A New Indole Alkaloid from the Fruits of *Capparis masaiikai*

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One new indole alkaloid (**1**), together with a known indole alkaloid (**2**), one triterpene (**3**) and two sterols (**4-5**), were isolated from the fruits of *Capparis masaiikai* (Capparaceae). Their structures were identified on the basis of their MS, 1D NMR and 2D NMR spectra and by comparison of their data with those reported previously in the related literatures. To our best of knowledge the compounds **1-5** were isolated from this plant material for the first time.

Keywords: *Capparis masaiikai*, Capparaceae, indole alkaloids.

INTRODUCTION

The genus *Capparis* (Capparaceae) distributed principally in tropical and subtropical regions comprises about 250 species in the world and about 30 species are distributed in China¹. The fruits of *Capparis masaiikai* were used as a traditional folk Chinese medicine for the treatment of pharyngitis². Its seeds are commonly chewed for their sweet taste, due to the presence of sweet proteins³. Previous phytochemical studies on the seeds have resulted in the isolation of two compounds, oxazolidine-2-thione⁴ and 2-hydroxyethyl glucosinolate⁵. During our investigation on the chemical constituents of this plant, one new and four known compounds were isolated from 90 % ethanol extracts and identified as methyl 2-methylsulfinyl-6-methoxy-3-indole carbonate (**1**), indole-3-carboxaldehyde (**2**), betulin (**3**), (3 β , 5 α , 8 α , 22*E*)-5,8-diepoxy-ergosta-6,22-dien-3-ol (**4**) and 5,8-epidioxy-(3 β , 5 α , 8 α , 22*E*)-ergosta-6,9(11), 22-trien-3-ol (**5**).

EXPERIMENTAL

NMR spectra were recorded on a Bruker AM-400 and Avance III 600 spectrometers with TMS as internal standard. A Bruker HCT/E squire and a Waters Autospec Premier P776 spectrum was used to measure ESIMS and HREIMS spectra, respectively. Chromatorex RP-C₁₈ gel (20-45 μ m, Merck, Darmstadt, Germany), Column chromatography was performed

on silica gel (100-200, 200-300 and 300-400 mesh, Qingdao Marine Chemical Inc.) and Sephadex LH-20 (40-70 μ m, Amersham Pharmacia Biotech AB, Uppsala, Sweden). TLC spots were visualized under UV light and by dipping into 5 % H₂SO₄ in EtOH followed by heating.

The fruits of *C. masaiikai* were collected from Wenshan, Yunnan Province, China, in September 2012 and identified by Prof. Hua Peng (Kunming Institute of Botany, Chinese Academy of Sciences). A voucher specimen (kmust 20120910) was deposited at Faculty of Life Science and Technology, Kunming University of Science and Technology.

Extraction and isolation: The air-dried and powdered fruits of *C. masaiikai* (5 kg) were extracted by refluxing with 90 % EtOH for three times. In a vacuum, the EtOH solvent was concentrated to give a crude residue (225 g), which was suspended in water. The water layer was partitioned with EtOAc. The EtOAc portion (80 g) was submitted to column chromatography (CC) over silica gel (100-200 mesh) using PE (petroleum ether)/acetone (100:1 $\rightarrow$ 6:4) and CHCl₃/CH₃OH (9:1 $\rightarrow$ 0:1) to give seven fractions (Fr.A-Fr.G). Fr.C (9.87 g) was subjected to chromatography on a RP-C₁₈ (MeOH/H₂O from 6:4 $\rightarrow$ 10:0) to give ten fractions (Fr.C1-Fr.C10). Fr.C5 (0.35 g) was purified by Sephadex LH-20 (chloroform/MeOH) and then was chromatographed over repetitive silica gel eluted by gradient PE/acetone (50:1 $\rightarrow$ 1:1) to yield compounds **1** (2 mg), **2** (2 mg), **3** (2 mg), **4** (10 mg) and **5** (8 mg) (Fig. 1).

