SHORT REPORT

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A New 4,5-Secofurancadinene from the Rhizome of *Curcuma kwangsiensis*

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Abstract: The rhizome of *Curcuma kwangsiensis* S. G. Lee et C. F. Liang is a Traditional Chinese Medicine indexed in Chinese Pharmacopoeia. A new compound, 4,5-seco-pyrocurzerenone (**1**), was isolated from the species along with sixteen sesquiterpenoids (**2**-**17**). Their structures were elucidated based on the spectroscopic evidence, mainly including NMR and HRESIMS. All the compounds were reported for the first time from this species.

Keywords: Sesquiterpenoid; 4,5-secofurancadinene; *Curcuma kwangsiensis*.

1. Plant Source

The rhizome of *Curcuma kwangsiensis* S. G. Lee et C. F. Liang was purchased from the Juhua Traditional Chinese Medicine Market, Kunming, China, on July, 2015, and identified by Prof. Shiming Guo, Yunnan Institute of Traditional Chinese Medicine and Material Medica, China. The voucher specimen (CK-2015-07) was deposited in the laboratory of Faculty of Life Science and Technology, Kunming University of Science and Technology.

2. Previous Studies

Curcuma kwangsiensis S. G. Lee et C. F. Liang belongs to the genus *Curcuma*, in which many plants were rich of diphenylheptanes and sesquiterpenoids [2,3]. However, the constituents in *Curcuma kwangsiensis* S. G. Lee et C. F. Liang are found to have more diphenylheptanes, but less sesquiterpenoids [4-9].

3. Present Study

The rhizome of *Curcuma kwangsiensis* S. G. Lee et C. F. Liang is one of three base source plants of Rhizoma Curcumae indexed in Chinese Pharmacopoeia (2015 edition) [1], which has good effects on treating blood stasis, amenorrhea, indigestion and abdominal distension. Currently, seventeen

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sesquiterpenoids (**1**-**17**) were isolated from the rhizome of *Curcuma kwangsiensis* S. G. Lee et C. F. Liang for the first time, including a new 4,5-secofurancadinene (**1**) (Figure 1).

The rhizome of *Curcuma kwangsiensis* S. G. Lee et C. F. Liang (10.6 kg) was extracted with 75% ethanol (10 L × 4 h × 4 times) to obtain a residue (1036.0 g), which then was suspended in H_2O (3 L) and partitioned successively with petroleum ether (3 L× 4 times) and EtOAc (3 L× 4 times). The petroleum ether extract (98.6 g) was subjected to a column of silica gel eluted with petroleum ether − EtOAc (1:0 to 1:2 v/v) to obtain 4 fractions (PA−PD). Fr. PB (14.3 g) was subjected to a column of silica gel eluted with petroleum ether − EtOAc to afford sub-fractions, which were further purified by Sephadex LH-20 with $CHCl_3$-MeOH (1:1), followed semi-preparative HPLC (Zorbax SB-C_{18}, 9.4 mm × 250 mm, 0.5 μm) with MeOH−H_2O to obtain **6** (0.9 mg), **7** (1.0 mg), **8** (1.0 mg), **9** (0.8 mg), **10** (1.0 mg) and **11** (0.9 mg). Fr. PC (9.5 g) was also purified by a series of silica gel column (petroleum ether − EtOAc), Sephadex LH-20 ($CHCl_3$-MeOH) and semi-preparative HPLC (MeOH − H_2O) to yield **12** (1.0 mg), **13** (1.3 mg), **14** (12.2 mg), **15** (26.0 mg) and **16** (16.9 mg). Fr. PD (7.1 g) was separated by a silica gel column (petroleum ether − EtOAc), followed Sephadex LH-20 ($CHCl_3$-MeOH) and semi-preparative HPLC (MeOH − H_2O) to obtain **17** (1.7 mg). The EtOAc extract (938.6 g) was also subjected to a column of silica gel eluted with petroleum ether − EtOAc (1:0 to 1:2 v/v) to obtain 12 fractions (EA−EL). Fr. EA (9.6 g) was purified by a series of silica gel column (petroleum ether − EtOAc), Sephadex LH-20 ($CHCl_3$-MeOH) and semi-preparative HPLC (MeOH − H_2O) to obtain **1** (1.8 mg), **2** (14.8 mg), **3** (3.1 mg), **4** (21.3 mg) and **5** (6.7 mg).

