leaves and changes during fruit ripening. *J Agric. Food Chem.* **2011,** *59* (20), 11141-11149.

211. Cui, T.; Li, J. Z.; Kayahara, H.; Ma, L.; Wu, L. X.; Nakamura, K. Quantification of the polyphenols and triterpene acids in Chinese Hawthorn fruit by high-performance liquid chromatography. *J. Agric. Food Chem.* **2006,** *54* (13), 4574-4581.

212. Cui, T.; Nakamura, K.; Tian, S.; Kayahara, H.; Tian, Y. L. Polyphenolic content and physiological activities of Chinese hawthorn extracts. *Biosci. Biotechnol. Biochem.* **2006,** *70* (12), 2948-2956.

213. Fiorentino, A.; D'Abrosca, B.; Pacifico, S.; Mastellone, C.; Piscopo, V.; Caputo, R.; Monaco, P. Isolation and structure elucidation of antioxidant polyphenols from quince (*Cydonia vulgaris*) peels. *J Agric. Food Chem.* **2008,** *56* (8), 2660-2667.

214. Silva, B. M.; Andrade, P. B.; Ferreres, F.; Domingues, A. L.; Seabra, R. M.; Ferreira, A. A. Phenolic profile of quince fruit (*Cydonia oblonga* Miller) (pulp and peel). *J. Agric. Food Chem.* **2002,** *50* (16), 4615-4618.

215. Wojdylo, A.; Oszmianski, J.; Bielicki, P. Polyphenolic composition, antioxidant activity, and polyphenol oxidase (PPO) activity of quince (Cydonia oblonga Miller) varieties. *J. Agric. Food Chem.* **2013,** *61* (11), 2762-2772.

216. Carbonell-Barrachina, A. A.; Szychowski, P. J.; VÃ¡squez, M. V.; Hernandez, F.; Wojdylo, A. Technological aspects as the main impact on quality of quince liquors. *Food Chem.* **2014,** (0).

217. Silva, B. M.; Andrade, P. B.; Ferreres, F.; Seabra, R. M.; Oliveira, M. B.; Ferreira, M. A. Composition of quince (*Cydonia oblonga* Miller) seeds: phenolics, organic acids and free amino acids. *Nat. Prod. Res.* **2005,** *19* (3), 275-281.

218. Karar, M. G. E.; Pletzer, D.; Jaiswal, R.; Weingart, H.; Kuhnert, N. Identification, characterization, isolation and activity against *Escherichia coli* of quince (*Cydonia oblonga*) fruit polyphenols. *Food Research International* **2014,** *85* (0), 121-129.

219. Ding, C. K.; Chachin, K.; Ueda, Y.; Imahori, Y.; Wang, C. Y. Metabolism of phenolic compounds during loquat fruit development. *J. Agric. Food Chem.* **2001,** *49* (6), 2883-2888.

220. Whiting, G. C.; Coggins, R. A. 4-*p*-coumaroylquinic acid in apple fruits. *Phytochem.* **1975,** *14*, 593.

221. Clifford, M. N.; Johnston, K. L.; Knight, S.; Kuhnert, N. A hierarchical scheme for LC–MS^n identification of chlorogenic acids. *J. Agric. Food Chem.* **2003,** *51*, 2900-2911.

222. Marks, S. C.; Mullen, W.; Crozier, A. Flavonoid and hydroxycinnamate profiles of english apple ciders. *J. Agric. Food Chem.* **2007,** *55* (21), 8723-8730.

223. Sommella, E.; Pepe, G.; Pagano, F.; Ostacolo, C.; Tenore, G. C.; Russo, M. T.; Novellino, E.; Manfra, M.; Campiglia, P. Detailed polyphenolic profiling of Annurca apple (*M. pumila* Miller cv Annurca) by a

combination of RP-UHPLC and HILIC, both hyphenated to IT-TOF mass spectrometry. *Food Research International* **2015,** *76, Part 3*, 466-477.

224. Ramirez-Ambrosi, M.; Abad-Garcia, B.; Viloria-Bernal, M.; Garmon-Lobato, S.; Berrueta, L. A.; Gallo, B. A new ultrahigh performance liquid chromatography with diode array detection coupled to electrospray ionization and quadrupole time-of-flight mass spectrometry analytical strategy for fast analysis and improved characterization of phenolic compounds in apple products. *J. Chromatogr. A* **2013,** *1316* (0), 78-91.

225. Fromm, M.; Loos, H. M.; Bayha, S.; Carle, R.; Kammerer, D. R. Recovery and characterisation of coloured phenolic preparations from apple seeds. *Food Chem.* **2001,** *136* (3â€“4), 1277-1287.

226. Escarpa, A.; Gonzalez, M. C. Evaluation of high-performance liquid chromatography for determination of phenolic compounds in pear horticultural cultivars. *Chromatographia* **2000,** *51*, 37-43.

227. Wald, B.; Wray, V.; Galensa, R.; Herrmann, K. Malonated flavonol glycosides and 3,5-dicaffeoylquinic acid from pears. *Phytochem.* **1989,** *28*, 663-664.

228. Kodoma, M.; Wada, H.; Otani, H.; Kohmoto, K.; Kimura, Y. 3,5-di-*O*-caffeoylquinic acid, an infection-inhibiting factor from *Pyrus pyrifolia* induced by infection with *Alternaria alternata*. *Phytochem.* **1997,** *47*, 371-373.

229. Lee, Y. G.; Cho, J. Y.; Kim, C. M.; Lee, S. H.; Kim, W. S.; Jeon, T. I.; Park, K. H.; Moon, J. H. Coumaroyl quinic acid derivatives and flavonoids from immature pear (*Pyrus pyrifolia nakai*) fruit. *Food Science and Biotechnology* **2013,** *22* (3), 803-810.

230. Duckstein, S. M.; Lotter, E. M.; Meyer, U.; Lindequist, U.; Stintzing, F. C. Phenolic constituents from *Alchemilla vulgaris* L. and *Alchemilla mollis* (Buser) Rothm. at different dates of harvest. *Z. Naturforsch. C.* **2013,** *68* (1-2), 529-540.

231. Bagdonaite, E.; Jakstas, V.; Raudonis, R.; Janulis, V. Chlorogenic acid, rutin and hyperoside content in *Fragaria vesca*, *F. viridis* and *F. moschata* in Lithuania. *Nat. Prod. Res.* **2013,** *27* (2), 181-184.

232. Fecka, I.; Kucharska, A. Z.; Kowalczyk, A. Quantification of tannins and related polyphenols in commercial products of Tormentil (*Potentilla tormentilla*). *Phytochemical Analysis* **2015,** n/a.

233. Ieri, F.; Innocenti, M.; Lucia, P.; Sandra, G.; Mulinacci, N. Phenolic composition of bud extracts of *Ribes nigrum* L., *Rosa canina* L. and *Tilia tomentosa* M. *J. Pharm. Biomed. Anal.* **2015,** (0).

234. Dall'Acqua, S.; Cervellati, R.; Loi, M. C.; Innocenti, G. Evaluation of in vitro antioxidant properties of some traditional Sardinian medicinal plants: Investigation of the high antioxidant capacity of *Rubus ulmifolius*. *Food Chem.* **2008,** *106* (2), 745-749.

235. Ruiz, A.; Bustamante, L.; Vergara, C.; Von Baer, D.; Hermosin-Gutierrez, I.; Mardones, C. Hydroxycinnamic acid and flavonols in native edible berries of South Patagonia. *Food Chem.* **2015,** *167*, 84-90.

236. Martins, A.; Barros, L.; Carvalho, A. M.; Santos-Buelga, C.; Fernandes, I. P.; Barreiro, F.; Ferreira, I. C. F. R. Phenolic extracts of *Rubus ulmifolius* Schott flowers: characterization, microencapsulation and incorporation into yogurts as nutraceutical sources. *Food & Funct.* **2014,** *5* (6), 1091-1100.

237. Gouveia-Figueira, S. C.; Castilho, P. C. Phenolic screening by HPLC–DAD–ESI/MSn and antioxidant capacity of leaves, flowers and berries of *Rubus grandifolius* Lowe. *Industrial Crops and Products* **2015,** *73* (0), 28-40.

238. Granica, S.; Krupa, K.; Klebowska, A.; Kiss, A. K. Development and validation of HPLC-DAD-CAD-MS^3 method for qualitative and quantitative standardization of polyphenols in Agrimoniae eupatoriae herba (Ph. Eur). *J. Pharm. Biomed. Anal.* **2013,** *86* (0), 112-122.

239. Vallejo, F.; Marin, J. G.; Tomás-Barberán, F. A. Phenolic compound content of fresh and dried figs (*Ficus carica* L.). *Food Chem.* **2011,** *130*, 485-492.

240. Takahashi, T.; Okiura, A.; Saito, K.; Kohno, M. Identification of phenylpropanoids in Fig (*Ficus carica* L.) leaves. *J. Agric. Food Chem.* **2014,** *62* (41), 10076-10083.

241. El-Sakhawy, F.; Kassem, H.; Abou-Hussein, D.; El-Gayed, S.; Mostafa, M.; Ahmed, R. Phytochemical investigation of the bioactive extracts of the leaves of *Ficus cyathistipula* Warb. *Zeitschrift fur Naturforschung. C, Journal of biosciences* **2016,** *71* (5-6), 141-154.

242. Russo, F.; Caporaso, N.; Paduano, A.; Sacchi, R. Phenolic compounds in fresh and dried figs from Cilento (Italy), by vonsidering Breba Crop and Full Crop, in comparison to Turkish and Greek Dried Figs. *J. Food Sci.* **2014**.

243. Omar, M. H.; Mullen, W.; Crozier, A. Identification of proanthocyanidin dimers and trimers, flavone *C*-glycosides, and antioxidants in *Ficus deltoidea*, a Malaysian herbal tea. *J. Agric. Food Chem.* **2011**.

244. Farag, M. A.; Abdelfattah, M. S.; Badr, S. E.; Wessjohann, L. A. Profiling the chemical content of *Ficus lyrata* extracts via UPLC-PDA-qTOF-MS and chemometrics. *Nat. Prod. Res.* **2014,** *28*, 1-8.

245. Imran, M.; Rasool, N.; Rizwan, K.; Zubair, M.; Riaz, M.; Zia-Ul-Haq, M.; Rana, U. A.; Nafady, A.; Jaafar, H. Z. Chemical composition and biological studies of *Ficus benjamina*. *Chem. Cent. J.* **2014,** *8* (1), 12.

246. Jahan, I. A.; Nahar, N.; Mosihuzzaman, M.; Rokeya, B.; Ali, L.; Azad Khan, A.; Makhmur, T.; Iqbal Choudhary, M. Hypoglycaemic and antioxidant activities of *Ficus racemosa* Linn. fruits. *Natural Product Research* **2009,** *23* (4), 399-408.

247. Pawlowska, A. M.; Oleszek, W.; Braca, A. Quali-quantitative analyses of flavonoids of *Morus nigra* L. and *Morus alba* L. (Moraceae) fruits. *J Agric. Food Chem.* **2008,** *56* (9), 3377-3380.

248. Zhang, W.; Han, F.; He, J.; Duan, C. HPLC-DAD-ESI-MS/MS analysis and antioxidant activities of nonanthocyanin phenolics in mulberry (*Morus alba* L.). *J Food Sci.* **2008,** *73* (6), C512-C518.

249. Sanchez-Salcedo, E. M.; Mena, P.; Garcia-Viguera, C.; Hernandez, F.; Jose Martinez, J. (Poly)phenolic compounds and antioxidant activity of white (*Morus alba*) and black (*Morus nigra*) mulberry leaves: Their potential for new products rich in phytochemicals. *Journal of Functional Foods* **2015,** *18*, 1039-1046.

250. Sanchez-Salcedo, E. M.; Tassotti, M.; Del Rio, D.; Hernandez, F.; Martinez, J. J.; Mena, P. (Poly)phenolic fingerprint and chemometric analysis of white (*Morus alba* L.) and black (*Morus nigra* L.) mulberry leaves by using a non-targeted UHPLC-MS approach. *Food Chem.* **2016,** *212*, 250-255.

251. Seo, C. S.; Lim, H. S.; Jeong, S. J.; Ha, H.; Shin, H. K. HPLC-PDA analysis and anti-inflammatory effects of Mori Cortex Radicis. *Nat. Prod. Commun.* **2013,** *8* (10), 1443-1446.

252. Tanae, M. M.; Lima-Landman, M. T.; De Lima, T. C.; Souccar, C.; Lapa, A. J. Chemical standardization of the aqueous extract of *Cecropia glaziovii* Sneth endowed with antihypertensive, bronchodilator, antiacid secretion and antidepressant-like activities. *Phytomed.* **2007,** *14* (5), 309-313.

253. Paul, P.; Bansal, P.; Nayak, P. G.; Pannakal, S. T.; Priyadarsini, K. I.; Unnikrishnan, M. K. Polyphenolic fraction of *Pilea microphylla* (L.) protects Chinese hamster lung fibroblasts against gamma-radiation-induced cytotoxicity and genotoxicity. *Environ. Toxicol. Pharmacol.* **2012,** *33* (1), 107-119.

254. Kartika, H.; Li, Q. X.; Wall, M. M.; Nakamoto, S. T.; Iwaoka, W. T. Major phenolic acids and total antioxidant activity in Mamaki leaves, *Pipturus albidus*. *J Food Sci.* **2007,** *72* (9), S696-S701.

255. Gorzalczany, S.; Marrassini, C.; Mino, J.; Acevedo, C.; Ferraro, G. Antinociceptive activity of ethanolic extract and isolated compounds of *Urtica circularis*. *J Ethnopharmacol.* **2011,** *134* (3), 733-738.

256. Marrassini, C.; Acevedo, C.; Mino, J.; Ferraro, G.; Gorzalczany, S. Evaluation of antinociceptive, antinflammatory activities and phytochemical analysis of aerial parts of *Urtica urens* L. *Phytother. Res* **2010,** *24* (12), 1807-1812.

257. Pinelli, P.; Ieri, F.; Vignolini, P.; Bacci, L.; Baronti, S.; Romani, A. Extraction and HPLC analysis of phenolic compounds in leaves, stalks, and textile fibers of *Urtica dioica* L. *J Agric. Food Chem.* **2008,** *56* (19), 9127-9132.

258. Orcic, D.; Franciskovic, M.; Bekvalac, K.; Svircev, E.; Beara, I.; Lesjak, M.; Mimica-Dukic, N. Quantitative determination of plant phenolics in *Urtica dioica* extracts by high-performance liquid chromatography coupled with tandem mass spectrometric detection. *Food Chem.* **2014,** *143*, 48-53.

259. Lopes-Lutz, D.; Dettmann, J.; Nimalaratne, C.; Schieber, A. Characterization and quantification of polyphenols in Amazon grape (*Pourouma cecropiifolia* Martius). *Molecules* **2010,** *15* (12), 8543-8552.

260. Loponen, J.; Lempa, K.; Ossipov, V.; Kozlov, M. V.; Girs, A.; Hangasmaa, K.; Haukioja, E.; Pihlaja, K. Patterns in content of phenolic compounds in leaves of mountain birches along a strong pollution gradient. *Chemosphere* **2001,** *45* (3), 291-301.

261. Kuokkanen, K.; Julkunen-Tiitto, R.; Keinanen, M.; Niemala, P.; Tahvanainen, J. The effect of elevated CO_2 and temperature on the secondary chemistry of *Betula pendula* seedlings. *Trees* **2001,** *15*, 378-384.

262. Kuokkanen, K.; Yan, S.; Niemelä, P. Effects of elevated CO2 and temperature on the leaf chemistry of birch *Betula pendula* (Roth) and the feeding behaviour of the weevil *Phyllobius maculicornis*. *Agricultural and Forest Entomology* **2003,** *5* (3), 209-217.

263. Kim, M. H.; Park, K. H.; Kim, S. R.; Park, K. J.; Oh, M. H.; Heo, J. H.; Yoon, K. H.; Yin, J.; Yoon, K. H.; Lee, M. W. Two new phenolic compounds from the leaves of *Alnus sibirica* Fisch ex Turcz. *Natural Product Research* **2016,** *30* (2), 206-213.

264. Lee, M. W.; Tanaka, T.; Nonaka, G. I.; Nishioka, I. Tannins and related compounds .115. Dimeric ellagitannins from *Alnus japonica*. *Phytochem.* **1992,** *31* (8), 2835-2839.

265. Amaral, J. S.; Ferreres, F.; Andrade, P. B.; Valentao, P.; Pinheiro, C.; Santos, A.; Seabra, R. Phenolic profile of hazelnut (*Corylus avellana* L.) leaves cultivars grown in Portugal. *Nat. Prod. Res.* **2005,** *19* (2), 157-163.

266. Bahnweg, G.; Heller, W.; Stich, S.; Knappe, C.; Betz, G.; Heerdt, C.; Kehr, R. D.; Ernst, D.; Langebartels, C.; Nunn, A. J.; Rothenburger, J.; Schubert, R.; Wallis, P.; Muller-Starck, G.; Werner, H.; Matyssek, R.; Sandermann, J. H. Beech leaf colonization by the endophyte *Apiognomonia errabunda* dramatically depends on light exposure and climatic conditions. *Plant Biol. (Stuttg)* **2005,** *7* (6), 659-669.

267. Almeida, I. F.; Valentao, P.; Andrade, P. B.; Seabra, R. M.; Pereira, T. M.; Amaral, M. H.; Costa, P. C.; Bahia, M. F. In vivo skin irritation potential of a *Castanea sativa* (Chestnut) leaf extract, a putative natural antioxidant for topical application. *Basic Clin. Pharmacol. Toxicol.* **2008,** *103* (5), 461-467.

268. Nishimura, H.; Nonaka, G.-I.; Nishioka, I. Seven quinic acid gallates from *Quercus stenophylla*. *Phytochem.* **1984,** *23*, 2621-2623.

269. Nishimura, H.; Nonaka, G.; Nishioka, I. Tannins and Related Compounds .19. 8 New gallotannins containing a proto-quercitol core from *Quercus stenophylla* Makino .3. *Chem. Pharm. Bull.* **1984,** *32* (5), 1741-1749.

270. Nishimura, H.; Nonaka, G.; Nishioka, I. Tannins and Related Compounds .20. 2 New ellagitannins containing a proto-quercitol core from *Quercus stenophylla* Makino .4. *Chem. Pharm. Bull.* **1984,** *32* (5), 1750-1753.

271. Nonaka, G.-I.; Ageta, M.; Nishioka, I. Tannins and related compounds. XXV. A new class of gallotannins possessing a (–)-shikimic acid core from C*astanopsis cuspidata* var. *sieboldii*. *Chem. Pharm. Bull.* **1985,** *33*, 96-101.

272. Huang, Y. L.; Tsujita, T.; Tanaka, T.; Matsuo, Y.; Kouno, I.; Li, D. P.; Nonaka, G. I. Triterpene hexahydroxydiphenoyl esters and a quinic acid purpurogallin carbonyl ester from the leaves of *Castanopsis fissa*. *Phytochem.* **2011,** *72* (16), 2006-2014.

273. Drynan, J. W.; Clifford, M. N.; Obuchowicz, J.; Kuhnert, N. The chemistry of low molecular weight black tea polyphenols. *Nat. Prod. Rep.* **2010,** *27* (3), 417-462.

274. Amaral, J. S.; Seabra, R. M.; Andrade, P. B.; Valentao, P.; Pereira, J. A.; Ferreres, F. Phenolic profile in the quality control of walnut (*Juglans regia* L.) leaves. *Food Chem.* **2004,** *88* (3), 373-379.

275. Gawlik-Dziki, U.; Durak, A.; Pecio, L.; Kowalska, I. Nutraceutical potential of tinctures from fruits, green husks, and leaves of *Juglans regia* L. *Scientific World Journal* **2014,** *2014*, 501392.

276. Regueiro, J.; Sanchez-Gonzalez, C.; Vallverdu-Queralt, A.; Simal-Gandara, J.; Lamuela-Raventos, R.; Izquierdo-Pulido, M. Comprehensive identification of walnut polyphenols by liquid chromatography coupled to linear ion trap-Orbitrap mass spectrometry. *Food Chem.* **2014,** *152*, 340-348.

277. Abu-Reidah, I. M.; Arraez-Roman, D.; Segura-Carretero, A.; Fernandez-Gutierrez, A. Profiling of phenolic and other polar constituents from hydro-methanolic extract of watermelon (*Citrullus lanatus*) by means of accurate-mass spectrometry (HPLC-ESI-QTOF-MS). *Food Research International* **2013,** *51* (1), 354-362.

278. Belles, J. M.; Lopez-Gresa, M. P.; Fayos, J.; Pallas, V.; Rodrigo, I.; Conejero, V. Induction of cinnamate 4-hydroxylase and phenylpropanoids in virus-infected cucumber and melon plants. *Plant Science* **2008,** *174* (5), 524-533.

279. Madala, N. E.; Tugizimana, F.; Steenkamp, P. A. Development and optimization of an UPLC-QTOF-MS/MS method based on an in-source collision induced dissociation approach for comprehensive discrimination of chlorogenic acids isomers from *Mormodica* plant species. *Journal of Analytical Methods in Chemistry* **2014,** 650879.

280. Yasir, M.; Sultana, B.; Nigam, P. S.; Owusu-Apenten, R. Antioxidant and genoprotective activity of selected cucurbitaceae seed extracts and LC-ESIMS/MS identification of phenolic components. *Food Chem.* **2016,** *199*, 307-313.

281. Ruiz, A. N. T. O.; Pastene, E. D. G. A.; Vergara, C. A. R. O.; Von Baer, D. I. E. T.; Avello, M. A. R. C.; Mardones, C. L. A. U. Hydroxycinnamic acid derivatives and flavonol profiles of Maqui (*Aristotelia chilensis*) fruits. *Journal of the Chilean Chemical Society* **2016,** *61* (1), 2792-2796.

282. Cao, S.; Ranarivelo, L.; Ratsimbason, M.; Randrianasolo, S.; Ratovoson, F.; Andrianjafy, M.; Kingston, D. G. Antiplasmodial activity of compounds from *Sloanea rhodantha* (Baker) Capuron var. rhodantha from the Madagascar rain forest. *Planta Med.* **2006,** *72* (15), 1438-1440.

283. Torre, J. C.; Schmidt, G. W.; Paetz, C.; Reichelt, M.; Schneider, B.; Gershenzon, J.; D'Auria, J. C. The biosynthesis of hydroxycinnamoyl quinate esters and their role in the storage of cocaine in *Erythroxylum coca*. *Phytochem.* **2013,** *91*, 177-186.

284. Yingngam, B.; Monschein, M.; Brantner, A. Ultrasound-assisted extraction of phenolic compounds from *Cratoxylum formosum* ssp. *formosum* leaves using central composite design and evaluation of its

protective ability against H_2O_2-induced cell death. *Asian Pacific journal of tropical medicine* **2014,** *7S1*, S497-S505.

285. Zhang, Y.; Liu, C.; Yu, M.; Zhang, Z.; Qi, Y.; Wang, J.; Wu, G.; Li, S.; Yu, J.; Hu, Y. Application of accelerated solvent extraction coupled with high-performance counter-current chromatography to extraction and online isolation of chemical constituents from *Hypericum perforatum* L. *J Chromatogr. A* **2011,** *1218* (20), 2827-2834.

286. Tusevski, O.; Petreska, S. J.; Stefova, M.; Simic, S. G. Phenolic profile of dark-grown and photoperiod-exposed *Hypericum perforatum* L. hairy root cultures. *Scientific World Journal* **2013,** *2013*, 602752.

287. Tusevski, O.; Stanoeva, J. P.; Markoska, E.; Brndevska, N.; Stefova, M.; Simic, S. G. Callus cultures of *Hypericum perforatum* L. a novel and efficient source for xanthone production. *Plant Cell Tissue and Organ Culture* **2016,** *125* (2), 309-319.

288. Demirkiran, O.; Mesaik, M.; Beynek, H.; Abbaskhan, A.; Choudhary, M., I Immunosupressive phenolic constituents from *Hypericum montbretii* Spach. *Records of Natural Products* **2013,** *7* (3), 210-219.

289. Caprioli, G.; Alunno, A.; Beghelli, D.; Bianco, A.; Bramucci, M.; Frezza, C.; Iannarelli, R.; Papa, F.; Quassinti, L.; Sagratini, G.; Tirillini, B.; Venditti, A.; Vittori, S.; Maggi, F. Polar constituents and biological activity of the berry-like fruits from *Hypericum androsaemum* L. *Front Plant Sci* **2016,** *7*, 232-243.

290. Jabeur, I.; Tobaldini, F.; Martins, N.; Barros, L.; Martins, I.; Calhelha, R. C.; Henriques, M.; Silva, S.; Achour, L.; Santos-Buelga, C.; Ferreira, I. C. F. R. Bioactive properties and functional constituents of *Hypericum androsaemum* L.: A focus on the phenolic profile. *Food Research International* **2016,** *89*, 422-431.

291. Capasso, A.; Balderrama, L.; Sivila, S. C.; De Tommasi, N.; Sorrentino, L.; Pizza, C. Phytochemical and pharmacological studies of *Guettarda acreana*. *Planta Med.* **1998,** *64* (4), 348-352.

292. Jurgenliemk, G.; Nahrstedt, A. Phenolic compounds from *Hypericum perforatum*. *Planta Med.* **2002,** *68* (1), 88-91.

293. Zdunic, G.; Godevac, D.; Savikin, K.; Novakovic, M.; Milosavljevic, S.; Petrovic, S. Isolation and identification of phenolic compounds from *Hypericum richeri* Vill. and their antioxidant capacity. *Nat. Prod. Res* **2011,** *25* (3), 175-187.

294. Kirmizibekmez, H.; Bassarello, C.; Piacente, S.; Celep, E.; Atay, I.; Mercanoglu, G.; Yesilada, E. Phenolic compounds from *Hypericum calycinum* and their antioxidant activity. *Nat. Prod. Commun.* **2009,** *4* (4), 531-534.

295. Rainha, N.; Koci, K.; Coelho, A. V.; Lima, E.; Baptista, J.; Fernandes-Ferreira, M. HPLC-UV-ESI-MS analysis of phenolic compounds and antioxidant properties of *Hypericum undulatum* shoot cultures and wild-growing plants. *Phytochem.* **2013,** *86* (0), 83-91.

296. Rainha, N.; Lima, E.; Baptista, J. Comparison of the endemic Azorean *Hypericum foliosum* with other *Hypericum* species: antioxidant activity and phenolic profile. *Natural Product Research* **2011,** *25* (2), 123-135.

297. da Silveira, C. V.; Trevisan, M. T.; Rios, J. B.; Erben, G.; Haubner, R.; Pfundstein, B.; Owen, R. W. Secondary plant substances in various extracts of the leaves, fruits, stem and bark of *Caraipa densifolia* Mart. *Food Chem. Toxicol.* **2010,** *48* (6), 1597-1606.

298. Ramos-Gomez, M.; Figueroa-Perez, M. G.; Guzman-Maldonado, H.; Loarca-Pina, G.; Mendoza, S.; Quezada-Tristan, T.; Reynoso-Camacho, R. Phytochemical profile, antioxidant properties and hypoglycemic effect of Chaya (*Cnidoscolus chayamansa*) in STZ-induced diabetic rats. *J. Food Biochem.* **2016,** *DOI: 10.1111/jfbc.12281*, n/a.

299. Chen, L. [Polyphenols from leaves of *Euphorbia hirta* L]. *Zhongguo Zhong. Yao Za Zhi.* **1991,** *16* (1), 38-9, 64.

300. Yoshida, T.; Chen, L.; Shingu, T.; Okuda, T. Tannins and related polyphenols of Euphorbiaceous plants .4. Euphorbin-A and Euphorbin-B, novel dimeric dehydroellagitannins from *Euphorbia hirta* l. *Chem. Pharm. Bull.* **1988,** *36* (8), 2940-2949.

301. Medina-Ortega, K. J. Poinsettia (*Euphorbia pulcherrima* Willd. ex Klotzsch: Euphorbiacea) Resistance Mechanisms against the Silverleaf Whitefly, *Bemisia tabaci* (Gennadius) (Hemiptera: Aleyrodidae) Biotype B . Ph.D. Ohio State University, 2011.

302. Ahn, B. T.; Zhang, B. K.; Lee, S. C.; Kim, J. G.; Ro, J. S.; Lee, K. S. Phenolic compounds of aerial parts of *Euphorbia pekinensis*. *Yakhak Hoeji* **1996,** *40* (2), 170-176.

303. Feng, W.; Gao, L.; Zheng, X.; Wang, Y. Polyphenols of *Euphorbia helioscopia*. *Chinese Journal of Natural Medicines* **2009,** *7* (1), 37-39.

304. Falsone, G. Constituents of Euphorbiaceae .3. Calcium salts of isomeric O-(Beta-Hydroxy-Beta-Methylglutaroyl)Shikimic Acids from *Euphorbia biglandulosa* Desf. *Justus Liebigs Annalen der Chemie* **1977,** (5), 727-731.

305. Falsone, G.; Peters, W. Constituents of Euphorbiaceae Part 4 Constitution of the isomeric O-Beta Hydroxy-Gamma-Hydroxycarbonyl-Beta-Methylbutanoyl Shikimic Acids from *Euphorbia biglandulosa*. *Justus Liebigs Annalen der Chemie* **1978,** (12), 1905-1912.

306. Devkota, H. P.; Basnet, P.; Yahara, S. Diterpene esters and phenolic compounds from *Sapium insigne* (ROYLE) BENTH. ex HOOK. fil. *Chem. Pharm. Bull. (Tokyo)* **2009,** *57* (11), 1289-1291.

307. Ahn, Y. J.; Lee, S. H.; Kang, S. J.; Hwang, B. Y.; Park, W. Y.; Ahn, B. T.; Ro, J. S.; Lee, K. S. The phenolic components of *Sapium japonicum*. *Yakhak Hoeji* **1996,** *40* (2), 183-192.

308. Maldini, M.; Montoro, P.; Pizza, C. Phenolic compounds from *Byrsonima crassifolia* L. bark: phytochemical investigation and quantitative analysis by LC-ESI MS/MS. *J. Pharm. Biomed. Anal.* **2011,** *56* (1), 1-6.

309. Sannomiya, M.; dos Santos, L. C.; Carbone, V.; Napolitano, A.; Piacente, S.; Pizza, C.; Souza-Brito, A. R.; Vilegas, W. Liquid chromatography/electrospray ionization tandem mass spectrometry profiling of compounds from the infusion of *Byrsonima fagifolia* Niedenzu. *Rapid Commun. Mass Spectrom.* **2007,** *21* (8), 1393-1400.

310. Mariutti, L. R. B.; Rodrigues, E.; Chisté, R. C.; Fernandes, E.; Mercadante, A. Z. The Amazonian fruit *Byrsonima crassifolia* effectively scavenges reactive oxygen and nitrogen species and protects human erythrocytes against oxidative damage. *Food Research International* **2014,** *64* (0), 618-625.

311. de Sousa, L. R. F.; Ramalho, S. D.; Fernandes, J. B.; da Silva, M. F. d. G. F.; Lemma, M. R. d. C.; Correa, C. J.; de Souza, D. H. F.; Lima, M. I. S.; Vieira, P. C. Leishmanicidal galloylquinic acids are noncompetitive inhibitors of arginase. *J. Brazil. Chem. Soc.* **2014**.

312. Neszmelyi, A.; Kreher, B.; Muller, A.; Dorsch, W.; Wagner, H. Tetragalloylquinic acid, the major antiasthmatic principle of *Galphimia glauca*. *Planta Med.* **1993,** *59* (2), 164-167.

313. Sharma, A.; Cardoso-Taketa, A.; Choi, Y. H.; Verpoorte, R.; Villarreal, M. L. A comparison on the metabolic profiling of the Mexican anxiolytic and sedative plant *Galphimia glauca* four years later. *J Ethnopharmacol.* **2012,** *141* (3), 964-974.

314. Sultana, T.; Stecher, G.; Abel, G.; Popp, M.; Bonn, G. K. Qualitative and quantitative analysis of multiple galloyl derivatives of quinic acid from the medicinal plant *Galphimia glauca* Cav. using HPLC-ESI-MS. *Planta Med.* **2007,** *73*, 917-918.

315. Bezerra, A. G.; Negri, G.; Duarte-Almeida, J. M.; Smaili, S. S.; Carlini, E. A. Phytochemical analysis of hydroethanolic extracts from powdered roots of *Panax ginseng* C. A. Meyer and *Heteropterys tomentosa* A. Juss and evaluation of their effects on astrocyte cell death. *Quimica Nova* **2016,** *39* (5), 581-587.

316. Yang, X. W.; Wang, J. S.; Ma, Y. L.; Xiao, H. T.; Zuo, Y. Q.; Lin, H.; He, H. P.; Li, L.; Hao, X. J. Bioactive phenols from the leaves of *Baccaurea ramiflora*. *Planta Med.* **2007,** *73* (13), 1415-1417.

317. Cimanga, K.; De, B. T.; Apers, S.; Pieters, L.; Totte, J.; Kambu, K.; Tona, L.; Bakana, P.; van Ufford, L. Q.; Beukelman, C.; Labadie, R.; Vlietinck, A. J. Complement-Inhibiting constituents of *Bridelia ferruginea* stem bark. *Planta Med.* **1999,** *65* (3), 213-217.

318. Agyare, C.; Lechtenberg, M.; Deters, A.; Petereit, F.; Hensel, A. Ellagitannins from *Phyllanthus muellerianus* (Kuntze) Exell.: Geraniin and furosin stimulate cellular activity, differentiation and collagen synthesis of human skin keratinocytes and dermal fibroblasts. *Phytomedicine.* **2011,** *18* (7), 617-624.

319. Estork, D. M.; Gusmao, D. F.; Paciencia, M. L.; Diaz, I. E.; Varella, A. D.; Younes, R. N.; Reis, L. F.; Montero, E. F.; Bernardi, M. M.; Suffredini, I. B. First chemical evaluation and toxicity of Casinga-cheirosa to Balb-c male mice. *Molecules* **2014,** *19* (4), 3973-3987.

320. Jayasinghe, L.; Lakdusinghe, M.; Hara, N.; Fujimoto, Y. Phenolic constituents from the fruit juice of *Flacourtia inermis*. *Nat. Prod. Res* **2012,** *26* (3), 278-281.

321. Alakolanga, A. G. A. W.; Siriwardene, A. M. D. A.; Savitri Kumar, N.; Jayasinghe, L.; Jaiswal, R.; Kuhnert, N. LC-MS^n identification and characterization of the phenolic compounds from the fruits of *Flacourtia indica* (Burm. F.) Merr. and *Flacourtia inermis* Roxb. *Food Research International* **2014,** *62*, 388-396.