Fig. 1. Structures of compounds 1-5

RESULTS AND DISCUSSION

Compound 1: 2-Methylsulfinyl-6-methoxy-3-indole-carbonate was obtained as a white powder and its molecular formula $C_{12}H_{13}NO_4S$ was deduced from the HR-EI-MS at m/z 267.0562 $[M]^+$ (calcd. for $C_{12}H_{13}NO_4S$, 267.0565). The IR spectrum displayed absorption bands at 3239 cm^{-1} $\nu(\text{NH})$, 1624 cm^{-1} $\nu(\text{C=O})$ and 832 cm^{-1} $\nu(\text{S=O})$. The $^1\text{H-NMR}$ spectrum was very informative with a NH signal (δ_{H} 13.80) and showed the presence of one methyl (δ_{H} 3.09), two methoxyl group (δ_{H} 3.88, 3.79) and three mutual coupled aromatic protons (δ_{H} 8.27, 7.31, 7.24). The $^{13}\text{C-NMR}$ spectrum of **1** indicated 12 resonances carbons, including one methyl (δ_{C} 43.0), two methoxyl (δ_{C} 55.9, 51.8), three methane (δ_{C} 123.3, 113.8, 96.3) and six quaternary carbons (δ_{C} 165.4, 158.5, 147.8, 138.8, 122.3, 106.0). The spectroscopic data mentioned above suggested that **1** was a indol alkaloid⁶. The NMR data of compound **1** resembled those of 6-methoxy-3-indolecarbonate⁶ except for the presence of an additional methylsulfinyl group in **1**. The HMBC correlation of Me (δ_{H} 3.09, s) with C-2 (δ_{C} 147.8) as well as an additional sulfinyl group indicated the methylsulfinyl group should be placed at C-2 (Table-1 and Fig. 2). Thus, the structure of **1** was assigned as 2-methylsulfinyl-6-methoxy-3-indole carbonate.

TABLE-1
 ^1H (600 MHz) AND ^{13}C (150 MHz) NMR SPECTRAL
DATA FOR COMPOUND **1** IN $\text{C}_5\text{D}_5\text{N}$

Position	δ_{H} (mult., J in Hz)	δ_{C}
2		147.8
3		106.0
4	8.27 d (8.8)	123.3
5	7.24 dd (8.8, 2.2)	113.8
6		158.5
7	7.31 d (2.2)	96.3
8		138.8
9		122.3
10		165.4
6-OMe	3.79 s	55.9
10-OMe	3.89 s	51.8
2-SOMe	3.09 s	43.0

Fig. 2. Key HMBC (arrow) and ^1H - ^1H COSY (bold) correlations of compound **1**

Compound 2: Indole-3-carboxaldehyde was obtained as a colourless needle and its molecular formula C_9H_7NO . It was identified as indole-3-carboxaldehyde by comparison of the physical and spectral data with the reported data⁷. $^1\text{H-NMR}$ (CD_3OD , 400 MHz) δ : 9.86 (1H, s, CHO), 8.16 (1H, d, J = 7.0 Hz, H-4), 8.02 (1H, s, H-2), 7.45 (1H, d, J = 7.4 Hz, H-7), 7.25 (2H, m, H-5,6); $^{13}\text{C-NMR}$ (CD_3OD , 100 MHz) δ : 187.1 (3-CHO), 139.3 (C-2), 138.5 (C-9), 125.4 (C-8), 124.8 (C-6), 123.4 (C-4), 122.1 (C-5), 119.8 (C-3), 112.9 (C-7).

Compound 3: Betulin was obtained as a colourless needle and its molecular formula $C_{30}H_{50}O_2$. It was identified as betulin by comparison of the physical and spectral data with the reported data⁸. $^1\text{H-NMR}$ ($\text{C}_5\text{D}_5\text{N}$, 600 MHz) δ : 5.55 (1H, s, H-29a), 5.15 (1H, s, H-29b), 4.51 (2H, H-28), 3.49 (1H, dd, J = 7.8, 1.5 Hz, H-3), 1.28 (3H, s, H-30), 1.07 (3H, s, H-26), 1.03 (3H, s, H-27), 0.98 (3H, s, H-23), 0.83 (3H, s, H-25), 0.81 (3H, s, H-24); $^{13}\text{C-NMR}$ ($\text{C}_5\text{D}_5\text{N}$, 150 MHz) δ : 157.0 (C-20), 106.6 (C-29), 78.6 (C-3), 64.6 (C-28), 56.3 (C-5), 51.2 (C-9), 49.3 (C-18), 44.6 (C-19), 43.7 (C-17), 43.4 (C-14), 41.6 (C-8), 40.6 (C-1), 40.0 (C-4), 39.7 (C-7), 38.7 (C-13), 37.9 (C-10), 36.2 (C-22), 35.1 (C-21), 32.6 (C-16), 29.1 (C-23), 28.7 (C-15), 28.2 (C-2), 27.3 (C-12), 21.6 (C-11), 19.2 (C-6), 18.3 (C-30), 16.9 (C-25), 16.8 (C-26), 16.6 (C-24), 15.2 (C-27).

