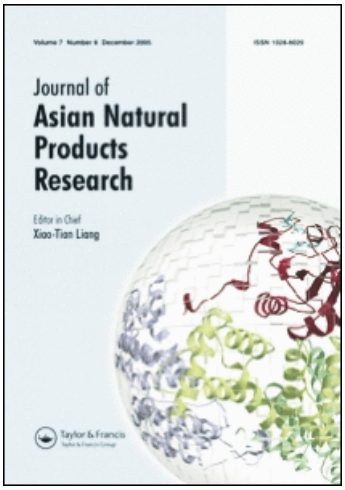

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Neolignan and lignan glycosides from branch bark of *Davidia involucrata*

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Two new neolignan glycosides, davidioside A (**1**) and davidioside B (**2**), have been isolated along with six known compounds from the branch bark of *Davidia involucrata*. Identification of their structures was achieved by 1D and 2D NMR experiments, including $^{1}H-^{1}H$ COSY, NOESY, HMQC, and HMBC methods as well as FAB mass spectral data.

Keywords: *Davidia involucrata*; Nyssaceae; Branch bark; Lignan glucosides; Davidioside A; Davidioside B

1. Introduction

Davidia involucrata is a famous Chinese peculiar tree, which only grows in the west of China [1]. For our interest in the chemical constituents of Chinese Nyssaceae species, we reported six flavones and flavonoid glycosides [2], seven caffeoyl derivatives from the leaves of *D. involucrata* [3], and seven phenolic glycosides from the stem bark of *D. involucrata* [4]. In this paper, we describe the isolation and structural elucidation of two new neolignan glycosides, davidioside A (**1**), davidioside B (**2**), and six known compounds: dihydrodehydrodiconiferyl alcohol-9-*O*-β-D-xylopyranoside (**3**) [5], dihydrodehydrodiconiferyl alcohol-4′-*O*-β-D-glucopyranoside (**4**) [6], dihydrodehydrodiconiferyl alcohol-9-*O*-β-D-glucopyranoside (**5**) [7], glochidioboside (**6**) [8], dihydrodehydrodiconiferyl alcohol (**7**) [9] and isolariciresinol-9-*O*-*β*-D-glucopyranoside (**8**) [10] from the branch bark of the title plant.

2. Results and discussion

Davidioside A (**1**) was obtained as a yellow amorphous powder, whose molecular formula was determined to be $C_{33}H_{38}O_{15}$ by observation of a quasi-molecular ion peak at *m*/*z* 673.2128 $[M - H]^-$ in the negative ion HRFAB mass spectrum. The IR spectrum indicated the presence of hydroxyl group (3340 cm^{-1}), conjugated ester (1682 cm^{-1}), and benzene ring

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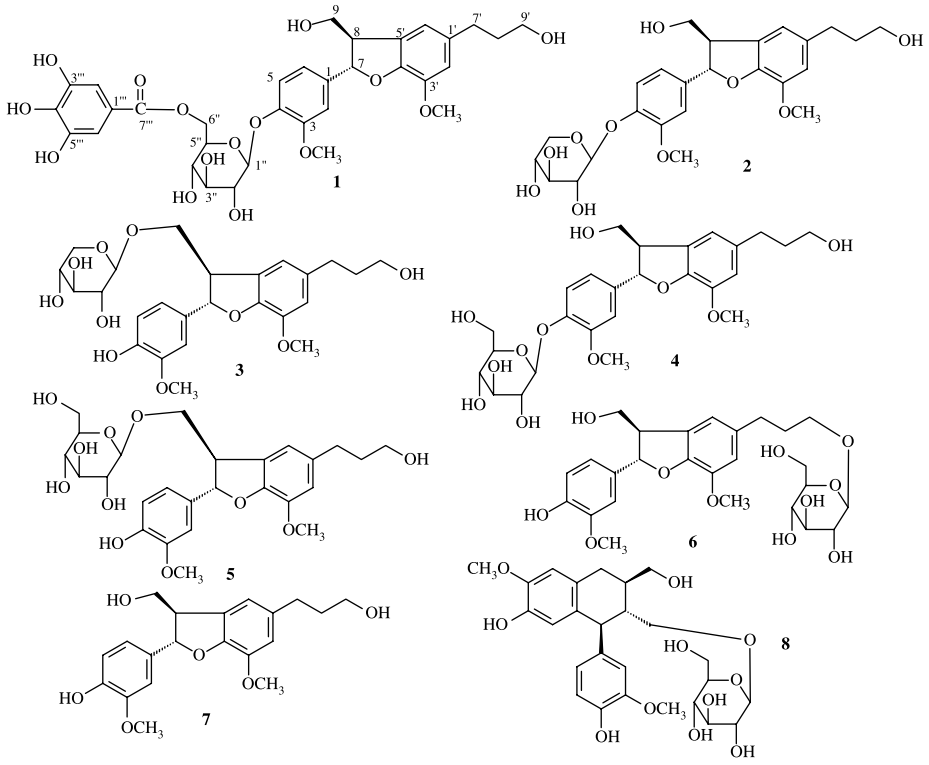

Figure 1. The structures of compounds **1**–**8**.

