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Qing-Hua Ye<sup>a</sup>; Wei-Min Zhao<sup>a</sup>; Guo-Wei Qin<sup>a</sup>

<sup>a</sup> Shanghai Institute of Materia Medica, Shanghai Institute of Biological Sciences, Shanghai, China

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## LIGNANS FROM *DENDROBIUM CHRYSANTHUM*

QING-HUA YE, WEI-MIN ZHAO and GUO-WEI QIN\*

Shanghai Institute of Materia Medica, Shanghai Institute of Biological Sciences,  
Chinese Academy of Sciences, Shanghai 200031, China

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A new neolignan glucoside denchryside B along with three known lignans have been isolated from the herbs of *Dendrobium chrysanthum* Wall. (Orchidaceae). The structures were elucidated on the basis of spectroscopic methods.

**Keywords:** *Dendrobium chrysanthum*; Orchidaceae; Neolignan glucoside; Denchryside B

### INTRODUCTION

The stems of several *Dendrobium* species (Orchidaceae) are used in traditional Chinese medicine as a Yin tonic to nourish the stomach, promote the production of body fluid, and reduce fever [1]. The products derived from *Dendrobium* plants are marketed in China as precious health-foods and nutrients. Chemical components of many *Dendrobium* plants have been widely investigated [2–5]. The species *Dendrobium chrysanthum* Wall. has been recorded in the Chinese Pharmacopoeia (2000 Edition) as one of the original materials of “Shi-Hu”, a famous tonic in traditional Chinese medicine. Earlier work on this species led to the isolation of alkaloids, fluorenones, bibenzyls and phenanthrenes [6–8]. In continuation of our research on *Dendrobium* species, the herbs of *Dendrobium chrysanthum* were investigated. We herein report the isolation and structure elucidation of one new neolignan glucoside denchryside B (**1**) and three known lignans (**2–4**) from the herbs of *Dendrobium chrysanthum*.

### RESULTS AND DISCUSSION

The ethanolic extracts of the herb *Dendrobium chrysanthum* were subjected to a series of column chromatographic steps on silica gel and filtration through Sephadex LH-20 to yield compounds **1–4** (Fig. 1).

\*Corresponding author. Tel.: +86-21-64311833. Fax: +86-21-64370269. E-mail: gwqin@mail.shcnc.ac.cn

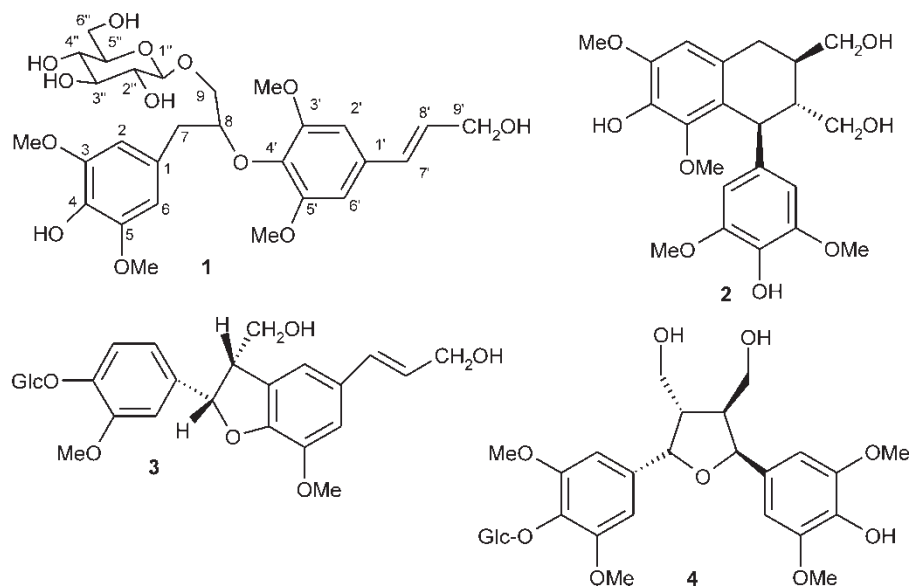


FIGURE 1 Compounds 1–4.

