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Two new lignans from *Dipteronia dyeriana*

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Abstract

A new sesquilignan, 7′,8′-didehydroherpetotriol (**1**), and a new lignan glycoside, (+)-isolariciresinol-9′-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside (**2**), were isolated from the branches of *Dipteronia dyeriana*. Their structures were elucidated by spectroscopic methods and chemical evidence. Compound **1** possessed inhibitory activity against human leukaemia K562 cells with an IC_{50} value of 39 μmol/L.
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Keywords: Aceraceae; *Dipteronia dyeriana*; Lignans; Didehydroherpetotriol; Leukaemia

Aceraceae comprises two genera, *Acer* and *Dipteronia* [1]. The plants of genus *Acer* contains various bioactive substances, such as triterpenoids with antitumor activity [2], stilbene glycosides with hepatoprotective and antioxidative activity [3,4], and diarylheptanoids as inhibitors of nitric oxide production [5]. To the best of our knowledge, there was not any report of chemical constituents and bioactivity on the genus *Dipteronia*. In our program to search antitumor agents from natural products, we have investigated *Dipteronia dyeriana* Henry collected from Pingbian County of Yunnan Province. In this paper, we report the structure elucidation of compounds **1** and **2** isolated from the branches of this plant, along with the inhibitory effects of compound **1** against human leukaemia K562 and human hepatoma HepG2 cells.

Compound **1** was obtained as pale yellow powder, $[\alpha]_D^{24.8}$ + 54.0 (*c* 0.50, MeOH), with UV (MeOH) absorption bands of 300 (4.11), 279 (4.15) and 234 (4.21) nm (λ_{max}: log ε). Its molecular formula was assigned as $C_{30}H_{30}O_9$ on the basis of the HR-ESI-MS *m/z* $[M-H]^-$ 533.1804 (calcd. 533.1811). In its IR (KBr) spectrum, absorption bands due to hydroxyl groups and aromatic ring were observed at 3406, 1608 and 1517 cm^{-1}. The ^{13}C NMR spectrum (Table 1) of **1** exhibited 30 carbon signals, including 13 quaternary carbons, 11 methines, three methylenes and three methoxy carbons. Extensive analysis and comparison of the ^1H and ^{13}C NMR spectra of **1** with herpetotriol [6] suggested that compound **1** was a sesquilignan. However, instead of two dihydrobenzofuran segments in herpetotriol, there was one dihydrobenzofuran [δ 150.4 (C-4′), 134.2 (C-5′), 89.6 (C-7″) and 55.1 (C-8″)] and one benzofuran segment [δ 143.9

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Table 1
^{1}H NMR (500 MHz) and ^{13}C NMR (100 MHz) data of **1** (CD_3OD, TMS, δ ppm)

No.	δ_H	δ_C	No.	δ_H	δ_C
1		134.6	7′		155.7
2	6.93 (d, 1H, 1.0)	105.9	8′		115.1
3		146.4	9′	4.78 (br s, 2H)	55.4
4		143.9	1″		130.8
5		132.9	2″	6.95 (d, 1H, 2.0)	110.6
6	7.25 (d, 1H, 1.0)	111.3	3″		149.2
7	6.65 (br d, 1H, 16.0)	132.4	4″		147.7
8	6.31 (ddd, 1H, 16.0, 6.0, 6.0)	128.8	5″	6.75 (d, 1H, 8.0)	116.2
9	4.21 (dd, 2H, 6.0, 1.5)	63.8	6″	6.82 (dd, 1H, 8.0, 2.0)	119.8
1′		125.1	7″	5.56 (d, 1H, 6.5)	89.6
2′	7.39 (d, 1H, 1.0)	113.0	8″	3.56 (dd, 1H, 12.5, 6.5)	55.1
3′		145.7	9″	3.84 (m, 2H)	64.6
4′		150.4	3-OCH_3	3.97 (s, 3H)	56.5
5′		134.2	3′-OCH_3	3.89 (s, 3H)	56.8
6′	7.36 (d, 1H, 1.0)	117.5	3″-OCH_3	3.79 (s, 3H)	56.4

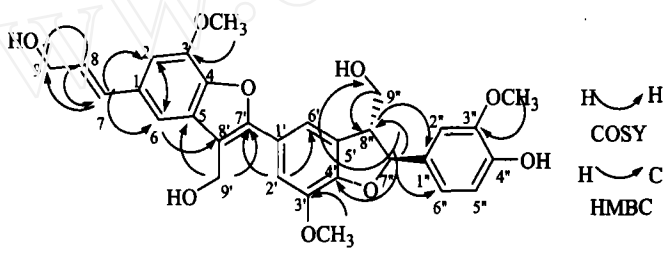

Fig. 1. The chemical structure and key ^{1}H–^{1}H COSY and HMBC correlations for **1**.

(C-4), 132.9 (C-5), 155.7 (C-7′), 115.1 (C-8′),] in **1**. The planar structure of **1** was established by the HMBC correlations (Fig. 1). A *trans*-configuration between H-7″ and H-8″ was inferred from the coupling constant (J = 6.5 Hz) [7]. Thus, **1** was identified as 7′,8′-didehydroherpetotriol. The absolute configuration of **1** has not been confirmed.