322. Kim, W. J.; Lee, K. T.; Lee, H. J.; Cho, S. T. Extractives from wood of *Euonymus japonica*. *Journal of Korean Forest Society* **2014,** *103* (1), 113-121.

323. Sulaiman, C. T.; Thushar, K. V.; George, S.; Balachandran, I. Phenolic characterisation of selected *Salacia* species using LC-ESI-MS/MS analysis. *Natural Product Research* **2014,** *28* (13), 1021-1024.

324. Bokesch, H. R.; McKee, T. C.; Currens, M. J.; Gulakowski, R. J.; McMahon, J. B.; Cardellina, J. H.; Boyd, M. R. HIV-inhibitory natural products. Part 27. HIV-inhibitory gallotannins from *Lepidobotrys stauditi*. *Nat. Prod. Lett.* **1996,** *8*, 133-136.

325. Hammoda, H. M.; Ghazy, N. M.; Harraz, F. M.; Radwan, M. M.; Elsohly, M. A.; Abdallah, I. I. Chemical constituents from *Tribulus terrestris* and screening of their antioxidant activity. *Phytochem.* **2013,** *92*, 153-159.

326. Lin, J. H.; Lin, M. F. Tannins and related compounds from *Erodium moschatum* (L.) L'Her . *J. Food Drug Anal.* **1997,** *5*, 347-354.

327. Fecka, I.; Cisowski, W. Tannins and flavonoids from the *Erodium cicutarium* herb. *Zeitschrift fur Naturforschung Section B-A Journal of Chemical Sciences* **2005,** *60* (5), 555-560.

328. Tuominen, A.; Toivonen, E.; Mutikainen, P.; Salminen, J. P. Defensive strategies in *Geranium sylvaticum*. Part 1: organ-specific distribution of water-soluble tannins, flavonoids and phenolic acids. *Phytochem.* **2013,** *95*, 394-407.

329. Miliauskas, G.; van Beek, T. A.; Venskutonis, P. R.; Linssen, J. P. H.; de Waard, P. Antioxidative activity of *Geranium macrorrhizum*. *Eur. Food Res. Technol.* **2004,** *218*, 253-261.

330. Bouchet, N.; Levesque, J.; Blond, A.; Bodo, B.; Pousset, J. L. 1,3-di-*O*-galloylquinic acid from *Guiera senegalensis*. *Phytochem.* **1996,** *42* (1), 189-190.

331. Bouchet, N.; Barrier, L.; Fauconneau, B. Radical scavenging activity and antioxidant properties of tannins from *Guiera senegalensis* (Combretaceae). *Phytotherapy Research* **1998,** *12*, 159-162.

332. Bouchet, N.; Lévesque, J.; Pousset, J. L. HPLC isolation, identification and quantification of tannins from *Guiera senegalensis*. *Phytochemical Analysis* **2000,** *11*, 52-56.

333. Lin, T. C.; Hsu, F. L. Tannins and related compounds from *Terminalia arborea*. *Chinese Pharmaceutical Journal* **1996,** *48* (2), 167-175.

334. Pfundstein, B.; El Desouky, S. K.; Hull, W. E.; Haubner, R.; Erben, G.; Owen, R. W. Polyphenolic compounds in the fruits of Egyptian medicinal plants (*Terminalia bellerica*, *Terminalia chebula* and *Terminalia horrida*): Characterization, quantitation and determination of antioxidant capacities. *Phytochem.* **2010,** *71* (10), 1132-1148.

335. Santos, S. A.; Vilela, C.; Freire, C. S.; Neto, C. P.; Silvestre, A. J. Ultra-high performance liquid chromatography coupled to mass spectrometry applied to the identification of valuable phenolic compounds from Eucalyptus wood. *J. Chromatogr. B Analyt. Technol. Biomed. Life Sci.* **2013,** *938*, 65-74.

336. Santos, S. A.; Freire, C. S.; Domingues, M. R.; Silvestre, A. J.; Pascoal, N. C. Characterization of phenolic components in polar extracts of *Eucalyptus globulus* Labill. bark by high-performance liquid chromatography-mass spectrometry. *J. Agric. Food Chem.* **2011,** *59* (17), 9386-9393.

337. Singab, A. N.; Ayoub, N.; Al-Sayed, E.; Martiskainen, O.; Sinkkonen, J.; Pihlaja, K. Phenolic Constituents of *Eucalyptus camaldulensis* Dehnh, with Potential Antioxidant and Cytotoxic Activities. *Records of Natural Products* **2011,** *5* (4), 271-280.

338. Fan, X.; Lin, S.; Zhu, C.; Liu, Y.; Hu, J.; Chen, X.; Wang, W.; Chen, N.; Shi, J. [Aromatic constituents of *Heteroplexis micocephal* and their bioactivities]. *Zhongguo Zhong. Yao Za Zhi.* **2011,** *36* (1), 48-56.

339. Ines, S.; Ines, B.; Wissem, B.; Mohamed, B. S.; Nawel, H.; joux-Franca, M. G.; Kamel, G.; Leila, C. G. *In vitro* antioxidant and antigenotoxic potentials of 3,5-O-di-galloylquinic acid extracted from *Myrtus communis* leaves and modulation of cell gene expression by H2O2. *J Appl Toxicol.* **2012,** *32* (5), 333-341.

340. Yoshimura, M.; Amakura, Y.; Tokuhara, M.; Yoshida, T. Polyphenolic compounds isolated from the leaves of *Myrtus communis*. *J. Nat. Med* **2008,** *62* (3), 366-368.

341. Taamalli, A.; Iswaldi, I.; Arraez-Roman, D.; Segura-Carretero, A.; Fernandez-Gutierrez, A.; Zarrouk, M. UPLC-QTOF/MS for a rapid characterisation of phenolic compounds from leaves of *Myrtus communis* L. *Phytochemical Analysis* **2014,** *25* (1), 89-96.

342. Romani, A.; Campo, M.; Pinelli, P. HPLC/DAD/ESI-MS analyses and anti-radical activity of hydrolyzable tannins from different vegetal species. *Food Chem.* **2012,** *130* (1), 214-221.

343. Nikhat, F.; Satynarayanaa, D.; Joshia, A. B. Phytochemical and pharmacological investigation of roots of *Syzygium cuminii* (L) Skeel. *Asian J. Res. Chem.* **2008,** *1*, 22-26.

344. Handoussa, H.; Hanafi, R.; Eddiasty, I.; El-Gendy, M.; El Khatib, A.; Linscheid, M.; Mahran, L.; Ayoub, N. Anti-inflammatory and cytotoxic activities of dietary phenolics isolated from *Corchorus olitorius* and *Vitis vinifera*. *Journal of Functional Foods* **2013,** *5* (3), 1204-1216.

345. Azuma, K.; Nakayama, M.; Koshioka, M.; Ippoushi, K.; Yamaguchi, Y.; Kohata, K.; Yamauchi, Y.; Ito, H.; Higashio, H. Phenolic Antioxidants from the Leaves of *Corchorus olitorius* L. *J. Agric. Food Chem.* **1999,** *47* (10), 3963-3966.

346. Taiwo, B. J.; Taiwo, G. O.; Olubiyi, O. O.; Fatokun, A. A. Polyphenolic compounds with anti-tumour potential from *Corchorus olitorius* (L.) Tiliaceae, a Nigerian leaf vegetable. *Bioorganic & Medicinal Chemistry Letters* **2016,** *26* (15), 3404-3410.

347. Ramirez-Rodrigues, M. M.; Plaza, M. L.; Azeredo, A.; Balaban, M. O.; Marshall, M. R. Physicochemical and phytochemical properties of cold and hot water extraction from *Hibiscus sabdariffa*. *J. Food Sci.* **2011,** *76* (3), C428-C435.

348. Zhen, J.; Villani, T.; Guo, Y.; Qi, Y.; Chin, K.; Pan, M. H.; Ho, C. T.; Simon, J. E.; Wu, Q. Phytochemistry, antioxidant capacity, total phenolic content and anti-inflammatory activity of *Hibiscus sabdariffa* leaves. *Food Chem.* **2015,** (0).

349. Ifie, I.; Marshall, L. J.; Ho, P.; Williamson, G. *Hibiscus sabdariffa* (Roselle) extracts and wine: phytochemical profile, physicochemical properties, and carbohydrase inhibition. *J. Agric. Food Chem.* **2016,** *64* (24), 4921-4931.

350. Borras-Linares, I.; Fernandez-Arroyo, S.; Arraez-Roman, D.; Palmeros-Suarez, P. A.; Del Val-Diaz, R.; Andrade-Gonzales, I.; Fern+índez-Gutierrez, A.; Gomez-Leyva, J. F.; Segura-Carretero, A. Characterization of phenolic compounds, anthocyanidin, antioxidant and antimicrobial activity of 25 varieties of Mexican Roselle (*Hibiscus sabdariffa*). *Industrial Crops and Products* **2015,** *69* (0), 385-394.

351. Algamdi, N.; Mullen, W.; Crozier, A. Tea prepared from *Anastatica hirerochuntica* seeds contains a diversity of antioxidant flavonoids, chlorogenic acids and phenolic compounds. *Phytochem.* **2011,** *72* (2-3), 248-254.

352. Brandl, W.; Herrmann, K. Hydroxycinnamic acid esters in brassicaceous vegetables and garden cress. *Z. Lebensm. Unters. -Forsch.* **1983,** *176* (6), 444-447.

353. Jansen, J. J.; Allwood, J. W.; Marsden-Edwards, E.; van der Putten, W. H.; Goodacre, R.; van Dam, N. M. Metabolomic analysis of the interaction between plants and herbivores. 5 ed.; 2009; pp 150-161.

354. Harbaum, B.; Hubbermann, E. M.; Wolff, C.; Herges, R.; Zhu, Z.; Schwarz, K. Identification of flavonoids and hydroxycinnamic acids in pak choi varieties (*Brassica campestris* L. ssp. *chinensis* var. *communis*) by HPLC-ESI-MSn and NMR and their quantification by HPLC-DAD. *J. Agric. Food Chem.* **2007,** *55* (20), 8251-8260.

355. Jaiswal, R.; Patras, M. A.; Eravuchira, P. J.; Kuhnert, N. Profile and characterization of the chlorogenic acids in green Robusta coffee beans by LC-MS(n): identification of seven new classes of compounds. *J. Agric. Food Chem.* **2010,** *58* (15), 8722-8737.

356. Lin, L. Z.; Harnly, J. M. Phenolic component profiles of mustard greens, yu choy, and 15 other brassica vegetables. *J Agric. Food Chem.* **2010,** *58* (11), 6850-6857.

357. Lin, L. Z.; Harnly, J. M. Identification of the phenolic components of collard greens, kale, and Chinese broccoli. *J. Agric. Food Chem.* **2009,** *57* (16), 7401-7408.

358. Wubshet, S. G.; Schmidt, J. S.; Wiese, S.; Staerk, D. High-resolution screening combined with HPLC-HRMS-SPE-NMR for identification of potential health-promoting constituents in Sea Aster and Sea Rocket: New Nordic food ingredients. *J. Agric. Food Chem.* **2013,** *61* (36), 8616-8623.

359. Siracusa, L.; Kulisic-Bilusic, T.; Politeo, O.; Krause, I.; Dejanovic, B.; Ruberto, G. Phenolic composition and antioxidant activity of aqueous infusions from *Capparis spinosa* L. and *Crithmum maritimum* L. before and after submission to a two-step in vitro digestion model. *J. Agric. Food Chem.* **2011,** *59* (23), 12453-12459.

360. Bakr, R. O.; El Bishbishy, M. H. Profile of bioactive compounds of *Capparis spinosa* var. *aegyptiaca* growing in Egypt. *Revista Brasileira de Farmacognosia-Brazilian Journal of Pharmacognosy* **2016,** *26* (4), 514-520.

361. Zunjar, V.; Mammen, D.; Trivedi, B. Antioxidant activities and phenolics profiling of different parts of *Carica papaya* by LCMS-MS. *Natural Product Research* **2015,** *29* (22), 2097-2099.

362. Kashiwada, Y.; Ahmed, F. A.; Kurimoto, S.; Kim, S. Y.; Shibata, H.; Fujioka, T.; Takaishi, Y. New alpha-glucosides of caffeoyl quinic acid from the leaves of *Moringa oleifera* Lam. *J. Nat. Med.* **2012,** *66* (1), 217-221.

363. Khoza, B. S.; Chimuka, L.; Mukwevho, E.; Steenkamp, P. E.; Madala, N. E. The effect of temperature on pressurised hot water extraction of pharmacologically-important metabolites as analysed by UPLC-qTOF-MS and PCA. *Evidence-Based Complementary and Alternative Medicine* **2014**.

364. Nouman, W.; Anwar, F.; Gull, T.; Newton, A.; Rosa, E.; Dominguez-Perles, R. Profiling of polyphenolics, nutrients and antioxidant potential of germplasm's leaves from seven cultivars of *Moringa oleifera* Lam. *Industrial Crops and Products* **2016,** *83*, 166-176.

365. Makita, C.; Chimuka, L.; Cukrowska, E.; Steenkamp, P. A.; Kandawa-Schutz, M.; Ndhlala, A. R.; Madala, N. E. UPLC-qTOF-MS profiling of pharmacologically important chlorogenic acids and associated glycosides in *Moringa ovalifolia* leaf extracts. *South African Journal of Botany* **2017,** *108*, 193-199.

366. Perez, C.; Mendiola, J. A.; Quirantes-Pine, R.; Ibanez, E.; Segura-Carretero, A. Green downstream processing using supercritical carbon dioxide, CO_2-expanded ethanol and pressurized hot water extractions for recovering bioactive compounds from *Moringa oleifera* leaves. *Journal of Supercritical Fluids* **2016,** *116*, 90-100.

367. Clifford, M. N. Miscellaneous phenols in foods and beverages — nature, occurrence and dietary burden. *J. Sci. Food Agric.* **2000,** *80*, 1126-1137.

368. Palafox-Carlos, H.; Yahia, E. M.; González-Aguilar, G. A. Identification and quantification of major phenolic compounds from mango (*Mangifera indica*, cv. Ataulfo) fruit by HPLC–DAD–MS/MS-ESI and their individual contribution to the antioxidant activity during ripening. *Food Chem.* **2012,** *135*, 105-111.

369. Hou, A. J.; Peng, L. Y.; Liu, Y. Z.; Lin, Z. W.; Sun, H. D. Two new gallotannins from *Pistacia weinmannifolia*. *Chinese Chemical Letters* **2000,** *11* (1), 53-56.

370. Hou, A. J.; Peng, L. Y.; Liu, Y. Z.; Lin, Z. W.; Sun, H. D. Gallotannins and related polyphenols from *Pistacia weinmannifolia*. *Planta Med.* **2000,** *66* (7), 624-626.

371. Zhao, X.; Sun, H.; Hou, A.; Zhao, Q.; Wei, T.; Xin, W. Antioxidant properties of two gallotannins isolated from the leaves of *Pistacia weinmannifolia*. *Biochim. Biophys. Acta* **2005,** *1725* (1), 103-110.

372. Minami, K.; Nakasugi, T.; Sun, H. D.; Hou, A. J.; Ihara, M.; Morimoto, M.; Komai, K. Isolation and identification of histamine-release inhibitors from *Pistacia weinmannifolia* J. Pisson ex. Franch. *Journal of Natural Medicines* **2006,** *60*, 138-140.

373. Ben Ahmed, Z.; Yousfi, M.; Viaene, J.; Dejaegher, B.; Demeyer, K.; Mangelings, D.; Vander Heyden, Y. Antioxidant activities of *Pistacia atlantica* extracts modeled as a function of chromatographic fingerprints in order to identify antioxidant markers. *Microchemical Journal* **2016,** *128*, 208-217.

374. Bampouli, A.; Kyriakopoulou, K.; Papaefstathiou, G.; Louli, V.; Aligiannis, N.; Magoulas, K.; Krokida, M. Evaluation of total antioxidant potential of *Pistacia lentiscus* var. *chia* leaves extracts using UHPLC-HRMS. *Journal of Food Engineering* **2015,** *167*, 25-31.

375. Baratto, M. C.; Tattini, M.; Galardi, C.; Pinelli, P.; Romani, A.; Visioli, F.; Basosi, R.; Pogni, R. Antioxidant activity of galloyl quinic derivatives isolated from *P. lentiscus* leaves. *Free Radic. Res.* **2003,** *37* (4), 405-412.

376. Romani, A.; Pinelli, P.; Galardi, C.; Mulinacci, N.; Tattini, M. Identification and quantification of galloyl derivatives, flavonoid glycosides and anthocyanins in leaves of *Pistacia lentiscus* L. *Phytochem. Anal.* **2002,** *13* (2), 79-86.

377. Rodriguez-Perez, C.; Quirantes-Pine, R.; Amessis-Ouchemoukh, N.; Madani, K.; Segura-Carretero, A.; Fernandez-Gutierrez, A. A metabolite-profiling approach allows the identification of new compounds from *Pistacia lentiscus* leaves. *J. Pharm. Biomed. Anal.* **2013,** *77*, 167-174.

378. Foddai, M.; Kasabri, V.; Afifi, F. U.; Azara, E.; Petretto, G. L.; Pintore, G. In vitro inhibitory effects of Sardinian *Pistacia lentiscus* L. and *Pistacia terebinthus* L. on metabolic enzymes: Pancreatic lipase, α-amylase, and α-glucosidase. *Starch - Stärke* **2014,** *66*, 1-9.

379. Ersan, S.; Ustundag, U. G.; Carle, R.; Schweiggert, R. M. Identification of phenolic compounds in red and green Pistachio (*Pistacia vera* L.) hulls (exo- and mesocarp) by HPLC-DAD-ESI-(HR)-MS^n. *J. Agric. Food Chem.* **2016,** *64*, 5334-5344.

380. Abu-Reidah, I. M.; Ali-Shtayeh, M. S.; Jamous, R. M.; Arraez-Romad, D.; Segura-Carratero, A. HPLC-DAD-ESI-MS/MS screening of bioactive components from *Rhus coriaria* L. (Sumac) fruits. *Food Chem.* **2015,** *166*, 179-191.

381. Marzouk, M. S.; Moharram, F. A.; Haggag, E. G.; Ibrahim, M. T.; Badary, O. A. Antioxidant flavonol glycosides from *Schinus molle*. *Phytother. Res.* **2006,** *20* (3), 200-205.

382. Feuereisen, M. M.; Hoppe, J.; Zimmermann, B. F.; Weber, F.; Schulze-Kaysers, N.; Schieber, A. Characterization of phenolic compounds in Brazilian Pepper (*Schinus terebinthifolius* Raddi) exocarp. *J. Agric. Food Chem.* **2014,** *62* (26), 6219-6226.

383. He, Z.; Xia, W.; Liu, Q.; Chen, J. Identification of a new phenolic compound from Chinese olive (*Canarium album* L.) fruit. *Eur. Food Res. Technol.* **2009,** *228*, 339-343.

384. Risch, B.; Herrmann, K.; Wray, V.; Grotjahn, L. 2'-(*E*)-*O*-*p*-coumaroylgalactaric acid and 2'-(*E*)-*O*-feruloylgalactaric acid in citrus. *Phytochem.* **1987,** *26*, 509-510.

385. Risch, B.; Herrmann, K.; Wray, V. (E)-O-p-Coumaroyl-, (E)-O-Feruloyl-derivatives of glucaric acid in citrus. *Phytochem.* **1988,** *27* (10), 3327-3329.

386. Risch, B.; Herrmann, K. Contents of hydroxycinnamic acid derivatives in citrus fruits. *Z. Lebensm. Unters. - Forsch.* **1988,** *187*, 530-534.

387. Wang, Y. C.; Chuang, Y. C.; Ku, Y. H. Quantitation of bioactive compounds in citrus fruits cultivated in Taiwan. *Food Chem.* **2007,** *102* (4), 1163-1171.

388. Sdiri, S.; Navarro, P.; Monterde, A.; Benabda, J.; Salvador, A. Effect of postharvest degreening followed by a cold-quarantine treatment on vitamin C, phenolic compounds and antioxidant activity of early-season citrus fruit. *Postharvest Biology and Technology* **2012,** *65* (0), 13-21.

389. He, D.; Shan, Y.; Wu, Y.; Liu, G.; Chen, B.; Yao, S. Simultaneous determination of flavanones, hydroxycinnamic acids and alkaloids in citrus fruits by HPLC–DAD–ESI/MS. *Food Chem.* **2011,** *127* (2), 880-885.

390. Fuzfai, Z.; Molnar-Perl, I. Gas chromatographic-mass spectrometric fragmentation study of flavonoids as their trimethylsilyl derivatives: analysis of flavonoids, sugars, carboxylic and amino acids in model systems and in citrus fruits. *J Chromatogr. A* **2007,** *1149* (1), 88-101.

391. Tao, B.; Ye, F.; Li, H.; Hu, Q.; Xue, S.; Zhao, G. Phenolic profile and in vitro antioxidant capacity of insoluble dietary fiber powders from citrus (*Citrus junos* Sieb. ex Tanaka) pomace as affected by ultrafine grinding. *J. Agric. Food Chem.* **2014**.

392. Girones-Vilaplana, A.; Moreno, D. A.; Garcia-Viguera, C. Phytochemistry and biological activity of Spanish citrus fruits. *Food Funct.* **2014,** *5* (4), 764-772.

393. Nogata, Y.; Sekiya, K.; Ohta, H.; Kusumoto, K. I.; Ishizu, T. Inhibitors of platelet lipoxygenase from Ponkan fruit. *Phytochem.* **2001,** *56* (7), 729-732.

394. Strack, D.; Gross, W.; Wray, V.; Grotjahn, L. Enzymic synthesis of caffeoylglucaric acid from chlorogenic acid and glucaric acid by a protein preparation from tomato cotyledons. *Plant Physiol.* **1987,** *83* (3), 475-478.

395. Ouattara, B.; Angenot, L.; Guissou, P.; Fondu, P.; Dubois, J.; Frederich, M.; Jansen, O.; van Heugen, J. C.; Wauters, J. N.; Tits, M. LC/MS/NMR analysis of isomeric divanilloylquinic acids from the root bark of *Fagara zanthoxyloides* Lam. *Phytochem.* **2004,** *65* (8), 1145-1151.

396. Pacifico, S.; Piccolella, S.; Galasso, S.; Fiorentino, A.; Kretschmer, N.; Pan, S. P.; Bauer, R.; Monaco, P. Influence of harvest season on chemical composition and bioactivity of wild rue plant hydroalcoholic extracts. *Food Chem. Toxicol.* **2016,** *90*, 102-111.

397. Yang, L. C.; Li, R.; Tan, J.; Jiang, Z. T. Polyphenolics composition of the leaves of *Zanthoxylum bungeanum* Maxim. grown in Hebei, China, and their radical scavenging activities. *J. Agric. Food Chem.* **2013,** *61* (8), 1772-1778.

398. Braguine, C. G.; Costa, E. S.; Magalhaes, L. G.; Rodrigues, V.; da Silva Filho, A. A.; Bastos, J. K.; Silva, M. L.; Cunha, W. R.; Januario, A. H.; Pauletti, P. M. Schistosomicidal evaluation of *Zanthoxylum naranjillo* and its isolated compounds against *Schistosoma mansoni* adult worms. *Zeitschrift fur Naturforschung Section C-A Journal of Biosciences* **2009,** *64* (11-12), 793-797.

399. Oszmianski, J.; Kalisz, S.; Aneta, W. The content of phenolic compounds in leaf tissues of White (*Aesculus hippocastanum* L.) and Red Horse Chestnut (*Aesculus carea* H.) colonized by the Horse Chestnut Leaf Miner (*Cameraria ohridella* Deschka & Dimic). *Molecules* **2014,** *19* (9), 14625-14636.

400. Chen, C. H.; Chen, P. Y.; Wang, K. C.; Lee, C. K. Rapid identification of the antioxidant constituent of *Koelreuteria henryi*. *Journal of the Chinese Chemical Society* **2010,** *57* (3A), 404-410.

401. Liu, L.; Zeng, Q. S.; Zhang, R. F.; We, Z. C.; Deng, Y. Y.; Zhang, Y.; Tang, X. J.; Zhang, M. W. Comparative Study on Phenolic Profiles and Antioxidant Activity of Litchi Juice Treated by High Pressure Carbon Dioxide and Thermal Processing. *Food Science and Technology Research* **2015,** *21* (1), 41-49.

402. Zhang, R. F.; Zeng, Q. S.; Deng, Y. Y.; Zhang, M. W.; Wei, Z. C.; Zhang, Y.; Tang, X. J. Phenolic profiles and antioxidant activity of litchi pulp of different cultivars cultivated in Southern China. *Food Chem.* **2013,** *136* (3-4), 1169-1176.

403. Sun, Y.; Li, H.; Hu, J.; Li, J.; Fan, Y. W.; Liu, X. R.; Deng, Z. Y. Qualitative and quantitative analysis of phenolics in *Tetrastigma hemsleyanum* and their antioxidant and antiproliferative activities. *J. Agric. Food Chem.* **2013,** *61* (44), 10507-10515.

404. Anttonen, M. J.; Karjalainen, R. O. High-performance liquid chromatography analysis of black currant (*Ribes nigrum* L.) fruit phenolics grown either conventionally or organically. *J. Agric. Food Chem.* **2006,** *54* (20), 7530-7538.

405. Makila, L.; Laaksonen, O.; Alanne, A. L.; Kortesniemi, M.; Kallio, H.; Yang, B. R. Stability of hydroxycinnamic acid derivatives, flavonol glycosides, and anthocyanins in black currant juice. *J. Agric. Food Chem.* **2016,** *64* (22), 4584-4598.

406. Jimenez-Aspee, F.; Theoduloz, C.; Vieira, M. N.; Rodriguez-Werner, M. A.; Schmalfuss, E.; Winterhalter, P.; Schmeda-Hirschmann, G. Phenolics from the Patagonian currants *Ribes* spp.: Isolation, characterization and cytoprotective effect in human AGS cells. *Journal of Functional Foods* **2016,** *26*, 11-26.

407. Duckstein, S. M.; Stintzing, F. C. Investigation on the phenolic constituents in *Hamamelis virginiana* leaves by HPLC-DAD and LC-MS/MS. *Anal. Bioanal. Chem.* **2011,** *401* (2), 677-688.

408. Salminen, J. P.; Shikov, A. N.; Karonen, M.; ozharitskaya, O. N.; im, J.; akarov, V. G.; iltunen, R.; alambosi, B. Rapid profiling of phenolic compounds of green and fermented *Bergenia crassifolia* L. leaves by UPLC-DAD-QqQ-MS and HPLC-DAD-ESI-QTOF-MS. *Natural Product Research* **2014,** *28* (19), 1530-1533.

409. Simirgiotis, M. J.; Quispe, C.; Areche, C.; Sepulveda, B. Phenolic compounds in Chilean Mistletoe (Quintral, *Tristerix tetrandus*) analyzed by UHPLC-Q/Orbitrap/MS/MS and Its antioxidant properties. *Molecules* **2016,** *21* (3).

410. Furbacher, T. R. Bioassay-guided isolation of potential antineoplastic natural products from Southwestern plants. University of Arizona, 2001.

411. Abdallah, H. M.; Farag, M. A.; Abdel-Naim, A. B.; Ghareib, S. A.; Abdel-Sattar, E. A. Mechanistic evidence of *Viscum schimperi* (Viscaceae) antihyperglycemic activity: from a bioactivity-guided approach to comprehensive metabolite profiling. *Phytotherapy Research* **2015,** *29* (11), 1737-1743.

412. Meddeb, E.; Charni, M.; Ghazouani, T.; Cozzolino, A.; Fratianni, F.; Raboudi, F.; Nazzaro, F.; Fattouch, S. Biochemical and molecular study of *Carpobrotus edulis* bioactive properties and their effects on *Dugesia sicula* (Turbellaria, Tricladida) regeneration. *Applied Biochemistry and Biotechnology* **2017,** 1-13.

413. Stintzing, F. C.; Kammerer, D.; Schieber, A.; Adama, H.; Nacoulma, O. G.; Carle, R. Betacyanins and phenolic compounds from *Amaranthus spinosus* L. and *Boerhavia erecta* L. *Zeitschrift fur Naturforschung C-A Journal of Biosciences* **2004,** *59* (1-2), 1-8.

414. Li, H.; Deng, Z.; Liu, R.; Zhu, H.; Draves, J.; Marcone, M.; Sun, Y.; Tsao, R. Characterization of phenolics, betacyanins and antioxidant activities of the seed, leaf, sprout, flower and stalk extracts of three *Amaranthus* species. *Journal of Food Composition and Analysis* **2015,** *37*, 75-81.

415. Maroli, A. S.; Nandula, V. K.; Dayan, F. E.; Duke, S. O.; Gerard, P.; Tharayil, N. Metabolic profiling and enzyme analyses indicate a potential role of antioxidant systems in complementing glyphosate resistance in an *Amaranthus palmeri* biotype. *J. Agric. Food Chem.* **2015,** *63* (41), 9199-9209.

416. Paucar-Menacho, L. M.; Penas, E.; Duenas, M.; Frias, J.; Martinez-Villaluenga, C. Optimizing germination conditions to enhance the accumulation of bioactive compounds and the antioxidant activity of kiwicha (*Amaranthus caudatus*) using response surface methodology. *LWT - Food Science and Technology* **2016**.

417. Arens, N.; Backhaus, A.; Doll, S.; Fischer, S.; Seiffert, U.; Mock, H. P. Non-invasive presymptomatic detection of *Cercospora beticola* infection and identification of early metabolic responses in sugar beet. *Frontiers in Plant Science* **2016,** *7*.

418. An, R. B.; Sohn, D. H.; Jeong, G. S.; Kim, Y. C. In vitro hepatoprotective compounds from *Suaeda glauca*. *Arch. Pharm. Res.* **2008,** *31* (5), 594-597.

419. Shen, T.; Heo, S. I.; Wang, M. H. Involvement of the p38 MAPK and ERK signaling pathway in the anti-melanogenic effect of methyl 3,5-dicaffeoyl quinate in B16F10 mouse melanoma cells. *Chem. Biol. Interact.* **2012,** *199* (2), 106-111.

420. Chung, Y. C.; Chun, H. K.; Yang, J. Y.; Kim, J. Y.; Han, E. H.; Kho, Y. H.; Jeong, H. G. Tungtungmadic acid, a novel antioxidant, from *Salicornia herbacea*. *Arch. Pharm. Res.* **2005,** *28* (10), 1122-1126.

421. Kim, J. Y.; Cho, J. Y.; Ma, Y. K.; Park, K. Y.; Lee, S. H.; Ham, K. S.; Lee, H. J.; Park, K. H.; Moon, J. H. Dicaffeoylquinic acid derivatives and flavonoid glucosides from glasswort (*Salicornia herbacea* L.) and their antioxidative activity. *Food Chem.* **2011,** *125* (1), 55-62.

422. das Neves Costa, F.; Jerz, G.; de Souza Figueiredo, F.; Winterhalter, P.; Leitao, G. G. Solvent system selectivities in countercurrent chromatography using *Salicornia gaudichaudiana* metabolites as practical example with off-line electrospray mass-spectrometry injection profiling. *Journal of chromatography. A* **2015,** *1385*, 20-27.

423. Tuan, N. Q.; Lee, W.; Oh, J.; Kwak, S.; Lee, H. G.; Ferreira, D.; Bae, J. S.; Na, M. K. Quinic acid derivatives from *Salicornia herbacea* alleviate HMGB1-mediated endothelial dysfunction. *Journal of Functional Foods* **2015,** *15*, 326-338.

424. Cho, J. Y.; Kim, J. Y.; Lee, Y. G.; Lee, H. J.; Shim, H. J.; Lee, J. H.; Kim, S. J.; Ham, K. S.; Moon, J. H. Four new dicaffeoylquinic acid derivatives from Glasswort (*Salicornia herbacea* L.) and their antioxidative activity. *Molecules* **2016,** *21* (8).

425. Chang, S. W.; Kim, K. H.; Lee, I. K.; Choi, S. U.; Ryu, S. Y.; Lee, K. R. Phytochemical constituents of *Bistorta manshuriensis*. *Natural Product Sciences* **2009,** *15* (4), 234-240.

426. Guo, X. D.; Wu, C. S.; Ma, Y. J.; Parry, J.; Xu, Y. Y.; Liu, H.; Wang, M. Comparison of milling fractions of tartary buckwheat for their phenolics and antioxidant properties. *Food Research International* **2012,** *49* (1), 53-59.

427. Ren, Q.; Wu, C.; Ren, Y.; Zhang, J. Characterization and identification of the chemical constituents from tartary buckwheat (*Fagopyrum tataricum* Gaertn) by high performance liquid chromatography/photodiode array detector/linear ion trap FTICR hybrid mass spectrometry. *Food Chem* **2013,** *136* (3-4), 1377-1389.

428. Li, F.; Zhang, X.; Zheng, S.; Lu, K.; Zhao, G.; Ming, J. The composition, antioxidant and antiproliferative capacities of phenolic compounds extracted from tartary buckwheat bran [*Fagopyrum tartaricum* (L.) Gaerth]. *Journal of Functional Foods* **2016,** *22*, 145-155.

429. Karamac, M.; Biskup, I.; Kulczyk, A. Fractionation of Buckwheat seed phenolics and analysis of their antioxidant activity. *Polish Journal of Food and Nutrition Sciences* **2015,** *65* (4), 243-249.

430. Kurita, S.; Kashiwagi, T.; Ebisu, T.; Shimamura, T.; Ukeda, H. Identification of neochlorogenic acid as the predominant antioxidant in *Polygonum cuspidatum* leaves. *Ital. J. Food Sci.* **2016,** *28* (1), 25-31.

431. Liu, J.; Nakamura, S.; Zhuang, Y.; Yoshikawa, M.; Hussein, G. M.; Matsuo, K.; Matsuda, H. Medicinal flowers. XXXX . Structures of dihydroisocoumarin glycosides and inhibitory effects on aldose reducatase from the flowers of *Hydrangea macrophylla* var.*thunbergii*. *Chem. Pharm. Bull. (Tokyo)* **2013,** *61* (6), 655-661.

432. Zhao, T.; He, J.; Wang, X.; Ma, B.; Wang, X.; Zhang, L.; Li, P.; Liu, N.; Lu, J.; Zhang, X. Rapid detection and characterization of major phenolic compounds in Radix Actinidia chinensis Planch by ultra-performance liquid chromatography tandem mass spectrometry. *J. Pharm. Biomed. Anal.* **2014,** *98*, 311-320.