Denchryside B (**1**), obtained as a yellowish oil, has the molecular formula  $C_{28}H_{38}O_{13}$  by HR-ESIMS ( $m/z$  605.2205,  $[M + Na]^+$ ). Complete hydrolysis of **1** with HCl yielded glucose by comparison with authentic samples on TLC. The  $^1H$  NMR spectrum (Table I) displayed signals for four aromatic protons [two singlets at  $\delta$  6.37 (2H) and 6.58 (2H)], two olefinic protons ( $\delta$  6.39 and 6.15) which appeared as the AB part of an ABX<sub>2</sub> system, four methoxyl groups at  $\delta$  3.64 (6H), 3.66 (6H) and an anomeric glucose proton ( $\delta$  4.12, 1H, d). The large coupling constant ( $J = 7.7$  Hz) proves the  $\beta$ -configuration of the anomeric center. As well as the sugar and four methyl (as methoxyls) moieties, the  $^{13}C$  NMR spectrum exhibited 18 carbon signals as three methylenes (two oxygenated), seven

TABLE I  $^1H$  NMR (500 MHz) and  $^{13}C$  NMR (125 MHz) data of compound **1** in  $CD_3OD$  ( $\delta$  ppm,  $J$  in Hz)

No.	$^{13}C$	$^1H$	No.	$^{13}C$	$^1H$
1	130.6 s		1''	105.1 d	4.12 d (7.7)
2	108.1 d	6.37 brs	2''	75.4 d	3.11 m
3	149.3 s		3''	78.2 d	3.20 m
4	135.2 s		4''	71.9 d	3.19 m
5	149.3 s		5''	78.2 d	3.09 m
6	108.1 d	6.37 brs	6''	62.9 t	3.50 dd (11.9, 5.5), 3.68 m
7	38.7 t	2.72 dd (13.9, 5.5); 2.88 dd (13.9, 7.7)	3-OCH <sub>3</sub>	57.1 q	3.64 s
8	84.2 d	4.28 m	5-OCH <sub>3</sub>	57.1 q	3.64 s
9	71.4 t	3.40 dd (10.6, 4.4) 3.88 dd (10.6, 4.1)	3'-OCH <sub>3</sub>	57.0 q	3.66 s
1'	135.0 s		5'-OCH <sub>3</sub>	57.0 q	3.66 s
2'	105.2 d	6.58 brs			
3'	155.0 s				
4'	136.9 s				
5'	155.0 s				
6'	105.2 d	6.58 brs			
7'	131.8 t	6.39 brd (16.1)			
8'	130.0 d	6.15 dt (16.1, 5.9)			
9'	63.9 t	4.06 dd (5.9, 1.5)			

methines (one oxygenated) and eight quaternary carbons (six oxygenated). Analysis of the  $^1\text{H}$ – $^1\text{H}$  COSY and HMQC spectra of **1** revealed the following structural fragments in the aglycon:  $-\text{CH}_2-\text{CH}-\text{CH}_2-$  (C-7  $\rightarrow$  C-9) and  $-\text{CH}=\text{CH}-\text{CH}_2-$  (C-7'  $\rightarrow$  C-9'). This was also supported by HMBC correlations from C-9 to H-7 and H-8, and from C-9' to H-7' and H-8'. The *trans* form of the double bond was established by  $J_{7',8'} = 16.1$  Hz. The HMBC correlations between H-7'/C-1, 2, 6, and between H-7'/C-1', 2', 6', indicated the connection of C-1 to C-7, and C-1' to C-7', respectively. The presence of a  $-\text{C}-8-\text{O}-\text{C}-4'-$  linkage was revealed by significant HMBC cross-peak from the oxymethine proton H-8 to C-4'. Thus, structure **1** was revealed as a neolignan of type 8-O-4' [9]. The  $^{13}\text{C}$ – $^1\text{H}$  long-range correlation signals between C-9 and  $\text{H}_{\text{glc}-1}$  in the HMBC spectrum and the correlation signals between H-9 and  $\text{H}_{\text{glc}-1}$  in the NOESY spectrum of **1** indicated the linkage of the glucose unit to C-9 of the aglycon. The positions of the other functional groups were assigned by  $^1\text{H}$ – $^1\text{H}$  COSY, HMQC, HMBC and NOESY correlations, which resulted in the assignment of all proton and carbon signals of **1**. Accordingly, the structure of **1** was established as 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-[2,6-dimethoxy-4-(*E*)-propenylphenoxy]-propan-3-hydroxy- $\beta$ -D-glucopyranoside.

From the extract of *Dendrobium chrysanthum*, three known lignans (+)-lyoniresinol (**2**) [10,11], dehydrodiconiferyl alcohol-4- $\beta$ -D-glucoside (**3**) [12] and 7,7'-bis-(4-hydroxy-3,5-dimethoxyphenyl)-8,8'-dihydroxymethyltetrahydrofuran-4 $\beta$ -D-glucoside (**4**) [13] were identified for the first time from the genus *Dendrobium*. The structures of all above compounds were identified by spectral analysis and by comparison of spectral data with literature values.

