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A NEW SESQUITERPENOID FROM *Mallotus apelta*

Jian-fu Xu,[1,2] Fu-shuang Li,[1] Zi-ming Feng,[1] Jian-shuang Jiang,[1] and Pei-cheng Zhang[1]*

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*A new sesquiterpenoid, malloapelin D (**1**), and a known schizandriside (**2**) were isolated from the roots of* Mallotus apelta. *Their structures were elucidated on the basis of spectroscopic methods including IR, MS, and 1D and 2D NMR.*

Keywords: *Mallotus apelta*, sesquiterpenoid, malloapelin D.

Mallotus apelta Muell. Arg. (Euphorbiaceae), which belongs to the Mallotus family, is widely distributed in the south of China and used as a folk medicine for the treatment of chronic hepatitis, ulcer, eczema, and hemostasis in traditional Chinese medicine. Extracts of *M. apelta* showed significant anti-HIV activity in recent study [1]. Various types of compounds with biological activities such as alkaloids, diterpenoids, coumarinolignoids, and benzopyran derivatives have been found from *M. apelta* [2–6]. In our study on the phytochemical constituents of this plant, the 70% ethanolic extract of the roots of *M. apelta* has been investigated. A new sesquiterpenoid, malloapelin D (**1**), and a known compound schizandriside (**2**) were isolated and their structures were elucidated on the basis of spectroscopic methods including IR, MS, and 1D and 2D NMR.

The air-dried and powdered roots of *Mallotus apelta* Muell. Arg. (5.5 kg) were exhaustively extracted with 70% EtOH at reflux temperature. The EtOH extract (275 g) was suspended in H_2O and partitioned successively with petroleum ether, EtOAc, and BuOH to yield petroleum ether (28 g), EtOAc (43 g), and BuOH (56 g) soluble fractions, respectively. The BuOH fraction was chromatographed on a column of silica gel eluting with $CHCl_3$–MeOH (in gradient) to give six fractions (F1–F6). Fraction 3 was rechromatographed on LH-20 to afford compound **1** (6 mg), **2** (10 mg).

Malloapelin D (**1**) was obtained as a colorless oil, $[\alpha]_D^{25}$ +7.5° (*c* 0.50, MeOH). The molecular formula of **1** was determined to be $C_{16}H_{24}O_7$ on the basis of the negative HR-ESI-MS (*m*/*z* 327.1451 $[M - H]^-$, calcd 327.1438 for $C_{16}H_{23}O_7$). The UV maximum at 264 nm exhibited absorption characteristic of a conjugated ketone. The presence of hydroxy (3600–2500 cm^{-1}), conjugated ketone (1693 cm^{-1}), and two double bond (1636 and 1603 cm^{-1}) groups were indicated in its IR spectrum. The ^1H NMR spectrum (Table 1) of **1** in CD_3OD showed signals attributed to four tertiary methyls at δ 1.03 (Me-5′), 1.21 (Me-1′), 2.05 (Me-3), and 3.41 (MeO-6′), a methylene at δ 1.69 (dd, J = 11.0, 14.0 Hz, H-2′), 2.14 (dd, J = 8.0, 14.0 Hz, H-2′), three methines attached to oxygen at δ 3.50 (1H, d, J = 7.5 Hz, H-4′), 3.65 (1H, m, H-3′), and 4.78 (1H, s, H-6′), and three olefinic protons at δ 5.74, 6.19, and 7.92. The ^{13}C NMR spectra (see Table 1) showed 16 carbon signals. In the HMBC spectrum, correlations from δ 1.03 (Me-5′) to δ 77.5 (C-4′), 106.0 (C-6′), 58.0 (C-5′), and 82.8 (C-8′), from δ 1.21 (Me-1′) to δ 42.1 (C-2′), 82.8 (C-8′), and 88.6 (C-1′), and from δ 3.41 (MeO-6′) to δ 106.0 (C-6′) indicated that there was a 1,5-dimethyl-3,4,8-trihydroxy-6-methoxy-7-oxabicyclo-[3,2,1]-octane skeleton. Correlations from δ 5.74 (H-2) to δ 170.0 (C-1), 132.4 (C-5), and 21.1 (Me-3) and from δ 2.05 (Me-3) to δ 119.4 (C-2) and 132.4 (C-4) indicated that there was a 3-methyl-2,4-pentadienoic acid moiety in **1**. Correlations from δ 6.19 (H-5) and 7.92 (H-4) to 82.8 (C-8′) and from δ 1.21 (Me-1′) and 1.03 (Me-5′) to 82.8 (C-8′) showed that the 3-methyl-2,4-pentadienoic acid moiety is attached to 1,5-dimethyl-3,4,8-trihydroxy-6-methoxy-7-oxabicyclo-[3,2,1]-octane at the C-8′ position. Therefore, the structure of **1** was determined as 5-(1,5-dimethyl-3,4,8-trihydroxy-6-methoxy-7-oxabicyclo-[3,2,1]-oct-8-yl)-3-methyl-2,4-pentadienoic acid, named malloapelin D.