433. Llorent-Martinez, E. J.; Gouveia, S.; Castilho, P. C. Analysis of phenolic compounds in leaves from endemic trees from Madeira Island. A contribution to the chemotaxonomy of Laurisilva forest species. *Industrial Crops and Products* **2015,** *64* (0), 135-151.

434. Dastmalchi, K.; Flores, G.; Petrova, V.; Pedraza-Penalosa, P.; Kennelly, E. J. Edible neotropical blueberries: antioxidant and compositional fingerprint analysis. *J Agric. Food Chem.* **2011,** *59* (7), 3020-3026.

435. Pawlowska, A. M.; De, L. M.; Braca, A. Phenolics of *Arbutus unedo* L. (Ericaceae) fruits: identification of anthocyanins and gallic acid derivatives. *J Agric. Food Chem.* **2006,** *54* (26), 10234-10238.

436. Mosele, J. I.; Macia, A.; Romero, M. P.; Motilva, M. J. Stability and metabolism of *Arbutus unedo* bioactive compounds (phenolics and antioxidants) under *in vitro* digestion and colonic fermentation. *Food Chem.* **2016,** *201*, 120-130.

437. Jaiswal, R.; Jayasinghe, L.; Kuhnert, N. Identification and characterization of proanthocyanidins of 16 members of the *Rhododendron* genus (Ericaceae) by tandem LC-MS. *J Mass Spectrom.* **2012,** *47* (4), 502-515.

438. Moze, S.; Polak, T.; Gasperlin, L.; Koron, D.; Vanzo, A.; Poklar, U. N.; Abram, V. Phenolics in Slovenian bilberries (*Vaccinium myrtillus* L.) and blueberries (*Vaccinium corymbosum* L.). *J. Agric. Food Chem.* **2011,** *59* (13), 6998-7004.

439. Rodriguez-Mateos, A.; Cifuentes-Gomez, T.; Tabatabaee, S.; Lecras, C.; Spencer, J. P. Procyanidin, anthocyanin, and chlorogenic acid contents of highbush and lowbush blueberries. *J Agric. Food Chem.* **2012,** *60*, 5772-5778.

440. Ayaz, F. A.; Hayirlioglu-Ayaz, S.; Gruz, J.; Novak, O.; Strnad, M. Separation, characterization, and quantitation of phenolic acids in a little-known Blueberry (*Vaccinium arctostaphylos* L.) fruit by HPLC–MS. *J. Agric. Food Chem.* **2005,** *53* (21), 8116-8122.

441. Ieri, F.; Martini, S.; Innocenti, M.; Mulinacci, N. Phenolic distribution in liquid preparations of *Vaccinium myrtillus* L. and *Vaccinium vitis idaea* L. *Phytochem. Anal.* **2013,** *24* (5), 467-475.

442. Mane, C.; Loonis, M.; Juhel, C.; Dufour, C.; Malien-Aubert, C. Food grade lingonberry extract: polyphenolic composition and *in vivo* protective effect against oxidative stress. *J. Agric. Food Chem.* **2011,** *59* (7), 3330-3339.

443. Hokkanen, J.; Mattila, S.; Jaakola, L.; Pirttila, A. M.; Tolonen, A. Identification of phenolic compounds from lingonberry (*Vaccinium vitis-idaea* L.), bilberry (*Vaccinium myrtillus* L.) and hybrid bilberry (*Vaccinium x intermedium* Ruthe L.) leaves. *J. Agric. Food Chem.* **2009,** *57* (20), 9437-9447.

444. Bujor, O. C.; Le Bourvellec, C.; Volf, I.; opa, V. I.; ufour, C. Seasonal variations of the phenolic constituents in bilberry (*Vaccinium myrtillus* L.) leaves, stems and fruits, and their antioxidant activity. *Food Chem.* **2016,** *213*, 56-68.

445. Vasco, C.; Riihinen, K.; Ruales, J.; Kamal-Eldin, A. Chemical composition and phenolic compound profile of mortino (*Vaccinium floribundum* Kunth). *J Agric. Food Chem.* **2009,** *57* (18), 8274-8281.

446. Gavrilova, V.; Kajdzanoska, M.; Gjamovski, V.; Stefova, M. Separation, characterization and quantification of phenolic compounds in blueberries and red and black currants by HPLC-DAD-ESI-MSn. *J Agric. Food Chem.* **2011,** *59* (8), 4009-4018.

447. Kim, S. M.; Shang, Y. F.; Um, B. H. Preparative separation of chlorogenic acid by centrifugal partition chromatography from highbush blueberry leaves (*Vaccinium corymbosum* L.). *Phytochemical Analysis* **2010,** *21* (5), 457-462.

448. Ramirez, J. E.; Zambrano, R.; Sepulveda, B.; Kennelly, E. J.; Simirgiotis, M. J. Anthocyanins and antioxidant capacities of six Chilean berries by HPLC-HR-ESI-ToF-MS. *Food Chem.* **2015,** *176*, 106-114.

449. Wang, L. J.; Wu, J.; Wang, H. X.; Li, S. S.; Zheng, X. C.; Du, H.; Xu, Y. J.; Wang, L. S. Composition of phenolic compounds and antioxidant activity in the leaves of blueberry cultivars. *Journal of Functional Foods* **2015,** *16* (0), 295-304.

450. Li, C.; Feng, J.; Huang, W. Y.; An, X. T. Composition of polyphenols and antioxidant activity of rabbiteye blueberry (*Vaccinium ashei*) in Nanjing. *J. Agric. Food Chem.* **2013,** *61* (3), 523-531.

451. Stefkov, G.; Hristovski, S.; Petreska Stanoeva, J.; Stefova, M.; Melovski, L.; Kulevanova, S. Resource assessment and economic potential of bilberries (*Vaccinium myrtillus* and *Vaccinium uliginosum*) on Osogovo Mtn., R. Macedonia. *Industrial Crops and Products* **2014,** *61* (0), 145-150.

452. Ma, J.; Luo, X. D.; Protiva, P.; Yang, H.; Ma, C.; Basile, M. J.; Weinstein, I. B.; Kennelly, E. J. Bioactive novel polyphenols from the fruit of *Manilkara zapota* (Sapodilla). *J. Nat. Prod.* **2003,** *66* (7), 983-986.

453. van der Hooft, J. J.; Akermi, M.; Unlu, F. Y.; Mihaleva, V.; Roldan, V. G.; Bino, R. J.; De Vos, R. C.; Vervoort, J. Structural annotation and elucidation of conjugated phenolic compounds in black, green, and white tea extracts. *J Agric. Food Chem.* **2012,** *60* (36), 8841-8850.

454. Del Rio, D.; Stewart, A. J.; Mullen, W.; Burns, J.; Lean, M. E.; Brighenti, F.; Crozier, A. HPLC–MS^n analysis of phenolic compounds and purine alkaloids in green and black tea. *J. Agric. Food Chem.* **2004,** *52* (10), 2807-2815.

455. Cartwright, R. A.; Roberts, E. A. H. Theogallin, a polyphenol occurring in tea. *J. Sci. Food Agric.* **1954,** *5*, 593-597.

456. Cartwright, R. A.; Roberts, E. A. H. Theogallin as a galloyl ester of quinic acid. *Chem. Ind.* **1955,** 230-231.

457. Fang, R.; Redfern, S. P.; Kirkup, D.; Porter, E. A.; Kite, G. C.; Terry, L. A.; Berry, M. J.; Simmonds, M. S. J. Variation of theanine, phenolic, and methylxanthine compounds in 21 cultivars of *Camellia sinensis* harvested in different seasons. *Food Chem.* **2017,** *220*, 517-526.

458. Yagi, K.; Goto, K.; Nanjo, F. Identification of a major polyphenol and polyphenolic composition in leaves of *Camellia irrawadiensis*. *Chem. Pharm. Bull. (Tokyo)* **2009,** *57* (11), 1284-1288.

459. Liu, Q.; Zhang, Y. J.; Yang, C. R.; Xu, M. Phenolic antioxidants from green tea produced from *Camellia crassicolumna* Var. *multiplex*. *J Agric. Food Chem.* **2009,** *57* (2), 586-590.

460. Zhou, Z. H.; Yang, C. R. Chemical constituents of crude green tea, the material of Pu-er tea in Yunnan. *Acta Botanica Yunnanica* **2000,** *22*, 343-350.

461. Clifford, M. N.; Ramìrez-Martìnez, J. R. Chlorogenic acids and purine alkaloid content of Maté (*Ilex paraguariensis*) leaf and beverage. *Food Chem.* **1990,** *35*, 13-21.

462. Filip, R.; Lopez, P.; Giberti, G.; Coussio, J.; Ferraro, G. Phenolic compounds in seven South American *Ilex* species. *Fitoterapia* **2001,** *72* (7), 774-778.

463. Filip, R.; Ferraro, G.; Gabriela, M. A.; Anesini, C. *Ilex brasiliensis*: phytochemical composition and mechanism of action against the proliferation of a lymphoma cell line. *J. Food Biochem.* **2008,** *32*, 752-765.

464. Kerr, M.; Fischer, J. E.; Purushotham, K. R.; Gao, D.; Nakagawa, Y.; Maeda, N.; Ghanta, V.; Hiramoto, R.; Chegini, N.; Humphreys Beher, M. G. Characterization of the synthesis and expression of the GTA-kinase from transformed and normal rodent cells. *Biochim. Biophys. Acta* **1994,** *1218*, 375-387.

465. Jaiswal, R.; Sovdat, T.; Vivan, F.; Kuhnert, N. Profiling and characterization by LC-MS^n of the chlorogenic acids and hydroxycinnamoylshikimate esters in maté (*Ilex paraguariensis*). *J. Agric. Food Chem.* **2010,** *58* (9), 5471-5484.

466. de Souza, L. M.; Dartora, N.; Scoparo, C. T.; Cipriani, T. R.; Gorin, P. A.; Iacomini, M.; Sassaki, G. L. Comprehensive analysis of mate (*Ilex paraguariensis*) compounds: development of chemical strategies for matesaponin analysis by mass spectrometry. *J Chromatogr. A* **2011,** *1218* (41), 7307-7315.

467. Dugo, P.; Cacciola, F.; Donato, P.; Jacques, R. A.; Caramao, E. B.; Mondello, L. High efficiency liquid chromatography techniques coupled to mass spectrometry for the characterization of maté extracts. *J. Chromatogr. A* **2009,** *1216* (43), 7213-7221.

468. Peres, R. G.; Tonin, F. G.; Tavares, M. F.; Rodriguez-Amaya, D. B. HPLC-DAD-ESI/MS identification and quantification of phenolic compounds in *Ilex paraguariensis* beverages and on-line evaluation of individual antioxidant activity. *Molecules.* **2013,** *18* (4), 3859-3871.

469. Souza, A. H. P.; Correa, R. C. G.; Barros, L.; Calhelha, R. C.; Santos-Buelga, C.; Peralta, R. M.; Bracht, A.; Matsushita, M.; Ferreira, I. C. F. R. Phytochemicals and bioactive properties of *Ilex paraguariensis*: An in-vitro comparative study between the whole plant, leaves and stems. *Food Research International* **2015,** *78*, 286-294.

470. Negishi, O.; Negishi, Y.; Yamaguchi, F.; Sugahara, T. Deodorization with ku-ding-cha containing a large amount of caffeoyl quinic acid derivatives. *J Agric. Food Chem.* **2004,** *52* (17), 5513-5518.

471. Thuong, P. T.; Su, N. D.; Ngoc, T. M.; Hung, T. M.; Dang, N. H.; Thuan, N. D.; Bae, K. H.; Oh, W. K. Antioxidant activity and principles of Vietnam bitter tea *Ilex kudingcha*. *Food Chem.* **2009,** *113*, 139-145.

472. Peng, B.; Qiao, C. F.; Zhao, J.; Huang, W. H.; Hu, D. J.; Liu, H. G.; Li, S. P. Simultaneous determination of flavonoids, isochlorogenic acids and triterpenoids in *Ilex hainanensis* using high performance liquid chromatography coupled with diode array and evaporative light scattering detection. *Molecules.* **2013,** *18* (3), 2934-2941.

473. Jiang, Y. P.; Li, H.; Pan, X. Z.; Sun, X. G.; Tang, Q. F.; Shao, M. [Chemical constituents from the roots of *Ilex pubescens*]. *Zhong. Yao Cai.* **2013,** *36* (11), 1774-1778.

474. Che, Y.; Wang, Z.; Zhu, Z.; Ma, Y.; Zhang, Y.; Gu, W.; Zhang, J.; Rao, G. Simultaneous qualitation and quantitation of chlorogenic acids in Kuding Tea using ultra-high-performance liquid chromatography-diode array detection coupled with linear ion trap Orbitrap mass spectrometer. *Molecules* **2016,** *21* (12), 1728 doi:10.3390/molecules21121728.

475. Jaiswal, R.; Halabi, E. A.; Karar, M. G.; Kuhnert, N. Identification and characterisation of the phenolics of *Ilex glabra* L. Gray (Aquifoliaceae) leaves by liquid chromatography tandem mass spectrometry. *Phytochem.* **2014,** *106*, 141-155.

476. Chen, Y. L.; Hwang, T. L.; Yu, H. P.; Fang, J. Y.; Chong, K. Y.; Chang, Y. W.; Chen, C. Y.; Yang, H. W.; Chang, W. Y.; Hsieh, P. W. *Ilex kaushue* and Its bioactive component 3,5-dicaffeoylquinic acid protected mice from lipopolysaccharide-induced acute lung injury. *Scientific Reports* **2016,** *6*, 34243; doi: 10.1038/srep34243.

477. Funk, V. A.; Susana, A.; Steussy, T. F.; Robinson, H. E. Classification of Compositae. In *Systematics, Evolution, and Biogeography of Compositae.*, Funk, V. A.; Susana, A.; Steussy, T. F.; Bayer, R. J., Eds.; International Association for Plant Taxonomy: Vienna, 2009; pp 171-189.

478. Nugroho, A.; Kim, K. H.; Lee, K. R.; Alam, M. B.; Choi, J. S.; Kim, W. B.; Park, H. J. Qualitative and quantitative determination of the caffeoylquinic acids on the Korean mountainous vegetables used for chwinamul and their peroxynitrite-scavenging effect. *Arch. Pharm. Res.* **2009,** *32* (10), 1361-1367.

479. Wang, Y.; Liu, B. Preparative isolation and purification of dicaffeoylquinic acids from the *Ainsliaea fragrans* champ by high-speed counter-current chromatography. *Phytochemical Analysis* **2007,** *18* (5), 436-440.

480. Chen, X.; Miao, J.; Wang, H.; Zhao, F.; Hu, J.; Gao, P.; Wang, Y.; Zhang, L.; Yan, M. The anti-inflammatory activities of *Ainsliaea fragrans* Champ. extract and its components in lipopolysaccharide-stimulated RAW264.7 macrophages through inhibition of NF-kappa B pathway. *J. Ethnopharmacol.* **2015,** *170*, 72-80.

481. Kim, H. M.; Lee, D. G.; Cho, E. J. Analysis of phenolic compounds in chwinamul by HPLC/UV . *Horticulture, Environement and Biotechnology* **2013,** *54* (2), 183-189.

482. Kim, T.; Jo, C.; Kim, H. S.; Park, Y. M.; Wu, Y. X.; Cho, J. H.; Kim, T. H. Chemical constituents from *Ainsliaea acerifolia* as potential anti-obesity agents. *Phytochemistry Letters* **2016,** *16*, 146-151.

483. Maruta, Y.; Kawabata, J.; Niki, R. Antioxidative caffeoylquinic acid-derivatives in the roots of Burdock (*Arctium-Lappa* L). *J. Agric. Food Chem.* **1995,** *43* (10), 2592-2595.

484. Saleem, A.; Walshe-Roussel, B.; Harris, C.; Asim, M.; Tamayo, C.; Sit, S.; Arnason, J. T. Characterisation of phenolics in Flor-Essence--a compound herbal product and its contributing herbs. *Phytochem. Anal.* **2009,** *20* (5), 395-401.

485. da Silva, L. M.; Allemand, A.; Mendes, D. A.; Dos Santos, A. C.; Andre, E.; de Souza, L. M.; Cipriani, T. R.; Dartora, N.; Marques, M. C.; Baggio, C. H.; Werner, M. F. Ethanolic extract of roots from *Arctium lappa* L. accelerates the healing of acetic acid-induced gastric ulcer in rats: Involvement of the antioxidant system. *Food Chem. Toxicol.* **2013,** *51*, 179-187.

486. Haghi, G.; Hatami, A.; Mehran, M. UPLC and HPLC of caffeoyl esters in wild and cultivated *Arctium lappa* L. *Food Chem.* **2013,** *138* (1), 321-326.

487. Carlotto, J.; da Silva, L. M.; Dartora, N.; Maria-Ferreira, D.; Sabry, D.; Filho, A. P.; de Paula Werner, M. F.; Sassaki, G. L.; Gorin, P. A.; Iacomini, M.; Cipriani, T. R.; de Souza, L. M. Identification of a dicaffeoylquinic acid isomer from Arctium lappa with a potent anti-ulcer activity. *Talanta* **2015,** *135*, 50-57.

488. Jaiswal, R.; Kuhnert, N. Identification and characterization of five new classes of chlorogenic acids in burdock (*Arctium lappa* L.) roots by liquid chromatography/tandem mass spectrometry. *Food & Funct.* **2011,** *2* (1), 63-71.

489. Liu, J.; Cai, Y. Z.; Wong, R. N.; Lee, C. K.; Tang, S. C.; Sze, S. C.; Tong, Y.; Zhang, Y. Comparative analysis of caffeoylquinic acids and lignans in roots and seeds among various burdock (*Arctium lappa*) genotypes with high antioxidant activity. *J Agric. Food Chem.* **2012,** *60* (16), 4067-4075.

490. Tousch, D.; Bidel, L. P.; Cazals, G.; Ferrare, K.; Leroy, J.; Faucanie, M.; Chevassus, H.; Tournier, M.; Lajoix, A. D.; Azay-Milhau, J. Chemical analysis and antihyperglycemic activity of an original extract from Burdock roots (*Arctium lappa*). *J. Agric. Food Chem.* **2014**.

491. Bai, J. P.; Hu, X. L.; Jiang, X. W.; Tian, X.; Zhao, Q. C. Caffeic acids from roots of *Arctium lappa* and their neuroprotective activity. *Chinese Traditional and Herbal Drugs* **2015,** *2015*, 163-168.

492. Tian, X.; An, L.; Gao, L. Y.; Bai, J. P.; Wang, J.; Meng, W. H.; Ren, T. S.; Zhao, Q. C. Compound MQA, a caffeoylquinic acid derivative, protects against NMDA-induced neurotoxicity and potential mechanisms *in vitro*. *CNS Neuroscience & Therapeutics* **2015,** *21* (7), 575-584.

493. Jiang, X. W.; Bai, J. P.; Zhang, Q.; Hu, X. L.; Tian, X.; Zhu, J.; Liu, J.; Meng, W. H.; Zhao, Q. C. Caffeoylquinic acid derivatives from the roots of *Arctium lappa* L. (burdock) and their structure-activity relationships (SARs) of free radical scavenging activities. *Phytochemistry Letters* **2016,** *15*, 159-163.

494. Shabana, M. M.; El-Sherei, M. M.; Moussa, M. Y.; Sleem, A. A.; Abdallah, H. M. Investigation of phenolic constituents of *Carduncellus eriocephalus* Boiss. var. *albiflora* Gauba and their biological activities. *Natural Product Communications* **2007,** *2* (8), 823-828.

495. Li, R.; Liu, S. K.; Song, W.; Wang, Y.; Li, Y. J.; Qiao, X.; Liang, H.; Ye, M. Chemical analysis of the Tibetan herbal medicine *Carduus acanthoides* by UPLC/DAD/qTOF-MS and simultaneous determination of nine major compounds. *Anal. Methods* **2014,** DOI: 10.1039/C4AY01138D.

496. Jaiswal, R.; Deshpande, S.; Kuhnert, N. Profiling the chlorogenic acids of R*udbeckia hirta*, *Helianthus tuberosus*, *Carlina acaulis* and *Symphyotrichum novae-angliae* leaves by LC-MS(n). *Phytochem. Anal.* **2011,** *22*, 432-441.

497. Flamini, G.; Antognoli, E.; Morelli, I. Two flavonoids and other compounds from the aerial parts of *Centaurea bracteata* from Italy. *Phytochem.* **2001,** *57* (4), 559-564.

498. Abbet, C.; Slacanin, I.; Corradi, E.; De Mieri, M.; Hamburger, M.; Potterat, O. Comprehensive analysis of *Cirsium spinosissimum* Scop., a wild alpine food plant. *Food Chem.* **2014,** *160* (0), 165-170.

499. Nugroho, A.; Lim, S. C.; Byeon, J. S.; Choi, J. S.; Park, H. J. Simultaneous quantification and validation of caffeoylquinic acids and flavonoids in *Hemistepta lyrata* and peroxynitrite-scavenging activity. *J. Pharm. Biomed. Anal.* **2013,** *76*, 139-144.

500. Nugroho, A.; Choi, J. S.; Park, H. J.; Kim, M. H.; Lim, S. C.; Choi, J. W. Validation of high-performance liquid chromatography analysis on phenolic substances of *Cirsium setidens* and sedative effect of pectolinarin as the active principle. *Natural Product Sciences* **2011,** *17* (4), 342-349.

501. Jaiswal, R.; Kiprotich, J.; Kuhnert, N. Determination of the hydroxycinnamate profile of 12 members of the Asteraceae family. *Phytochem.* **2011,** *72* (8), 781-790.

502. Slanina, J.; Paulová, H.; Humpa, O.; Bochoráková, H.; Taborárská, E. 1,5-Dicaffeoylquinic acid, and antioxidant component of *Cynara cardunculus* leaves. *Scripta Medica* **1999,** *72*, 9-18.

503. Pandino, G.; Courts, F. L.; Lombardo, S.; Mauromicale, G.; Williamson, G. Caffeoylquinic acids and flavonoids in the immature inflorescence of globe artichoke, wild cardoon, and cultivated cardoon. *J. Agric. Food Chem.* **2010,** *58* (2), 1026-1031.

504. Gouveia, S. C.; Castilho, P. C. Phenolic composition and antioxidant capacity of cultivated artichoke, Madeira cardoon and artichoke-based dietary supplements. *Food Research International* **2012,** *48* (2), 712-724.

505. Ramos, P. A. B.; Santos, S. A. O.; Guerra, Ã. R.; Guerreiro, O.; Freire, C. S. R.; Rocha, S. M.; Duarte, M. F.; Silvestre, A. J. D. Phenolic composition and antioxidant activity of different morphological parts of *Cynara cardunculus* L. var. *altilis* (DC). *Industrial Crops and Products* **2014,** *61* (0), 460-471.

506. Schütz, K.; Kammerer, D.; Carle, R.; Schieber, A. Identification and quantification of caffeoylquinic acids and flavonoids from artichoke (*Cynara scolymus* L.) heads, juice, and pomace by HPLC-DAD-ESI/MS(n). *J. Agric. Food Chem.* **2004,** *52* (13), 4090-4096.

507. Zhu, X. F.; Zhang, H. X.; Lo, R. Three di-O-caffeoylquinic acid derivatives from the heads of *Cynara scolymus* L. *Nat. Prod. Res.* **2009,** *23* (6), 527-532.

508. Pereira, C.; Barros, L.; Carvalho, A. M.; Santos-Buelga, C.; Ferreira, I. C. Infusions of artichoke and milk thistle represent a good source of phenolic acids and flavonoids. *Food & Funct.* **2015,** *6* (1), 55-61.

509. Wu, J.; Qian, Y.; Mao, P.; Chen, L.; Lu, Y.; Wang, H. Separation and identification of phenolic compounds in canned artichoke by LC/DAD/ESI-MS using core-shell C18 column: A comparative study. *J Chromatogr. B Analyt. Technol. Biomed. Life Sci.* **2012**.

510. Wei, H.; Ma, G.; Peng, Y.; He, C.; Xiao, P. Chemical constituents of the roots of *Dolomiaea souliei*. *Chemistry Of Natural Compounds* **2014,** *50* (3), 455-457.

511. Abdallah, H. M.; Ezzat, S. M.; El Dine, R. S.; Abdel-Sattar, E.; Abdel-Naim, A. B. Protective effect of *Echinops galalensis* against CCl4-induced injury on the human hepatoma cell line (Huh7). *Phytochemistry Letters* **2013,** *6* (1), 73-78.

512. Verotta, L.; Belvisi, L.; Bertocci, V.; Loi, M. C. Complete characterization of extracts of *Onopordum illyricum* L. (Asteraceae) by HPLC/PDA/ESIMS and NMR. *Nat. Prod. Commun.* **2014,** *3*, 2037-2042.

513. Skala, E.; Kicel, A.; Olsewska, N. A.; Kiss, A. K.; Wysokinska, H. Establishment of hairy root cultures of *Rhaponticum carthamoides* (Willd.) Iljin for the production of biomass and caffeic acid derivatives. *BioMed Research International* **2015,** *2015*, http://dx.doi.org/10.1155/2015/181098 .

514. Yi, T.; Chen, H.-B.; Zhao, Z.-Z.; Jiang, Z.-H.; Cai, S.-Q.; Wang, T.-M. Comparative analysis of the major constituents in the traditional Tibetan medicinal plants *Saussurea laniceps* and *S. medusa* by LC–DAD–MS. *Chromatographia* **2009,** *70*, 957-962.

515. Yi, T.; Chen, H.-B.; Zhao, Z.-Z.; Jang, Z.-H.; Cai, S.-Q.; Wang, T. M. Identification and determination of the major constituents in the traditional Uighur medicinal plant *Saussurea involucrata* by LC-DAD-MS. *Chromatographia* **2009,** *69*, 537-542.

516. Yi, T.; Lo, H.; Zhao, Z.; Yu, Z.; Yang, Z.; Chen, H. Comparison of the chemical composition and pharmacological effects of the aqueous and ethanolic extracts from a Tibetan "Snow Lotus" (*Saussurea laniceps*) herb. *Molecules* **2012,** *17* (6), 7183-7194.

517. Yi, T.; Zhu, L.; Tang, Y. N.; Zhang, J. Y.; Liang, Z. T.; Xu, J.; Zhao, Z. Z.; Yu, Z. L.; Bian, Z. X.; Yang, Z. J.; Chen, H. B. An integrated strategy based on UPLC-DAD-QTOF-MS for metabolism and pharmacokinetic studies of herbal medicines: Tibetan Snow Lotus herb (*Saussurea laniceps*), a case study. *J. Ethnopharmacol.* **2014,** *153* (3), 701-713.

518. Nugroho, A.; Lim, S. C.; Lee, C. M.; Choi, J. S.; Park, H. J. Simultaneous quantitative determination and validation of quercetin glycosides with peroxynitrite-scavenging effects from *Saussurea grandifolia*. *J Pharm. Biomed. Anal.* **2012,** *61*, 247-251.

519. Wang, T. M.; Wang, R. F.; Chen, H. B.; Shang, M. Y.; Cai, S. Q. Alkyl and phenolic glycosides from *Saussurea stella*. *Fitoterapia* **2013,** *88*, 38-43.

520. Yang, M. C.; Kim, S. M.; Lee, K. H.; Kim, K. H.; Lee, K. R. A new sesquiterpene glycoside from the aerial parts of *Saussurea triangulata*. *Molecules* **2007,** *12*, 2270-2276.

521. Chung, I.-M.; Kim, M.-Y.; Park, W.-H.; Moon, H.-I. Quinic acid derivatives from *Saussurea triangulata* attenuates glutamate-induced neurotoxicity in primary cultured rat cortical cells. *Journal of Enzyme Inhibition and Medicinal Chemistry* **2009,** *24*, 188-191.

522. Chen, R.; Liu, X.; Zou, J.; Yang, L.; Dai, J. Qualitative and quantitative analysis of phenylpropanoids in cell culture, regenerated plantlets and herbs of *Saussurea involucrata*. *J Pharm. Biomed. Anal.* **2013,** *74*, 39-46.

523. Zou, X.; Liu, D.; Liu, Y.; Fu, Y.; Zhang, X.; Xiu, Z.; Xiao, H. Isolation and characterization of two new phenolic acids from cultured cells of *Saussurea involucrata*. *Phytochemistry Letters* **2014,** *7* (0), 133-136.

524. Zou, X.; Liu, D.; Liu, Y.; Xiu, Z.; Xiao, H. A new polyphenol, 1, 3-di-O-caffeoyl-5-O-(1-methoxyl-2-O-caffeoyl-4-maloyl)-quinic acid, isolated from cultured cells of *Saussurea involucrata*. *Chinese Journal of Natural Medicines* **2015,** *13* (4), 295-298.

525. Pereira, C.; Barros, L.; Alves, M. J.; Santos-Buelga, C.; Ferreira, I. C. F. R. Artichoke and milk thistle pills and syrups as sources of phenolic compounds with antimicrobial activity. *Food & Funct.* **2016,** *7*, 3083-3090.

526. Soliman, F. M.; Shehata, A. H.; Khaleel, A. E.; Ezzat, S. M.; Sleem, A. A. Caffeoyl derivatives and flavonoids from three Compositae species. *Pharmacognosy Magazine* **2008,** *4* (13), 1-11.

527. Gouveia, S.; Gonçalves, J.; Castilho, P. C. Characterization of phenolic compounds and antioxidant activity of ethanolic extracts from flowers of *Andryala glandulosa* ssp. *varia* (Lowe ex DC.) R.Fern., an endemic species of Macaronesia region. *Industrial Crops and Products* **2013,** *42* (0), 573-582.

528. Fusani, P.; Zidorn, C. Phenolics and a sesquiterpene lactone in the edible shoots of *Cicerbita alpina* (L.) Wallroth. *Journal of Food Composition and Analysis* **2010,** *23* (6), 658-663.

529. Goupy, P. M.; Varoquaux, P. J. A.; Nicolas, J. J.; Macheix, J.-J. Identification and localization of hydroxycinnamoyl and flavonol derivatives from endive (*Cichorium endivia* L. cv. Geante Maraichere) leaves. *J. Agric. Food Chem.* **1990,** *38*, 2116-2121.

530. Mascherpa, D.; Carazzone, C.; Marrubini, G.; Gazzani, G.; Papetti, A. Identification of phenolic constituents in *Cichorium endivia* Var. *crispum* and Var. *latifolium* salads by high-performance liquid chromatography with diode array detection and electrospray ioniziation tandem mass spectrometry. *J Agric. Food Chem.* **2012,** *60* (49), 12142-12150.

531. Dalar, A.; Konczak, I. *Cichorium intybus* from Eastern Anatolia: Phenolic composition, antioxidant and enzyme inhibitory activities. *Industrial Crops and Products* **2014,** *60* (0), 79-85.

532. Petropoulos, S. A.; Levizou, E.; Ntatsi, G.; Fernandes, A.; Petrotos, K.; Akoumianakis, K.; Barros, L.; Ferreira, I. C. F. R. Salinity effect on nutritional value, chemical composition and bioactive compounds content of Cichorium spinosum L. *Food Chem.* **2017,** *214*, 129-136.

533. Brieudes, V.; Angelis, A.; Vougogiannopoulou, K.; Pratsinis, H.; Kletsas, D.; Mitakou, S.; Halabalaki, M.; Skaltsounis, L. A. Phytochemical analysis and antioxidant potential of the phytonutrient-rich decoction of *Cichorium spinosum* and *C. intybus*. *Planta Med* **2016,** *24.05.2016* (EFirst).

534. Tong, J.; Ma, B.; Ge, L.; Mo, Q.; Zhou, G.; He, J.; Wang, Y. Dicaffeoylquinic acid-enriched fraction of *Cichorium glandulosum* seeds attenuates experimental Type 1 Diabetes via multipathway protection. *J. Agric. Food Chem.* **2015,** *63* (50), 10791-10802.

535. Ahn, H. R.; Lee, H. J.; Kim, K. A.; Kim, C. Y.; Nho, C. W.; Jang, H.; Pan, C. H.; Lee, C. Y.; Jung, S. H. Hydroxycinnamic acids in *Crepidiastrum denticulatum* protect oxidative stress-induced retinal damage. *J. Agric. Food Chem.* **2014,** *62* (6), 1310-1323.

536. Zidorn, C.; Schubert, B.; Stuppner, H. Altitudinal differences in the contents of phenolics in flowering heads of three members of the tribe Lactuceae (Asteraceae) occurring as introduced species in New Zealand. *Biochem. Syst. Ecol.* **2005,** *33* (9), 855-872.

537. Zidorn, C.; Schubert, B.; Stuppner, H. Phenolics as chemosystematic markers in and for the genus *Crepis* (Asteraceae, Cichorieae). *Sci. Pharm.* **2008,** *76*, 743-750.

538. Enke, N.; Gemeinholzer, B.; Zidorn, C. Molecular and phytochemical systematics of the subtribe Hypochaeridinae (Asteraceae, Cichorieae). *Organisms Diversity & Evolution* **2012,** *12* (1), 1-16.

539. Zidorn, C.; Gottschlich, G.; Stuppner, H. Chemosystematic investigations on phenolics from flowerheads of Central European taxa of *Hieracium sensu lato* (Asteraceae). *Plant Systematics and Evolution* **2002,** *231* (1-4), 39-58.

540. Petrovic, S. D.; Löscher, R.; Gorunovic, M. S.; Merfort, I. Flavonoid and phenolic acid patterns in seven *Hieracium* species. *Biochem. Syst. Ecol.* **1999,** *27* (6), 651-656.

541. Svehlikova, V.; Mraz, P.; Piacente, S.; Marhold, K. Chemotaxonomic significance of flavonoids and phenolic acids in the *Hieracium rohacsense* group (Hieracium sect. Alpina; Lactuceae, Compositae). *Biochem. Syst. Ecol.* **2002,** *30* (11), 1037-1049.

542. Liu, Y.; Lu, J. Q.; Zhagn, J. Y.; Wang, F.; Wang, Q.; Qiao, Y. J. [Identification of chemical component from *Ixeris sonchifolia* and its injection by HPLC-ESI-MS(n)]. *Zhongguo Zhong. Yao Za Zhi.* **2013,** *38* (16), 2675-2681.

543. Luna, M. C.; Tudela, J. A.; Tomas-Barberan, F. A.; Gil, M. I. Modified atmosphere (MA) prevents browning of fresh-cut romaine lettuce through multi-target effects related to phenolic metabolism. *Postharvest Biology and Technology* **2016,** *119*, 84-93.