## EXPERIMENTAL

### General Experimental Procedures

Optical rotations were measured with a Perkin-Elmer 341 polarimeter. LR-ESIMS were measured using a Finnigan LCQ-DECA instrument, and HR-ESIMS data were obtained on a Mariner spectrometer. LR-EIMS were obtained on a MAT-95 spectrometer; HR-EIMS were obtained on a Kratos 1H spectrometer. NMR spectra were run on a Bruker DRX-500 spectrometer with TMS as internal standard. Column chromatographic separations were carried out using silica gel H60 (Qingdao Haiyang Chemical Group Corporation, Qingdao, China), Sephadex LH-20 (Pharmacia Biotech AB, Uppsala, Sweden) and RP-18 (100–200 mesh, Tianjin No. 2 Chemical Reagent Factory, Tianjin, China) as packing materials, and using a LiChroprep RP-18 Lobar column (40–63  $\mu\text{m}$ , Merck). HSGF254 silica gel TLC plates (Yantai Chemical Industrial Institute, Yantai, China) were used for analytical TLC.

### Plant Material

The fresh herbs of *Dendrobium chrysanthum* were collected in the suburb of Guiyang, Guizhou Province in February of 2001 and identified by Professor Yongping Wang of Guizhou Botanical Garden, Guizhou Province, China. A voucher specimen is deposited at the herbarium of the Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

### Extraction and Isolation

Powdered air-dried herbs of *D. chrysanthum* (2.0 kg) were refluxed with 95% EtOH thrice (12 L  $\times$  3) at room temperature. After evaporation of EtOH *in vacuo*, the aqueous residue (2.0 L) was successively extracted with light petroleum, EtOAc and n-BuOH

(2.0 L  $\times$  3 each). The n-BuOH extract (40 g) was subjected to column chromatography over RP-18 (5.0 cm i.d.  $\times$  40 cm) eluted with an EtOH–H<sub>2</sub>O gradient (H<sub>2</sub>O, 3:7, 1:1, 3:2 and 95% EtOH) (2000 mL each). The fraction from the eluent EtOH–H<sub>2</sub>O (3:7) (1.5 g) was filtered through a Sephadex LH-20 column (3.0 cm i.d.  $\times$  150 cm) eluted with EtOH and over a Lobar RP-18 column (2.5 cm i.d.  $\times$  31 cm) eluted with a MeOH–H<sub>2</sub>O gradient (3:7 and 2:3) (500 mL each) to yield compounds **1** (12 mg), **3** (15 mg) and **4** (10 mg). The fraction from the eluent of 95% EtOH (0.40 g) was chromatographed over a silica gel column (3.0 cm i.d.  $\times$  40 cm) eluted with a CHCl<sub>3</sub>–MeOH–H<sub>2</sub>O gradient (5:1:0.1 and 4:1:0.1) (300 mL each) to yield compound **2** (5 mg).

### Identification

Denchryside B (**1**), a yellowish oil;  $[\alpha]_D^{20} - 53$  (c 0.35, MeOH); ESIMS  $m/z$  605  $[M + Na]^+$ ; HR-ESIMS  $m/z$  605.2205  $[M + Na]^+$  (calcd for C<sub>28</sub>H<sub>38</sub>O<sub>13</sub>Na, 605.2208); for <sup>1</sup>H and <sup>13</sup>C NMR data: see Table I.

(+)-Lyoniresinol (**2**), an amorphous white solid;  $[\alpha]_D^{20} + 11$  (c 0.10, MeOH); EIMS  $m/z$  420  $[M]^+$ , 371, 217, 205, 183, 167; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm): 6.95 (2H, s, H-2', 6'), 6.78 (1H, s, H-5), 5.11 (1H, d,  $J = 5.5$  Hz, H-1), 4.24 (1H, dd,  $J = 10.5, 5.0$  Hz, H-3a); 4.18 (2H, d,  $J = 5.0$  Hz, H-2a); 4.16 (1H, dd,  $J = 10.5, 5.0$  Hz, H-3a); 3.85 (3H, s, 8-OCH<sub>3</sub>), 3.84 (3H, s, 6-OCH<sub>3</sub>), 3.73 (6H, s, 3',5'-OCH<sub>3</sub>), 3.19 (2H, d,  $J = 5.0$  Hz, H-4), 2.75 (1H, m, H-2), 2.33 (1H, m, H-3).

