

A New Phenolic Compound from *Dendrobium longicornu*Jiangmiao Hu,<sup>†,\*</sup> Weiwei Fan,<sup>†,‡</sup> Lu Zhou,<sup>§</sup> Youxing Zhao,<sup>†</sup> and Jun Zhou<sup>†,\*</sup><sup>†</sup>State Key Laboratory of Phytochemistry and Plant Resource in West China, Kunming Institute of Botany, the Chinese Academy of Science, Kunming 650204, P. R. China

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The stems of several *Dendrobium* species (Orchidaceae) are used as "Shi-Hu" in traditional Chinese medicine mainly for the good of throat and immune ability.<sup>1-3</sup> *D. longicornu* belongs to Sect. Formosae of *Dendrobium* species and mainly distributed in southwest of China,<sup>1</sup> and chemical research of this Sect. plant is not common. First chemical report of this species at 2004<sup>4</sup> described five new phenolic compounds, and continual experiments of the species lead to the isolation of an interesting new phenolic compound (**1**) having an oxepine parent nucleus, together with three known compounds, trigonol A (**2**),  $\beta$ -sitosterol and daucosterol. To the best of our knowledge, it is the first time for the isolation of this kind of compound from *Dendrobium* species. This paper describes the isolation and structural elucidation of the new compound **1**.

Compound **1** was obtained as a yellow amorphous powder, possessing a molecular-ion peak at  $m/z$  283 in its negative FABMS. The molecular formula of C<sub>16</sub>H<sub>12</sub>O<sub>5</sub> was deduced from the negative HR FABMS ( $m/z$  283.0604 [M-H]<sup>-</sup>) and its NMR data, indicating 11 degrees of unsaturation. The UV spectrum of **1** ( $\lambda_{\max}$  (log  $\epsilon$ ): 344 (3.9), 244 (4.2), 207 (4.4) nm) indicated an extended conjugated system. The <sup>13</sup>C NMR spectrum of **1** exhibited 16 carbon signals, including one methoxyl, 7 methine and 8 quaternary carbons. The <sup>1</sup>H NMR spectrum of **1** exhibited three correlated aromatic methine signals at  $\delta$  7.41 (1H, d,  $J$  = 8.4 Hz), 6.56 (1H, dd,  $J$  = 8.4, 1.8 Hz) and 6.62 (1H, d,  $J$  = 1.8 Hz) indicating a 1,3,4-trisubstituted aromatic ring. Another set of three correlated aromatic atoms at  $\delta$  6.93 (1H, d,  $J$  = 1.7 Hz), 6.84 (1H, dd,  $J$  = 8.4, 1.7 Hz) and 7.86 (1H, d,  $J$  = 8.4 Hz) suggested the presence of the second 1,3,4-trisubstituted aromatic ring. A proton signal at  $\delta$  9.93 correlated with the carbon signal at  $\delta$  187.6 (C-12) in the HSQC spectrum indicated an aldehyde group. The aldehyde group was linked to a quaternary carbon (C-10), which in turn was connected to another quaternary carbon (C-11), as appreciated by their correlations [H-12/C-10, C-11] in the HMBC spectrum. These two quaternary carbons, two 1,3,4-trisubstituted aromatic rings and an oxygen constituted an oxepine nucleus. The observed correlations [H-12/C-9a, H-1/C-4a, C-11, H-9/C-5a, C-10] in the HMBC spectrum of **1** was in perfect agreement with the proposed structure. Therefore, compound **1** was determined as (Z)-7,11-dihydroxy-3-methoxy-10,11-dihydrodibenzo [b,f] oxepine-10-carbaldehyde and named as longicornuol B.

The structure of compound **2** was confirmed to be trigonol

A,<sup>5</sup> a bibenzyl which was first reported from *Dendrobium* species by us recently. Other two known compounds,  $\beta$ -sitosterol and daucosterol, were elucidated by comparing with authentic compound by TLC means.

### Experimental Section

**General procedures.** Melting points were measured on a XRC-1 micro-melting point apparatus (Beijing, China) and were uncorrected. Optical rotations were measured with a Horiba SEAP-300 spectropolarimeter. UV spectra were measured on a Hitachi UV-3210 spectrophotometer (Shanghai, China). IR spectra were measured with a Bio-Rad FTS-135 IR spectrometer (Richmond, CA) with KBr pellets. FABMS was obtained on a VG Auto Spec-3000 mass spectrometer (VG, Manchester, England). 1D and 2D NMR spectra were recorded on Bruker AM-400 MHz and DRX-500 spectrometers (Karlsruhe, Germany), with chemical shifts ( $\delta$ ) in ppm relative to trimethylsilane (TMS) as internal standard and coupling constants in hertz (Hz). Column chromatography was carried out on silica gel (200 - 300 mesh) and TLC was carried out on plates precoated with silica gel (10 - 40  $\mu$ m, Qindao Marine Chemical Ltd., Qingdao, PRC). Sephadex LH-20 was purchased from Amersham Biosciences.