544. Romani, A.; Pinelli, P.; Galassi, G.; Sanins, S. M.; Cimen, M. Y.; Heinecke, J. W. Polyphenols in greenhouse and open-air-grown lettuce. *Food Chem.* **2002,** *79*, 337-342.

545. Ribas-Agusti, A.; Gratacos-Cubarsi, M.; Sarraga, C.; Garcia-Regueiro, J. A.; Castellari, M. Analysis of eleven phenolic compounds including novel p-coumaroyl derivatives in lettuce (*Lactuca sativa* L.) by ultra-

high-performance liquid chromatography with photodiode array and mass spectrometry detection. *Phytochem. Anal.* **2011,** *22* (6), 555-563.

546. Abu-Reidah, I. M.; Contreras, M. M.; Arraez-Roman, D.; Segura-Carretero, A.; Fernandez-Gutierrez, A. Reversed-phase ultra-high-performance liquid chromatography coupled to electrospray ionization-quadrupole-time-of-flight mass spectrometry as a powerful tool for metabolic profiling of vegetables: *Lactuca sativa* as an example of its application. *J. Chromatogr. A* **2013,** *1313*, 212-227.

547. Ferreres, F.; Pereira, D. M.; Valentao, P.; Andrade, P. B.; Seabra, R. M.; Sottomayor, M. New phenolic compounds and antioxidant potential of *Catharanthus roseus*. *J. Agric. Food Chem.* **2008,** *56* (21), 9967-9974.

548. Stojakowska, A.; Michalska, K.; Malarz, J.; Beharav, A.; Kisiel, W. Root tubers of *Lactuca tuberosa* as a source of antioxidant phenolic compounds and new furofuran lignans. *Food Chem.* **2013,** *138* (2-3), 1250-1255.

549. Kim, K. H.; Kim, Y. H.; Lee, K. R. Isolation of quinic acid derivatives and flavonoids from the aerial parts of *Lactuca indica* L. and their hepatoprotective activity *in vitro*. *Bioorg. Med. Chem. Lett.* **2007,** *17* (24), 6739-6743.

550. Nugroho, A.; Jang, S.-W.; Kim, W.-B.; Lee, K. R.; Choi, J. S.; Park, H. J. Analysis of quinic acid derivatives on seven cultivars of the lettuce (*Lactuca sativa* L.) and peroxynitrite scavenging effect. *Korean Journal of Pharmacognosy* **2009,** *40*, 376-381.

551. Zidorn, C.; Stuppner, H. Evaluation of chemosystematic characters in the genus *Leontodon* (Asteraceae). *Taxon* **2001,** *50* (1), 115-133.

552. Zidorn, C.; Stuppner, H. Chemosystematics of taxa from the Leontodon section Oporinia. *Biochem. Syst. Ecol.* **2001,** *29* (8), 827-837.

553. Zidorn, C.; Petersen, B. O.; Udovicic, V.; Larsen, T. O.; Duus, J. A.; Rollinger, J. M.; Ongania, K. H.; Ellmerer, E. P.; Stuppner, H. Podospermic acid, 1,3,5-tri-O-(7,8-dihydrocaffeoyl)quinic acid from *Podospermum laciniatum* (Asteraceae). *Tetrahedron Lett.* **2005,** *46* (8), 1291-1294.

554. Zidorn, C.; Ellmerer, E. P.; Sturm, S.; Stuppner, H. Tyrolobibenzyls E and F from *Scorzonera humilis* and distribution of caffeic acid derivatives, lignans and tyrolobibenzyls in European taxa of the subtribe Scorzonerinae (Lactuceae, Asteraceae). *Phytochem.* **2003,** *63* (1), 61-67.

555. Recio, M. C.; Giner, R. M.; Hermenegildo, M.; Peris, J. B.; Manez, S.; Rios, J. L. Phenolics of *Reichardia* and their taxonomic implications. *Biochem. Syst. Ecol.* **1992,** *20* (5), 449-452.

556. Jehle, M.; Bano, J.; Ellmerer, E. P.; Zidorn, C. Natural products from *Scorzonera aristata* (Asteraceae). *Nat. Prod. Commun.* **2010,** *5* (5), 725-727.

557. Granica, S.; Lohwasser, U.; Jöhrer, K.; Zidorn, C. Qualitative and quantitative analyses of secondary metabolites in aerial and subaerial of *Scorzonera hispanica* L. (black salsify). *Food Chem.* **2015,** *173* (0), 321-331.

558. Tsevegsuren, N.; Edrada, R.; Lin, W.; Ebel, R.; Torre, C.; Ortlepp, S.; Wray, V.; Proksch, P. Biologically active natural products from Mongolian medicinal plants *Scorzonera divaricata* and *Scorzonera pseudodivaricata*. *J. Nat. Prod.* **2007,** *70* (6), 962-967.

559. Yang, Y. J.; Liu, X.; Wu, H. R.; He, X. F.; Bi, Y. R.; Zhu, Y.; Liu, Z. L. Radical scavenging activity and cytotoxicity of active quinic acid derivatives from *Scorzonera divaricata* roots. *Food Chem.* **2013,** *138* (2-3), 2057-2063.

560. Sari, A. Two new 3-benzylphthalides from *Scorzonera veratrifolia* Fenzl. *Nat. Prod. Res.* **2010,** *24* (1), 56-62.

561. Sari, A. Phenolic compounds from *Scorzonera latifolia* (Fisch. & Mey.) DC. *Nat. Prod. Res* **2012,** *26* (1), 50-55.

562. Wang, Y.; Wray, V.; Tsevegsuren, N.; Lin, W.; Proksch, P. Phenolic compounds from the Mongolian medicinal plant *Scorzonera radiata*. *Z. Naturforsch. C.* **2012,** *67* (3-4), 135-143.

563. Wang, Y. Isolation and Structure Elucidation of Bioactive Secondary Metabolites from Mongolian Medicinal Plants. Ph.D. Heinrich Heine University, Düsseldorf, 2009.

564. Acikara, O. B.; Hosek, J.; Babula, P.; Cvacka, J.; Budesinsky, M.; Dracinsky, M.; Iscan, G. S.; Kadlecova, D.; Ballova, L.; Smejkal, K. Turkish *Scorzonera* species extracts attenuate cytokine secretion via inhibition of NF-kappa B activation, showing anti-inflammatory effect *in vitro*. *Molecules* **2016,** *21* (1), 43.

565. Xu, Y. J.; Sun, S. B.; Sun, L. M.; Qiu, D. F.; Liu, X. J.; Jiang, Z. B.; Yuan, C. S. Quinic acid esters and sesquiterpenes from *Sonchus arvensis*. *Food Chem.* **2008,** *111* (1), 92-97.

566. Sprogoe, K.; Staerk, D.; Jager, A. K.; Adsersen, A.; Hansen, S. H.; Witt, M.; Landbo, A. K.; Meyer, A. S.; Jaroszewski, J. W. Targeted natural product isolation guided by HPLC-SPE-NMR: constituents of *Hubertia* species. *J. Nat Prod.* **2007,** *70* (9), 1472-1477.

567. Sareedenchai, V.; Ganzera, M.; Ellmerer, E. P.; Lohwasser, U.; Zidorn, C. Phenolic compounds from *Tragopogon porrifolius* L. *Biochem. Syst. Ecol.* **2009,** *37* (3), 234-236.

568. Granica, S.; Piwowarski, J. P.; Randazzo, A.; Schneider, P.; Zyzynska-Granica, B.; Zidorn, C. Novel stilbenoids, including cannabispiradienone glycosides, from *Tragopogon tommasinii* (Asteraceae, Cichorieae) and their potential anti-inflammatory activity. *Phytochem.* **2015,** *117*, 254-266.

569. Li, Y.; Zhang, C. Y.; Lin, T.; Wang, G. H.; Zeng, D. Q.; Guo, Z. J.; Zou, X. H.; Chen, H. F. [Chemical constituents from *Elephantopus tomentosus*]. *Zhongguo Zhong. Yao Za Zhi.* **2013,** *38* (11), 1751-1756.

570. Ooi, K. L.; Muhammad, T. S.; Tan, M. L.; Sulaiman, S. F. Cytotoxic, apoptotic and anti-alpha-glucosidase activities of 3,4-di-O-caffeoyl quinic acid, an antioxidant isolated from the polyphenolic-rich extract of *Elephantopus mollis* Kunth. *J. Ethnopharmacol.* **2011,** *135* (3), 685-695.

571. Geng, H. W.; Zhang, X. L.; Wang, G. C.; Yang, X. X.; Wu, X.; Wang, Y. F.; Ye, W. C.; Li, Y. L. Antiviral dicaffeoyl derivatives from *Elephantopus scaber*. *Journal of Asian Natural Products Research* **2011,** *13* (7), 665-669.

572. Silva, E. L.; Lobo, J. F. R.; Vinther, J. M.; Borges, R. M.; Staerk, D. High-resolution alpha-glucosidase inhibition profiling combined with HPLC-HRMS-SPE-NMR for identification of antidiabetic compounds in *Eremanthus crotonoides* (Asteraceae). *Molecules (Basel, Switzerland)* **2016,** *21* (6).

573. Gobbo-Neto, L.; Lopes, N. P. Online identification of chlorogenic acids, sesquiterpene lactones, and flavonoids in the Brazilian arnica *Lychnophora ericoides* Mart. (Asteraceae) leaves by HPLC-DAD-MS and HPLC-DAD-MS/MS and a validated HPLC-DAD method for their simultaneous analysis. *J Agric. Food Chem.* **2008,** *56* (4), 1193-1204.

574. dos Santos, M. D.; Chen, G.; Almeida, M. C.; Soares, D. M.; Petto de Souza, G. E.; Lopes, N. P.; Lantz, R. Effects of caffeoylquinic acid derivatives and *C*-flavonoid from *Lychnophora ericoides* on *in vitro* inflammatory mediator production. *Natural Product Communications* **2010,** *5* (5), 733-740.

575. Wang, Y.; Wang, E.; Shang, J.; Wang, H. [Caffeoylquinic acid derivatives from the seeds of *Vernonia anthelmintica*]. *Zhongguo Zhong. Yao Za Zhi.* **2012,** *37* (11), 1590-1592.

576. Tuerxuntayi, A.; Liu, Y. Q.; Tulake, A.; Kabas, M.; Eblimit, A.; Aisa, H. A. Kaliziri extract upregulates tyrosinase, TRP-1, TRP-2 and MITF expression in murine B16 melanoma cells. *BMC. Complement Altern. Med* **2014,** *14* (1), 166.

577. Liu, J.; Ding, G.; Yu, S. [Chemical constituents from stem barks of *Vernonia cumingiana*]. *Zhongguo Zhong yao za zhi = Zhongguo zhongyao zazhi = China journal of Chinese materia medica* **2010,** *35* (11), 1421-1424.

578. Igual, M. O.; Martucci, M. E. P.; Da Costa, F. B.; Gobbo-Neto, L. Sesquiterpene lactones, chlorogenic acids and flavonoids from leaves of *Vernonia polyanthes* Less (Asteraceae). *Biochem. Syst. Ecol.* **2013,** *51* (0), 94-97.

579. Johnson, C. E.; Lin, L. Z.; Harnly, J. M.; Oladeinde, F. O.; Kinyue, A. M.; Michelin, R.; Bronner, Y. Identification of the phenolic components of *Vernonia amygdalina* and *Russelia equisetiformis*. *J. Nat. Prod.* **2011,** *4*, 57-64.

580. Lin, L. Z.; Harnly, J. M. Identification of hydroxycinnamoylquinic acids of Arnica flowers and Burdock roots using a standardized LC-DAD-ESI/MS profiling method. *J. Agric. Food Chem.* **2008,** *56* (21), 10105-10114.

581. Benedek, B.; Geisz, N.; Jager, W.; Thalhammer, T.; Kopp, B. Choleretic effects of yarrow (*Achillea millefolium* s.l.) in the isolated perfused rat liver. *Phytomedicine.* **2006,** *13* (9-10), 702-706.

582. Benedek, B.; Gjoncaj, N.; Saukel, J.; Kopp, B. Distribution of phenolic compounds in Middleeuropean taxa of the *Achillea millefolium* L. aggregate. *Chem. Biodivers.* **2007,** *4* (5), 849-857.

583. Vitalini, S.; Beretta, G.; Iriti, M.; Orsenigo, S.; Basilico, N.; Dall'Acqua, S.; Iorizzi, M.; Fico, G. Phenolic compounds from *Achillea millefolium* L. and their bioactivity. *Acta Biochim. Pol.* **2011,** *58* (2), 203-209.

584. Radulovic, N.; Stojanovic, G.; Asakawa, Y. Hydroxycinnamoyl conjugates from the roots of *Achillea holosericea* Sibth. et Sm. *Biochem. Syst. Ecol.* **2006,** *34* (1), 83-87.

585. Kundakovic, T.; Fokialakis, N.; Magiatis, P.; Kovacevic, N.; Chinou, I. Triterpenic derivatives of *Achillea alexandri-regis* BORNM. & RUDSKI. *Chem. Pharm. Bull. (Tokyo)* **2004,** *52* (12), 1462-1465.

586. Dias, M. I.; Barros, L.; DueÃ±as, M.; Pereira, E.; Carvalho, A. M.; Alves, R. C.; Oliveira, M. B.; Santos-Buelga, C.; Ferreira, I. C. F. R. Chemical composition of wild and commercial *Achillea millefolium* L. and bioactivity of the methanolic extract, infusion and decoction. *Food Chem.* **2013,** *141* (4), 4152-4160.

587. Karaköse, H.; Jaiswal, R.; Deshpande, S.; Kuhnert, N. Investigating the photochemical changes of chlorogenic acids Induced by UV light in model systems and in agricultural practice with *Stevia rebaudiana* cultivation as an example. *J. Agric. Food Chem.* **2015**.

588. Pavlovic, M.; Kovacevic, N.; Couladis, M.; Tzakou, O. Phenolic constituents of *Anthemis triumfetti* (L.) DC. *Biochem. Syst. Ecol.* **2006,** *34*, 449-452.

589. Morishita, H.; Iwahashi, H.; Osaka, N.; Kido, R. Chromatographic separation and identification of naturally occurring chlorogenic acids by ^{1}H nuclear magnetic resonance spectroscopy and mass spectrometry. *J. Chromatogr.* **1984,** *315*, 253-260.

590. Iwai, K.; Kishimoto, N.; Kakino, Y.; Mochida, K.; Fujita, T. *In vitro* antioxidative effects and tyrosinase inhibitory activities of seven hydroxycinnamoyl derivatives in green coffee beans. *J. Agric. Food Chem.* **2004,** *52* (15), 4893-4898.

591. Peron, G.; Baldan, V.; Sut, S.; Faggian, M.; Roccabruna, L.; Zanini, D.; Manzini, P.; Maggi, F.; Dall'Acqua, S. Phytochemical investigations on Artemisia alba Turra growing in the North-East of Italy. *Natural Product Research* **2016,** 1-8.

592. Niranjan, A.; Barthwal, J.; Govindrajan, R.; Singh, D. P.; Lehri, L.; Amla, D. V. Development and validation of HPLC-UV-MS/MS methods for identification and quantification of polyphenols in *Artemisia pallens*. *Acta Chromatographica* **2009,** *21*, 105-116.

593. Fiamegos, Y. C.; Kastritis, P. L.; Exarchou, V.; Han, H.; Bonvin, A. M.; Vervoort, J.; Lewis, K.; Hamblin, M. R.; Tegos, G. P. Antimicrobial and efflux pump inhibitory activity of caffeoylquinic acids from *Artemisia absinthium* against gram-positive pathogenic bacteria. *PLoS ONE* **2011,** *6* (4), e18127.

594. Lee, H. J.; Lee, J. Y.; Kim, S. M.; Nho, C. W.; Jung, S. H.; Song, D.-J.; Kim, C. Y.; Pan, C.-H. Inhibitory effects of dicaffeoylquinic acids from *Artemisia dubia* on aldo-keto reductase family 1b10 . *Journal of the Korean Society for Applied Biological Chemistry* **2010,** *53*, 826-830.

595. Jung, H. A.; Park, J. J.; Islam, M. N.; Jin, S. E.; Min, B. S.; Lee, J. H.; Sohn, H. S.; Choi, J. S. Inhibitory activity of coumarins from *Artemisia capillaris* against advanced glycation endproduct formation. *Arch. Pharm. Res.* **2012,** *35* (6), 1021-1035.

596. Nurul, I. M.; Jung, H. A.; Sohn, H. S.; Kim, H. M.; Choi, J. S. Potent alpha-glucosidase and protein tyrosine phosphatase 1B inhibitors from *Artemisia capillaris*. *Arch. Pharm. Res.* **2013,** *36* (5), 542-552.

597. Park, K. M.; Li, Y.; Kim, B.; Zhang, H.; Hwangbo, K.; Piao, D. G.; Chi, M. J.; Woo, M. H.; Choi, J. S.; Lee, J. H.; Moon, D. C.; Chang, H. W.; Kim, J. R.; Son, J. K. High-performance liquid chromatographic analysis for quantitation of marker compounds of *Artemisia capillaris* Thunb. *Arch. Pharm. Res.* **2012,** *35* (12), 2153-2162.

598. Zhao, Y.; Geng, C. A.; Ma, Y. B.; Huang, X. Y.; Chen, H.; Cao, T. W.; He, K.; Wang, H.; Zhang, X. M.; Chen, J. J. UFLC/MS-IT-TOF guided isolation of anti-HBV active chlorogenic acid analogues from *Artemisia capillaris* as a traditional Chinese herb for the treatment of hepatitis. *J. Ethnopharmacol.* **2014,** *156*, 147-154.

599. Yamamoto, N.; Ueda, M.; Kawabata, K.; Sato, T.; Kawasaki, K.; Hashimoto, T.; Ashida, H. *Artemisia princeps* extract promoted glucose uptake in cultured L6 muscle cells via glucose transporter 4 translocation. *Biosci. Biotechnol. Biochem.* **2010,** *74* (10), 2036-2042.

600. Yang, H.; Lee, D. Y.; Jeon, M.; Suh, Y.; Sung, S. H. Determination of five active compounds in *Artemisia princeps* and *A. capillaris* based on UPLC-DAD and discrimination of two species with multivariate analysis. *Arch. Pharm. Res.* **2014,** *37* (5), 617-625.

601. Akihisa, T.; Kawashima, K.; Orido, M.; Akazawa, H.; Matsumoto, M.; Yamamoto, A.; Ogihara, E.; Fukatsu, M.; Tokuda, H.; Fuji, J. Antioxidative and melanogenesis-inhibitory activities of caffeoylquinic acids and other compounds from moxa. *Chem. Biodivers.* **2013,** *10* (3), 313-327.

602. Zhang, Y. H.; Xue, M. Q.; Bai, Y. C.; Yuan, H. H.; Zhao, H. L.; Lan, M. B. 3,5-Dicaffeoylquinic acid isolated from *Artemisia argyi* and its ester derivatives exert anti-leucyl-tRNA synthetase of *Giardia lamblia* (GlLeuRS) and potential anti-giardial effects. *Fitoterapia* **2012,** *83* (7), 1281-1285.

603. Ornano, L.; Venditti, A.; Ballero, M.; Sanna, C.; Quassinti, L.; Bramucci, M.; Lupidi, G.; Papa, F.; Vittori, S.; Maggi, F.; Bianco, A. Chemopreventive and antioxidant activity of the chamazulene-rich essential oil obtained from *Artemisia arborescens* L. growing on the Isle of La Maddalena, Sardinia, Italy. *Chem. Biodivers.* **2013,** *10* (8), 1464-1474.

604. Anaya-Eugenio, G. D.; Rivero-Cruz, I.; Rivera-Chavez, J.; Mata, R. Hypoglycemic properties of some preparations and compounds from *Artemisia ludoviciana* Nutt. *J. Ethnopharmacol.* **2014,** *155* (1), 416-425.

605. Könczöl, A.; Beni, Z.; Sipos, M. M.; Rill, A.; Hada, V.; Hohmann, J.; Mathe, I.; Szantay, C., Jr.; Keseru, G. M.; Balogh, G. T. Antioxidant activity-guided phytochemical investigation of *Artemisia gmelinii* Webb. ex Stechm.: isolation and spectroscopic challenges of 3,5-O-dicaffeoyl (epi?) quinic acid and its ethyl ester. *J Pharm. Biomed. Anal.* **2012,** *59*, 83-89.

606. Lee, J. S.; Kim, H. J.; Lee, Y. S. A new anti-HIV flavonoid glucuronide from *Chrysanthemum morifolium*. *Planta Med.* **2003,** *69* (9), 859-861.

607. Zhang, L.; Tu, Z. C.; Yuan, T.; Wang, H.; Fu, Z. F.; Wen, Q. H.; Wang, X. Q. Solvent optimization, antioxidant activity, and chemical characterization of extracts from *Artemisia selengnesis* Turcz. *Industrial Crops and Products* **2014,** *56* (0), 223-230.

608. Zhang, L.; Tu, Z. C.; Wang, H.; Fu, Z. F.; Wen, Q. H.; Fan, D. Metabolic profiling of antioxidants constituents in *Artemisia selengensis* leaves. *Food Chem.* **2015,** *186*, 123-132.

609. Zhang, L.; Tu, Z. C.; Wang, H.; Wen, Q. H.; Fu, Z. F.; Xie, X. Antioxidant activity and phenolic acids profiles of *Artemisia selengensis* Turcz extracted with various methods by HPLC-QTOF-MS/MS. *J. Food Biochem.* **2016,** *40* (4), 603-612.

610. Dahmani-Hamzaoui, N.; Salido, S.; Linares-Palomino, P. J.; Baaliouamer, A.; Altarejos, J. On-line radical scavenging detection and characterization of antioxidants from *Artemisia herba-alba*. *HCA* **2012,** *95* (4), 564-576.

611. Boudjelal, A.; Siracusa, L.; Henchiri, C.; Sarri, M.; Abderrahim, B.; Baali, F.; Ruberto, G. Antidiabetic effects of aqueous infusions of *Artemisia herba-alba* and *Ajuga iva* in alloxan-induced diabetic rats. *Planta Med.* **2015,** *81* (9), 696-704.

612. Younsi, F.; Trimech, R.; Boulila, A.; Ezzine, O.; Dhahri, S.; Boussaid, M.; Messaoud, C. Essential oil and phenolic compounds of *Artemisia herba-alba* (Asso.): composition, antioxidant, antiacetylcholinesterase, and antibacterial activities. *International Journal of Food Properties* **2016,** *19* (7), 1425-1438.

613. Gu, D.; Yang, Y.; Abdulla, R.; Aisa, H. A. Characterization and identification of chemical compositions in the extract of *Artemisia rupestris* L. by liquid chromatography coupled to quadrupole time-of-flight tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* **2012,** *26* (1), 83-100.

614. Gouveia, S. C.; Castilho, P. C. *Artemisia annua* L.: Essential oil and acetone extract composition and antioxidant capacity. *Industrial Crops and Products* **2013,** *45*, 170-181.

615. Carbonara, T.; Pascale, R.; Argentieri, M. P.; Papadia, P.; Fanizzi, F. P.; Villanova, L.; Avato, P. Phytochemical analysis of a herbal tea from *Artemisia annua* L. *J. Pharm. Biomed. Anal.* **2012,** *62* (0), 79-86.

616. Han, J.; Ye, M.; Qiao, X.; Xu, M.; Wang, B. r.; Guo, D. A. Characterization of phenolic compounds in the Chinese herbal drug *Artemisia annua* by liquid chromatography coupled to electrospray ionization mass spectrometry. *J. Pharm. Biomed. Anal.* **2008,** *47* (3), 516-525.

617. Li, L.; Wang, Z.; Peng, Y.; Fu, X.; Wang, Y.; Xiao, W.; Song, S. Screening and identification of multi-components in Re Du Ning injections using LC/TOF-MS coupled with UV-irradiation. *Journal of Chromatographic Science* **2014**.

618. Zhao, Y. W.; Ni, F. Y.; Song, Y. L.; Wang, S. Y.; Huang, W. Z.; Wang, Z. Z.; Xiao, W. [Chemical constituents from *Artemisia annua*]. *Zhongguo Zhong yao za zhi = Zhongguo zhongyao zazhi = China journal of Chinese materia medica* **2014,** *39* (24), 4816-4821.

619. Zhao, W. W.; Zhang, W. N.; Chen, Y. R.; Yang, F. P.; Cao, Q. M.; Chen, W. Z.; Liu, J. L.; Dai, K. W. Identification and purification of novel chlorogenic acids in *Artemisia annua* L. *Journal of Experimental Biology and Agricultural Sciences* **2015,** *3* (5), 415-422.

620. Gouveia, S.; Castilho, P. C. Antioxidant potential of *Artemisia argentea* L'Her alcoholic extract and its relation with the phenolic composition. *Food Research International* **2011,** *44* (6), 1620-1631.

621. Gouveia, S.; Castilho, P. C. *Helichrysum monizii* Lowe: phenolic composition and antioxidant potential. *Phytochem. Anal.* **2012,** *23* (1), 72-83.

622. Ma, C. M.; Hattori, M.; Chen, H. B.; Cai, S. Q.; Daneshtalab, M. Profiling the phenolic compounds of *Artemisia pectinata* by HPLC-PAD-MS^n. *Phytochem. Anal.* **2008,** *19* (4), 294-300.

623. Melguizo-Melguizo, D.; Diaz-de-Cerio, E.; Quirantes-Pine, R.; Svarc-Gajic, J.; Segura-Carretero, A. The potential of *Artemisia vulgaris* leaves as a source of antioxidant phenolic compounds. *Journal of Functional Foods* **2014,** *10* (0), 192-200.

624. Carnat, A.; Heitz, A.; Fraisse, D.; Carnat, A. P.; Lamaison, J. L. Major dicaffeoylquinic acids from *Artemisia vulgaris*. *Fitoterapia* **2000,** *71*, 587-589.

625. Lin, L. Z.; Harnly, J. M. LC-PDA-ESI/MS identification of the phenolic components of three compositae spices: chamomile, tarragon, and Mexican arnica. *Nat. Prod. Commun.* **2012,** *7* (6), 749-752.

626. Jung, H. A.; Islam, M. D. N.; Kwon, Y. S.; Jin, S. E.; Son, Y. K.; Park, J. J.; Sohn, H. S.; Choi, J. S. Extraction and identification of three major aldose reductase inhibitors from *Artemisia montana*. *Food Chem. Toxicol.* **2011,** *49* (2), 376-384.

627. Ornano, L.; Venditti, A.; Donno, Y.; Sanna, C.; Ballero, M.; Bianco, A. Phytochemical analysis of non-volatile fraction of *Artemisia caerulescens* subsp *densiflora* (Viv.) (Asteraceae), an endemic species of La Maddalena Archipelago (Sardinia - Italy). *Natural Product Research* **2016,** *30* (8), 920-925.

628. Lin, F. D.; Luo, D. W.; Ye, J.; Xiao, M. T. [Chemical constituents of *Artemisia lactiflora*(II)]. *Zhongguo Zhong yao za zhi = Zhongguo zhongyao zazhi = China journal of Chinese materia medica* **2014,** *39* (13), 2531-2535.

629. Yan, X. T.; Ding, Y.; Li, W.; Sun, Y. N.; Yang, S. Y.; Koh, Y. S.; Kim, Y. H. Two new phenolic compounds from *Artemisia iwayomogi*. *HCA* **2014,** *97* (2), 283-289.

630. Nugroho, A.; Lim, S. C.; Karki, S.; Choi, J. S.; Park, H. J. Simultaneous quantification and validation of new peroxynitrite scavengers from *Artemisia iwayomogi*. *Pharmaceutical biology* **2015,** *53* (5), 653-661.

631. Lima, T. C.; Souza, R. J.; Santos, A. D.; Moraes, M. H.; Biondo, N. E.; Barison, A.; Steindel, M.; Biavatti, M. W. Evaluation of leishmanicidal and trypanocidal activities of phenolic compounds from *Calea uniflora* Less. *Natural Product Research* **2016,** *30* (5), 551-557.

632. Torres-Rodriguez, L.; Garcia-Chavez, E.; Berhow, M.; De Mejia, E. G. Anti-inflammatory and anti-oxidant effect of *Calea urticifolia* lyophilized aqueous extract on lipopolysaccharide-stimulated RAW 264.7 macrophages. *J. Ethnopharmacol.* **2016,** *188*, 266-274.

633. Chuda, Y.; Ono, H.; Ohnishi-Kameyama, M.; Nagata, T.; Tsushida, T. Structural identification of two antioxidant quinic acid derivatives from Garland (*Chrysanthemum coronarium.L.*). *J. Agric. Food Chem.* **1996,** *44*, 2037-2039.

634. Hosni, K.; Hassen, I.; Sebei, H.; Casabianca, H. Secondary metabolites from *Chrysanthemum coronarium* (Garland) flowerheads: Chemical composition and biological activities. *Industrial Crops and Products* **2013,** *44*, 263-271.

635. Murayama, T.; Yada, H.; Kobori, M.; Shinmoto, H.; Tsushida, T. Evaluation of three antioxidants and their identification and radical scavenging activities in edible chrysanthemums. *J. Jpn. Soc. Hort. Sci.* **2002,** *71*, 236-242.

636. Lai, J. P.; Lim, Y. H.; Su, J.; Shen, H. M.; Ong, C. N. Identification and characterization of major flavonoids and caffeoylquinic acids in three Compositae plants by LC/DAD-APCI/MS. *J Chromatogr. B Analyt. Technol. Biomed. Life Sci.* **2007,** *848* (2), 215-225.

637. Nguyen, M. T.; Awale, S.; Tezuka, Y.; Tran, Q. L.; Watanabe, H.; Kadota, S. Xanthine oxidase inhibitory activity of Vietnamese medicinal plants. *Biol. Pharm. Bull.* **2004,** *27* (9), 1414-1421.

638. Leiss, K. A.; Maltese, F.; Choi, Y. H.; Verpoorte, R.; Klinkhamer, P. G. Identification of chlorogenic acid as a resistance factor for thrips in chrysanthemum. *Plant Physiol.* **2009,** *150* (3), 1567-1575.

639. Beninger, C. W.; Abou-Zaid, M. M.; Kistner, A. L.; Hallett, R. H.; Iqbal, M. J.; Grodzinski, B.; Hall, J. C. A flavanone and two phenolic acids from *Chrysanthemum morifolium* with phytotoxic and insect growth regulating activity. *J. Chem. Ecol.* **2004,** *30* (3), 589-606.

640. Kim, H. J.; Lee, Y. S. Identification of new dicaffeoylquinic acids from *Chrysanthemum morifolium* and their antioxidant activities. *Planta Med.* **2005,** *71* (9), 871-876.

641. Xie, Y. Y.; Qu, J. L.; Wang, Q. L.; Wang, Y.; Yoshikawa, M.; Yuan, D. Comparative evaluation of cultivars of *Chrysanthemum morifolium* flowers by HPLC-DAD-ESI/MS analysis and antiallergic assay. *J Agric. Food Chem.* **2012,** *60* (51), 12574-12583.

642. Lin, L. Z.; Harnly, J. M. Identification of the phenolic components of chrysanthemum flower (*Chrysanthemum morifolium* Ramat). *Food Chem.* **2010,** *120* (1), 319-326.

643. Clifford, M. N.; Wu, W.; Kirkpatrick, J.; Kuhnert, N. Profiling the chlorogenic acids and other caffeic acid derivatives of herbal Chrysanthemum by LC–MS^{n}. *J. Agric. Food Chem.* **2007,** *55*, 929-936.

644. Niu, Y.; Yin, L.; Luo, S.; Dong, J.; Wang, H.; Hashi, Y.; Chen, S. Identification of the anti-oxidants in Flos Chrysanthemi by HPLC-DAD-ESI/MS(n) and HPLC coupled with a post-column derivatisation system. *Phytochem. Anal.* **2013,** *24* (1), 59-68.

645. Wang, S.; Hao, L.-J.; Zhu, J.-J.; Wang, Z.-M.; Zhang, X.; Song, X.-M. Comparative evaluation of Chrysanthemum Flos from different origins by HPLC-DAD-MS^{n} and relative response factors. *Food Anal. Methods* **2014**.

646. He, J.; Wu, X.; Kuang, Y.; Wang, T.; Bi, K.; Li, Q. Quality assessment of *Chrysanthemum indicum* flower by simultaneous quantification of six major ingredients using a single reference standard combined with HPLC fingerprint analysis. *Asian Journal of Pharmaceutical Sciences* **2016**.

647. Wang, T.; Zhu, Z.; Guo, Q.; Mao, P. Variation in major flavonoids glycosides and caffeoylquinic acids during florescence of three *Chrysanthemum morifolium* Ramat cv. *Hangju* genotypes. *Biochem. Syst. Ecol.* **2013,** *47* (0), 74-79.

648. Dai, S.; Zhang, M.; Cheng, W. M.; Zhang, X.; Zhang, Q. L.; Li, J. [Simultaneous determination of eight active components in *Chrysanthemum indicum* by HPLC]. *Zhongguo Zhong. Yao Za Zhi.* **2013,** *38* (12), 1961-1965.

649. Sun, Y.; Ma, X.; Liu, J. [Compounds from fraction with cardiovascular activity of *Chrysanthemum indicum*]. *Zhongguo Zhong. Yao Za Zhi.* **2012,** *37* (1), 61-65.

650. Farag, N. F.; Farag, M. A.; Abdelrahman, E. H.; Azzam, S. M.; El-Kashoury, E. S. Metabolites profiling of *Chrysanthemum pacificum* Nakai parts using UPLC-PDA-MS coupled to chemometrics. *Natural Product Research* **2015,** *29*, 1342-1349.

651. Nugroho, A.; Lim, S. C.; Choi, J.; Park, H. J. Identification and quantification of the sedative and anticonvulsant flavone glycoside from *Chrysanthemum boreale*. *Archives of Pharmacal Research* **2013,** *36* (1), 51-60.

652. Bessada, S. M. F.; Barreira, J. C. M.; Barros, L.; Ferreira, I. C. F. R.; Oliveira, M. B. Phenolic profile and antioxidant activity of *Coleostephus myconis* (L.) Rchb.f.: An underexploited and highly disseminated species. *Industrial Crops and Products* **2016,** *89*, 45-51.

653. Catarino, M. D.; Silva, A. M. S.; Saraiva, S.; Sobral, A. J. F. N.; Cardoso, S. M. Characterization of phenolic constituents and evaluation of antioxidant properties of leaves and stems of *Eriocephalus africanus*. *Arabian Journal of Chemistry* **2015,** (0).

