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A new sesquiterpene from the roots of *Vladimiria souliei*

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Abstract

A new sesquiterpene, named vladimenal (**1**), was isolated from the roots of *Vladimiria souliei*. The structure was elucidated on the basis of spectroscopic analysis.

Keywords: *Vladimiria souliei*; Sesquiterpene; Vladimenal

Vladimiria souliei (Franch.) Ling as a medicinal plant is mainly distributed in Sichuan Province, China. Its roots, a traditional Chinese medicine, were used for relieving pain and stomach diseases since ancient times [1]. Previous phytochemical investigations on this species resulted in the isolation of sesquiterpene lactones [2], and ligans [3]. In the course of our study on searching biological active constituents from medicinal plants, a new sesquiterpene aldehyde, named vladimenal (**1**), was isolated from the roots of *V. souliei* (Franch.) Ling. The structure was elucidated by spectroscopic methods. In this paper, we presented the isolation and structural elucidation of the new sesquiterpene based on the spectral analysis.

The roots of *V. souliei* (Franch.) Ling were collected from Sichuan Province, China, in July 2006. A voucher specimen (No. 20060703) was deposited at laboratory of the Research Department of Natural Medicine, College of Pharmaceutical Sciences, Nankai University, China. The dried roots (8.0 kg) of *V. souliei* (Franch.) Ling were extracted with methanol three times under reflux. Removing the solvent, the methanol extract was partitioned three times by petroleum ether to give 210.0 g residues. The petroleum ether soluble part was fractionated by silica gel column chromatography and PHPLC to afford compound **1** (Fig. 1).

Compound **1** was obtained as a colorless oil. $[\alpha]_D^{26}$: + 46.1 (*c* 0.4, MeOH). Its EI-MS spectrum showed a quasi-molecular ion peak at *m/z* 234 $[M]^+$. Its molecular formula was determined as $C_{15}H_{22}O_2$ from its HR-EI-MS spectrum (*m/z* 234.1607 $[M]^+$, calcd. for $C_{15}H_{22}O_2$, 234.1620). Its IR spectrum showed the presence of the hydroxyl (3006 cm^{-1}) and carbonyl (1639 cm^{-1}) groups. The ^1H NMR (Table 1) spectrum showed one aldehyde proton at δ 9.46 (d, 1H, J = 1.3 Hz, H-15), two olefinic protons at δ 6.46 (dd, 1H, J = 3.4, 1.3 Hz, H-5), δ 5.45 (dd, 1H, J = 11.0, 4.8 Hz, H-9) and one methine proton of oxygenated carbon at δ 4.22 (dd, 1H, J = 12.4, 3.4 Hz, H-1). In addition, three

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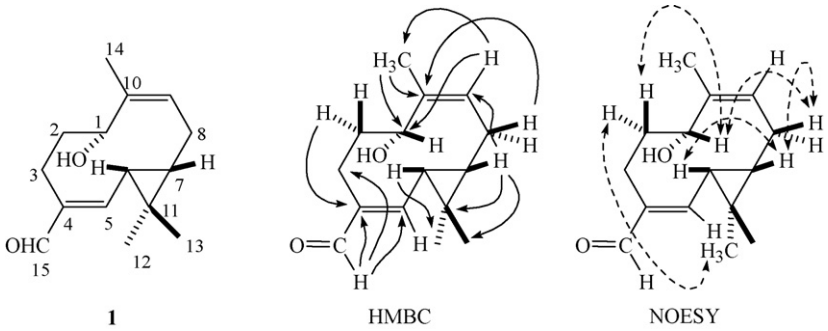

Fig. 1. Structure and selected correlations in HMBC and NOESY spectra of compound **1**.

Table 1
^{1}H and ^{13}C NMR data for compound **1** (^{1}H, 600 MHz; ^{13}C, 150 MHz; in $CDCl_3$, ppm, *J* Hz).