1) Key Laboratory of Bioactive Substances and Resources Utilization of Chinese Herbal Medicine (Ministry of Education), Institute of Materia Medica, Peking Union Medical College and Chinese Academy of Medical Sciences, Beijing, 100050, P. R. China, fax: +86 10 63 01 77 57, e-mail: pczhang@imm.ac.cn; 2) Beijing Institute of Medicinal Chemistry, Beijing, 102205, P. R. China. Published in Khimiya Prirodnykh Soedinenii, No. 2, pp. 201–202, March–April, 2011. Original article submitted January 27, 2010.

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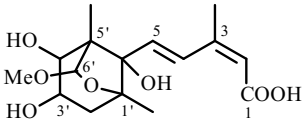
TABLE 1. ^{1}H and ^{13}C NMR Data of Compound **1** in CD_3OD (δ, ppm, J/Hz*)

Position	δ_H	δ_C	Position	δ_H	δ_C
1		170.0	4′	3.50 (1H, d, J = 7.5)	77.5
2	5.74 (1H, br.s)	119.4	5′		58.0
3		151.4	6′	4.78 (1H, s)	106.0
4	7.92 (1H, d, J = 15.0)	132.4	8′		82.8
5	6.19 (1H, d, J = 15.0)	132.4	Me-3	2.05 (3H, s)	21.1
1′		88.6	Me-1′	1.21 (3H, s)	19.7
2′	1.69 (1H, dd, J = 11.0, 14.0)	42.1	Me-5′	1.03 (3H, s)	10.8
	2.14 (1H, dd, J = 8.0, 14.0)		MeO-6′	3.41 (3H, s)	56.5
3′	3.65 (1H, m)	72.0			

*^{1}H and ^{13}C NMR data were measured at 500 and 125 MHz, respectively.



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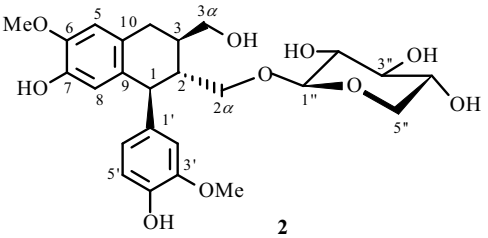

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The known compound, schizandriside (**2**), isolated from this plant for the first time, was identified by ^{1}H and ^{13}C NMR spectroscopy analysis as well as by comparison of their spectral data with those reported [7].

EXPERIMENTAL

Malloapelin D (1), 5-(1,5-dimethyl-3,4,8-trihydroxy-6-methoxy-7-oxabicyclo-[3,2,1]-oct-8-yl)-3-methyl-2,4-pentadienoic acid, colorless oil, $[\alpha]_D^{25}$ +7.5° (*c* 0.50, MeOH). UV (MeOH, λ_{max}, nm): 264. IR (KBr, ν_{max}, cm^{-1}): 3600–2500 (OH), 1693 (C=O), 1636, 1603 (C=C), 1172. ^{1}H and ^{13}C NMR, see Table 1. HR-ESI-MS: *m/z* 327.1451 $[M - H]^-$ (calcd 327.1438 for $C_{16}H_{23}O_7$).

Schizandriside (2), isolariciresinol-2α-*O*-β-D-xyloside, white powder. UV (MeOH, λ_{max}, nm): 284, 230. ESI-MS: *m/z* 515.1 $[M + Na]^+$. ^{1}H NMR (500 MHz, CD_3OD, δ, ppm, J/Hz): 6.79 (1H, d, J = 8.0, H-5′), 6.74 (1H, s, H-5), 6.69 (1H, br.s, H-2′), 6.64 (1H, d, J = 8.0, H-6′), 6.17 (1H, s, H-8), 4.10 (1H, d, J = 7.0, H-1″), 3.99 (1H, m, H-3α), 3.94 (1H, m, H-3α), 3.81 (1H, d, J = 7.0, H-1), 3.81 (3H, s, MeO-6), 3.78 (3H, s, MeO-3′), 3.75 (1H, m, H-2α), 3.68 (1H, m, H-2α), 2.81 (2H, d, J = 7.0, H-4), 2.05 (1H, m, H-2), 2.05 (1H, m, H-3). ^{13}C NMR (125 MHz, CD_3OD, δ): 148.8 (C-3′), 147.0 (C-6), 145.3 (C-4′), 144.7 (C-7), 138.6 (C-1′), 134.0 (C-9), 129.3 (C-10), 123.1 (C-6′), 117.1 (C-8), 116.0 (C-5′), 114.1 (C-5), 112.5 (C-2′), 105.5 (C-1″), 77.5 (C-3″), 74.6 (C-2″), 70.8 (C-4″), 69.8 (C-2α), 66.5 (C-5″), 65.0 (C-3α), 56.5 (C-MeO-6), 56.5 (C-MeO-3′), 47.7 (C-1), 45.6 (C-2), 39.4 (C-3), 33.4 (C-4).

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