Table 2
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data of **2** (CD_3OD, TMS, δ ppm)

No.	δ_H	δ_C	No.	δ_H	δ_C
1		129.1	8′	1.85 (m, 1H)	45.8
2		134.4	9′	4.00 (dd, 1H, 9.6, 2.4)	69.2
				3.22 (m, 1H)	
3	6.17 (s, 1H)	117.4	5-OCH_3	3.79 (s, 3H)	56.4
4		145.1	3′-OCH_3	3.80 (s, 3H)	56.5
5		147.2	1″	4.07 (d, 1H, 8.0)	105.1
6	6.64 (s, 1H)	112.4	2″	3.19 (dd, 1H, 9.2, 8.0)	75.1
7	2.86 (dd, 1H, 16.0, 11.2)	33.9	3″	3.32 (m, 1H)	78.1
	2.79 (dd, 1H, 16.0, 5.2)				
8	2.08 (m, 1H)	39.4	4″	3.26 (m, 1H)	71.8
9	3.77 (m, 2H)	65.0	5″	3.35 (m, 1H)	76.8
1′		138.7	6″	3.93 (dd, 1H, 11.6, 1.6)	68.2
				3.57 (m, 1H)	
2′	6.78 (d, 1H, 2.0)	114.3	1‴	4.74 (d, 1H, 1.2)	102.3
3′		148.9	2‴	3.80 (m, 1H)	72.2
4′		145.8	3‴	3.64 (m, 1H)	72.3
5′	6.74 (d, 1H, 8.0)	116.1	4‴	3.34 (m, 1H)	74.0
6′	6.64 (dd, 1H, 8.0, 2.0)	123.2	5‴	3.63 (m, 1H)	69.8
7′	4.08 (d, 1H, 11.2)	47.9	6‴	1.22 (d, 3H, 6.0)	18.1

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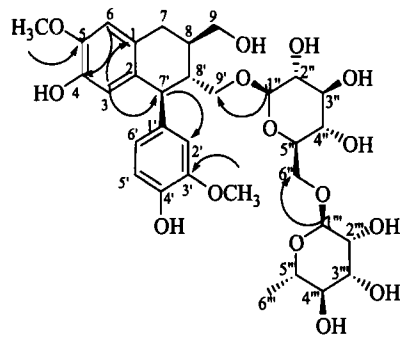

Fig. 2. The chemical structure and HMBC correlations for **2**.

Compound **2** was isolated as white powder, $[\alpha]_D^{24.7}$ + 3.9 (*c* 0.43, MeOH). UV (MeOH) absorption band was at λ_{max} (log ε): 283 (3.77) nm. The FABMS spectrum of compound **2** showed a molecular ion peak at *m/z* 667 $[M-H]^-$, besides significant fragment peaks at *m/z* 521 $[M-(\text{rhamnose-OH})]^-$. Its molecular formula was determined as $C_{32}H_{44}O_{15}$ on the basis of the HR-ESI-MS *m/z* $[M-H]^-$ 667.2586 (calcd. 667.2601). In its IR (KBr) spectrum, absorption bands due to hydroxyl groups and aromatic double bonds were observed at 3424, 1627 and 1513 cm^{-1}. The ^{13}C NMR spectrum (Table 2) of **2** showed 32 carbon signals, including two methoxyl, one methyl, four methylenes, eighteen methines and seven quaternary carbons. There was a (+) or (−) isolariciresinol moiety in **2** by comparison of the ^1H and ^{13}C NMR spectra of **2** with those in the literatures [8,9]. The spectral data of δ_H 4.07 (d, 1H, *J* = 8.0 Hz) and δ_C 105.1 (d), 78.1 (d), 76.8 (d), 75.1 (d), 71.8 (d), 68.2 (t) showed the presence of a β-glucose moiety [10]. In addition, the remaining six carbon signals [δ 102.3 (d), 74.0 (d), 72.3 (d), 72.2 (d), 69.8 (d), 18.1 (q)] and an anomeric proton resonance at δ 5.49 (d, 1H, *J* = 1.2 Hz) was the characteristic of α-rhamnoside [10]. Acidic hydrolysis of **2** in 2 mol/L HCl water solution [11] gave a rhamnose, a β-D-glucose ($[\alpha]_D^{20.6}$ + 83.3 (*c* 0.060, H_2O)), and a (+)-isolariciresinol ($[\alpha]_D^{20.7}$ + 25.6 (*c* 0.065, Me_2CO)). And the location of the glucose and rhamnose were established on the basis of HMBC correlations from δ 4.07 (d, 1H, H-1″) to δ 69.2 (C-9′) and δ 4.74 (d, 1H, H-1‴) to δ 68.2 (C-6″) (Fig. 2). Thus, the structure of **2** was elucidated as (+)-isolariciresinol-9′-*O*-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside.

The bioassay results showed that **1** inhibited the growth of K562 and HepG2 cells with an IC_{50} of 39 and 312 μmol/L, respectively [12,13].

Acknowledgments

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