**Plant material.** The stems of *D. longicornu* were collected in January 2004 from Xiaoshao of Kunming in Yunnan Province, P. R. China, and identified by Professor Hong Yu of Yunnan University. A voucher specimen (No. Zsh-1) was preserved at the State Key Laboratory of Phytochemistry and Plant Resource in West China, Kunming Institute of Botany, the Chinese Academy of Science, P. R. China.

**Extraction and isolation.** Extraction of the plant material (4.5 kg) with 95% EtOH and evaporated under reduced pressure and then fractionated successively into CHCl<sub>3</sub> soluble (76 g) and *n*-BuOH soluble (73 g) fractions were reported previously.<sup>4</sup> Got CHCl<sub>3</sub> soluble (70 g) isolated into five fractions (A-E) and got *n*-BuOH soluble (60 g) isolated into six fractions (I - VI)<sup>4</sup> were also reported.<sup>4</sup> Fraction B (5.2 g) from CHCl<sub>3</sub> soluble was then applied to column chromatography over silica gel (petroleum ether-EtOAc, 3:1, v/v) to yield  $\beta$ -sitosterol. Fraction D (3.0 g) was applied to column chromatography over silica gel (petroleum ether-Acetone, 7:3, v/v) and purified further on Sephadex LH-20 ( $\emptyset$  2  $\times$  120 cm, MeOH) to afford compound **1**

**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments and two-dimensional NMR correlations of **1**

Position	$\delta_{\text{H}}$ (mult, $J$ in Hz)	$\delta_{\text{C}}$ (mult)	HMBC (H $\rightarrow$ C)
1	7.41 (1H, d, $J = 8.4$ )	133.6 (d)	C-4a, 10
2	6.56 (1H, dd, $J = 8.4, 1.8$ )	108.8 (d)	C-3, 4
3		160.0 (s)	
4	6.62 (1H, d, $J = 1.8$ )	100.5 (d)	C-2, 3, 4a
4a		162.4 (s)	
5a		157.2 (s)	
6	6.93 (1H, d, $J = 1.7$ )	98.4 (d)	C-4b, 6, 7, 8a
7		156.3 (s)	
8	6.84 (1H, dd, $J = 8.4, 1.7$ )	114.2 (d)	C-5, 8a
9	7.86 (1H, d, $J = 8.4$ )	123.0 (d)	C-4b, 9
9a		118.5 (s)	
10		118.1 (s)	
11		163.2 (s)	
11a		110.0 (s)	
12	9.93 (1H, s)	187.6 (d)	C-8a, 9, 10
13	3.77 (3H, s)	56.1 (q)	C-3

(4 mg). Fraction III (2.1 g) from *n*-BuOH soluble was then subjected to column chromatography over silica gel ( $\text{CHCl}_3$ -MeOH, 20:1, v/v) and Sephadex LH-20 ( $\text{O} 1.7 \times 120$  cm, MeOH) to give trigonopol A (6 mg). Fraction IV (12.0 g) was subjected to column chromatography over silica gel ( $\text{CHCl}_3$ -MeOH, 20:1, v/v) and got daucosterol (42 mg).

**Longicornuol B (1):** Yellow amorphous powder, mp 96 - 98  $^{\circ}\text{C}$ ; UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 344 (3.9), 244 (4.2), 207 (4.4) nm; IR (KBr):  $\nu_{\text{max}}$  3405, 2956, 2925, 2854, 1702, 1646, 1613, 1496, 1467, 1438, 1377, 1309, 1264, 1202, 1135, 1061, 1029,

954, 894, 835, 813  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 400 MHz) and  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 100 MHz) spectra data with chemical shifts ( $\delta$ ) in ppm, see Table 1; FAB MS  $m/z$  (%): 283  $[\text{M-H}]^-$  (100); HR FABMS 283.0604  $[\text{M-H}]^-$  (calcd. for  $\text{C}_{16}\text{H}_{11}\text{O}_5$ , 283.0606).

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**Supplementary Material.** FABMS (negative) and HR FABMS and 1D and 2D NMR spectra and of compound **1** can be available at supplementary material (Fig. S2-S8).

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