(1607 and 1500 cm^{-1}). Acid hydrolysis of **1** with 2 M TFA afforded glucose, which was identified by HPTLC. The ^{1}H NMR spectrum of **1** showed an ABX spin system signals at δ_H 6.99 (1H, d, $J = 2.0$ Hz), 7.04 (1H, d, $J = 8.3$ Hz), 6.79 (1H, dd, $J = 8.3$, 2.0 Hz), aromatic proton signals at δ_H 6.70 (1H, br. s, overlap), 6.71 (1H, br. s, overlap) and 7.09 (2H, s), an anomeric proton signal at δ_H 4.88 (1H, d, $J = 7.8$ Hz), and two methoxyl signals at δ_H 3.84 (6H, s, $-OCH_3$). The ^{13}C NMR spectrum of **1** gave a carbonyl signal at δ_C 168.2 (ester group), 18 aromatic carbon signals, a hexose signals and two methoxyl signals (see table 1). Evaluation of spin–spin coupling and chemical shifts of the hexose allowed the identification of one β-glucopyranosyl unit. The ^{1}H NMR and ^{13}C NMR spectra of **1** suggested the presence of two primary alcohols, two characteristic signals (δ_C 88.2 with δ_H 5.48 and 55.4 with a proton resonating at δ_H 3.89) for a benzofuran type neolignan, and a galloyl group due to the signals at δ_H 7.09 (2H, s) in the ^{1}H NMR spectrum and δ_C 168.2, 146.5 × 2, 139.8, 121.5, 110.4 × 2 in the ^{13}C NMR spectrum. Because the molecular elemental composition of **1** was 33 carbons, besides the galloyl group and the glucose, the compound **1** must be 20 carbons including 12 aromatic carbons (sp^2 carbons), six sp^3 carbons and two methoxy carbons. Comparing the NMR data of **1** with the reported reference [9] revealed the aglycone of compound **1** was dihydrodehydrodiconiferyl alcohol. The cross-peaks in the HMBC experiment between H-2‴, H-6‴ and C-7‴, C-4‴, C-3‴, C-5‴, C-1‴, between H-6″ and C-7‴, between H-1″ and C-4, indicated that the gallic acid was linked at C-6″ of the glucose and the sugar linked at C-4 of the genin. On the basis of above evidences, **1** was determined to be 4-*O*-(6-galloyl)-β-D-glucopyranosyl dihydrodehydrodiconiferyl alcohol.

Table 1. ^{1}H NMR and ^{13}C NMR data of compounds **1** and **2** (**CD_3OD**).

