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A NEW LIGNAN FROM THE LEAVES OF *Loropetalum chinensis*

Xiao-Jiang Zhou,[1,2] Zhou Xie,[2] Yong-Ming Yan,[1] Xue-Song Li,[1,2] Bing Wang,[2] and Yong-Xian Cheng[1]*

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Investigation on the EtOH extract of the leaves of Loropetalum chinensis *led to the isolation of seven compounds (**1**–**7**). Their structures were identified using spectroscopic methods. Among these compounds, compound **1** is a new lignan, and **2**–**7** were isolated from this plant for the first time.*

Keywords: *Loropetalum chinensis*, Hamamelidaceae, lignan.

The leaves of *Loropetalum chinensis* (Hamamelidaceae), known as ''Ji-Mu-Ye,'' have been used as an important herb for the treatment of bleeding in China, whereas the roots, flowers, and fruits of *L. chinensis* are also medically used in traditional Chinese medicine [1]. Previous reports indicated that the major principles of *L. chinensis* are flavonoids and tannins [2], which possessed antimicrobial activities [3]. Considering that only a limited number of compounds have been characterized from the leaves of this plant, we initiated this study, and seven compounds were isolated. Among them, compound **1** is a new lignan, and the others were isolated from this plant for the first time.

Compound **1** has the molecular formula $C_{19}H_{22}O_4$, derived from its HR-ESI-MS (*m/z* 313.1434 ($[M - H]^+$; calcd 131.1439). The ^1H NMR spectrum showed an AA′BB′ and an ABX spin systems in the aromatic region. The ^{13}C NMR exhibited 17 carbon signals (Table 1), corresponding to 19 carbons, which were attributed to two benzene rings, one methoxy group, two methyls, one methylene, two methines, and one carbonyl group. These data indicate that compound **1** is a lignan. The ^1H, ^1H COSY spectrum showed cross peaks of H-2/H-3, H-9/H-8/H-8′/H-7′, and H-5′/H-6′, which confirmed the substituted patterns of two benzene rings, and suggested two C_6-C_3 units were linked via C-8–C-8′. HMBC correlations (Fig. 1) of OMe, H-2′, H-5′/C-3′ (δ 146.3), H-5′/C-4′ (δ 143.5), and NOESY correlation of OMe/H-2′ indicated that the OMe and hydroxyl were located at C-3′ and C-4′, respectively. HMBC correlations of H-9, H-2/C-7 (δ 204.9) indicated the position of the carbonyl group. The absolute configurations at C-8 and C-8′ remain as yet unknown.

The known compounds were identified as 4-methoxyphenol (**2**), (+)-syringaresinol (**3**) [4], (–)-(7*R*,8*S*,8′*S*)-lyoniresiol (**4**) [5], α-tocopherol (**5**) [6], 2-phyten-1-ol (**6**) [6], and zingiberone (**7**) by comparison of their spectroscopic data with literature data or directly by spectroscopic data.

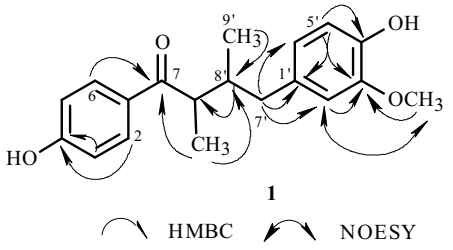

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Fig. 1. Important HMBC and NOESY correlations for compound **1**.

1) State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, P. R. China, fax: +86 871 522 30 48, e-mail: yxcheng@mail.kib.ac.cn; 2) College of Pharmacy, Hunan University of Chinese Medicine, Changsha 410208, P. R. China. Published in Khimiya Prirodnykh Soedinenii, No. 5, pp. 609–610, September–October, 2011. Original article submitted September 27, 2010.

TABLE 1. NMR Data of **1** (500 and 125 MHz, δ, ppm, J/Hz)

C atom	δ_C (DEPT)	δ_H	C atom	δ_C (DEPT)	δ_H
1	129.5 (C)		3′	146.3 (C)	
2,6	131.0 (CH)	7.86 (d, J = 8.0)	4′	143.5 (C)	
3,5	115.6 (CH)	6.92 (d, J = 8.0)	5′	114.0 (CH)	6.78 (d, J = 8.1)
4	161.2 (C)		6′	121.7 (CH)	6.54 (d, J = 8.1)
7	204.9 (C)		7′	38.9 (CH_2)	2.79 (d, J = 9.1)
8	45.2 (CH)	3.40 (m)	8′	38.4 (CH)	2.19 (m)
9	14.1 (CH_3)	1.24 (d, J = 6.6)	9′	17.8 (CH_3)	0.85 (d, J = 5.6)
1′	132.7 (C)		OMe	55.8	3.77 (s)
2′	111.6 (CH)	6.52 (br.s)			