Dehydrodiconiferyl alcohol-4- $\beta$ -D-glucoside (**3**), C<sub>26</sub>H<sub>32</sub>O<sub>11</sub>, a yellowish oil;  $[\alpha]_D^{20} - 65$  (c 0.20, MeOH); EIMS  $m/z$  520  $[M]^+$ , 358, 340, 324, 312, 137, 115; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm): 7.14 (1H, d,  $J = 8.4$  Hz, H-5), 7.00 (1H, d,  $J = 1.9$  Hz, H-2), 6.93 (2H, d,  $J = 3.2$  Hz, H-2',6'), 6.92 (1H, dd,  $J = 8.4, 1.9$  Hz, H-6), 6.53 (1H, d,  $J = 15.9$  Hz, H- $\alpha'$ ), 6.22 (1H, dd,  $J = 15.9, 5.9$  Hz, H- $\beta'$ ); 5.58 (1H, d,  $J = 5.9$  Hz, H- $\alpha$ ), 4.88 (1H, d,  $J = 7.4$  Hz, H-G<sub>1</sub>), 4.19 (2H, dd,  $J = 5.9, 1.2$  Hz, H- $\gamma'$ ), 3.88 (3H, s, 4-OCH<sub>3</sub>), 3.82 (3H, s, 5'-OCH<sub>3</sub>), 3.75 (1H, m, H-G<sub>2</sub>), 3.67 (1H, m, H-G<sub>5</sub>), 3.65 (1H, m, H-G<sub>3</sub>), 3.48 (1H, m, H- $\beta$ ), 3.47 (1H, m, H-G<sub>6</sub>), 3.45 (1H, m, H-G<sub>4</sub>), 3.40 (1H, m, H-G<sub>6</sub>). <sup>13</sup>C NMR data (125 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm): 151.0 (s, C-3), 149.2 (s, C-3'), 147.7 (s, C-4), 145.6 (s, C-1'), 138.1 (s, C-1), 132.8 (s, C-5'), 132.0 (s, C- $\alpha'$ ), 130.1 (s, C-4'), 127.7 (d, C- $\beta'$ ), 119.4 (d, C-6), 118.1 (d, C-5), 116.5 (d, C-6'), 112.2 (d, C-2'), 111.2 (d, C-2), 102.8 (d, C-G<sub>1</sub>), 88.8 (d, C- $\alpha$ ), 78.1 (d, C-G<sub>3</sub>), 77.8 (d, C-G<sub>5</sub>), 75.0 (d, C-G<sub>2</sub>), 71.3 (d, C-G<sub>4</sub>), 65.0 (t, C- $\gamma$ ), 63.9 (t, C- $\gamma'$ ), 62.5 (t, C-G<sub>6</sub>), 56.8 (q, C-4-OCH<sub>3</sub>), 56.7 (q, C-5'-OCH<sub>3</sub>), 55.4 (d, C- $\beta$ ).

7,7'-Bis-(4-hydroxy-3,5-dimethoxyphenyl)-8,8'-dihydroxymethyl-tetrahydrofuran-4- $\beta$ -D-glucoside (**4**), a yellowish oil;  $[\alpha]_D^{20} - 13$  (c 0.10, MeOH); EIMS  $m/z$  418 C<sub>22</sub>H<sub>26</sub>O<sub>8</sub>  $[M - \text{glucose}]^+$ , 388, 181; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm): 6.70 (2H, s, H-2, 6), 6.65 (2H, s, H-2',6'), 4.76 (1H, d,  $J = 7.2$  Hz, H-G<sub>1</sub>), 4.75 (1H, d,  $J = 4.0$  Hz, H-7); 4.25 (1H, m, H-9), 4.26 (1H, m, H-9'), 3.88 (1H, m, H-9), 3.86 (1H, m, H-9'), 3.84 (6H, s, 3',5'-OCH<sub>3</sub>), 3.83 (6H, s, 3, 5-OCH<sub>3</sub>), 3.77 (1H, dd,  $J = 12.0, 2.4$  Hz, H-G<sub>6</sub>); 3.66 (1H, dd,  $J = 12.0, 4.8$  Hz, H-G<sub>6</sub>), 3.47 (1H, m, H-G<sub>2</sub>), 3.42 (1H, m, H-G<sub>4</sub>), 3.40 (1H, m, H-G<sub>3</sub>), 3.19 (1H, m, H-G<sub>5</sub>), 3.12 (1H, m, H-8). <sup>13</sup>C NMR data (125 MHz, CD<sub>3</sub>OD):  $\delta$  (ppm): 154.0 (s, C-3,5), 149.7 (s, C-3',5'), 139.9 (s, C-14), 136.6 (s, C-4'), 135.9 (s, C-4), 133.0 (s, C-1'), 105.0 (d, C-G<sub>1</sub>), 104.9 (d, C-2,6), 104.7 (d, C-2',6'), 88.1 (d, C-7'), 87.5 (d, C-7), 78.5 (d, C-G<sub>5</sub>), 78.0 (d, C-G<sub>3</sub>), 76.0 (d, C-G<sub>2</sub>), 73.3 (t, C-9'), 73.2 (t, C-9), 62.5 (t, C-G<sub>6</sub>), 57.4 (q, C-3, 5-OCH<sub>3</sub>), 57.1 (q, C-3',5'-OCH<sub>3</sub>), 55.8 (d, C-8), 55.6 (d, C-8').

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