654. Gafner, S.; Wolfender, J. L.; Hostettmann, K.; Stoeckli-Evans, H.; Mavi, S. Phenols, acetylenes, and sesquiterpene lactones from *Inulanthera nuda*. *HCA* **1998,** *81* (11), 2062-2071.

655. Shi, S.; Huang, K.; Zhang, Y.; Zhao, Y.; Du, Q. Purification and identification of antiviral components from *Laggera pterodonta* by high-speed counter-current chromatography. *Journal of chromatography. B, Analytical technologies in the biomedical and life sciences* **2007,** *859* (1), 119-124.

656. Petrulova, V.; Ducaiova, Z.; Repcak, M. Short-term UV-B dose stimulates production of protective metabolites in *Matricaria chamomilla* leaves. *Photochem. Photobiol.* **2014**.

657. Ganzera, M.; Guggenberger, M.; Stuppner, H.; Zidorn, C. Altitudinal variation of secondary metabolite profiles in flowering heads of *Matricaria chamomilla* cv. BONA. *Planta Med.* **2008,** *74* (4), 453-457.

658. Ducaiova, Z.; Sajko, M.; Mihalicova, S.; Repcak, M. Dynamics of accumulation of coumarin-related compounds in leaves of *Matricaria chamomilla* after methyl jasmonate elicitation. *Plant Growth Regulation* **2016,** *79* (1), 81-94.

659. Raal, A.; Pussa, T.; Sepp, J.; Malmiste, B.; Arak, E. Content of phenolic compounds in aerial parts of *Chamomilla suaveolens* from Estonia. *Nat. Prod. Commun.* **2011,** *6* (8), 1107-1110.

660. Wu, C.; Chen, F.; Wang, X.; Wu, Y.; Dong, M.; He, G.; Galyean, R. D.; He, L.; Huang, G. Identification of antioxidant phenolic compounds in feverfew (*Tanacetum parthenium*) by HPLC-ESI-MS/MS and NMR. *Phytochem. Anal.* **2007,** *18* (5), 401-410.

661. Kwon, H. C.; Jung, C. M.; Shin, C. G.; Lee, J. K.; Choi, S. U.; Kim, S. Y.; Lee, K. R. A new caffeoyl quinic acid from *Aster scaber* and its inhibitory activity against human immunodeficiency virus-1 (HIV-1) integrase. *Chem. Pharm. Bull.* **2000,** *48* (11), 1796-1798.

662. Nugroho, A.; Kim, M. H.; Choi, J.; Choi, J. S.; Jung, W. T.; Lee, K. T.; Park, H. J. Phytochemical studies of the phenolic substances in *Aster glehni* extract and its sedative and anticonvulsant activity. *Arch. Pharm. Res.* **2012,** *35* (3), 423-430.

663. Ko, R. K.; Kang, M. C.; Kim, B. S.; Han, J. H.; Kim, G. O.; Lee, N. H. A new phloroglucinol glycoside from *Aster subulatus* Michx. *Bulletin of the Korean Chemical Society* **2009,** *30* (5), 1167-1169.

664. Jaiswal, R.; Dickman, M. H.; Kuhnert, N. First diastereoselective synthesis of methyl caffeoyl- and feruloyl-*muco*-quinates. *Org. Biomol. Chem.* **2012,** *10* (27), 5266-5277.

665. Jaiswal, R.; Matei, M. F.; Golon, A.; Witt, M.; Kuhnert, N. Understanding the fate of chlorogenic acids in coffee roasting using mass spectrometry based targeted and non-targeted analytical strategies. *Food Funct.* **2012,** *3*, 976-984.

666. Zhong, R. F.; Xu, G. B.; Wang, Z.; Wang, A. M.; Guan, H. Y.; Li, J.; He, X.; Liu, J. H.; Zhou, M.; Li, Y. J.; Wang, Y. L.; Liao, S. G. Identification of anti-inflammatory constituents from *Kalimeris indica* with UHPLC-ESI-Q-TOF-MS/MS and GC-MS. *J. Ethnopharmacol.* **2015,** *165*, 39-45.

667. Sang-Cheol, L.; Juhn, P. H. HPLC Analysis on the caffeoylquinic acids of *Aster altaicus* var. *uchiyamae* Kitamura and peroxynitrite-scavenging effect. *Korean Journal of Plant Reources* **2016,** *29* (1), 20-25.

668. Zhao, D. X.; Hu, B. Q.; Zhang, M.; Zhang, C. F.; Xu, X. H. Simultaneous separation and determination of phenolic acids, pentapeptides, and triterpenoid saponins in the root of *Aster tataricus* by high-performance liquid chromatography coupled with electrospray ionization quadrupole time-of-flight mass spectrometry. *J. Sep. Science* **2015,** *38* (4), 571-575.

669. Choi, S. Z.; Lee, S. O.; Choi, S. U.; Lee, K. R. A new sesquiterpene hydroperoxide from the aerial parts of *Aster oharai*. *Archives of Pharmacal Research* **2003,** *26* (7), 521-525.

670. Aboy, A. L.; Apel, M. A.; Debenedetti, S.; Francescato, L.; Rosella, M. A.; Henriques, A. T. Assay of caffeoylquinic acids in *Baccharis trimera* by reversed-phase liquid chromatography. *J Chromatogr. A* **2012,** *1219*, 147-153.

671. Grecco, S. S.; Felix, M. J.; Lago, J. H.; Pinto, E. G.; Tempone, A. G.; Romoff, P.; Ferreira, M. J.; Sartorelli, P. Anti-trypanosomal phenolic derivatives from *Baccharis uncinella*. *Nat. Prod. Commun.* **2014,** *9* (2), 171-173.

672. Argoti, J. C.; Linares-Palomino, P. J.; Salido, S.; Ramirez, B.; Insuasty, B.; Altarejos, J. On-line activity screening for radical scavengers from *Baccharis chilco*. *Chem. Biodivers.* **2013,** *10* (2), 189-197.

673. Cariddi, L.; Escobar, F.; Sabini, C.; Torres, C.; Reinoso, E.; Cristofolini, A.; Comini, L.; Nunez, M. S.; Sabini, L. Apoptosis and mutagenicity induction by a characterized aqueous extract of *Baccharis articulata* (Lam.) Pers. (Asteraceae) on normal cells. *Food Chem. Toxicol.* **2012,** *50* (2), 155-161.

674. de Oliveira, S. Q.; Kappel, V. D.; Pires, V. S.; Lencina, C. L.; Sonnet, P.; Moreira, J. C.; Gosmann, G. Antioxidant properties of phenolic compounds from *Baccharis articulata* and *B. usterii*. *Natural Product Communications* **2014,** *9* (7), 941-944.

675. dos Grecco, S.; Ferreira, M. J. P.; Romoff, P.; Favero, O. A.; Lago, J. H. Phenolic derivatives from *Baccharis retusa* DC. (Asteraceae). *Biochem. Syst. Ecol.* **2012,** *42*, 21-24.

676. Simões-Pires, C. A.; Queiroz, E. F.; Henriques, A. T.; Hostettmann, K. Isolation and on-line identification of anti-oxidant compounds from three *Baccharis* species by HPLC-UV-MS/MS with post-column derivatisation. *Phytochemical Analysis* **2005,** *16* (5), 307-314.

677. Chan, C. O.; Jin, D. P.; Dong, N. P.; Chen, S. B.; Mok, D. K. W. Qualitative and quantitative analysis of chemical constituents of *Centipeda minima* by HPLC-QTOF-MS & HPLC-DAD. *J. Pharm. Biomed. Anal.* **2016,** *125*, 400-407.

678. Timmermann, B. N.; Hoffmann, J. J.; Jolad, S. D.; Schram, K. H.; Klenk, R. E.; Bates, R. B. Constituents of *Chrysothamnus paniculatus.* 3. 3,4,5-tricaffeoylquinic acid (a new shikimate prearomatic) and 3,4-, 3,5- and 4,5-dicaffeoylquinic acids. *J. Nat. Prod.* **1983,** *46*, 365-368.

679. Lin, L. C.; Kuo, Y. C.; Chou, C. J. Immunomodulatory principles of *Dichrocephala bicolor*. *J. Nat Prod.* **1999,** *62* (3), 405-408.

680. Yue, J.-M.; Zhao, Q.-S.; Lin, Z.-W.; Sun, H.-D. Phenolic compounds from *Erigeron breviscapus* (Compositae). *Acta Botanica Sinica* **2000,** *42*, 311-315.

681. Li, X.-B.; Xu, J.-J.; Xie, S.-Q.; Meng, Z.-G.; Li, L.-G.; Yang, S.-C. Simultaneous determination of three active constituents in *Erigeron breviscapus* by highperformance liquid chromatography. *Journal of Medicinal Plants Research* **2013,** *7*, 250-256.

682. Ju, W. Z.; Zhao, Y.; Liu, F.; Wu, T.; Zhang, J.; Liu, S. J.; Zhou, L.; Dai, G. L.; Xiong, N. N.; Fang, Z. Y. Clinical tolerability and pharmacokinetics of Erigerontis hydroxybenzene injection: Results of a randomized phase I study in healthy Chinese volunteers. *Phytomed.* **2015,** *22* (2), 319-325.

683. Wang, L.-W.; Li, H.-J.; Li, P.; Wei, Y.-J.; Tang, D.; Yi, L.; Quian, Z.-M. Simultaneous quantification of two major classes of constituents in *Erigeron breviscapus* and Its extract injection by RP-HPLC. *Chromatographia* **2007,** *66*, 395-399.

684. Zhang, Y.; Shi, P.; Qu, H.; Cheng, Y. Characterization of phenolic compounds in *Erigeron breviscapus* by liquid chromatography coupled to electrospray ionization mass spectrometry. *Rapid Commun. Mass Spectrom.* **2007,** *21* (18), 2971-2984.

685. Liao, S. G.; Zhang, L. J.; Li, C. B.; Lan, Y. Y.; Wang, A. M.; Huang, Y.; Zhen, L.; Fu, X. Z.; Zhou, W.; Qi, X. L.; Guan, Z. Z.; Wang, Y. L. Rapid screening and identification of caffeic acid and its esters in *Erigeron*

breviscapus by ultra-performance liquid chromatography/tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* **2010,** *24* (17), 2533-2541.

686. Zhang, Y.; Zhao, Q.; Ma, J.; Wu, B.; Zeng, X. Chemical characterization of phenolic compounds in Erigeron injection by rapid-resolution LC coupled with multi-stage and quadrupole-TOF-MS. *Chromatographia* **2010,** *72*, 651-658.

687. Li, F.; Zhang, L. D.; Li, B. C.; Yang, J.; Yu, H.; Wan, J. B.; Wang, Y. T.; Li, P. Screening of free radical scavengers from *Erigeron breviscapus* using on-line HPLC-ABTS/DPPH based assay and mass spectrometer detection. *Free Radic. Res* **2012,** *46* (3), 286-294.

688. Wang, S. X.; Guo, H.; Hu, L. M.; Liu, Y. N.; Wang, Y. F.; Kang, L. Y.; Gao, X. M. Caffeic acid ester fraction from *Erigeron breviscapus* inhibits microglial activation and provides neuroprotection. *Chin J Integr. Med* **2012,** *18* (6), 437-444.

689. Li, J.; Yu, D. [Chemical constituents from herbs of *Erigeron breviscapus*]. *Zhongguo Zhong. Yao Za Zhi.* **2011,** *36* (11), 1458-1462.

690. Jang, D. S.; Yoo, N. H.; Kim, N. H.; Lee, Y. M.; Kim, C. S.; Kim, J.; Kim, J. H.; Kim, J. S. 3,5-Di-*O*-caffeoyl-*epi*-quinic acid from the leaves and stems of *Erigeron annuus* inhibits protein glycation, aldose reductase, and cataractogenesis. *Biol. Pharm. Bull.* **2010,** *33* (2), 329-333.

691. Berto, C.; Maggi, F.; Nya, P. C.; Pettena, A.; Boschiero, I.; Dall'Acqua, S. Phenolic constituents of *Erigeron floribundus* (Asteraceae), a Cameroonian medicinal plant. *Natural Product Communications* **2014,** *9* (12), 1691-1694.

692. Zahoor, A.; Hussain, H.; Khan, A.; Ahmed, I.; Ahmad, V. U.; Krohn, K. Chemical constituents from *Erigeron bonariensis* L. and their chemotaxonomic importance. *Records of Natural Products* **2012,** *6* (4), 376-380.

693. Ferreres, F.; Grosso, C.; Gil-Izquierdo, A.; Valentao, P.; Azevedo, C.; Andrade, P. B. HPLC-DAD-ESI/MS(n) analysis of phenolic compounds for quality control of *Grindelia robusta* Nutt. and bioactivities. *J. Pharm. Biomed. Anal.* **2014,** *94*, 163-172.

694. Schmeda-Hirschmann, G.; Quispe, C.; Gonzalez, B. Phenolic Profiling of the South American "Baylahuen" Tea (*Haplopappus* spp., Asteraceae) by HPLC-DAD-ESI-MS. *Molecules* **2015,** *20* (1), 913-928.

695. Wang, Y.; Hamburger, M.; Gueho, J.; Hostettmann, K. Cyclohexanecarboxylic acid derivatives from *Psiadia trinervia*. *HCA* **1992,** *75*, 269-275.

696. Choi, S. Z.; Choi, S. U.; Lee, K. R. Phytochemical constituents of the aerial parts from *Solidago virga-aurea* var. *gigantea*. *Arch. Pharm. Res.* **2004,** *27* (2), 164-168.

697. Abdel Motaal, A.; Ezzat, S. M.; Tadros, M. G.; El-Askary, H. I. *In vivo* anti-inflammatory activity of caffeoylquinic acid derivatives from *Solidago virgaurea* in rats. *Pharmaceutical biology* **2016,** *doi: 10.1080/13880209.2016.1190381*, 1-7.

698. Thiem, B.; Wesolowska, M.; Skrzypczak, L.; Budzianowski, J. Phenolic compounds in two *Solidago* L. species from *in vitro* culture. *Acta Pol. Pharm.* **2001,** *58* (4), 277-281.

699. Schmeda-Hirschmann, G.; Jordan, M.; Gerth, A.; Wilken, D. Secondary metabolite content in rhizomes, callus cultures and in vitro regenerated plantlets of *Solidago chilensis*. *Z. Naturforsch. C.* **2005,** *60* (1-2), 5-10.

700. Tamura, E. K.; Jimenez, R. S.; Waismam, K.; Gobbo-Neto, L.; Lopes, N. P.; Malpezzi-Marinho, E. A.; Marinho, E. A.; Farsky, S. H. Inhibitory effects of *Solidago chilensis* Meyen hydroalcoholic extract on acute inflammation. *J. Ethnopharmacol.* **2009,** *122* (3), 478-485.

701. Olennikov, D. N.; Kashchenko, N. I. Componential profile and amylase inhibiting activity of phenolic compounds from *Calendula officinalis* L. leaves. *Scientific World Journal* **2014,** *2014*, 654193.

702. Olennikov, D. N.; Kashchenko, N. I. 1,5-Di-O-isoferuloylquinic acid and other phenolic compounds from pollen of *Calendula officinalis*. *Chem Nat Compd* **2014,** 1-5.

703. Fernandes, A. E. F.; Meloni, F.; Borella, J. C.; Lopes, N. P. Effect of fertilisation and harvest period on polar metabolites of *Calendula officinalis*. *Revista Brasileira de Farmacognosia* **2013,** *23* (5), 731-735.

704. Engel, R.; Szabo, K.; Abranko, L.; Rendes, K.; Füzy, A.; Takacs, T. Effect of arbuscular mycorrhizal fungi on the growth and the polyphenol profile of Marjoram, Lemon Balm and Marigold. *J. Agric. Food Chem.* **2016,** *64*, 3733-3742.

705. Silva, D. B.; Okano, L. T.; Lopes, N. P.; de Oliveira, D. C. R. Flavanone glycosides from *Bidens gardneri* Bak. (Asteraceae). *Phytochem.* **2013,** *96* (0), 418-422.

706. Ping, L.; Wang, Y.; Guo, Z.; Wu, S.; Kennelly, E. J.; Wang, J.; Li, T.; Long, C. Separation of three bioactive isomers from *Bidens pilosa* by countercurrent chromatography. *Journal of Liquid Chromatography & Related Technologies* **2014,** *37* (18), 2598-2609.

707. Liang, X.; Xu, Q. Separation and identification of phenolic compounds in *Bidens pilosa* L. by ultra high performance liquid chromatography with quadrupole time-of-flight mass spectrometry. *J. Sep. Science* **2016,** *39*, 1853-1862.

708. Gbashi, S.; Njobeh, P.; Steenkamp, P.; Tutu, H.; Madala, N. The effect of temperature and methanol-water mixture on pressurized hot water extraction (PHWE) of anti-HIV analogoues from Bidens pilosa. *Chemistry Central Journal* **2016,** *10* (DOI 10.1186/s13065-016-0182-z).

709. Chen, L. X.; Hu, D. J.; Lam, S. C.; Ge, L.; Wu, D.; Zhao, J.; Long, Z. R.; Yang, W. J.; Fan, B.; Li, S. P. Comparison of antioxidant activities of different parts from Snow Chrysanthemum (*Coreopsis tinctoria* Nutt.) and Identification of their natural antioxidants using high performance liquid chromatography coupled with diode array detection and mass spectrometry. *J. Chromatogr. A* **2016,** *1428*, 134-142.

710. Ma, Z.; Zheng, S.; Han, H.; Meng, J.; Yang, X.; Zeng, S.; Zhou, H.; Jiang, H. The bioactive components of *Coreopsis tinctoria* (Asteraceae) capitula: Antioxidant activity *in vitro* and profile in rat plasma. *Journal of Functional Foods* **2016,** *20*, 575-586.

711. Shui, G. H.; Leong, L. P.; Wong, S. P. Rapid screening and characterisation of antioxidants of *Cosmos caudatus* using liquid chromatography coupled with mass spectrometry. *Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences* **2005,** *827* (1), 127-138.

712. Zhang, M.; Liu, W. X.; Zheng, M. F.; Xu, Q. L.; Wan, F. H.; Wang, J.; Lei, T.; Zhou, Z. Y.; Tan, J. W. Bioactive quinic acid derivatives from *Ageratina adenophora*. *Molecules* **2013,** *18* (11), 14096-14104.

713. Escandon-Rivera, S.; Gonzalez-Andrade, M.; Bye, R.; Linares, E.; Navarrete, A.; Mata, R. alpha-glucosidase inhibitors from *Brickellia cavanillesii*. *J. Nat Prod.* **2012,** *75* (5), 968-974.

714. Clavin, M.; Gorzalczany, S.; Macho, A.; Munoz, E.; Ferraro, G.; Acevedo, C.; Martino, V. Anti-inflammatory activity of flavonoids from *Eupatorium arnottianum*. *J. Ethnopharmacol.* **2007,** *112* (3), 585-589.

715. Maas, M.; Petereit, F.; Hensel, A. Caffeic acid derivatives from *Eupatorium perfoliatum* L. *Molecules* **2009,** *14*, 36-45.

716. Xu, Q.; Xie, H.; Xiao, H.; Wei, X. Phenolic constituents from the roots of *Mikania micrantha* and their allelopathic effects. *J. Agric. Food Chem.* **2013,** *61* (30), 7309-7314.

717. Wei, X.; Huang, H.; Wu, P.; Cao, H.; Ye, W. Phenolic constituents from *Mikania micrantha*. *Biochem. Syst. Ecol.* **2004,** *32* (11), 1091-1096.

718. de Souza, J. M.; Taleb-Contini, S. H.; de Oliveira, D. C. R. Phytochemical study of *Mikania pseudohoffmanianna* G. M. Barroso ex W. C. Holmes. *Brazilian Journal of Pharmaceutical Sciences* **2006,** *42*, 265-268.

719. de Melo, L. V.; Sawaya, A. C. H. F. UHPLC–MS quantification of coumarin and chlorogenic acid in extracts of the medicinal plants known as guaco (*Mikania glomerata* and *Mikania laevigata*). *Revista Brasileira de Farmacognosia* **2015,** (0).

720. Ferreira, F. P.; Rodrigues de Oliveira, D. C. New constituents from *Mikania laevigata* Shultz Bip. ex Baker. *Tetrahedron Lett.* **2010,** *51* (52), 6856-6859.

721. Karaköse, H.; Jaiswal, R.; Kuhnert, N. Characterization and quantification of hydroxycinnamate derivatives in *Stevia rebaudiana* leaves by LC–MS^n. *J. Agric. Food Chem.* **2011,** *59* (18), 10143-10150.

722. Karakose, H.; Muller, A.; Kuhnert, N. Profiling and quantification of phenolics in *Stevia rebaudiana* leaves. *J Agric Food Chem* **2015**.

723. Bender, C.; Graziano, S.; Zimmermann, B. F. Study of *Stevia rebaudiana* Bertoni antioxidant activities and cellular properties. *Int. J Food Sci Nutr* **2015,** *66* (5), 553-558.

724. Barroso, M.; Barros, L.; Rodrigues, M. A.; Sousa, M. J.; Santos-Buelga, C.; Ferreira, I. C. F. R. *Stevia rebaudiana* Bertoni cultivated in Portugal: A prospective study of its antioxidant potential in different conservation conditions. *Industrial Crops and Products* **2016,** *90*, 49-55.

725. Molina-Calle, M.; Priego-Capote, F.; de Castro, M. D. L. Characterization of *Stevia* leaves by LC-QTOF MS/MS analysis of polar and non-polar extracts. *Food Chem.* **2017,** *219*, 329-338.

726. Shikov, A. N.; Kundracikova, M.; Palama, T. L.; Pozharitskaya, O. N.; Kosman, V. M.; Makarov, V. G.; Galambosi, B.; Kim, H. J.; Jang, Y. P.; Choi, Y. H.; Verpoorte, R. Phenolic constituents of *Gnaphalium uliginosum* L. *Phytochemistry Letters* **2010,** *3* (1), 45-47.

727. Olennikov, D.; Chirikova, N.; Kashchenko, N., I Spinacetin, A New Caffeoylglycoside, and Other Phenolic Compounds from *Gnaphalium uliginosum*. *Chemistry Of Natural Compounds* **2015,** *51* (6), 1085-1090.

728. Rastrelli, S.; Saravia, A.; Hernandez, M.; de Simone, F. Anti-inflammatory activity-guided fractionation of *Gnaphalium stramineum*. *Pharma. Biol.* **1998,** *36*, 315-319.

729. Cicek, S. S.; Untersulzner, C.; Schwaiger, S.; Zidorn, C. Caffeoyl-D-glucaric acid derivatives in the genus *Gnaphalium* (Asteraceae: Gnaphalieae). *Records of Natural Products* **2012,** *6* (3), 311-315.

730. Kulisic-Bilusic, T.; Katalinic, V.; Dragovic-Uzelac, V.; Ljubenkov, I.; Krisko, A.; Dejanovic, B.; Jukic, M.; Politeo, O.; Pifat, G.; Milos, M. Antioxidant and acetylcholinesterase inhibiting activity of several aqueous tea Infusions *in vitro*. *Food Technology and Biotechnology* **2008,** *46* (4), 368-375.

731. Carini, M.; Aldini, G.; Furlanetto, S.; Stefani, R.; Facino, R. M. LC coupled to ion-trap MS for the rapid screening and detection of polyphenol antioxidants from *Helichrysum stoechas*. *J. Pharm. Biomed. Anal.* **2001,** *24*, 517-526.

732. Gouveia, S. C.; Castilho, P. C. Analysis of phenolic compounds from different morphological parts of *Helichrysum devium* by liquid chromatography with on-line UV and electrospray ionization mass spectrometric detection. *Rapid Commun. Mass Spectrom.* **2009,** *23* (24), 3939-3953.

733. Gouveia, S. C.; Castilho, P. C. Characterization of phenolic compounds in *Helichrysum melaleucum* by high-performance liquid chromatography with on-line ultraviolet and mass spectrometry detection. *Rapid Commun. Mass Spectrom.* **2010,** *24* (13), 1851-1868.

734. Gouveia, S.; Castilho, P. C. Characterisation of phenolic acid derivatives and flavonoids from different morphological parts of *Helichrysum obconicum* by a RP-HPLC-DAD-ESI-MSn method. *Food Chem.* **2011,** *129* (2), 333-344.

735. Heyman, H. M.; Senejoux, F.; Seibert, I.; Klimkait, T.; Maharaj, V. J.; Meyer, J. J. M. Identification of anti-HIV active dicaffeoylquinic- and tricaffeoylquinic acids in *Helichrysum populifolium* by NMR-based metabolomic guided fractionation. *Fitoterapia* **2015,** *103*, 155-164.

736. Martin, C.; Veale, A.; Gazendam, I.; Heyman, H.; Crampton, B. Elicitation of medicinally active dicaffeoylquinic acid derivatives from *Helichrysum populifolium*. *South African Journal of Botany* **2015,** *98*, 188.

737. Gouveia, S. C.; Castilho, P. C. Validation of a HPLC–DAD-ESI/MSn method for caffeoylquinic acids separation, quantification and identification in medicinal *Helichrysum* species from Macaronesia. *Food Research International* **2012,** *45*, 362-368.

738. Mari, A.; Napolitano, A.; Masullo, M.; Pizza, C.; Piacente, S. Identification and quantitative determination of the polar constituents in *Helichrysum italicum* flowers and derived food supplements. *J. Pharm. Biomed. Anal.* **2014,** *96* (0), 249-255.

739. Schwaiger, S.; Seger, C.; Wiesbauer, B.; Schneider, P.; Ellmerer, E. P.; Sturm, S.; Stuppner, H. Development of an HPLC-PAD-MS assay for the identification and quantification of major phenolic edelweiss (*Leontopodium alpium* Cass.) constituents. *Phytochemical Analysis* **2006,** *17* (5), 291-298.

740. Gongora, L.; Menez, S.; Giner, R. M.; Recio, M. D.; Schinella, G.; Rios, J. L. Inhibition of xanthine oxidase by phenolic conjugates of methylated quinic acid. *Planta Med.* **2003,** *69* (5), 396-401.

741. Gongora, L.; Giner, R. M.; Manez, S.; Recio, M. D.; Rios, J. L. *Phagnalon rupestre* as a source of compounds active on contact hypersensitivity. *Planta Med.* **2002,** *68* (6), 561-564.

742. Giner, E.; El, A. M.; Manez, S.; Recio, M. C.; Rios, J. L.; Giner, R. M. Phenolic substances from *Phagnalon rupestre* protect against 2,4,6-trinitrochlorobenzene-induced contact hypersensitivity. *J. Nat Prod.* **2011,** *74* (5), 1079-1084.

743. Kasper, J.; Melzig, M. F.; Jenett-Siems, K. New phenolic compounds of *Acmella ciliata*. *Planta Med.* **2010,** *76* (6), 633-635.

744. Tamura, Y.; Hattori, M.; Konno, K.; Kono, Y.; Honda, H.; Ono, H.; Yoshida, M. Triterpenoid and caffeic acid derivatives in the leaves of ragweed, *Ambrosia artemisiifolia* L. (Asterales : Asteraceae), as feeding stimulants of Ophraella communa LeSage (Coleoptera : Chrysomelidae). *Chemoecology* **2004,** *14* (2), 113-118.

745. Merfort, I. Caffeoylquinic acids from flowers of *Arnica montana* and *Arnica chamissonis*. *Phytochem.* **1992,** *31*, 2111-2113.

746. Spitaler, R.; Schlorhaufer, P. D.; Ellmerer, E. P.; Merfort, I.; Bortenschlager, S.; Stuppner, H.; Zidorn, C. Altitudinal variation of secondary metabolite profiles in flowering heads of *Arnica montana* cv. ARBO. *Phytochem.* **2006,** *67* (4), 409-417.

747. Ganzera, M.; Egger, C.; Zidorn, C.; Stuppner, H. Quantitative analysis of flavonoids and phenolic acids in *Arnica montana* L. by micellar electrokinetic capillary chromatography. *Anal. Chim. Acta* **2008,** *614* (2), 196-200.

748. Spitaler, R.; Winkler, A.; Lins, I.; Yanar, S.; Stuppner, H.; Zidorn, C. Altitudinal variation of phenolic contents in flowering heads of *Arnica montana* cv. ARBO: a 3-year comparison. *J Chem. Ecol.* **2008,** *34* (3), 369-375.

749. Albert, A.; Sareedenchai, V.; Heller, W.; Seidlitz, H. K.; Zidorn, C. Temperature is the key to altitudinal variation of phenolics in *Arnica montana* L. cv. ARBO. *Oecologia.* **2009,** *160* (1), 1-8.

750. Perry, N. B.; Burgess, E. J.; Rodriguez Guitian, M. A.; Romero Franco, R.; Lopez Mosquera, E.; Smallfield, B. M.; Joyce, N. I.; Littlejohn, R. P. Sesquiterpene lactones in *Arnica montana*: helenalin and dihydrohelenalin chemotypes in Spain. *Planta Med.* **2009,** *75* (6), 660-666.

751. Jaiswal, R.; Kuhnert, N. Identification and characterization of two new derivatives of chlorogenic acids in Arnica (*Arnica montana* L.) flowers by high-performance liquid chromatography/tandem mass spectrometry. *J. Agric. Food Chem.* **2011,** *59* (8), 4033-4039.

752. Clauser, M.; Aiello, N.; Scartezzini, F.; Innocenti, G.; Dall'Acqua, S. Differences in the chemical composition of *Arnica montana* flowers from wild populations of north Italy. *Nat. Prod. Commun.* **2014,** *9* (1), 3-6.

753. Cheminat, A.; Zawatzky, R.; Becker, H.; Brouillard, R. Caffeoyl conjugates from *Echinacea* species: Structures and biological activity. *Phytochem.* **1988,** *27* (9), 2787-2794.

754. Pellati, F.; Benvenuti, S.; Melegari, M.; Lasseigne, T. Variability in the composition of anti-oxidant compounds in *Echinacea* species by HPLC. *Phytochem. Anal.* **2005,** *16* (2), 77-85.

755. Lee, K. Y.; Kim, T. B.; Kim, Y. C.; Sung, S. H.; Ha, N. R. Characterization of triterpenoids, flavonoids and phenolic acids in *Eclipta prostrata* by high-performance liquid chromatography/diode-array detector/electrospray Ionization with multi-stage tandem mass spectroscopy. *Natural Product Sciences* **2010,** *16* (3), 164-168.

756. Fang, X.; Wang, J.; Hao, J.; Li, X.; Guo, N. Simultaneous extraction, identification and quantification of phenolic compounds in *Eclipta prostrata* using microwave-assisted extraction combined with HPLC–DAD–ESI–MS/MS. *Food Chem.* **2015,** *188* (0), 527-536.

757. Leung, J.; Fenton, T. W.; Clandinin, D. R. Phenolic components of sunflower flour. *J. Food Sci.* **1981,** *46*, 1386-1388 + 1393.

758. Dabrowski, K. J.; Sosulski, F. W. Composition of free and hydrolyzable phenolic acids in defatted flours of ten oilseeds. *J. Agric. Food Chem.* **1984,** *32*, 128-130.

759. Vaintraub, I. A.; Kratch, V. V. Changes in free and bound chlorogenic acid and in polyphenoloxidase activity during the industrial processing of sunflower seeds. *Nahrung* **1989,** *33*, 95-97.

760. Tomás-Barberán, F. A.; Martos, I.; Ferreres, F.; Radovic, B. S.; Anklam, E. HPLC flavonoid profiles as markers for the botanical origin of European unifloral honeys. *J. Sci. Food Agric.* **2001,** *81*, 485-496.

761. Yaoa, L.; Jiang, Y.; Singanusong, R.; Datta, N.; Raymont, K. Phenolic acids in Australian *Melaleuca*, *Guioa*, *Lophostemon*, *Banksia* and *Helianthus* honeys and their potential for floral authentication. *Food Research International* **2005,** *38* (6), 651-658.

762. Weisz, G. M.; Kammerer, D. R.; Carle, R. Identification and quantification of phenolic compounds from sunflower (*Helianthus annuus* L.) kernels and shells by HPLC-DAD/ESI-MSn. *Food Chem.* **2009,** *115* (2), 758-765.

763. Karamac, M.; Kosinska, A.; Estrella, I.; Hernandez, T.; Duenas, M. Antioxidant activity of phenolic compounds identified in sunflower seeds. *Eur. Food Res. Technol.* **2012,** *235*, 221-230.

764. Liang, Q.; Cui, J.; Li, H.; Liu, J.; Zhao, G. Florets of sunflower (*Helianthus annuus* L.): potential new sources of dietary fiber and phenolic acids. *J. Agric. Food Chem.* **2013,** *61* (14), 3435-3442.

765. Sun, Z.; Chen, J.; Ma, J.; Jiang, Y.; Wang, M.; Ren, G.; Chen, F. Cynarin-rich sunflower (*Helianthus annuus*) sprouts possess both antiglycative and antioxidant activities. *J Agric. Food Chem.* **2012,** *60* (12), 3260-3265.

766. Tchone, G.; Baerwald, G.; Annemueller, G.; Fleischer, L.-G. Separation and identification of phenolic compounds in Jerusalem artichoke (*Helianthus tuberosus* L.). *Science des Aliments* **2006,** *26*, 394-408.

767. Kays, S. J.; Nottingham, S. F. *Biology and chemistry of Jerusalem Artichoke: Helianthus tuberosus L.;* CRC Press: 2007.

768. Yuan, X.; Gao, M.; Xiao, H.; Tan, C.; Du, Y. Free radical scavenging activities and bioactive substances of Jerusalem artichoke (*Helianthus tuberosus* L.) leaves. *Food Chem.* **2012,** *133* (1), 10-14.

769. Chen, F.; Long, X.; Liu, Z.; Shao, H.; Liu, L. Analysis of phenolic acids of Jerusalem Artichoke (*Helianthus tuberosus* L.) responding to salt-stress by liquid chromatography/tandem mass spectrometry. *Scientific World Journal* **2014,** http://dx.doi.org/10.1155/2014/568043.

770. Lee, S. Y.; Shin, Y. J.; Choi, S. U.; Lee, K. R. A new flavonol glycoside from the aerial part of *Rudbeckia laciniata*. *Arch. Pharm. Res.* **2013**.

771. Wang, L.; Wang, T.; Guo, Q. S.; Huang, Y.; Xu, H. K. [Comparative study on four major active compounds of *Sanvitalia procumbens* and *Chrysanthemum morifolium* cv 'Hangju' and 'Gongju']. *Zhongguo Zhong. Yao Za Zhi.* **2013,** *38* (20), 3442-3445.