EXPERIMENTAL

Optical rotation was recorded on a Horiba SEPA-300 polarimeter. The UV spectrum was measured on a Shimadzu UV-2401PC spectrophotometer. The IR spectrum was obtained on a Tensor 27 spectrometer, with KBr pellet. The NMR spectra were recorded on a Bruker AV-400 or DRX-500 spectrometer. ESI-MS were recorded on a VG Auto Spec-3000 spectrometer, and HR-ESI-MS were determined on an API QSTAR Pulsar 1 spectrometer. Column chromatography (CC) was carried out on silica gel (200–300 mesh; Qingdao Marine Chemical Inc., Qingdao, China), RP-18 (40–60 μm; Daiso Co., Osaka, Japan), MCI gel CHP 20P (75–150 μm, Tokyo, Japan), and Sephadex LH-20 (Amersham Pharmacia, Uppsala, Sweden).

Plant Material. The leaves of *L. chinensis* were purchased from Hunan Corporation of Materia Medica, Hunan Province, P. R. China, in September 2008, and authenticated by one of our authors (X. J. Zhou). A voucher specimen (CHYX-0093) was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, P. R. China.

Extraction and Separation. The dried powdered leaves of *L. chinensis* (10 kg) were extracted with 70% EtOH (2 × 80 L) to give an extract (930 g), which was suspended in water and partitioned by petroleum ether, EtOAc, and *n*-BuOH (each 4 × 4 L). The EtOAc extract (210 g) was subjected to silica gel CC and eluted with a gradient of $CHCl_3$–MeOH (100:0, 98:2, 96:4, 94:6, 90:10, 85:15, 80:20, 70:30) to give fractions A–H. Fraction E (8.5 g) was submitted to CC over MCI gel CHP 20P eluting with a gradient of aqueous MeOH to yield three portions (E1–E3), Fraction E1 (1.8 g) was passed through Sephadex LH-20 (MeOH) to yield compound **1** (21 mg). Fraction E2 (1 g) was separated by RP-18 eluting with gradient MeOH–H_2O (30–100%) followed by Sephadex LH-20 (MeOH) to yield compound **2** (5 mg). Fraction E3 (2.2 g) was separated by RP-18 eluting with gradient MeOH–H_2O (40–100%) followed by Sephadex LH-20 (MeOH), and then purified by preparative TLC (petroleum ether–EtOAc–^{i}PrOH, 3:1:1) to afford **3** (20 mg). Fraction D (14 g) was submitted to CC over MCI gel CHP 20P eluting with a gradient of aqueous MeOH to yield two portions (D1 and D2). Fraction D1 (2.5 g) was submitted to silica gel CC (petroleum ether–EtOAc, 20:1) followed by Sephadex LH-20 (MeOH) to yield **5** (75 mg). Fraction D2 (0.6 g) was purified by preparative TLC (petroleum ether–EtOAc–^{i}PrOH, 3:2:0.6) followed by semipreparative HPLC (Agilent 1200 liquid chromatograph with a Zorbax SB-C18 column, 9.4 mm × 25 cm, i.d.) eluting with 30% aqueous MeOH to produce **4** (14 mg). Fraction A (15 g) was fractionated by silica gel CC (petroleum ether–EtOAc, 50:1) to yield two portions (A1 and A2). Fraction A1 (1.2 g) was purified by preparative TLC (petroleum ether–EtOAc, 20:1) to yield **6** (64 mg). Fraction A2 (2.3 g) was purified by silica gel CC ($CHCl_3$–Me_2CO, 100:0.5) followed by Sephadex LH-20 (MeOH) to yield compound **7** (6 mg).

4-(4-Hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)-2,3-dimethylbutan-1-one (1). Colorless gum; $[\alpha]_D^{21}$ –6.4° (*c* 0.51, $CHCl_3$). UV ($CHCl_3$, λ_{max}, nm): 272 (log ε 4.30). IR (KBr, ν_{max}, cm^{-1}): 3439, 2961, 2920, 2850, 1648, 1602, 1514, 1462, 1378, 1271, 1224, 1171, 1034. ^1H and ^{13}C NMR, see Table 1. ESI-MS (negative) *m/z* 313 $[M - H]^-$; HR-ESI-MS (negative) *m/z* $[M - H]^-$ 313.1434 (calcd for $C_{19}H_{21}O_4$, 313.1439).

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