No.	δ_C	δ_H[a] (*J* in Hz)	No.	δ_C	δ_H[a] (*J* in Hz)
1	68.4	4.22 (dd, 1H, *J* = 12.4, 3.4)	8	24.1	2.06 (m, 1H)
2	29.8	2.09 (m, 1H)			1.57 (m, 1H)
		1.72 (m, 1H)	9	128.2	5.45 (dd, 1H, *J* = 11.0, 4.8)
3	22.2	2.33 (m, 1H)	10	134.9	
		2.23 (m, 1H)	11	18.9	
4	146.8		12	15.9	1.03 (s, 3H)
5	151.8	6.46 (dd, 1H, *J* = 3.4, 1.3)	13	27.6	1.12 (s, 3H)
6	24.9	1.25 (m, 1H)	14	16.5	1.70 (s, 3H)
7	32.6	0.95 (m, 1H)	15	195.4	9.46 (d, 1H, *J* = 1.3)

[a] α-Hydrogen listed first. All assignments based on the extensive 1D and 2D NMR spectra (HMQC, HMBC, ^{1}H-^{1}H COSY, NOESY).

methyl protons at δ 1.03 (s, 3H, H-12), 1.12 (s, 3H, H-13), 1.70 (s, 3H, H-14) and other protons in the upfield region were also observed in the ^{1}H NMR spectrum of compound **1**.

The ^{13}C NMR (Table 1) spectrum revealed fifteen carbon signals, including four sp^2 carbon signals (δ_C 146.8 (C-4), 151.8 (C-5), 128.2 (C-9), 134.9 (C-10)), one oxygenated carbon signals (δ_C 68.4 (C-1)), one aldehyde carbonyl carbon signal (δ_C 195.4 (C-15)), and other carbon signals in the upfield region. The other carbon signals were further classified into methyls (δ_C 15.9 (C-12), 27.6 (C-13), 16.5 (C-14)), methylenes (δ_C 29.8 (C-2), 22.2 (C-3), 24.1 (C-8)), methines (δ_C 24.9 (C-6), 32.6 (C-7)), and quaternary carbon (δ_C 18.9 (C-11)), which were confirmed by the HMQC spectrum. According to the ^{1}H, ^{13}C and HMQC NMR spectra, the aldehyde carbonyl carbon signal (δ_C 195.4 (C-15)) and sp^2 carbon signals (δ_C 146.8 (C-4), 151.8 (C-5)) showed the presence of an *a*, β-unsaturated carbonyl moiety in **1**. Another double bond moiety – CH=C (CH_3) – (C-9 (128.2), C-10 (134.9), C-14 (16.5)) in **1** were also deduced from 1D and 2D NMR spectral data of **1**. In addition, a comparison of chemical shifts of the upfield proton signals (δ_H 1.25 (m, 1H, H-6), 0.95 (m, 1H, H-7)) and the carbon signals (δ_C 24.9 (C-6), 32.6 (C-7), 18.9 (C-11)) with those of cyclopropane moieties reported in the literature [4,5] revealed the presence of a cyclopropane moiety, which was further confirmed by HMQC and HMBC (Fig. 1) spectra. The linkages of these moieties, which formed a 10-membered big ring, were confirmed by the following HMBC correlations (Fig. 1). The carbonyl signal at δ 195.4 in the downfield region of ^{13}C NMR spectrum was assigned to C-15 position by the correlations H-3/C-15 and H-5/C-15 in the HMBC spectrum. The HMBC correlations H-6/C-4 (5, 7, 8), H-7/C-5 (6, 8, 9), and H-6 (7)/C-11 (12, 13) revealed that the methine of the cyclopropane moiety at δ_C 24.9, 32.6 were attributable to C-6 and C-7, respectively. From the correlations of HMBC spectrum of **1**, the sp^2 carbon signals of the other double bond moiety – C=C (CH_3) – at δ_C 128.2, 134.9 and the oxygenated carbon signal at δ_C 68.4 were assigned to C-9, C-10, and C-1, respectively. Furthermore, the H–H correlations H-1/H-2, H-2/H-3, H-5/H-6, H-6/H-7, H-7/H-8, and H-8/H-9 in the ^{1}H-^{1}H COSY spectrum of **1** confirmed the above conclusions. These spectral data disclosed the planar structure of **1**.

The planar structure of **1** is very similar to that of isobicyclogermacrenal, whose stereochemistry was determined by NOE correlations [4,5]. From the NOESY spectrum of **1**, the NOE correlations (Fig. 1) between H-6 and H-7,

suggested that H-6, and H-7 have the same conformation in a β-position. The other NOE correlations of H-7/H-8β, H-8β/H-1β, H-1β/H-2β, H-2β/H-3β, H-2α/H-3α were also observed. Thereby, the relative stereochemical structure of **1** was confirmed. By analyzing the HMQC, HMBC, ^{1}H-^{1}H COSY and NOESY NMR spectra, all the proton and carbon signals were assigned unambiguously. The structure of compound **1** was elucidated as the new sesquiterpene, named vladimenal.

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