1		δ_H	δ_C	***2***		δ_H	δ_C
1	C		138.3	1	C		138.7
2	CH	6.99 (1H, d, $J = 2.0$ Hz)	111.1	2	CH	7.02 (1H, d, $J = 1.7$ Hz)	112.2
3	C		150.8	3	C		151.3
4	C		147.4	4	C		147.5
5	CH	7.04 (1H, d, $J = 8.3$ Hz)	118.0	5	CH	6.70 (1H, d, $J = 8.3$ Hz)	118.0
6	CH	6.79 (1H, dd, $J = 8.3$, 2.0 Hz)	119.7	6	CH	6.90 (1H, dd, $J = 8.3$, 1.7 Hz)	119.2
7	CH	5.48 (1H, d, $J = 5.9$ Hz)	88.2	7	CH	5.54 (1H, d, $J = 6.0$ Hz)	88.5
8	CH	3.89 (1H, m)	55.4	8	CH	3.90 (1H, m)	55.7
9	CH_2	3.81 (1H,m)	65.0	9	CH_2	3.43 (2H, m, overlap)	65.1
		3.74 (1H,m)					
3-OCH_3		3.84 (3H,s)	56.7	3-OCH_3		3.89 (3H, s)	56.7
1′	C		129.8	1′	C		129.6
2′	CH	6.70 (1H, br. s, overlap)	114.3	2′	CH	6.72 (1H, br. s, overlap)	114.2
3′	C		145.1	3′	C		145.2
4′	C		147.4	4′	C		147.3
5′	C		137.0	5′	C		137.1
6′	CH	6.71 (1H, br. s, overlap)	118.1	6′	CH	6.72 (1H, br. s, overlap)	118.5
7′	CH_2	2.60 (2H, t, $J = 7.9$ Hz)	32.9	7′	CH_2	2.61 (2H, t, $J = 7.7$ Hz)	32.9
8′	CH_2	1.80 (2H, m)	35.7	8′	CH_2	1.80 (2H,m)	35.8
9′	CH_2	3.56 (2H, t, $J = 6.4$ Hz)	62.3	9′	CH_2	3.83 (2H, overlap)	62.2
3-OCH_3		3.84 (3H, s)	56.9	3-OCH_3		3.84 (3H, s)	56.7
1″	CH	4.88 (1H,d, $J = 7.8$ Hz)	102.7	1″	CH	4.85 (1H, d, $J = 7.2$ Hz)	103.5
2″	CH	3.50 (1H, t, $J = 7.8$ Hz)	74.9	2″	CH	3.42 (1H, overlap)	74.6
3″	CH	3.52 (1H, t, $J = 9.3$ Hz)	77.8	3″	CH	3.31 (1H, overlap)	77.4
4″	CH	3.42 (1H, t, $J = 9.3$ Hz)	71.8	4″	CH	3.55 (1H, t, $J = 6.4$ Hz)	71.0
5″	CH	3.70 (1H, m)	75.6	5″	CH_2	3.29 (2H, overlap)	66.8
6″	CH_2	4.53 (1H, br. d, $J = 12.0$ Hz)	64.8				
		4.41 (1H, dd, $J = 12.0$, 7.2 Hz)					
1‴	C		121.5				
2‴,6′	CH	7.09 (2H, s)	110.4				
3‴,5′	C		146.5				
4‴	C		139.8				
7‴	C		168.2				

Measured in CD_3OD at 400 MHz for ^{1}H and 100 MHz for ^{13}C.

Compound **2** exhibited the presence of hydroxyl group (3330 cm^{-1}) and benzene ring (1606 and 1500 cm^{-1}). Acid hydrolysis of **2** with 2 M TFA gave xylose, which was identified by HPTLC. The HRFAB-MS of **2** exhibited a quasi-molecular ion peak at *m/z* 491.1914 $[M - H]^-$, which was consistent with the molecular formula $C_{25}H_{31}O_{10}$, representing ten degrees of unsaturation. The ^1H NMR spectrum of **2** showed ABX spin system signals at δ_H 7.02 (1H, d, $J = 1.7$ Hz), 6.70 (1H, d, $J = 8.3$ Hz), 6.90 (1H, dd, $J = 8.3$, 1.7 Hz), aromatic proton signal at δ_H 6.72 (2H, br. s, overlap), an anomeric proton signal δ_H 4.85 (1H, d, $J = 7.2$ Hz) and two methoxy signals at δ_H 3.89 (3H, s, $-OCH_3$), 3.84 (3H, s, $-OCH_3$). Comparing the NMR spectral data of **2** with those of **7** showed that their data were similar except the positions C-4, C-3, and C-5. This evidence indicated the structures of **2** and **7** were the same genin. The correlation of the HMBC experiment indicated that the xylose was linked at C-4, due to the cross-peak between H-1 of xylose and C-4. Thus, compound **2** was elucidated to be 4-*O*-β-D-xylopyranosyl dihydrodehydrodiconiferyl alcohol.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a Yanaco MP-S3 apparatus and are uncorrected. UV spectra were recorded with a Backman DU-64 spectrometer. Optical rotations were measured with a Jasco DIP-180 digital polarimeter spectrophotometer. The IR spectrum was recorded with a Perkin-Elmer 1750 FTIR spectrometer. ^1H, ^{13}C, DEPT, $^1H-^1H$ COSY, NOESY, HMQC and HMBC NMR spectra were obtained on a Varian Unity Plus 400 instrument. FAB mass spectra were recorded on a Jeol JMS-HX 110 instrument. Chromatographic stationary phases were RP-8 (40–60 μm, Merck), silica gel (160–200 mesh), Sephadex LH-20 (25–100 μm, Pharmacia Fine Chemical Co. Ltd.) and MCI-gel CHP20P (75–150 μm, Mitsubish Chemical Industries Ltd.). The following solvent systems were used: (a) $CHCl_3$/MeOH/H_2O (80:20:3), $CHCl_3$/MeOH/H_2O (70:30:5) and MeOH/H_2O (0–100%) for the glycosides; (b) $CHCl_3$/MeOH/H_2O (7:3:1) lower-layer 9 ml + 1 ml HOAc for sugars. Spot of TLC was detected by spraying with 5% H_2SO_4, then by heating. Sugars were detected by spraying with aniline-phthalate reagent.