772. Fucina, G.; Rocha, L. W.; da Silva, G. F.; Hoepers, S. M.; Ferreira, F. P.; Guaratini, T.; Cechinel Filho, V.; Lucinda-Silva, R. M.; Quintão, N. L. M.; Bresolin, T. M. B. Topical anti-inflammatory phytomedicine based on *Sphagneticola trilobata* dried extracts. *Pharmaceutical biology* **2016,** *101*, 530-536.

773. Agata, I.; Goto, S.; Hatano, T.; Ishibe, S.; Okuda, T. 1,3,5-tri-*O*-caffeoylquinic acid from *Xanthium strumarium*. *Phytochem.* **1997,** *33*, 508-509.

774. Yoon, H. N.; Lee, M. Y.; Kim, J. K.; Suh, H. W.; Lim, S. S. Aldose reductase inhibitory compounds from *Xanthium strumarium*. *Archives of Pharmacal Research* **2013,** *36* (9), 1090-1095.

775. Han, T.; Zhang, Q. Y.; Zhang, H.; Wen, J.; Wang, Y.; Huang, B. K.; Rahman, K.; Zheng, H. C.; Qin, L. P. Authentication and quantitative analysis on the chemical profile of *Xanthium* fruit (Cang-Er-Zi) by high-performance liquid chromatography-diode-array detection tandem mass spectrometry method. *Analytica Chimica Acta* **2009,** *634* (2), 272-278.

776. Yang, L.; Su, Z.; Zeng, X.; Li, X.; Wu, Z.; Xu, S.; Yan, Y. Quality assessment of Fructus xanthii based on fingerprinting using high-performance liquid chromatography. *J AOAC Int* **2012,** *95* (4), 1053-1058.

777. Sato, M.; Hiraoka, A.; Watanabe, M. Inhibition of γ–irradiation-induced oxidation of chlorogenate by 1,3-dicaffeoylquinate in *Xanthium occidentale*. *Phytochem.* **1993,** *33*, 1357-1360.

778. Ma, Y. T.; Huang, M. C.; Hsu, F. L.; Chang, H. F. Thiazinedione from *Xanthium strumarium*. *Phytochem.* **1998,** *48* (6), 1083-1085.

779. Yoon, H. N.; Lee, M. Y.; Kim, J. K.; Suh, H. W.; Lim, S. S. Aldose reductase inhibitory compounds from *Xanthium strumarium*. *Arch. Pharm. Res.* **2013,** *36* (9), 1090-1095.

780. Ranger, C. M.; Singh, A. P.; Frantz, J. M.; Canas, L.; Locke, J. C.; Reding, M. E.; Vorsa, N. Influence of Silicon on Resistance of *Zinnia elegans* to *Myzus persicae* (Hemiptera: Aphididae) . *Environmental Entomology* **2009,** *38* (1), 129-136.

781. Toffoli-Kadri, M. C.; Carollo, C. A.; Lourenco, L. D.; Felipe, J. L.; Nespoli, J. H.; Wollf, L. G.; Resende, G. M.; de Lima, J. R.; Franco, V. N.; Vieira, M. C.; de Siqueira, J. M. *In vivo* and *in vitro* anti-inflammatory properties of *Achyrocline alata* (Kunth) DC. *J. Ethnopharmacol.* **2014,** *153* (2), 461-468.

782. Zheleva-Dimitrova, D.; Gevrenova, R.; Zaharieva, M. M.; Najdenski, H.; Ruseva, S.; Lozanov, V.; Balabanova, V.; Yagi, S.; Momekov, G.; Mitev, V. HPLC-UV and LC-MS analyses of acylquinic acids in *Geigeria alata* (DC) Oliv. & Hiern. and their contribution to antioxidant and antimicrobial capacity. *Phytochemical Analysis* **2017**.

783. Stojakowska, A.; Malarz, J.; Kiss, A. K. Hydroxycinnamates from elecampane (*Inula helenium* L.) callus culture. *Acta Physiologiae Plantarum* **2016,** *38* (2).

784. Kinoshita, K.; Kawai, T.; Imaizumi, T.; Akita, Y.; Koyama, K.; Takahashi, K. Anti-emetic principles of *Inula linariaefolia* flowers and *Forsythia suspensa* fruits. *Phytomed.* **1996,** *3* (1), 51-58.

785. Stojakowska, A.; Malarz, J.; Zubek, S.; Turnau, K.; Kisiel, W. Terpenoids and phenolics from *Inula ensifolia*. *Biochem. Syst. Ecol.* **2010,** *38* (2), 232-235.

786. Aboul-Ela, M. A.; El-Lakany, A. M.; Shams Eldin, S. M.; Hammoda, H. M. A new validated HPTLC method for quantitative determination of 1, 5-dicaffeoylquinic acid in *Inula crithmoides* roots. *Pak. J Pharm. Sci.* **2012,** *25* (4), 721-725.

787. Ela, M. A.; El-Lakany, A. M.; Abdel-Kader, M. S.; Alqasoumi, S. I.; Shams-El-Din, S. M.; Hammoda, H. M. New quinic acid derivatives from hepatoprotective *Inula crithmoides* root extract. *HCA* **2012,** *95* (1), 61-66.

788. Mahmoudi, H.; Hosni, K.; Zaouali, W.; Amri, I.; Zargouni, H.; Hamida, N. B.; Kaddour, R.; Hamrouni, L.; Nasri, M. B.; Ouerghi, Z. Comprehensive phytochemical analysis, antioxidant and antifungal activities of *Inula viscosa* Aiton leaves. *J Food Saf* **2015,** n/a.

789. Boussaha, S.; Bekhouche, K.; Boudjerda, A.; Leon, F.; Koldas, S.; Yaglioglu, A. S.; Demirtas, I.; Brouard, I.; Marchioni, E.; Zama, D.; Benayache, S.; Benayache, F. Chemical constituents, *in vitro* antioxidant and antiproliferative activities of *Perralderia coronopifolia* Coss. subsp *eu-coronopifolia* M. var. *typica* M. extract. *Records of Natural Products* **2015,** *9* (3), 312-322.

790. Venditti, A.; Bianco, A.; Muscolo, C.; Zorzetto, C.; SÃ¡nchez-Mateo, C. C.; Rabanal, R. M.; Quassinti, L.; Bramucci, M.; Damiano, S.; Iannarelli, R.; Lupidi, G.; Papa, F.; Petrelli, D.; Vitali, L. A.; Vittori, S.; Maggi, F. Bioactive secondary metabolites from *Schizogyne sericea* (Asteraceae) endemic to Canary Islands. *Chemistry & Biodiversity* **2016,** *13*, 826-836.

791. Stojakowska, A.; Malarz, J.; Zylewski, M.; Kisiel, W. Acylated hydroxycinnamic acid glucosides from flowers of *Telekia speciosa*. *Phytochemistry Letters* **2015,** *12* (0), 257-261.

792. Ono, M.; Masuoka, C.; Odake, Y.; Ikegashira, S.; Ito, Y.; Nohara, T. Antioxidative constituents from *Tessaria integrifolia*. *Food Science and Technology Research* **2000,** *6* (2), 106-114.

793. Takenaka, M.; Yan, X.; Ono, H.; Yoshida, M.; Nagata, T.; Nakanishi, T. Caffeic acid derivatives in the roots of Yacon (*Smallanthus sonchifolius*). *J. Agric. Food Chem.* **2003,** *51* (3), 793-796.

794. Serra-Barcellona, C.; Coll Araoz, M. V.; Cabrera, W. M.; Habib, N. C.; Honore, S. M.; Catalan, C. A.; Grau, A.; Genta, S. B.; Sanchez, S. S. *Smallanthus macroscyphus*: a new source of antidiabetic compounds. *Chem. Biol. Interact.* **2014,** *209*, 35-47.

795. Barcellona, C. S.; Cabrera, W. M.; HonorÃ©, S. M.; Mercado, M. a. I. s.; SÃ¡nchez, S. S.; Genta, S. B. Safety assessment of aqueous extract from leaf *Smallanthus sonchifolius* and its main active lactone, enhydrin. *J. Ethnopharmacol.* **2012,** *144* (2), 362-370.

796. Russo, D.; Valentao, P.; Andrade, P. B.; Fernandez, E. C.; Milella, L. Evaluation of antioxidant, antidiabetic and anticholinesterase activities of *Smallanthus sonchifolius* Landraces and correlation with their phytochemical profiles. *International Journal of Molecular Sciences* **2015,** *16* (8), 17696-17718.

797. Martino, V.; Debenedetti, S. L.; Coussio, J. D. Caffeoylquinic acids from *Pterocaulon virgatum* and *Pluchea sagittalis*. *Phytochem.* **1979,** *18*, 2052-2053.

798. Scholz, E.; Heinrich, M.; Hunkler, D. Caffeoylquinic acids and some biological activities of *Pluchea symphytifolia*. *Planta Med.* **1994,** *60* (4), 360-364.

799. Arsiningtyas, I. S.; Gunawan-Puteri, M. D.; Kato, E.; Kawabata, J. Identification of alpha-glucosidase inhibitors from the leaves of *Pluchea indica* (L.) Less., a traditional Indonesian herb: promotion of natural product use. *Nat. Prod. Res.* **2014,** *28*, 1350-1353.

800. Cordova, W. H. P.; Kevers, C.; Michiels, J. A.; Salabarria, I. S.; Dommes, J. Variation in phenolic constituents and antioxidant capacities of plant organs of three Cuban species of *Pluchea* Cass. (Asteraceae) under *ex vitro* and *in vitro* growth conditions. *J. Med. Plants Res.* **2013,** *7*, 2523-2532.

801. Park, H.-J.; Nugroho, A.; Lee, J. H.; Kim, J.-D.; Kim, W.-B.; Lee, K. R.; Choi, J. S. HPLC analysis of caffeoylquinic acids in the extract of *Cacalia firma* and peroxynitrite scavenging effect. *Korean Journal of Pharmacognosy* **2009,** *40*, 365-369.

802. Wan, C.; Yu, Y.; Zhou, S.; Tian, S.; Cao, S. Isolation and identification of phenolic compounds from *Gynura divaricata* leaves. *Pharmacogn. Mag.* **2011,** *7* (26), 101-108.

803. Chen, J.; Mangelinckx, S.; Ma, L.; Wang, Z.; Li, W.; De Kimpe, N. Caffeoylquinic acid derivatives isolated from the aerial parts of *Gynura divaricata* and their yeast α-glucosidase and PTP1B inhibitory activity. *Fitoterapia* **2014,** (0).

804. Chen, J.; Mangelinckx, S.; Lu, H.; Wang, Z.-T.; Li, W.-L.; De Kimpe, N. Profiling and elucidation of the phenolic compounds in the aerial parts of *Gynura bicolor* and *G. divaricata* collected from different Chinese origins. *Chemistry & Biodiversity* **2015,** *12* (1), 96-115.

805. Teoh, W. Y.; Tan, H. P.; Ling, S. K.; Abdul Wahab, N.; Sim, K. S. Phytochemical investigation of *Gynura bicolor* leaves and cytotoxicity evaluation of the chemical constituents against HCT 116 cells. *Natural Product Research* **2016,** *30* (4), 448-451.

806. Siriwatanametanon, N.; Heinrich, M. The Thai medicinal plant *Gynura pseudochina* var. *hispida*: chemical composition and *in vitro* NF-KB inhibitory activity. *Natural Product Communications* **2011,** *6* (5), 627-630.

807. Nuringtyas, T. R.; Choi, Y. H.; Verpoorte, R.; Klinkhamer, P. G.; Leiss, K. A. Differential tissue distribution of metabolites in *Jacobaea vulgaris*, *Jacobaea aquatica* and their crosses. *Phytochem.* **2012,** *78*, 89-97.

808. Shang, Y. F.; Kim, S. M.; Song, D. G.; Pan, C. H.; Lee, W. J.; Um, B. H. Isolation and identification of antioxidant compounds from *Ligularia fischeri*. *J. Food Sci.* **2010,** *75* (6), C530-C535.

809. Lee, B. I.; Nugroho, A.; Bachri, M. S.; Choi, J.; Lee, K. R.; Choi, J. S.; Kim, W. B.; Lee, K. T.; Lee, J. D.; Park, H. J. Anti-ulcerogenic effect and HPLC analysis of the caffeoylquinic acid-rich extract from *Ligularia stenocephala*. *Biol. Pharm. Bull.* **2010,** *33* (3), 493-497.

810. Nugroho, A.; Park, H. J.; Choi, J.; Choi, J. S.; Kim, W. B.; Kim, J. D.; Bachri, M. S.; Lee, B. I. The inhibitory effect of the caffeoylquinic acid-rich extract of *Ligularia stenocephala* leaves on obesity in the high fat diet-induced rat. *Natural Product Sciences* **2010,** *16* (2), 80-87.

811. Kim, S. M.; Jeon, J. S.; Kang, S. W.; Jung, Y. J.; Ly, L. N.; Um, B. H. Content of antioxidative caffeoylquinic acid derivatives in field-grown *Ligularia fischeri* (Ledeb.) Turcz and responses to sunlight. *J Agric. Food Chem.* **2012,** *60* (22), 5597-5603.

812. Park, C. H.; Ahn, M. J.; Hwang, G. S.; An, S. E.; Whang, W. K. Cosmeceutical bioactivities of isolated compounds from *Ligularia fischeri* Turcz leaves. *Applied Biological Chemistry* **2016,** *59* (3), 485-494.

813. Hussain, S. H.; Latif, A.; Cox, R. J.; Simpson, T. J.; Ali, M.; Arfan, M.; Uddin, G. Phytochemicals from the aerial parts of *Ligularia thomsonii* and their radical scavenging activity. *Phytochemistry Letters* **2014,** *7* (0), 6-10.

814. Kim, S. M.; Kang, S. W.; Jeon, J. S.; Jung, Y. J.; Kim, C. Y.; Pan, C. H.; Um, B. H. Rapid identification and evaluation of antioxidant compounds from extracts of *Petasites japonicus* by hyphenated-HPLC techniques. *Biomed. Chromatogr.* **2012,** *26* (2), 199-207.

815. Zhang, Y.; Guo, F.; Zeng, P.; Jia, Q.; Li, Y.; Zhu, W.; Chen, K. [Phenolic components from *Petasites tricholobus*]. *Zhongguo Zhong. Yao Za Zhi.* **2012,** *37* (12), 1782-1787.

816. Arciniegas, A.; Perez-Castorena, A. L.; Villasen¦or, J. L.; Romo de Vivar, A. Chemical constituents of *Roldana aschenborniana*. *Biochem. Syst. Ecol.* **2004,** *32* (6), 615-618.

817. Tan, D. P.; Chou, G. X.; Wang, Z. T. Phenolic compounds from *Senecio scandens*. *Biochem. Syst. Ecol.* **2010,** *38* (1), 122-124.

818. Yang, X.; Yang, L.; Xiong, A.; Li, D.; Wang, Z. Authentication of *Senecio scandens* and *S. vulgaris* based on the comprehensive secondary metabolic patterns gained by UPLC-DAD/ESI-MS. *J. Pharm. Biomed. Anal.* **2011,** *56* (2), 165-172.

819. de Souza, R. R.; Bretanha, L. C.; Dalmarco, E. M.; Pizzolatti, M. G.; Fröde, T. S. Modulatory effect of *Senecio brasiliensis* (Spreng) Less. in a murine model of inflammation induced by carrageenan into the pleural cavity. *J. Ethnopharmacol.* **2015,** (0).

820. Gao, H.; Huang, Y. N.; Gao, B.; Xu, P. Y.; Inagaki, C.; Kawabata, J. α-Glucosidase inhibitory effect by the flower buds of *Tussilago farfara* L. *Food Chem.* **2008,** *106* (3), 1195-1201.

821. Li, Z. Y.; Zhi, H. J.; Xue, S. Y.; Sun, H. F.; Zhang, F. S.; Jia, J. P.; Xing, J.; Zhang, L. Z.; Qin, X. M. Metabolomic profiling of the flower bud and rachis of *Tussilago farfara* with antitussive and expectorant effects on mice. *J Ethnopharmacol.* **2012,** *140* (1), 83-90.

822. Li, Z. Y.; Zhi, H. J.; Zhang, F. S.; Sun, H. F.; Zhang, L. Z.; Jia, J. P.; Xing, J.; Qin, X. M. Metabolomic profiling of the antitussive and expectorant plant *Tussilago farfara* L. by nuclear magnetic resonance spectroscopy and multivariate data analysis. *J Pharm. Biomed. Anal.* **2013,** *75*, 158-164.

823. Tian, D.; Li, Z. Y.; Jia, J. P.; Qin, X. M. Characterization of Farfarae Flos by proton nuclear magnetic resonance fingerprinting and chemometrics. *Analytical Letters* **2015,** *48* (1), 127-136.

824. Kang, U.; Park, J.; Nam, J. W.; Lee, S. K.; Woo, M. H.; Lee, J. H.; Woo, H. A.; Seo, E. K. Identification of phenolic compounds from the flower buds of *Tussilago farfara* and their antioxidative effects. *Planta Med.* **2014,** *80*, PD29.

825. Scognamiglio, M.; Esposito, A.; DəAbrosca, B.; Pacifico, S.; Fiumano, V.; Tsafantakis, N.; Monaco, P.; Fiorentino, A. Isolation, distribution and allelopathic effect of caffeic acid derivatives from *Bellis perennis* L. *Biochem. Syst. Ecol.* **2012,** *43*, 108-113.

826. Fontanel, D.; Galtier, C.; Viel, C.; Gueiffier, A. Caffeoyl quinic and tartaric acids and flavonoids from *Lapsana communis* L. subsp. *communis* (Asteraceae). *Zeitschrift fur Naturforschung C-A Journal of Biosciences* **1998,** *53* (11-12), 1090-1092.

827. Kühnl, T.; Koch, U.; Heller, W.; Wellmann, E. Chlorogenic acid biosynthesis: characterisation of a light-induced microsomal 5-*O*-(4-coumaroyl)-D-quinate/shikimate 3'-hydroxylase from carrot (*Daucus carota*) cell suspension cultures. *Arch. Biochem. Biophys.* **1987,** *258*, 226-232.

828. Grimmig, B.; Matern, U. Structure of the parsley caffeoyl-CoA *O*-methyltransferase gene, harbouring a novel elicitor responsive cis-acting element. *Plant Mol. Biol.* **1997,** *33* (2), 323-341.

829. Brandl, W.; Galensa, R.; Herrmann, K. HPLC analysis of celery components (hydroxycinnamic acid esters, sugars, mannitol, phthalides). *Z. Lebensm. Unters. -Forsch.* **1983,** *177*, 325-327.

830. Haghi, G.; Hatami, A.; Mehran, M.; Hosseini, H. Caffeic acid derivatives from *Bupleurum chinense*. *Research in pharmaceutical sciences* **2014,** *9* (5), 323-330.

831. Nguyen, H. T.; Uto, T.; Morinaga, O.; Shoyama, Y. Chemical constituents from the aerial parts of *Bupleurum falcatum* L. and biological evidences. *Natural Product Sciences* **2015,** *21* (2), 71-75.

832. Dirks, U.; Herrmann, K. Hochleistungsflüssigkeitschromatographie der Hydroxycinnamoylchinäsauren und der 4-(β-D-Glucopyranosyloxy)-benzoesäure in Gewürzen. *Lebensm. Unters. Forsch.* **1984,** *179*, 12-16.

833. Plazonic, A.; Bucar, F.; Males, Z.; Mornar, A.; Nigovic, B.; Kujundzic, N. Identification and quantification of flavonoids and phenolic acids in burr parsley (*Caucalis platycarpos* L.), using high-performance liquid chromatography with diode array detection and electrospray ionization mass spectrometry. *Molecules* **2009,** *14* (7), 2466-2490.

834. Kaiser, A.; Kammerer, D. R.; Carle, R. Impact of blanching on polyphenol stability and antioxidant capacity of innovative coriander (*Coriandrum sativum* L.) pastes. *Food Chem.* **2013,** *140* (1-2), 332-339.

835. Antognoni, F.; Perellino, N. C.; Crippa, S.; Dal, T. R.; Danieli, B.; Minghetti, A.; Poli, F.; Pressi, G. Irbic acid, a dicaffeoylquinic acid derivative from *Centella asiatica* cell cultures. *Fitoterapia* **2011,** *82* (7), 950-954.

836. Long, H. S.; Stander, M. A.; Van Wyk, B. E. Notes on the occurrence and significance of triterpenoids (asiaticoside and related compounds) and caffeoylquinic acids in *Centella* species. *South African Journal of Botany* **2012,** *82*, 53-59.

837. Maulidiani, A. F.; Khatib, A.; Shaari, K.; Lajis, N. H. Chemical characterization and antioxidant activity of three medicinal Apiaceae species. *Industrial Crops and Products* **2014,** *55* (0), 238-247.

838. Satake, T.; Kamiya, K.; An, Y.; Oishi, T.; Yamamoto, J. The anti-thrombotic active constituents from *Centella asiatica*. *Biol. Pharm. Bull.* **2007,** *30* (5), 935-940.

839. Dall'Acqua, S.; Viola, G.; Piacente, S.; Cappelletti, E. M.; Innocenti, G. Cytotoxic constituents of roots of *Chaerophyllum hirsutum*. *J. Nat Prod.* **2004,** *67* (9), 1588-1590.

840. Martins, N.; Barros, L.; Santos-Buelga, C.; Ferreira, I. C. F. R. Antioxidant potential of two Apiaceae plant extracts: A comparative study focused on the phenolic composition. *Industrial Crops and Products* **2016,** *79*, 188-194.

841. Clifford, M. N.; Knight, S. The cinnamoyl–amino acid conjugates of green robusta coffee beans. *Food Chem.* **2004,** *87*, 457-463.

842. Kammerer, D.; Carle, R.; Schieber, A. Characterization of phenolic acids in black carrots (*Daucus carota* ssp. *sativus* var. *atrorubens* Alef.) by high-performance liquid chromatography/electrospray ionization mass spectrometry. *Rapid Commun. Mass Spectrom.* **2004,** *18* (12), 1331-1340.

843. Ma, T.; Tian, C.; Luo, J.; Zhou, R.; Sun, X.; Ma, J. Influence of technical processing units on polyphenols and antioxidant capacity of carrot (*Daucus carrota* L.) juice. *Food Chem.* **2013,** *141* (3), 1637-1644.

844. Delnavazi, M. R.; Hadjiakhoondi, A.; Delazar, A.; Ajani, Y.; Yassa, N. Azerosides A and B: Two new phloroacetophenone glycosides from the roots of *Dorema glabrum* Fisch & CA Mey. *Medicinal Chemistry Research* **2015,** *24* (2), 787-796.

845. Delnavazi, M. R.; Hadjiakhoondi, A.; Delazar, A.; Ajani, Y.; Tavakoli, S.; Yassa, N. Phytochemical and antioxidant investigation of the aerial parts of *Dorema glabrum* Fisch & CA Mey. *Iranian Journal of Pharmaceutical Research* **2015,** *14* (3), 925-931.

846. Cadiz-Gurrea, M. d. l. L.; Fernandez-Arroyo, S.; Joven, J.; Segura-Carretero, A. Comprehensive characterization by UHPLC-ESI-Q-TOF-MS from an *Eryngium bourgatii* extract and their antioxidant and anti-inflammatory activities. *Food Research International* **2013,** *50*, 197-204.

847. Matei, M. F.; Jaiswal, R.; Kuhnert, N. Investigating the chemical changes of chlorogenic acids during coffee brewing - conjugate addition of water to the olefinic moiety of chlorogenic acids and their quinides. *J Agric. Food Chem.* **2012,** *60*, 12105-12115.

848. Matei, M. F.; Jaiswal, R.; Kuhnert, N. LC-MSn study of the chemical transformations of hydroxycinnamates during yerba maté (*Ilex paraguariensis*) tea brewing. *Food Research International* **2016**.

849. Jaiswal, R.; Müller, H.; Müller, A.; Karar, M. G. E.; Kuhnert, N. Identification and characterization of chlorogenic acids, chlorogenic acid glycosides and flavonoids from *Lonicera henryi* L. (Caprifoliaceae) leaves by LC--MS^n. *Phytochem.* **2014,** *108* (0), 252-263.

850. Gohari, A.; Saeidnia, S.; Moghaddam, M. K.; Yassa, N.; Malmir, M.; Shahverdi, A. Isolation of a new quinic acid derivative and its antibacterial modulating activity. *Daru-Journal of Faculty of Pharmacy* **2010,** *18* (1), 69-73.

851. Znati, M.; Ben Jannet, H.; Cazaux, S.; Souchard, J. P.; Skhiri, F. H.; Bouajila, J. Antioxidant, 5-lipoxygenase inhibitory and cytotoxic activities of compounds isolated from the *Ferula lutea* flowers. *Molecules* **2014,** *19* (10), 16959-16975.

852. Alkhatib, R.; Hennebelle, T.; Roumy, V.; Sahpaz, S.; Suzgec, S.; Akalin, E.; Mericli, A. H.; Bailleul, F. Coumarins, caffeoyl derivatives and a monoterpenoid glycoside from *Ferulago asparagifolia*. *Biochem. Syst. Ecol.* **2009,** *37* (3), 230-233.

853. Krizman, M.; Baricevic, D.; Prosek, M. Determination of phenolic compounds in fennel by HPLC and HPLC-MS using a monolithic reversed-phase column. *J. Pharm. Biomed. Anal.* **2007,** *43* (2), 481-485.

854. Parejo, I.; Viladomat, F.; Bastida, J.; Schmeda-Hirschmann, G.; Burillo, J.; Codina, C. Bioguided isolation and identification of the nonvolatile antioxidant compounds from fennel (Foeniculum vulgare Mill.) waste. *J Agric. Food Chem.* **2004,** *52* (7), 1890-1897.

855. Parejo, I.; Jauregui, O.; Sanchez-Rabaneda, F.; Viladomat, F.; Bastida, J.; Codina, C. Separation and characterization of phenolic compounds in fennel (*Foeniculum vulgare*) using liquid chromatography-negative electrospray ionization tandem mass spectrometry. *J Agric. Food Chem.* **2004,** *52* (12), 3679-3687.

856. Parejo, I.; Viladomat, F.; Bastida, J.; Codina, C. Development and validation of a high-performance liquid chromatographic method for the analysis of antioxidative phenolic compounds in fennel using a narrow bore reversed phase C18 column. *Analytica Chimica Acta* **2004,** *512* (2), 271-280.

857. Pacifico, S.; Galasso, S.; Piccolella, S.; Kretschmer, N.; Pan, S. P.; Nocera, P.; Lettieri, A.; Bauer, R.; Monaco, P. Winter Wild Fennel leaves as source of anti-inflammatory and antioxidant polyphenols. *Arabian Journal of Chemistry* **2015,** (0).

858. Salami, M.; Rahimmalek, M.; Ehtemam, M. H. Inhibitory effect of different fennel (*Foeniculum vulgare*) samples and their phenolic compounds on formation of advanced glycation products and comparison of antimicrobial and antioxidant activities. *Food Chem.* **2016,** *213*, 196-205.

859. Nacef, S.; Jannet, H. B.; Abreu, P.; Mighri, Z. Phenolic constituents of *Convolvulus dorycnium* L. flowers. *Phytochemistry Letters* **2010,** *3* (2), 66-69.

860. Adhikari, B.; Devkota, H. P.; Joshi, K. R.; Watanabe, T.; Yahara, S. Two new diacetylene glycosides: bhutkesoside A and B from the roots of *Ligusticopsis wallichiana*. *Natural Product Research* **2016,** *30* (14), 1577-1584.

861. Sieniawska, E.; Baj, T.; Los, R.; Skalicka-Wozniak, K.; Malm, A.; Glowniak, K. Phenolic acids content, antioxidant and antimicrobial activity of *Ligusticum mutellina* L. *Nat. Prod. Res.* **2013,** *27* (12), 1108-1110.

862. Ruan, M.; Li, Y.; Li, X.; Luo, J.; Kong, L. Qualitative and quantitative analysis of the major constituents in Chinese medicinal preparation Guan-Xin-Ning injection by HPLC-DAD-ESI-MS(n). *J Pharm. Biomed. Anal.* **2012,** *59*, 184-189.

863. Li, M. J.; Wang, F. Q.; Huang, Y. H.; Du, F. F.; Zhong, C. C.; Olaleye, O. E.; Jia, W. W.; Li, Y. F.; Xu, F.; Dong, J. J.; Li, J.; Lim, J. B. R.; Zhao, B. C.; Jia, L. F.; Li, L.; Li, C. Systemic exposure to and disposition of catechols derived from *Salvia miltiorrhiza* roots (Danshen) after Intravenous dosing DanHong injection in human subjects, rats, and dogs. *Drug Metab. Disp.* **2015,** *43* (5), 679-690.

864. Li, X. X.; Cheng, C.; Wang, F. Q.; Huang, Y. H.; Jia, W. W.; Olaleye, O. E.; Li, M. J.; Li, Y. F.; Li, C. Pharmacokinetics of catechols in human subjects intravenously receiving XueBiJing injection, an emerging antiseptic herbal medicine. *Drug Metabolism and Pharmacokinetics* **2016,** *31* (1), 95-98.

865. Barron, D.; Kaouadji, M.; Mariotte, A. M. Cinnamic Acid Esters from *Meum athamanticum*. *J. Nat. Prod.* **1984,** *47* (4), 737-738.

866. Barron, D.; Kaouadji, M.; Mariotte, A.-M. New cinnamoyl esters of quinic acid from *Meum athamanticum*. *Z. Naturforsch.* **1984,** *39*, 167-170.

867. Barron, D.; Kolodie, L.; Mariotte, A. M. Mise en evidence d'une activité antiagrégante plaquettaire *in vitro* chez les ombelliféres. 1. *Meum athamanticum* Jacq. *Plantes Médicinales et Phytothérapie* **1983,** *17*, 107-113.

868. Sieniawska, E.; Skalicka-Wozniak, K. Isolation of chlorogenic acid from *Mutellina purpurea* L. herb using high-performance counter-current chromatography. *Natural Product Research* **2014,** *28* (21), 1936-1939.

869. Sieniawska, E.; Baj, T.; Dudka, J.; Mroczek, T.; Glowniak, K. TLC-DPPH center dot activity-guided separation and LC-DAD-MS identification of antioxidant compounds from *Mutellina purpurea* L. herb. *Acta Chromatographica* **2016,** *28* (1), 51-58.

870. Spinola, V.; Castilho, P. C. Phytochemical profile, chemotaxonomic studies and in vitro antioxidant activities of two endemisms from Madeira archipelago: *Melanoselinum decipiens* and *Monizia edulis* (Apiaceae). *Chemistry & Biodiversity* **2016,** n/a.

871. Farag, M. A.; Ezzat, S. M.; Salama, M. M.; Tadros, M. G. Anti-acetylcholinesterase potential and metabolome classification of 4 *Ocimum* species as determined via UPLC/qTOF/MS and chemometric tools. *J Pharm. Biomed Anal* **2016,** *125*, 292-302.

872. Fotakis, C.; Tsigrimani, D.; Tsiaka, T.; Lantzouraki, D. Z.; Strati, I. F.; Makris, C.; Tagkouli, D.; Proestos, C.; Sinanoglou, V. J.; Zoumpoulakis, P. Metabolic and antioxidant profiles of herbal infusions and decoctions. *Food Chem.* **2016,** *211*, 963-971.

873. Liu, H.; Zheng, A.; Liu, H.; Yu, H.; Wu, X.; Xiao, C.; Dai, H.; Hao, F.; Zhang, L.; Wang, Yu.; ang, H. Identification of three novel polyphenolic compounds, Origanine A–C, with unique skeleton from *Origanum vulgare* L. using the hyphenated LC-DAD-SPE-NMR/MS methods. *J. Agric. Food Chem.* **2012,** *60* (1), 129-135.

874. Nikolic, N. C.; Lazic, M. M.; Karabegovic, I. T.; Stojanovic, G. S.; Todorovic, Z. B. A characterization of content, composition and scavenging capacity of phenolic compounds in parsnip roots of various weight. *Nat. Prod. Commun.* **2014,** *9* (6), 811-814.

875. Kaiser, A.; Carle, R.; Kammerer, D. R. Effects of blanching on polyphenol stability of innovative paste-like parsley (*Petroselinum crispum* (Mill.) Nym ex A. W. Hill) and marjoram (*Origanum majorana* L.) products. *Food Chem.* **2013,** *138* (2-3), 1648-1656.

876. Lee, S. Y.; Moon, E.; Kim, S. Y.; Lee, K. R. Quinic acid derivatives from *Pimpinella brachycarpa* exert anti-neuroinflammatory activity in lipopolysaccharide-induced microglia. *Bioorg. Med. Chem. Lett.* **2013,** *23* (7), 2140-2144.

877. Dahia, M.; Siracusa, L.; Laouer, H.; Ruberto, G. Constituents of the polar extracts from Algerian *Pituranthos scoparius*. *Natural Product Communications* **2009,** *4* (12), 1691-1692.

878. Santos-Gomes, P. C.; Seabra, R. M.; Andrade, P. B.; Fernandes-Ferreira, M. Determination of phenolic antioxidant compounds produced by calli and cell suspensions of sage (Salvia officinalis L.). *J. Plant Physiol.* **2003,** *160* (9), 1025-1032.

879. Gao, J. F.; Ding, L.; Zhang, P.; Liu, J. X. [Chemical constituents of *Salvia chinensis*]. *Zhongguo Zhong. Yao Za Zhi.* **2013,** *38* (10), 1556-1559.

880. Gao, C. Y.; Tian, C. R.; Zhou, R.; Zhang, R. G.; Lu, Y. H. Phenolic composition, DNA damage protective activity and hepatoprotective effect of free phenolic extract from *Sphallerocarpus gracilis* seeds. *International Immunopharmacology* **2014,** *20* (1), 238-247.

881. Hyun, S. K.; Jung, H. A.; Min, B. S.; Jung, J. H.; Choi, J. S. Isolation of phenolics, nucleosides, saccharides and an alkaloid from the root of *Aralia cordata*. *Natural Product Sciences* **2010,** *16* (1), 20-25.

882. Papajewski, S.; Vogler, B.; Conrad, J.; Klaiber, I.; Roos, G.; Walter, C. U.; Sussmuth, R.; Kraus, W. Isolation from *Cussonia barteri* of 1'-*O*-chlorogenoylchlorogenic acid and 1'-*O*-chlorogenoylneochlorogenic acid, a new type of quinic acid esters. *Planta Med.* **2001,** *67* (8), 732-736.