Compound 4: ($3\beta,5\alpha,8\alpha,22E$)-5,8-Diepoxy-ergosta-6,22-dien-3-ol was obtained as a white amorphous powder and its molecular formula $C_{28}H_{44}O_3$. It was identified as ($3\beta,5\alpha,8\alpha,22E$)-5,8-diepoxy-ergosta-6,22-dien-3-ol by comparison of the physical and spectral data with the reported data⁹. $^1\text{H-NMR}$ (CD_3COCD_3 , 400 MHz) δ : 6.48 (1H, d, J = 8.5 Hz, H-7), 6.22 (1H, d, J = 8.5 Hz, H-6), 5.26 (1H, dd, J = 15.2, 7.3 Hz, H-23), 5.19 (1H, dd, J = 15.2, 7.3 Hz, H-22), 3.76 (1H, m, H-3), 1.0 (3H, d, J = 6.6 Hz, H-21), 0.92 (3H, d, J = 6.8 Hz, H-28), 0.88 (3H, s, H-19), 0.85 (3H, d, J = 6.8 Hz, H-26), 0.84 (3H, s, H-18), 0.82 (3H, d, J = 6.7 Hz, H-27); $^{13}\text{C-NMR}$ (CD_3COCD_3 , 100 MHz) δ : 136.6 (C-6), 136.4 (C-22), 132.8 (C-23), 131.1 (C-7), 82.3 (C-5), 79.4 (C-8), 66.2 (C-3), 56.9 (C-17), 52.6 (C-14), 52.4 (C-9), 45.1 (C-13), 43.7 (C-24), 40.6 (C-20), 40.2 (C-12), 38.0 (C-4), 37.9 (C-10), 35.6 (C-1), 33.8 (C-25), 31.0 (C-2), 30.2 (C-16), 24.0 (C-11), 21.3 (C-21), 21.2 (C-15), 20.3 (C-27), 19.9 (C-26), 18.5 (C-19), 18.0 (C-28), 13.2 (C-18).

Compound 5: 5,8-Epidioxy-($3\beta,5\alpha,8\alpha,22E$)-ergosta-6,9(11),22-trien-3-ol was obtained as a white amorphous powder and its molecular formula $C_{28}H_{42}O_3$. It was identified as 5,8-epidioxy-($3\beta,5\alpha,8\alpha,22E$)-ergosta-6,9(11),22-trien-3-ol by comparison of the physical and spectral data with the reported data⁹. $^1\text{H-NMR}$ (CD_3OD , 400 MHz) δ : 6.78 (1H, d, J = 8.4 Hz, H-7), 6.48 (1H, d, J = 8.4 Hz, H-6), 5.58 (1H, d, J = 4.2 Hz, H-11), 5.32 (1H, dd, J = 15.4, 7.7 Hz, H-23), 5.22 (1H, dd, J = 15.4, 7.7 Hz, H-22), 4.50 (1H, m, H-3), 1.23 (3H, s,

H-19), 1.06 (3H, d, $J = 6.4$ Hz, H-21), 1.0 (3H, d, $J = 6.8$ Hz, H-28), 0.92 (3H, d, $J = 5.4$ Hz, H-26), 0.90 (3H, d, $J = 6.5$ Hz, H-27), 0.82 (3H, s, H-18); ^{13}C -NMR (CD_3OD , 100 MHz) δ : 144.3 (C-9), 136.6 (C-6), 136.2 (C-22), 133.0 (C-23), 131.4 (C-7), 112.0 (C-11), 83.7 (C-5), 79.0 (C-8), 66.4 (C-3), 56.5 (C-17), 49.3 (C-14), 44.3 (C-13), 43.5 (C-24), 41.9 (C-12), 40.7 (C-20), 39.0 (C-10), 37.4 (C-4), 33.8 (C-25), 33.7 (C-1), 31.8 (C-2), 29.5 (C-16), 26.3 (C-19), 21.8 (C-15), 21.4 (C-21), 20.7 (C-26), 20.4 (C-27), 18.3 (C-28), 13.7 (C-18).

Compounds (**1-5**) were isolated from this plant material for the first time. These results in this study may provide some important information for the research of *C. masaikai* from the perspective of plant taxonomy.

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