*Compound **1***: Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 2.22 (3H, s, H-14), 2.40 (3H, s, H-13), 2.45 (3H, s, H-15), 2.70 (2H, m, H-3), 3.28 (2H, m, H-2), 7.48 (1H, s, H-9), 7.49 (1H, s, H-12), 10.80 (1H, s, H-5); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm):12.9 (CH_3, C-13), 20.2 (CH_3, C-15), 24.1 (CH_2, C-2), 30.0 (CH_3, C-14), 44.2 (CH_2, C-3), 115.6 (C, C-11), 118.3 (CH, C-9), 128.7 (C, C-7), 129.2 (C, C-6), 134.1 (C, C-10), 137.0 (C, C-1), 144.3 (CH, C-12), 155.1 (C, C-8), 192.2 (CHO, C-5), 208.4 (C, C-4); HRESIMS *m/z* 267.0990 $[M + Na]^+$ (calcd for $C_{15}H_{16}O_3Na$, 267.0997).

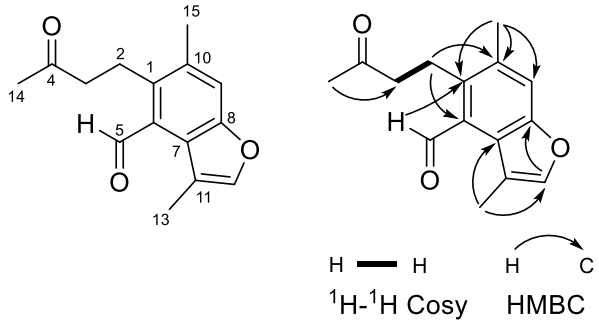

Figure 1. The structure and the key correlations in ^{1}H-^{1}H Cosy and HMBC of compound **1**

Compound **1** was isolated as a yellow oil, whose molecular formula was determined as $C_{15}H_{16}O_3$ by HRESIMS (*m/z* 267.0990 $[M + Na]^+$, calcd 267.0997) with eight indices of hydrogen deficiency. In the ^{1}H NMR spectrum of **1**, three methyl at δ_H 2.22 (3H, s), 2.40 (3H, s) and 2.45 (3H, s), two methylene at δ_H 2.71 (2H, m) and 3.28 (2H, m), two olefinic methine at δ_H 7.48 (1H, s) and 7.49 (1H, s), and one aldehydic proton at δ_H 10.80 (1H, s) were shown, which were further assigned to the corresponding carbons at δ_C 30.0 (C-14), 12.9 (C-13), 20.2 (C-15), 44.2 (C-3), 24.1 (C-2), 118.3 (C-9), 144.3 (C-12), and 192.2 (C-5), according to ^{13}C NMR, DEPT and HSQC spectra. Except those eight assigned carbon signals, other seven quaternary carbons were shown in the downfield of ^{13}C NMR, including six olefinic (δ_C 115.6, 128.7, 129.2, 134.1, 137.0, 155.1) and a ketocarbonyl (δ_C 208.4), which were also supported by the DEPT and HSQC spectra. In HMBC spectrum, the correlations from Me-14 to C-3, and from H-5 to C-1 and 7 indicated **1** contains one formyl and one acetyl located in C-3 and C-6, respectively. Other correlations from Me-13 to C-7, 11 and 12, Me-15 to C-1, 9 and 10 observed in HMBC, together with the eight indices of hydrogen deficiency, further suggested **1** was a furancadinene, structurally similar with pyrocurzerenone (**4**) [12], except two more carbonyl carbons

(δ_C 192.2, 208.4) presented in compound **1**, instead of one olefinic secondary and one olefinic quaternary carbons in pyrocurzerenone (**4**). These evidence also revealed the olefinic bond in C-4 and -5 in pyrocurzerenone (**4**) was oxidized and transformed into one formyl and one acetyl in compound **1** (Figure 1). Thus,compound **1** was named as 4,5-seco-pyrocurzerenone.

The sixteen known sesquiterpenes were identified as (±)-commyrrin A (**2**) [10], furanocadalene (**3**) [11], pyrocurzerenone (**4**) [12], 4,10-*E*-pizedoarondiol (**5**) [13], procurcumadiol (**6**) [14], doarondiol (**7**) [14], sozedoarondiol (**8**) [15], (1*S*,4*S*,5*S*,10*R*)-zedoarondiol (**9**) [16], aerugidiol (**10**) [16], curzereone (**11**) [17], isoprocurcumenol (**12**) [16], zedoalactone F (**13**) [18], zederone (**14**) [19], 1*α*,4*β*-dihydroxyeudesman-8-one (**15**) [20], germacrone (**16**) [13], and procurcumadiol (**17**) [21] by comparing their NMR and MS date with those reported in the literature. All of them were found in this plant for the first time.

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Supporting Information

Supporting Information accompanies this paper on http://www.acgpubs.org/journal/records-of-natural-products

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