883. Liu, S. P.; An, J. T.; Wang, R.; Li, Q. Simultaneous quantification of five bioactive components of *Acanthopanax senticosus* and its extract by ultra performance liquid chromatography with electrospray ionization time-of-flight mass spectrometry. *Molecules* **2012,** *17* (7), 7903-7913.

884. Tolonen, A.; Joutsamo, T.; Mattlla, S.; Kamarainen, T.; Jalonen, J. Identification of isomeric dicaffeoylquinic acids from *Eleutherococcus senticosus* using HPLC-ESI/TOF/MS and 1H-NMR methods. *Phytochem. Anal.* **2002,** *13* (6), 316-328.

885. Yang, G.; Li, W.; Huang, C.; Lin, L.; Zhang, Q.; Koike, K. Phenolic constituents from the stems of *Acanthopanax senticosus*. *Chem. Nat. Compd* **2011,** *46*, 876-879.

886. Sithisarn, P.; Muensaen, S.; Jarikasem, S. Determination of caffeoyl quinic acids and flavonoids in *Acanthopanax trifoliatus* leaves by HPLC. *Nat. Prod. Commun.* **2011,** *6* (9), 1289-1291.

887. Zhang, X. D.; Liu, X. Q.; Kim, Y. H.; Whang, W. K. Chemical constituents and their acetyl cholinesterase inhibitory and antioxidant activities from leaves of *Acanthopanax henryi*: potential complementary source against Alzheimer's disease. *Archives of Pharmacal Research* **2014,** *37* (5), 606-616.

888. Trute, A.; Nahrstedt, A. Identification and quantitative analysis of phenolic compounds from the dry extract of *Hedera helix*. *Planta Med.* **1997,** *63* (2), 177-179.

889. Bai, G.; Cao, X.; Zhang, H.; Xiang, J.; Ren, H.; Tan, L.; Tang, Y. Direct screening of G-quadruplex ligands from *Kalopanax septemlobus* (Thunb.) Koidz extract by high performance liquid chromatography. *J. Chromatogr. A* **2011,** *1218* (37), 6433-6438.

890. You, Q.; Chen, F.; Ni, H.; Wang, X.; Jiang, Y.; McCoy, J. A. HPLC-MS analyses and bioactivities of novel chemicals in Devil's club (*Oplopanax horridus* (Sm.) Miq.). *Food Chem.* **2012,** *135* (1), 199-207.

891. Buchanan, M. S.; Carroll, A. R.; Edser, A.; Parisot, J.; Addepalli, R.; Quinn, R. J. Tyrosine kinase inhibitors from the rainforest tree *Polyscias murrayi*. *Phytochem.* **2005,** *66* (4), 481-485.

892. Li, Y.; But, P. P.; Ooi, V. E. Antiviral activity and mode of action of caffeoylquinic acids from *Schefflera heptaphylla* (L.) Frodin. *Antiviral Res.* **2005,** *68* (1), 1-9.

893. Tan, P. N.; Thi, T. V.; Dinh, T. M.; Tien, D. L.; Nhat, M. P.; Trong, D. B. New C-20-gibberellin diterpene from the leaves of *Schefflera sessiliflora* De P. V. *Natural Product Research* **2015,** *29* (15), 1432-1436.

894. Bäcker, C.; Jenett-Siems, K.; Bodtke, A.; Lindequist, U. Polyphenolic compounds from the leaves of *Pittosporum angustifolium*. *Biochem. Syst. Ecol.* **2014,** *55*, 101-103.

895. Mikulic-Petkovsek, M.; Ivancic, A.; Todorovic, B.; Veberic, R.; Stampar, F. Fruit phenolic composition of different Elderberry species and hybrids. *J. Food Sci.* **2015,** *80* (10), C2180-C2190.

896. Mikulic-Petkovsek, M.; Samoticha, J.; Eler, K.; Stampar, F.; Veberic, R. Traditional elderflower beverages: a rich source of phenolic compounds with high antioxidant capacity. *J. Agric. Food Chem.* **2015,** *63*, 1477-1487.

897. Lin, L. Z.; Harnly, J. M. A screening method for the identification of glycosylated flavonoids and other phenolic compounds using a standard analytical approach for all plant materials. *J. Agric. Food Chem.* **2007,** *55* (4), 1084-1096.

898. Hlila, M. B.; Mosbah, H.; Zanina, N.; Ben Nejma, A.; Ben Jannet, H.; Aouni, M.; Selmi, B. Characterisation of phenolic antioxidants in *Scabiosa arenaria* flowers by LC-ESI-MS/MS and NMR. *J. Pharm. Pharmacol.* **2016,** *68*, 932-940.

899. Ma, J. N.; Bolraa, S.; Ji, M.; He, Q. Q.; Ma, C. M. Quantification and antioxidant and anti-HCV activities of the constituents from the inflorescences of *Scabiosa comosa* and *S. tschilliensis*. *Natural Product Research* **2016,** *30* (5), 590-594.

900. Kikuchi, M.; Onoguchi, R.; Yaoita, Y.; Machida, K. Two new glycosides from *Viburnum plicatum* Thunb. ex Murray var. plicatum f. plicatum. *J. Nat. Med.* **2011,** *65* (1), 202-205.

901. Yu, Y.; Feng, X. L.; Gao, H.; Xie, Z. L.; Dai, Y.; Huang, X. J.; Kurihara, H.; Ye, W. C.; Zhong, Y.; Yao, X. S. Chemical constituents from the fruits of *Gardenia jasminoides* Ellis. *Fitoterapia* **2012,** *83* (3), 563-567.

902. Kraujalyte, V.; Venskutonis, P. R.; Pukalskas, A.; Cesoniene, L.; Daubaras, R. Antioxidant properties and polyphenolic compositions of fruits from different European cranberrybush (*Viburnum opulus* L.) genotypes. *Food Chem.* **2013,** *141* (4), 3695-3702.

903. Karacelik, A. A.; Kucuk, M.; Iskefiyeli, Z.; Aydemir, S.; De Smet, S.; Miserez, B.; Sandra, P. Antioxidant components of *Viburnum opulus* L. determined by on-line HPLC-UV-ABTS radical scavenging and LC-UV-ESI-MS methods. *Food Chem.* **2015,** *175*, 106-114.

904. Iwai, K.; Kim, M. Y.; Onodera, A.; Matsue, H. α-Glucosidase-inhibitory and antihyperglycemic effects of polyphenols in the fruit of *Viburnum dilatatum* Thunb. *J. Agric. Food Chem.* **2006,** *54* (13), 4588-4592.

905. Kim, M. Y.; Iwai, K.; Matsue, H. Phenolic compositions of *Viburnum dilatatum* Thunb. fruits and their antiradical properties. *Journal of Food Composition and Analysis* **2005,** *18* (8), 789-802.

906. Al-Taweel, A. M.; Perveen, S.; Fawzy, G. A.; Khan, A.; Mehmood, R.; Malik, A. Abeliaside, a new phenolic glucoside from *Abelia triflora*. *Natural Product Research* **2015,** *29* (21), 1978-1984.

907. Moldoch, J.; Szajwaj, B.; Masullo, M.; Pecio, L.; Oleszek, W.; Piacente, S.; tochmal, A. Phenolic constituents of *Knautia arvensis* aerial parts. *Natural Product Communications* **2011,** *6* (11), 1627-1630.

908. Zhang, J.-Y.; Zhang, Q.; Li, N.; Wang, Z.-J.; Lu, J.-Q.; Qiao, Y.-J. Diagnostic fragment-ion-based and extension strategy coupled to DFIs intensity analysis for identification of chlorogenic acids isomers in Flos Lonicerae Japonicae by HPLC–ESI–MS^n. *Talanta* **2013,** *104*, 1-9.

909. Palikova, I.; Heinrich, J.; Bednar, P.; Marhol, P.; Kren, V.; Cvak, L.; Valentova, K.; Ruzicka, F.; Hola, V.; Kolar, M.; Simanek, V.; Ulrichova, J. Constituents and antimicrobial properties of blue honeysuckle: a novel source for phenolic antioxidants. *J Agric. Food Chem.* **2008,** *56* (24), 11883-11889.

910. Li, X. Q.; Sun, X. H.; Cai, S.; Ying, X. X.; Li, F. M. Investigation on the chemical constituents and variation of the flower buds of *Lonicera* species by UPLC-ESI-MS/MS and principle component analysis. *Yao Xue. Xue. Bao.* **2009,** *44* (8), 895-904.

911. Gao, W.; Wang, R.; Li, D.; Liu, K.; Chen, J.; Li, H. J.; Xu, X.; Li, P.; Yang, H. Comparison of five Lonicera flowers by simultaneous determination of multi-components with single reference standard method and principal component analysis. *J. Pharm. Biomed. Anal.* **2016,** *117*, 345-351.

912. Peng, L. Y.; Mei, S. X.; Jiang, B.; Zhou, H.; Sun, H. D. Constituents from *Lonicera japonica*. *Fitoterapia* **2000,** *71* (6), 713-715.

913. Zhang, C.; Yin, Z.; Ye, W.; Guan, Y.; Guo, L.; Zhang, J.; Shen, W. [Chemical constituents from stems of *Lonicera japonica*]. *Zhongguo Zhong. Yao Za Zhi.* **2009,** *34* (23), 3051-3053.

914. Ma, J.; Li, N.; Li, X. [Caffeoylquinic acid derivatives from leaves of *Lonicera japonica*]. *Zhongguo Zhong. Yao Za Zhi.* **2009,** *34* (18), 2346-2348.

915. Lee, E. J.; Kim, J. S.; Kim, H. P.; Lee, J. H.; Kang, S. S. Phenolic constituents from the flower buds of *Lonicera japonica* and their 5-lipoxygenase inhibitory activities. *Food Chem.* **2010,** *120* (1), 134-139.

916. Park, H. S.; Park, K. I.; Lee, D. H.; Kang, S. R.; Nagappan, A.; Kim, J. A.; Kim, E. H.; Lee, W. S.; Shin, S. C.; Hah, Y. S.; Kim, G. S. Polyphenolic extract isolated from Korean *Lonicera japonica* Thunb. induce G2/M cell cycle arrest and apoptosis in HepG2 Cells: Involvements of PI3K/Akt and MAPKs. *Food Chem. Toxicol.* **2012,** *50* (7), 2407-2416.

917. Yu, Y.; Jiang, Z.; Song, W.; Yang, Y.; Li, Y.; Jiang, J.; Shi, J. Glucosylated caffeoylquinic acid derivatives from the flower buds of *Lonicera japonica*. *Acta Pharmaceutica Sinica B* **2015,** *5* (3), 210-214.

918. Chen, Y.; Shan, Y.; Zhao, Q. Z.; Wang, M.; Wang, X.; Xu, F.; Liang, J. Y. Two new tri.terpenoid saponins from *Lonicera macranthoides*. *Chinese Chemical Letters* **2012,** *23*, 325-328.

919. Liu, J.; Zhang, J.; Wang, F.; Chen, X. F. Chemical constituents from the buds of *Lonicera macranthoides* in Sichuan, China. *Biochem. Syst. Ecol.* **2014,** *54* (0), 68-70.

920. Hu, X.; Chen, L.; Shi, S.; Cai, P.; Liang, X.; Zhang, S. Antioxidant capacity and phenolic compounds of *Lonicerae macranthoides* by HPLC–DAD–QTOF-MS/MS. *J. Pharm. Biomed. Anal.* **2016,** *124*, 254-260.

921. Zhang, S. H.; Hu, X.; Shi, S. Y.; Huang, L. Q.; Chen, W.; Chen, L.; Cai, P. Typical ultraviolet spectra in combination with diagnostic mass fragmentation analysis for the rapid and comprehensive profiling of chlorogenic acids in the buds of *Lonicera macranthoides*. *Analytical and Bioanalytical Chemistry* **2016,** 1-14.

922. Barreira, J. C. M.; Pereira, E.; Dueñas, M.; Carvalho, A. M.; Santos-Buelga, C.; Ferreira, I. C. F. R. *Bryonia dioica*, *Tamus communis* and *Lonicera periclymenum* fruits: Characterization in phenolic compounds and incorporation of their extracts in hydrogel formulations for topical application. *Industrial Crops and Products* **2013,** *49* (0), 169-176.

923. Qian, Z. M.; Li, H. J.; Li, P.; Ren, M. T.; Tang, D. Simultaneous qualitation and quantification of thirteen bioactive compounds in Flos lonicerae by high-performance liquid chromatography with diode array detector and mass spectrometry. *Chem. Pharm. Bull. (Tokyo)* **2007,** *55* (7), 1073-1076.

924. Zhang, J. Y.; Wang, Z. J.; Li, Y.; Li, Y.; Cai, W.; Li, C.; Lu, J. Q.; Qiao, Y. J. A strategy for comprehensive identification of sequential constituents using ultra-high-performance liquid chromatography coupled with linear ion trap Orbitrap mass spectrometer, application study on chlorogenic acids in Flos Lonicerae Japonicae. *Talanta* **2016,** *147*, 16-27.

925. Teng, R. W.; Zhou, Z. H.; Wang, D. Z.; Yand, C. G. Four caffeoylquinic acids from *Morina nepalensis* var. *alba* Hand. Mazz. *Chinese Journal of Magnetic Resonance* **2002,** *19*, 167-174.

926. Hung, T. M.; Na, M. K.; Thuong, P. T.; Su, N. D.; Sok, D. E.; Song, K. S.; Seong, Y. H.; Bae, K. H. Antioxidant activity of caffeoyl quinic acid derivatives from the roots of *Dipsacus asper* Wall. *J. Ethnopharmacol.* **2006,** *108* (2), 188-192.

927. Hung, T. M.; Thuong, P. T.; Youn, U.; Zhang, X. F.; Min, B.-S.; Woo, M. H.; Lee, H.-K.; Bae, K. H. Antioxidant acticities of phenolic derivatives from *Dipsacus asper* Wall.(II). *Natural Product Sciences* **2008,** *14* (2), 107-112.

928. Ling, Y.; Liu, K.; Zhang, Q.; Liao, L.; Lu, Y. High performance liquid chromatography coupled to electrospray ionization and quadrupole time-of-flight-mass spectrometry as a powerful analytical strategy for systematic analysis and improved characterization of the major bioactive constituents from Radix Dipsaci. *J. Pharm. Biomed. Anal.* **2014,** *98*, 120-129.

929. Kacem, N.; Hay, A. E.; Marston, A.; Zellagui, A.; Rhouati, S.; Hostettmann, K. Antioxidant compounds from Algerian *Convolvulus tricolor* (Convolvulaceae) seed husks. *Nat. Prod. Commun.* **2012,** *7* (7), 873-874.

930. Fan, L.; Wang, Y.; Liang, N.; Huang, X. J.; Li, M. M.; Fan, C. L.; Wu, Z. L.; Li, Y. L.; Ye, W. C. Chemical constituents from the roots and stems of *Erycibe obtusifolia* and their *in vitro* antiviral activity. *Planta Med.* **2013,** *79* (16), 1558-1564.

931. Löffler, C.; Czygan, F. C.; Proksch, P. Phenolic constituents as taxonomic markers in the genus Cuscuta (Cuscutaceae). *Biochem. Syst. Ecol.* **1997,** *25* (4), 297-303.

932. Löffler, C.; Sahm, A.; Wray, V.; Czygan, F. C.; Proksch, P. Soluble phenolic constituents from *Cuscuta reflexa* and *Cuscuta platyloba*. *Biochem. Syst. Ecol.* **1995,** *23* (2), 121-128.

933. Li, W. L.; Zhang, Y.; Mu, Y. Y.; Bai, J.; Ding, J. X.; Xiang, Z.; Ji, Y. B. Identification of estrogenic constituents in serum after oral administration of Tu-Si-Zi extract using HPLC-ESI/Q-TOF MS/MS. *Journal of Liquid Chromatography & Related Technologies* **2015,** *38* (16), 1521-1525.

934. Liu, J.; Feng, Z.; Xu, J.; Wang, Y.; Zhang, P. Rare biscoumarins and a chlorogenic acid derivative from *Erycibe obtusifolia*. *Phytochem.* **2007,** *68* (13), 1775-1780.

935. Liu, Z.; Feng, Z.; Yang, Y.; Jiang, J.; Zhang, P. Acyl quinic acid derivatives from the stems of *Erycibe obtusifolia*. *Fitoterapia* **2014,** *99*, 109-116.

936. Fan, L.; Wang, Y.; Liang, N.; Huang, X. J.; Fan, C. L.; Wu, Z. L.; He, Z. D.; Li, Y. L.; Ye, W. C. Quinic acid derivatives and coumarin glycoside from the roots and stems of *Erycibe obtusifolia*. *Phytochemistry Letters* **2015,** *14*, 185-189.

937. Song, S.; Li, Y.; Feng, Z.; Jiang, J.; Zhang, P. Hepatoprotective constituents from the roots and stems of *Erycibe hainanesis*. *J Nat. Prod.* **2010,** *73* (2), 177-184.

938. Feng, Z.; Song, S.; An, Y.; Yang, Y.; Jiang, J.; Zhang, P. Hepatoprotective acyl glycosides obtained from *Erycibe hainanesis*. *Phytochemistry Letters* **2014,** *9*, 163-167.

939. Itoh, A.; Tanaka, Y.; Nagakura, N.; Nishi, T.; Tanahashi, T. A quinic acid ester from *Strychnos lucida*. *J. Nat. Med* **2006,** *60*, 146-148.

940. Madala, N. E.; Steenkamp, P. A.; Piater, L. A.; Dubery, I. A. Metabolomic analysis of isonitrosoacetophenone-induced perturbations in phenolic metabolism of Nicotiana tabacum cells. *Phytochem.* **2013,** *94*, 82-90.

941. Islam, M. S.; Yoshimoto, M.; Yahara, S.; Okuno, S.; Ishiguro, K.; Yamakawa, O. Identification and characterization of foliar polyphenolic composition in sweetpotato (*Ipomoea batatas* L.) genotypes. *J Agric. Food Chem.* **2002,** *50* (13), 3718-3722.

942. Kurata, R.; Adachi, M.; Yamakawa, O.; Yoshimoto, M. Growth suppression of human cancer cells by polyphenolics from sweetpotato (*Ipomoea batatas* L.) leaves. *J Agric. Food Chem.* **2007,** *55* (1), 185-190.

943. Yoshimoto, M.; Yahara, S.; Okuno, S.; Islam, M. S.; Ishiguro, K.; Yamakawa, O. Antimutagenicity of mono-, di-, and tricaffeoylquinic acid derivatives isolated from sweetpotato (*Ipomoea batatas* L.) leaf. *Biosci. Biotechnol. Biochem.* **2002,** *66* (11), 2336-2341.

944. Sun, H.; Mu, T.; Xi, L.; Zhang, M.; Chen, J. Sweet potato (*Ipomoea batatas* L.) leaves as nutritional and functional foods. *Food Chem.* **2014,** *156* (0), 380-389.

945. Sasaki, K.; Oki, T.; Kai, Y.; Nishiba, Y.; Okuno, S. Effect of repeated harvesting on the content of caffeic acid and seven species of caffeoylquinic acids in sweet potato leaves. *Bioscience Biotechnology and Biochemistry* **2015,** *79* (8), 1308-1314.

946. Zhang, L.; Tu, Z. C.; Yuan, T.; Wang, H.; ie, X.; u, Z. F. Antioxidants and alpha-glucosidase inhibitors from *Ipomoea batatas* leaves identified by bioassay-guided approach and structure-activity relationships. *Food Chem.* **2016,** *208*, 61-67.

947. Dini, I.; Tenore, G. C.; Dini, A. New polyphenol derivative in *Ipomoea batatas* tubers and its antioxidant activity. *J Agric. Food Chem.* **2006,** *54* (23), 8733-8737.

948. Wang, Z.; Clifford, M. N. Profiling the chlorogenic acids of sweet potato (*Ipomoea batatas*) from China. *Food Chem.* **2008,** *106*, 147-152.

949. Nandutu, A. M.; Clifford, M. N.; Howell, N. K. Analysis of phenolic compounds in Ugandan sweet potato varieties (NSP, SPK AND TZ). *African Journal of Biochemistry Research* **2007,** *1*, 29-36.

950. Teramachi, F.; Koyano, T.; Kowithayakorn, T.; Hayashi, M.; Komiyama, K.; Ishibashi, M. Collagenase inhibitory quinic acid esters from *Ipomoea pes-caprae*. *J Nat. Prod.* **2005,** *68* (5), 794-796.

951. Truong, V. D.; McFeeters, R. F.; Thompson, R. T.; Dean, L. L.; Shofran, B. Phenolic acid content and composition in leaves and roots of common commercial sweetpotato (*Ipomea batatas* L.) cultivars in the United States. *J Food Sci.* **2007,** *72* (6), C343-C349.

952. Jeng, T. L.; Lai, C. C.; Liao, T. C.; Lin, S. Y.; Sung, J. M. Effects of drying on caffeoylquinic acid derivative content and antioxidant capacity of sweet potato leaves. *Journal of Food and Drug Analysis* **2014,** (0).

953. Meira, M.; David, J. M.; David, J. P.; Araujo, S. V.; Regis, T. L.; Giulietti, A. M.; de Queirz, L. P. Chemical constituents of *Ipomoea subincana* Meisn. (Convolvulaceae). *Quimica Nova* **2008,** *31* (4), 751-754.

954. Hallmann, E.; Rembialkowska, E. Characterisation of antioxidant compounds in sweet bell pepper (*Capsicum annuum* L.) under organic and conventional growing systems. *J Sci. Food Agric.* **2012,** *92* (12), 2409-2415.

955. Kim, W. R.; Kim, E. O.; Kang, K.; Oidovsambuu, S.; Jung, S. H.; Kim, B. S.; Nho, C. W.; Um, B. H. Antioxidant activity of phenolics in leaves of three red pepper (*Capsicum annuum*) cultivars. *J. Agric. Food Chem.* **2014,** *62* (4), 850-859.

956. Mudric, S. Z.; Gagic, U. M.; Dramicanin, A. M.; Ciric, I. Z.; Milojkovic-Opsenica, D. M.; Popovic-Dordevic, J. B.; Momirovic, N. M.; Tesic, Z. L. The polyphenolics and carbohydrates as indicators of botanical and geographical origin of Serbian autochthonous clones of red spice paprika. *Food Chem.* **2017,** *217*, 705-715.

957. Quispe, C.; Viveros-Valdez, E.; Schmeda-Hirschmann, G. Phenolic constituents of the Chilean herbal tea *Fabiana imbricata* R. et P. *Plant Foods Hum. Nutr* **2012,** *67* (3), 242-246.

958. Dong, J. Z.; Gao, W. S.; Lu, D. Y.; Wang, Y. Simultaneous extraction and analysis of four polyphenols from leaves of *Lycium barbarum* L. *J. Food Biochem.* **2011,** *35*, 914-931.

959. Bondia-Pons, I.; Savolainen, O.; Torronen, R.; Martinez, J.; Poutanen, K.; Hanhineva, K. Metabolic profiling of Goji berry extracts for discrimination of geographical origin by non-targeted liquid chromatography coupled to quadrupole time-of-flight mass spectrometry. *Food Research International* **2014,** *63*, 132-138.

960. Wu, W. B.; Hung, D. K.; Chang, F. W.; Ong, E. T.; Chen, B. H. Anti-inflammatory and anti-angiogenic effects of flavonoids isolated from *Lycium barbarum* Linnaeus on human umbilical vein endothelial cells. *Food & Funct.* **2012,** *3* (10), 1068-1081.

961. Dong, J. Z.; Wang, Y.; Wang, S. H.; Yin, L. P.; Xu, G. J.; Zheng, C.; Lei, C.; Zhang, M. Z. Selenium increases chlorogenic acid, chlorophyll and carotenoids of *Lycium chinense* leaves. *J. Sci. Food Agric.* **2013,** *93* (2), 310-315.

962. Abdennacer, B.; Karim, M.; Yassine, M.; Nesrine, R.; Mouna, D.; Mohamed, B. Determination of phytochemicals and antioxidant activity of methanol extracts obtained from the fruit and leaves of Tunisian *Lycium intricatum* Boiss. *Food Chem.* **2015,** *174*, 577-584.

963. Wang, J.; Lu, D.; Liang, Y.; Zhao, H.; Luo, M.; Ling, X.; Ouyang, P. Isolation of mono-caffeoylquinic acids from tobacco waste using continuous resin-based pre-separation and preparative HPLC. *J Sep. Sci.* **2012,** *35* (10-11), 1379-1387.

964. McGrath, T. E.; Brown, A. P.; Meruva, N. K.; Chan, W. G. Phenolic compound formation from the low temperature pyrolysis of tobacco. *Journal of Analytical and Applied Pyrolysis* **2009,** *84* (2), 170-178.

965. Chen, L. X.; Xia, G. Y.; Liu, Q. Y.; Xie, Y. Y.; Qiu, F. Chemical constituents from the calyces of *Physalis alkekengi* var. *franchetii*. *Biochem. Syst. Ecol.* **2014,** *54* (0), 31-35.

966. Stommel, J. R.; Whitaker, B. D.; Haynes, K. G.; Prohens, J. Genotype x environment interactions in eggplant for fruit phenolic acid content. *Euphytica* **2015,** *205* (3), 823-836.

967. Wu, S. B.; Meyer, R. S.; Whitaker, B. D.; Litt, A.; Kennelly, E. J. Antioxidant glucosylated caffeoylquinic acid derivatives in the invasive tropical Soda Apple, *Solanum viarum*. *J Nat. Prod.* **2012,** *75* (12), 2246-2250.

968. Wu, S. B.; Meyer, R. S.; Whitaker, B. D.; Litt, A.; Kennelly, E. J. A new liquid chromatography-mass spectrometry-based strategy to integrate chemistry, morphology, and evolution of eggplant (*Solanum*) species. *J. Chromatogr. A* **2013,** *1314* (0), 154-172.

969. Meyer, R. S.; Whitaker, B. D.; Little, D. P.; Wu, S. B.; Kennelly, E. J.; Long, C. L.; Litt, A. Parallel reductions in phenolic constituents resulting from the domestication of eggplant. *Phytochem.* **2015,** (0).

970. Ma, C.; Whitaker, B. D.; Kennelly, E. J. New 5-O-caffeoylquinic acid derivatives in fruit of the wild eggplant relative *Solanum viarum*. *J. Agric. Food Chem.* **2010,** *58* (20), 11036-11042.

971. Espin, S.; Gonzalez-Manzano, S.; Taco, V.; Poveda, C.; Ayuda-Dur+ín, B.; Gonzalez-Paramas, A. M.; Santos-Buelga, C. Phenolic composition and antioxidant capacity of yellow and purple-red Ecuadorian cultivars of tree tomato (*Solanum betaceum* Cav.). *Food Chem.* **2016,** *194*, 1073-1080.

972. Herraiz, F. J.; Villano, D.; Plazas, M.; Vilanova, S.; Ferreres, F.; Prohens, J.; Moreno, D. A. Phenolic profile and biological activities of the pepino (*Solanum muricatum*) fruit and Its wild relative *S. caripense*. *International Journal of Molecular Sciences* **2016,** *17* (3).

973. Im, H. W.; Suh, B. S.; Lee, S. U.; Kozukue, N.; Ohnisi-Kameyama, M.; Levin, C. E.; Friedman, M. Analysis of phenolic compounds by high-performance liquid chromatography and liquid chromatography/mass spectrometry in potato plant flowers, leaves, stems, and tubers and in home-processed potatoes. *J. Agric. Food Chem.* **2008,** *56* (9), 3341-3349.

974. Narváez-Cuenca, C. E.; Vincken, J. P.; Zheng, C.; Gruppen, H. Diversity of (dihydro) hydroxycinnamic acid conjugates in Colombian potato tubers. *Food Chem.* **2013**.

975. Andre, C. M.; Oufir, M.; Guignard, C.; Hoffmann, L.; Hausman, J. F.; Evers, D.; Larondelle, Y. Antioxidant profiling of native Andean potato tubers (*Solanum tuberosum* L.) reveals cultivars with high levels of beta-carotene, alpha-tocopherol, chlorogenic acid, and petanin. *J Agric. Food Chem.* **2007,** *55* (26), 10839-10849.

976. Narvaez-Cuenca, C. E.; Vincken, J. P.; Gruppen, H. Identification and quantification of (dihydro) hydroxycinnamic acids and their conjugates in potato by UHPLC-DAD-ESI-MS^n. *Food Chem.* **2012,** *130* (3), 730-738.

977. Narvaez-Cuenca, C. E.; Vincken, J. P.; Gruppen, H. Quantitative fate of chlorogenic acid during enzymatic browning of potato juice. *J Agric. Food Chem.* **2013,** *61* (7), 1563-1572.

978. Maldonado, A. F. S.; Mudge, E.; Ganzle, M. G.; Schieber, A. Extraction and Fractionation of Phenolic Acids and Glycoalkaloids from Potato Peels Using Acidified Water/Ethanol-based Solvents. *Food Research International* **2014,** (0).

979. Lachman, J.; Hamouz, K.; Musilova, J.; Hejtmankova, K.; Kotikova, Z.; Pazderu, K.; Domkarova, J.; Pivec, V.; Cimr, J. Effect of peeling and three cooking methods on the content of selected phytochemicals in potato tubers with various colour of flesh. *Food Chem.* **2013,** *138* (2-3), 1189-1197.

980. Zhu, F.; Cai, Y. Z.; Ke, J.; Corke, H. Compositions of phenolic compounds, amino acids and reducing sugars in commercial potato varieties and their effects on acrylamide formation. *J. Sci. Food Agric.* **2010,** *90* (13), 2254-2262.

981. Lopez-Cobo, A.; Gomez-Caravaca, A. M.; Cerretani, L.; Segura-Carretero, A.; Fernandez-Gutierrez, A. Distribution of phenolic compounds and other polar compounds in the tuber of *Solanum tuberosum* L. by HPLC-DAD-q-TOF and study of their antioxidant activity. *Journal of Food Composition and Analysis* **2014,** (0).

982. Karaköse, H. Ph.D. Jacobs University Bremen, Germany, 2012.

983. Navarre, D. A.; Payyavula, R. S.; Shakya, R.; Knowles, N. R.; Pillai, S. S. Changes in potato phenylpropanoid metabolism during tuber development. *Plant Physiol. Biochem.* **2013,** *65*, 89-101.

984. Navarre, D. A.; Pillai, S. S.; Shakya, R.; Holden, M. J. HPLC profiling of phenolics in diverse potato genotypes. *Food Chem.* **2011,** *127* (1), 34-41.

985. Torres-Contreras, A. M.; Nair, V.; Cisneros-Zevallos, L.; Jacobo-Velazquez, D. A. Plants as biofactories: Stress-induced production of chlorogenic acid isomers in potato tubers as affected by wounding intensity and storage time. *Industrial Crops and Products* **2014,** *62*, 61-66.

986. Whitaker, B. D.; Stommel, J. R. Distribution of hydroxycinnamic acid conjugates in fruit of commercial eggplant (*Solanum melongena* L.) cultivars. *J Agric. Food Chem.* **2003,** *51* (11), 3448-3454.

987. Ma, C.; Dastmalchi, K.; Whitaker, B. D.; Kennelly, E. J. Two new antioxidant malonated caffeoylquinic acid isomers in fruits of wild eggplant relatives. *J. Agric. Food Chem.* **2011,** *59* (17), 9645-9651.

988. Pereira, A. C.; Oliveira, D. F.; Silva, G. H.; Figueiredo, H. C.; Cavalheiro, A. J.; Carvalho, D. A.; Souza, L. P.; Chalfoun, S. M. Identification of the antimicrobial substances produced by *Solanum palinacanthum* (Solanaceae). *An. Acad. Bras. Cienc.* **2008,** *80* (3), 427-432.

989. Rodrigues, E.; Mariutti, L. R.; Mercadante, A. Z. Carotenoids and phenolic compounds from *Solanum sessiliflorum*, an unexploited Amazonian fruit, and their scavenging capacities against reactive oxygen and nitrogen species. *J. Agric. Food Chem.* **2013,** *61* (12), 3022-3029.

990. Garcia-Salas, P.; Gomez-Caravaca, A. M.; Morales-Soto, A.; Segura-Carretero, A.; Fernandez-Gutierrez, A. Identification and quantification of phenolic compounds in diverse cultivars of eggplant grown in different seasons by high-performance liquid chromatography coupled to diode array detector and electrospray-quadrupole-time of flight-mass spectrometry. *Food Research International* **2014,** *57* (0), 114-122.

991. Chideh, S.; Pilard, S.; Attoumbre, J.; Saguez, R.; Hassan-Abdallah, A.; Cailleu, D.; Wadouachi, A.; Baltora-Rosset, S. 5-O-Caffeoylshikimic acid from *Solanum somalense* leaves: Advantage of centrifugal partition chromatography over conventional column chromatography. *J. Sep. Sci.* **2014**.

992. Sanchez-Rodriguez, E.; Moreno, D. A.; Ferreres, F.; Rubio-Wilhelmi, M. M.; Ruiz, J. M. Differential responses of five cherry tomato varieties to water stress: changes on phenolic metabolites and related enzymes. *Phytochem.* **2011,** *72* (8), 723-729.

993. van der, R. B.; Danoun, S.; Boudet, A. M.; Rochange, S. F. Down-regulation of cinnamoyl-CoA reductase in tomato (*Solanum lycopersicum* L.) induces dramatic changes in soluble phenolic pools. *J. exp. Bot.* **2006,** *57* (6), 1399-1411.

994. Ribas-Agusti, A.; Caceres, R.; Gratacos-Cubarsi, M.; Sarraga, C.; Castellari, M. A validated HPLC-DAD method for routine determination of ten phenolic compounds in tomato fruits. *Food Analytical Methods* **2012,** *5* (5), 1137-1144.

995. Ferreres, F.; Taveira, M.; Gil-Izquierdo, A.; Oliveira, L.; Teixeira, T.; Valentao, P.; Simoes, N.; Andrade, P. B. High-performance liquid chromatography-diode array detection-electrospray ionization multi-stage mass spectrometric screening of an insect/plant system: the case of Spodoptera littoralis/Lycopersicon esculentum phenolics and alkaloids. *Rapid Commun. Mass Spectrom.* **2011,** *25* (14), 1972-1980.

996. Sanchez-Rodriguez, E.; Ruiz, J. M.; Ferreres, F.; Moreno, D. A. Phenolic profiles of cherry tomatoes as influenced by hydric stress and rootstock technique. *Food Chem.* **2012,** *134* (2), 775-782.