3.2 Plant material

The branch bark of *Davidia involucrata* was collected on the Yun-Long Mountain, Gong-Shan county of Yunnan province, China in 1995. The plant was identified by Dr. Y.P. Yang,

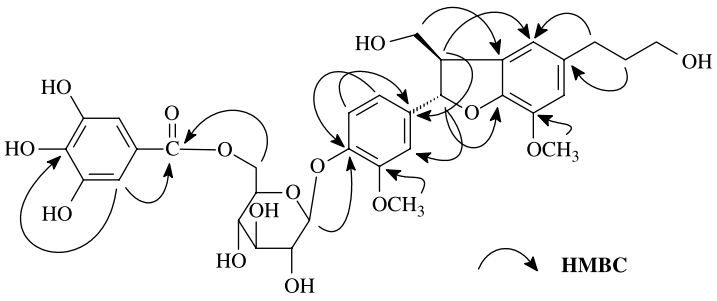

Figure 2. HMBC correlations for **1**.

A voucher specimen (No. 12245) is deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, China.

3.3 Extraction and isolation

The dry branch bark of *Davidia involucrata* (10 kg) was extracted (2 × 10 L) with MeOH at room temperature (7 days × 2). The extract was evaporated *in vacuo* to yield a residue, which was solubilised in water and then filtered. The water-soluble fraction was passed through a D_{101} macroporous adsorptive resin column and was eluted with water and methanol. Evaporation of the methanol eluate yielded 175 g of a brown fraction (A). The fraction A was subjected to dry column chromatography (DCC) on silica gel (2.0 kg), eluted with $CHCl_3$/MeOH/H_2O (10:2:0.2) to get 13 fractions. Each fraction was purified by Sephadex LH-20, RP-8 gel column chromatography (solvent: MeOH/H_2O, 10–70%) and finally purified repeatedly by chromatography on a silica gel column with $CHCl_3$/MeOH/H_2O (100:10:1–70:30:5) as eluent to yield **1** (59.9 mg), **2** (16 mg), **3** (12.7 mg), **4** (40 mg), **5** (74 mg), **6** (56 mg), **7** (48.7 mg), **8** (60 mg).

3.3.1 Davidioside A (1). Yellow amorphous powder, mp 136–138°C, HRFAB-MS *m/z* 673. 2128 $[M - H]^-$ (calcd for $C_{33}H_{38}O_{15}$, 673. 2132), $[\alpha]_D^{21}$ −21 (*c* 0.5, MeOH); IR ν_{max} cm^{-1}: 3340, 1682, 1607, 1520, 1500; UV λ_{MeOH} nm (log ε): 229 (3.92), 281 (3.45), 310 (3.14); FAB-MS *m/z* 673 $[M - H]^-$; ^1H NMR and ^{13}C NMR, see table 1.

3.3.2 Davidioside B (2). Colourless amorphous powder, mp 85–86°C, $[\alpha]_D^{21}$ −14 (*c* 0.16, MeOH); IR ν_{max} cm^{-1}: 3330, 1606, 1519, 1500; UV λ_{MeOH} nm (log ε): 229 (4.02), 282 (3.65); FAB-MS *m/z* 491 $[M - H]^-$, 359 $[M - H - 132]^-$; HR-FAB-MS *m/z* 491.1914 $[M - H]^-$ (calcd for $C_{25}H_{31}O_{10}$, 491.1917); ^1H NMR and ^{13}C NMR, see table 1.

3.4 Acid hydrolysis

A solution of each compound (8 mg) was heated at 100°C in 2 M aqueous CF_3COOH (5 ml) and refluxed in a water bath for 3 h. After this reaction, the reaction mixture was diluted with H_2O (15 ml) and extracted with CH_2Cl_2 (3 × 5 ml). The CH_2Cl_2 extracts were washed with H_2O and then evaporated to dryness *in vacuo*. After evaporation of the aqueous layer with MeOH until neutral to dryness, the sugars were analysed by comparison with authentic sample [solvent system $CHCl_3$/MeOH/H_2O (7:3:1) lower-layer 9 ml + 1 ml HOAc for sugars] on silica gel HPTLC.

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