997. Chanforan, C.; Loonis, M.; Mora, N.; Caris-Veyrat, C.; Dufour, C. The impact of industrial processing on health-beneficial tomato microconstituents. *Food Chem.* **2012,** *134* (4), 1786-1795.

998. Siracusa, L.; Patane, C.; Avola, G.; Ruberto, G. Polyphenols as chemotaxonomic markers in Italian "long-storage" tomato genotypes. *J. Agric. Food Chem.* **2012,** *60* (1), 309-314.

999. Vallverdu-Queralt, A.; Jauregui, O.; Medina-Remon, A.; Andres-Lacueva, C.; Lamuela-Raventos, R. M. Improved characterization of tomato polyphenols using liquid chromatography/electrospray ionization linear ion trap quadrupole Orbitrap mass spectrometry and liquid chromatography/electrospray ionization tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* **2010,** *24* (20), 2986-2992.

1000. Vallverdu-Queralt, A.; Jauregui, O.; Medina-Remon, A.; Lamuela-Raventos, R. M. Evaluation of a method to characterize the phenolic profile of organic and conventional tomatoes. *J. Agric. Food Chem.* **2012,** *60* (13), 3373-3380.

1001. Kirmizibekmez, H.; Demir, D. Iridoid glycosides and phenolic compounds from the flowers of *Vitex agnus-castus*. *HCA* **2016,** *99* (7), 518-522.

1002. Leitão, S. G.; Fonseca, E. N.; dos Santos, T. C.; França, F.; Delle Monache, F. Caffeoylquinic acid derivatives from two Brazilian *Vitex* species. *Biochem. Syst. Ecol.* **2008,** *36* (4), 312-315.

1003. Deng, Y.; Chin, Y. W.; Chai, H. B.; de Blanco, E. C.; Kardono, L. B. S.; Riswan, S.; Soejarto, D. D.; Farnsworth, N. R.; Kinghorn, A. D. Phytochemical and bioactivity studies on constituents of the leaves of *Vitex quinata*. *Phytochemistry Letters* **2011,** *4* (3), 213-217.

1004. Vitorino, L. C.; Silva, F. G.; Lima, W. C.; Soares, M. A.; Pedroso, R. C. N.; Silva, M. R.; Dias, H. J.; Crotti, A. E. M.; Silva, M. L. A. E.; Cunha, W. R.; Pauletti, P. M.; Januario, A. H. Metabolic response induced by endophytic fungi and bacteria in *H. marrubioides* Epling *in vitro* microplants. *Quimica Nova* **2013,** *36* (7), 1014-1020.

1005. Costa, P.; Goncalves, S.; Valentao, P.; Andrade, P. B.; Almeida, C.; Nogueira, J. M.; Romano, A. Metabolic profile and biological activities of *Lavandula pedunculata* subsp. *lusitanica* (Chaytor) Franco: studies on the essential oil and polar extracts. *Food Chem.* **2013,** *141* (3), 2501-2506.

1006. Torras-Claveria, L.; Jauregui, O.; Bastida, J.; Codina, C.; Viladomat, F. Antioxidant activity and phenolic composition of Lavandin (*Lavandula x intermedia* Emeric ex Loiseleur) waste. *J. Agric. Food Chem.* **2007,** *55* (21), 8436-8443.

1007. Kakasy, A.; Fuzfai, Z.; Kursinszki, L.; Molnar-Perl, I.; Lemberkovics, E. Analysis of non-volatile constituents in *Dracocephalum* species by HPLC and GC-MS. *Chromatographia* **2006,** *63*, S17-S22.

1008. Dai, L. M.; Zhao, C. C.; Jin, H. Z.; Tang, J.; Shen, Y. H.; Li, H. L.; Peng, C. Y.; Zhang, W. D. A new ferulic acid ester and other constituents from *Dracocephalum peregrinum*. *Arch. Pharm. Res.* **2008,** *31* (10), 1325-1329.

1009. Cirlini, M.; Mena, P.; Tassotti, M.; Herrlinger, K. A.; Nieman, K. M.; Dall'Asta, C.; Del Rio, D. Phenolic and volatile composition of a dry spearmint (*Mentha spicata* L.) extract. *Molecules* **2016,** (21), 1007 doi:10.3390/molecules21081007.

1010. Martins, N.; Barros, L.; Santos-Buelga, C.; Henriques, M.; Silva, S. Ã.; Ferreira, I. C. F. R. Decoction, infusion and hydroalcoholic extract of *Origanum vulgare* L.: Different performances regarding bioactivity and phenolic compounds. *Food Chem.* **2014,** *158* (0), 73-80.

1011. Vallverdu-Queralt, A.; Regueiro, J.; Martinez-Huelamo, M.; Rinaldi Alvarenga, J. F.; Leal, L. N.; Lamuela-Raventos, R. M. A comprehensive study on the phenolic profile of widely used culinary herbs and spices: rosemary, thyme, oregano, cinnamon, cumin and bay. *Food Chem.* **2014,** *154*, 299-307.

1012. Cabana, R.; Silva, L. R.; Valentao, P.; Viturro, C.; Andrade, P. Effect of different extraction methodologies on the recovery of bioactive metabolites from *Satureja parvifolia* (Phil.) Epling (Lamiaceae). *Industrial Crops and Products* **2013,** *48* (0), 49-56.

1013. Boros, B.; Jakabova, S.; Dornyei, A.; Horvath, G.; Pluhar, Z.; Kilar, F.; Felinger, A. Determination of polyphenolic compounds by liquid chromatography–mass spectrometry in *Thymus* species. *J Chromatogr. A* **2010,** *1217* (51), 7972-7980.

1014. Budzianowski, J.; Skrzypczak, L. Phenylpropanoid esters from *Lamium album* flowers. *Phytochem.* **1995,** *38* (4), 997-1001.

1015. Bernatoniene, J.; Kopustinskiene, D. M.; Jakstas, V.; Majiene, D.; Baniene, R.; Kursvietiene, L.; Masteikova, R.; Savickas, A.; Toleikis, A.; Trumbeckaite, S. The effect of *Leonurus cardiaca* herb extract and some of its flavonoids on mitochondrial oxidative phosphorylation in the heart. *Planta Med.* **2014,** *80* (7), 525-532.

1016. Boudjelal, A.; Henchiri, C.; Siracusa, L.; Sari, M.; Ruberto, G. Compositional analysis and *in vivo* anti-diabetic activity of wild Algerian *Marrubium vulgare* L. infusion. *Fitoterapia* **2012,** *83* (2), 286-292.

1017. Zhang, Y.; Wang, Z. Z. Phenolic composition and antioxidant activities of two *Phlomis* species: A correlation study. *C. R. Biol.* **2009,** *332* (9), 816-826.

1018. Delnavazi, M.; Mohammadifar, F.; Rustaie, A.; Aghaahmadi, M.; Yassa, N. Phytochemical constituents, antioxidant activity and toxicity potential of *Phlomis olivieri* Benth. *Research Journal of Pharmacognosy* **2016,** *3* (2), 9-15.

1019. Sarikurkcu, C.; Uren, M. C.; Tepe, B.; Cengiz, M.; Kocak, M. S. *Phlomis armeniaca*: Phenolic compounds, enzyme inhibitory and antioxidant activities. *Industrial Crops and Products* **2015,** *78*, 95-101.

1020. Kirmizibekmez, H.; Calis, I.; Perozzo, R.; Brun, R.; Donmez, A. A.; Linden, A.; Ruedi, P.; Tasdemir, D. Inhibiting activities of the secondary metabolites of *Phlomis brunneogaleata* against parasitic protozoa and plasmodial enoyl-ACP Reductase, a crucial enzyme in fatty acid biosynthesis. *Planta Med.* **2004,** *70* (8), 711-717.

1021. Karioti, A.; Bolognesi, L.; Vincieri, F. F.; Bilia, A. R. Analysis of the constituents of aqueous preparations of *Stachys recta* by HPLC-DAD and HPLC-ESI-MS. *J Pharm. Biomed. Anal.* **2010,** *53* (1), 15-23.

1022. Venditti, A.; Bianco, A.; Nicoletti, M.; Quassinti, L.; Bramucci, M.; Lupidi, G.; Vitali, L. A.; Papa, F.; Vittori, S.; Petrelli, D.; Maleci, B. L.; Giuliani, C.; Maggi, F. Characterization of secondary metabolites, biological activity and glandular trichomes of *Stachys tymphaea* Hausskn. from the Monti Sibillini National Park (Central Apennines, Italy). *Chem. Biodivers.* **2014,** *11* (2), 245-261.

1023. Leporini, L.; Menghini, L.; Foddai, M.; Petretto, G. L.; Chessa, M.; Tirillini, B.; Pintore, G. Antioxidant and antiproliferative activity of *Stachys glutinosa* L. ethanol extract. *Natural Product Research* **2015,** *29* (10), 899-907.

1024. Venditti, A.; Frezza, C.; Bianco, A.; Serafini, M.; Cianfaglione, K.; Nagy, D. U.; Iannarelli, R.; Caprioli, G.; Maggi, F. Polar constituents, essential oil and antioxidant activity of marsh woundwort (*Stachys palustris* L.). *Chemistry & Biodiversity* **2016,** n/a.

1025. Petreska, J.; Stefkov, G.; Kulevanova, S.; Alipieva, K.; Bankova, V.; Stefova, M. Phenolic compounds of mountain tea from the Balkans: LC/DAD/ESI/MSn profile and content. *Nat. Prod. Commun.* **2011,** *6* (1), 21-30.

1026. Goulas, V.; Exarchou, V.; Kanetis, L.; Gerothanassis, I. P. Evaluation of the phytochemical content, antioxidant activity and antimicrobial properties of mountain tea (*Sideritis syriaca*) decoction. *Journal of Functional Foods* **2014,** *6* (0), 248-258.

1027. Stanoeva, J. P.; tefova, M.; tefkov, G.; ulevanova, S.; lipieva, K.; ankova, V.; neva, I.; vstatieva, L. N. Chemotaxonomic contribution to the *Sideritis* species dilemma on the Balkans. *Biochem. Syst. Ecol.* **2015,** *61*, 477-487.

1028. Armata, A.; Gabrieli, C.; Termentzi, A.; Zervou, M.; Kokkalou, E. Constituents of *Sideritis syriaca*. ssp *syriaca* (Lamiaceae) and their antioxidant activity. *Food Chem.* **2008,** *111* (1), 179-186.

1029. Bongcheewin, B.; Grayer, R. J.; Porter, E. A.; Kite, G. C.; Simmonds, M. S. J.; Ingrouille, M. J.; Paton, A. J. A chemosystematic study of the genus *Gomphostemma* and related genera (Lamiaceae). *Biochem. Syst. Ecol.* **2014,** *57*, 305-316.

1030. Varga, L.; Engel, R.; Szabo, K.; Abranko, L.; Gosztola, B.; Nemeth, E. Z.; Sarosi, S. Seasonal variation in phenolic content and antioxidant activity of *Glechoma hederacea* L. harvested from six Hungarian populations. *Acta Aliment.* **2016,** *45* (2), 268-276.

1031. Döring, A. S.; Petersen, M. Production of caffeic, chlorogenic and rosmarinic acids in plants and suspension cultures of *Glechoma hederacea*. *Phytochemistry Letters* **2014,** (0), DOI: 10.1016/j.phytol.2014.05.012.

1032. Leyva-Lopez, N.; Nair, V.; Bang, W. Y.; Cisneros-Zevallos, L.; Heredia, J. B. Protective role of terpenes and polyphenols from three species of Oregano (*Lippia graveolens*, *Lippia palmeri* and *Hedeoma patens*) on the suppression of lipopolysaccharide-induced inflammation in RAW 264.7 macrophage cells. *J. Ethnopharmacol.* **2016,** *187*, 302-312.

1033. Dzamic, A. M.; Sokovic, M. D.; Novakovic, M.; Jadranin, M.; Ristic, M. S.; Tesevic, V.; Marin, P. D. Composition, antifungal and antioxidant properties of *Hyssopus officinalis* L. subsp. *pilifer* (Pant.) Murb. essential oil and deodorized extracts. *Industrial Crops and Products* **2013,** *51* (0), 401-407.

1034. Venditti, A.; Bianco, A.; Frezza, C.; Conti, F.; Bini, L. M.; Giuliani, C.; Bramucci, M.; Quassinti, L.; Damiano, S.; Lupidi, G.; Beghelli, D.; Caterbi, S.; Petrelli, D.; Vitali, L. A.; Papa, F.; Caprioli, G.; Maggi, F. Essential oil composition, polar compounds, glandular trichomes and biological activity of *Hyssopus officinalis* subsp *aristatus* (Godr.) Nyman from central Italy. *Industrial Crops and Products* **2015,** *77*, 353-363.

1035. Skrzypczak-Pietraszek, E.; Pietraszek, J. Chemical profile and seasonal variation of phenolic acid content in bastard balm (*Melittis melissophyllum* L., Lamiaceae). *J Pharm. Biomed. Anal.* **2012,** *66*, 154-161.

1036. Huang, G. J.; Liao, J. C.; Chiu, C. S.; Huang, S. S.; Lin, T. H.; Deng, J. S. Anti-inflammatory activities of aqueous extract of *Mesona procumbens* in experimental mice. *J Sci. Food Agric.* **2012,** *92* (6), 1186-1193.

1037. Sahin, S.; Demir, C.; Malyer, H. Determination of phenolic compounds in *Prunella* L. by liquid chromatography-diode array detection. *J Pharm. Biomed. Anal.* **2011,** *55* (5), 1227-1230.

1038. Jiang, H. L.; Xu, L. Z.; Yang, X. D.; Zhang, D.; Yang, S. L.; Zou, Z. M. [Quinic acid esters from herba of *Siphonostegia chinensis*]. *Zhongguo Zhong. Yao Za Zhi.* **2002,** *27* (12), 923-926.

1039. Lee, D. S.; Keo, S.; Ko, W.; Kim, K. S.; Ivanova, E.; Yim, J. H.; Kim, Y. C.; Oh, H. Secondary metabolites isolated from *Castilleja rubra* exert anti-inflammatory effects through NF-kappaB inactivation on lipopolysaccharide-induced RAW264.7 macrophages. *Arch. Pharm. Res.* **2014,** *37* (7), 947-954.

1040. Barreira, J. C. M.; Dias, M. I.; Zivovic, J.; Stojkovic, D.; Sokovic, M.; Santos-Buelga, C.; Ferreira, I. C. F. R. Phenolic profiling of *Veronica* spp. grown in mountain, urban and sandy soil environments. *Food Chem.* **2014,** *163*, 275-283.

1041. Ferreres, F.; Grosso, C.; Gil-Izquierdo, A.; Valenteo, P.; Andrade, P. B. Assessing *Jasminum grandiflorum* L. authenticity by HPLC-DAD-ESI/MSn and effects on physiological enzymes and oxidative species. *J. Pharm. Biomed. Anal.* **2014,** *88* (0), 157-161.

1042. Ryan, D.; Prenzler, P. D.; Lavee, S.; Antolovich, M.; Robards, K. Quantitative changes in phenolic content during physiological development of the olive (*Olea europaea*) cultivar Hardy's Mammoth. *J Agric. Food Chem.* **2003,** *51* (9), 2532-2538.

1043. Wu, Z. J.; Ma, X. L.; Fang, D. M.; Qi, H. Y.; Ren, W. J.; Zhang, G. L. Analysis of caffeic acid derivatives from *Osmanthus yunnanensis* using electrospray ionization quadrupole time-of-flight mass spectrometry. *Eur. J. Mass Spectrom. (Chichester, Eng)* **2009,** *15* (3), 415-429.

1044. Tang, J. S.; Gao, H.; Wang, C. X.; Dai, Y.; Bao, L.; Ye, W. C.; Yao, X. S. Antioxidative phenylpropanoid-substituted epicatechin glycosides from *Parabarium huaitingii*. *Planta Med.* **2009,** *75* (15), 1586-1590.

1045. An, H.; Wang, H.; Lan, Y.; Hashi, Y.; Chen, S. Simultaneous qualitative and quantitative analysis of phenolic acids and flavonoids for the quality control of *Apocynum venetum* L. leaves by HPLC-DAD-ESI-IT-TOF-MS and HPLC-DAD. *J. Pharm. Biomed. Anal.* **2013,** *85*, 295-304.

1046. Pereira, A. C.; Pereira, A. B.; Moreira, C. C.; Botion, L. M.; Lemos, V. S.; Braga, F. C.; Cortes, S. F. *Hancornia speciosa* Gomes (Apocynaceae) as a potential anti-diabetic drug. *J. Ethnopharmacol.* **2015,** *161*, 30-35.

1047. Zhu, W. M.; Lu, C. H.; Wang, Y.; Zhou, J.; Hao, X. J. Monoterpenoids and their glycosides from *Winchia calophylla*. *Journal of Asian Natural Products Research* **2004,** *6* (3), 193-198.

1048. Okonkwo, T. J.; Osadebe, P. O.; Proksch, P. Bioactive phenylpropanoids, phenolic acid and phytosterol from *Landolphia owariensis* P. Beauv stringy seed pulp. *Phytotherapy Research* **2016,** *30* (1), 78-83.

1049. Surveswaran, S.; Cai, Y. Z.; Xing, J.; Corke, H.; Sun, M. Antioxidant properties and principal phenolic phytochemicals of Indian medicinal plants from Asclepiadoideae and Periplocoideae. *Natural Product Research* **2010,** *24* (3), 206-221.

1050. Um, B. H.; Polat, M.; Lobstein, A.; Weniger, B.; Aragon, R.; Declercq, L.; Anton, R. A new dicaffeoylquinic acid butyl ester from *Isertia pittieri*. *Fitoterapia* **2002,** *73* (6), 550-552.

1051. Batista, J. C.; Santin, S. M. d. O.; Schuquel, I. T. A.; Arruda, L. L. M. d.; Bersani-Amado, C. A.; Oliveira, C. M. A. d.; Kato, L.; Ferreira, H. D.; Silva, C. C. d. Constituintes quimicos e avaliação das atividades antioxidante e anti-inflamatoria das raizes de *Sabicea brasiliensis* wernh (Rubiaceae). *Quimica Nova* **2014,** *37*, 638-642.

1052. Kapil, A.; Koul, I. B.; Suri, O. P. Antihepatotoxic effects of chlorogenic acid from *Anthocephalus cadamba*. *Phytotherapy Research* **1995,** *9*, 189.

1053. Lucarini, R.; Tozatti, M.; Silva, M.; Gimenez, V.; Pauletti, P.; Groppo, M.; Turatti, I.; Cunha, W.; Martins, C. Antibacterial and anti-inflammatory activities of an extract, fractions, and compounds isolated from *Gochnatia pulchra* aerial parts. *Braz. J. Med. Biol. Res.* **2015,** *48* (9), 822-830.

1054. Strapasson, R. L.; Ruediger, A. L.; Burrow, R. A.; Barison, A.; Stefanello, M. E. A new sesquiterpene lactone and other constituents of *Moquiniastrum polymorphum* subsp *floccosum* (Asteraceae). *Natural Product Communications* **2014,** *9* (11), 1541-1543.

1055. Chassevent, F.; D'Ornano, M.; Pougneaud, S. Composition et caractéristiques chimiques de Coffea sauvages de Madagascar. *Café Cacao Thé* **1967,** *11*, 343-349.

1056. Clifford, M. N.; Williams, T.; Bridson, D. Chlorogenic acids and caffeine as possible taxonomic criteria in *Coffea* and *Psilanthus*. *Phytochem.* **1989,** *28*, 829-838.

1057. Anthony, F.; Clifford, M. N.; Noirot, M. Biochemical diversity on the genus *Coffea L.:* chlorogenic acids, caffeine and mozambioside contents. *Gen. Res. Crop Evol.* **1993,** *40*, 61-70.

1058. Andrade, P. B.; Leitao, R.; Seabra, R. M.; Oliveira, M. B.; Ferreira, A. 3,4-Dimethoxycinnamic acid levels as a tool for differentiation of *Coffea canephora* and *Coffea arabica*. *Food Chem.* **1998,** *61*, 511-514.

1059. Bertrand, B.; Villarreal, D.; Laffargue, A.; Posada, H.; Lashermes, P.; Dussert, S. Comparison of the effectiveness of fatty acids, chlorogenic acids, and elements for the chemometric discrimination of coffee (*Coffea arabica* L.) varieties and growing origins. *J. Agric. Food Chem.* **2008,** *56* (6), 2273-2280.

1060. Campa, C.; Doulbeau, S.; Dussert, S.; Hamon, S.; Noirot, M. Qualitative relationship between caffeine and chlorogenic acid contents among wild *Coffea* species. *Food Chem.* **2005,** *93* (1), 135-139.

1061. Babova, O.; Occhipinti, A.; Maffei, M. E. Chemical partitioning and antioxidant capacity of green coffee (*Coffea arabica* and *Coffea canephora*) of different geographical origin. *Phytochem.* **2016,** *123*, 33-39.

1062. Baeza, G.; Sarria, B.; Bravo, L.; Mateos Briz, R. Exhaustive qualitative LC-DAD-MSn analysis of Arabica green coffee beans: cinnamoyl-glycosides and cinnamoylshikimic acids as new polyphenols in green coffee. *J. Agric. Food Chem.* **2016**.

1063. Clifford, M. N. Chlorogenic acids. In *Coffee 1. Chemistry*, Clarke, R. J.; Macrae, R., Eds.; Elsevier Applied Science: London, 1985; pp 153-202.

1064. Clifford, M. N.; Willson, K. C. *Coffee: botany, biochemistry and production of beans and beverage;* Chapman and Hall: London, 1985.

1065. Ky, C.-L.; Louarn, J.; Dussert, S.; Guyot, B.; Hamon, S.; Noirot, M. Caffeine, trigonelline, chlorogenic acids and sucrose diversity in wild *Coffea arabica* L. and *C. canephora* P. accessions. *Food Chem.* **2001,** *75*, 223-230.

1066. Clifford, M. N.; Marks, S.; Knight, S.; Kuhnert, N. Characterization by LC–MS^n of four novel classes of *p*-coumaric acid-containing diacyl chlorogenic acids in green coffee beans. *J. Agric. Food Chem.* **2006,** *54*, 4095-4101.

1067. Clifford, M. N.; Knight, S.; Surucu, B.; Kuhnert, N. Characterization by LC-MS^n of four new classes of chlorogenic acids in green coffee beans: dimethoxycinnamoylquinic acids, diferuloylquinic acids, caffeoyl-dimethoxycinnamoylquinic acids, and feruloyl-dimethoxycinnamoylquinic acids. *J. Agric. Food Chem.* **2006,** *54*, 1957-1969.

1068. Alonso-Salces, R. M.; Serra, F.; Reniero, F.; Heberger, K. Botanical and geographical characterization of green coffee (*Coffea arabica* and *Coffea canephora*): chemometric valuation of phenolic and methylxanthine contents. *J Agric. Food Chem.* **2009,** *57*, 4224-4235.

1069. Alonso-Salces, R. M.; Guillou, C.; Berrueta, L. A. Liquid chromatography coupled with ultraviolet absorbance detection, electrospray ionization, collision-induced dissociation and tandem mass spectrometry on a triple quadrupole for the on-line characterization of polyphenols and methylxanthines in green coffee beans. *Rapid Commun. Mass Spectrom.* **2009,** *23* (3), 363-383.

1070. Kuhnert, N.; Jaiswal, R.; Eravuchira, P.; El-Abassy, R. M.; Kammer, B. v. d.; Materny, A. Scope and limitations of principal component analysis of high resolution LC-TOF-MS data: the analysis of the chlorogenic acid fraction in green coffee beans as a case study. *Anal. Methods* **2011,** *3* (1), 144-155.

1071. Clifford, M. N.; Jarvis, T. The chlorogenic acids content of green robusta coffee beans as a possible index of geographic origin. *Food Chem.* **1988,** *29*, 291-298.

1072. Clifford, M. N.; Kellard, B.; Ah-Sing, E. Caffeoyl-tyrosine from green robusta coffee beans. *Phytochem.* **1989,** *28*, 1989-1990.

1073. Correia, A. M. N. G.; Leitao, M. C. A.; Clifford, M. N. Caffeoyl-tyrosine and Angola II as characteristic markers for Angolan robusta coffees. *Food Chem.* **1995,** *53*, 309-313.

1074. Garrett, R.; Rezende, C. M.; Ifa, D. R. Coffee origin discrimination by paper spray mass spectrometry and direct coffee spray analysis. *Anal. Methods* **2013,** *5* (21), 5944-5948.

1075. Mehari, B.; Redi-Abshiro, M.; Chandravanshi, B. S.; Combrinck, S.; Atlabachew, M.; McCrindle, R. Profiling of phenolic compounds using UPLC-MS for determining the geographical origin of green coffee beans from Ethiopia. *Journal of Food Composition and Analysis* **2016,** *45*, 16-25.

1076. Guerrero, G.; Suarez, M.; Moreno, G. Chlorogenic acids as a potential criterion in coffee genotype selections. *J Agric. Food Chem.* **2001,** *49* (5), 2454-2458.

1077. Guerrero, G. A.; Suarez, M.; Moreno, G. R. Derivados hidroxicinnamicos para la discriminacion de genotipos de cafe. *Cenicafe* **2003,** *54* (3), 234-241.

1078. Campa, C.; Noirot, M.; Bourgeois, M.; Pervent, M.; Ky, C. L.; Chrestin, H.; Hamon, S.; De Kochko, A. Genetic mapping of a caffeoyl-coenzyme A 3-*O*-methyltransferase gene in coffee trees. Impact on chlorogenic acid content. *Theor. Appl. Genet.* **2003,** *107*, 751-757.

1079. Koshiro, Y.; Jackson, M. C.; Katahira, R.; Wang, M. L.; Nagai, C.; Ashihara, H. Biosynthesis of chlorogenic acids in growing and ripening fruits of *Coffea arabica* and *Coffea canephora* plants. *Z. Naturforsch. C.* **2007,** *62* (9-10), 731-742.

1080. Joet, T.; Laffargue, A.; Salmona, J.; Doulbeau, S.; Descroix, F.; Bertrand, B.; de, K. A.; Dussert, S. Metabolic pathways in tropical dicotyledonous albuminous seeds: *Coffea arabica* as a case study. *New Phytol.* **2009,** *182* (1), 146-162.

1081. Garrett, R.; Vaz, B. G.; Hovell, A. M.; Eberlin, M. N.; Rezende, C. M. Arabica and Robusta coffees: identification of major polar compounds and quantification of blends by direct-infusion electrospray ionization-mass spectrometry. *J. Agric. Food Chem.* **2012,** *60*, 4253-4258.

1082. Clifford, M. N.; Ramìrez-Martìnez, J. R. Phenols and caffeine in wet processed coffee beans and pulp. *Food Chem.* **1991,** *40*, 35-42.

1083. Ramirez-Coronel, M. A.; Marnet, N.; Kolli, V. S.; Roussos, S.; Guyot, S.; Augur, C. Characterization and estimation of proanthocyanidins and other phenolics in coffee pulp (*Coffea arabica*) by thiolysis-high-performance liquid chromatography. *J Agric. Food Chem.* **2004,** *52* (5), 1344-1349.

1084. Mondolot, L.; La Fisca, P.; Buatois, B.; Talansier, E.; De Kochko, A.; Campa, C. Evolution in caffeoylquinic acid content and histolocalization during *Coffea canephora* leaf development. *Ann. Bot. (Lond)* **2006,** *98* (1), 33-40.

1085. Campa, C.; Mondolot, L.; Rakotondravao, A.; Bidel, L. P.; Gargadennec, A.; Couturon, E.; La, F. P.; Rakotomalala, J. J.; Jay-Allemand, C.; Davis, A. P. A survey of mangiferin and hydroxycinnamic acid ester accumulation in coffee (*Coffea*) leaves: biological implications and uses. *Ann Bot.* **2012,** *110* (3), 595-613.

1086. Davis, P. A. *Psilanthus mannii*, the type species of *Psilanthus*, transferred to *Coffea*. *Nordic Journal of Botany* **2011,** *29*, 471-472.

1087. Clifford, M. N.; Wu, W.; Kirkpatrick, J.; Jaiswal, R.; Kuhnert, N. Profiling and characterisation by liquid chromatography/multi-stage mass spectrometry of the chlorogenic acids in Gardeniae Fructus. *Rapid Commun. Mass Spectrom.* **2010,** *24* (21), 3109-3120.

1088. Kim, H. J.; Kim, E. J.; Seo, S. H.; Shin, C. G.; Jin, C.; Lee, Y. S. Vanillic acid glycoside and quinic acid derivatives from Gardeniae Fructus. *J. Nat. Prod.* **2006,** *69* (4), 600-603.

1089. Nishizawa, M.; Izuhara, R.; Kaneko, K.; Fujimoto, Y. 3-caffeoyl-4-sinapoylquinic acid, a novel lipoxygenase inhibitor from Gardeniae fructus. *Chem. Pharm. Bull.* **1987,** *35*, 2133-2135.

1090. Fu, X.; Chou, G.; Wang, Z. Chemical Constituents of *Gardenia jasminoides* Ellis. *Chinese Journal of Natural Medicines* **2008,** *6* (6), 418-420.

1091. Wu, X.; Zhou, Y.; Yin, F.; Mao, C.; Li, L.; Cai, B.; Lu, T. Quality control and producing areas differentiation of Gardeniae Fructus for eight bioactive constituents by HPLC-DAD-ESI/MS. *Phytomedicine.* **2014,** *21* (4), 551-559.

1092. Fu, Z.; Ling, Y.; Li, Z.; Chen, M.; Sun, Z.; Huang, C. HPLC-Q-TOF-MS/MS for analysis of major chemical constituents of Yinchen-Zhizi herb pair extract. *Biomed. Chromatogr.* **2014,** *28* (4), 475-485.

1093. Zou, L.; Li, X.; Shi, Q.; Feng, F. An effective integrated method for comprehensive identification of eighty-five compounds in Zhi-Zi-Da-Huang decoction by HPLC-DAD-ESI-MS (TOF) and HPLC-DAD-ESI-MS/MS (QqQ) without the help of reference standards. *Anal. Methods* **2014,** *6* (12), 4312-4327.

1094. Yang, L.; Peng, K.; Zhao, S.; Zhao, F.; Chen, L.; Qiu, F. 2-Methyl-l-erythritol glycosides from *Gardenia jasminoides*. *Fitoterapia* **2013,** *89* (0), 126-130.

1095. Bergonzi, M. C.; Righeschi, C.; Isacchi, B.; Bilia, A. R. Identification and quantification of constituents of *Gardenia jasminoides* Ellis (Zhizi) by HPLC-DAD-ESI-MS. *Food Chem.* **2012,** *134* (2), 1199-1204.

1096. Zhao, X.; Long, Z.; Dai, J.; Bi, K.; hen, X. Identification of multiple constituents in the traditional Chinese medicine formula Zhi-zi-chi decoction and rat plasma after oral administration by liquid chromatography coupled to quadrupole time-of-flight tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* **2012,** *26* (20), 2443-2453.

1097. Versiani, M. A.; Ikram, A.; Khalid, S.; Faizi, S.; Tahiri, I. A. Ixoroid: a new triterpenoid from the flowers of *Ixora coccinea*. *Nat. Prod. Commun.* **2012,** *7* (7), 831-834.

1098. Jaiswal, R.; Karar, M. G. E.; Gadir, H. A.; Kuhnert, N. Identification and characterisation of phenolics from *Ixora coccinea* L. (Rubiaceae) by liquid chromatography multi-stage mass spectrometry. *Phytochemical Analysis* **2014,** n/a.

1099. Bishay, D. W.; Backheet, E. Y.; Gouda, Y. G.; Mostafa, S. M. Phytochemical and biological study of *Vangueria edulis* cultivated in Egypt. *Bulletin of Pharmaceutical Sciences* **2012,** *35*, 67-81.

1100. Berger, A.; Preinfalk, A.; Robien, W.; Brecker, L.; Valant-Vetschera, K.; Schinnerl, J. New reports on flavonoids, benzoic- and chlorogenic acids as rare features in the *Psychotria* alliance (Rubiaceae). *Biochem. Syst. Ecol.* **2016,** *66*, 145-153.

1101. Jaiswal, R.; Kuhnert, N. How to identify and discriminate between the methyl quinates of chlorogenic acids by liquid chromatography-tandem mass spectrometry. *J. Mass Spectrom.* **2011,** *46* (3), 269-281.

1102. Jaiswal, R.; Matei, M. F.; Deshpande, S.; Kuhnert, N. Identification and characterization of hydroxycinnamates of six *Galium* species from the Rubiaceae family. In *Encyclopedia of Analytical Chemistry*, Hostettmann, K.; Stuppner, H.; Marston, H.; Chen, S., Eds.; John Wiley & Sons, Ltd: 2014; pp 505-524.

1103. Li, C.; Zhao, Y.; Guo, Z.; Zhang, X.; Xue, X.; Liang, X. Effective 2D-RPLC/RPLC enrichment and separation of micro-components from *Hedyotis diffusa* Willd. and characterization by using ultra-performance liquid chromatography/quadrupole time-of-flight mass spectrometry. *J. Pharm. Biomed. Anal.* **2014,** *99* (0), 35-44.

1104. Deshpande, S.; Jaiswal, R.; Matei, M. F.; Kuhnert, N. Investigation of acyl migration in mono- and dicaffeoylquinic acids under aqueous basic, aqueous acidic, and dry roasting conditions. *J. Agric. Food Chem.* **2014,** *62* (37), 9160-9170.

1105. Kang, U.; Park, J.; Han, A. R.; Woo, M. H.; Lee, J. H.; Lee, S. K.; Chang, T. S.; Woo, H. A.; Seo, E. K. Identification of cytoprotective constituents of the flower buds of *Tussilago farfara* against glucose oxidase-induced oxidative stress in mouse fibroblast NIH3T3 cells and human keratinocyte HaCaT cells. *Archives of Pharmacal Research* **2016,** *39* (4), 474-480.

1106. Nebehaj, E.; Hofmann, T. The leaf polyphenols of forest trees: optimization of the extraction solvent, seasonal changes and structural elucidation by HPLC-ESI-MS^n. Geneva, Switzerland, 2016.

1107. Wianowska, D.; Typek, R.; Dawidowicz, A. L. How to eliminate the formation of chlorogenic acids artefacts during plants analysis? Sea sand disruption method (SSDM) in the HPLC analysis of chlorogenic acids and their native derivatives in plants. *Phytochem.* **2015,** *117*, 489-499.