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## One new dihydrobenzofuran lignan from *Vitex trifolia*

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A new benzofuran-type lignan, vitrifol A (**1**), was isolated from the fruits of *Vitex trifolia*, along with three known compounds **2**–**4**. Their structures were elucidated mainly on the basis of 1D, 2D NMR and MS spectral data. Compound **1** was first isolated as a dimer of dihydrobenzofuran-type lignan.

**Keywords:** *Vitex trifolia*; Verbenaceae; vitrifol A; dimer of dihydrobenzofuran

### 1. Introduction

*Vitex trifolia* L. (Verbenaceae) has long been used as a medicinal plant and is widely distributed in Asia, Australia, and East Africa. The ripened fruits of this plant, *Viticis Fructus*, have traditionally been used as a folk medicine in China for the treatment of headache, cold, migraine, eyepain, and rheumatism, and its leaves have also been used for the treatment of wounds.<sup>1</sup> In early reports, flavonoids,<sup>2,3</sup> sterols,<sup>2</sup> and diterpenes<sup>4–7</sup> were isolated from this plant. In this paper, we present the isolation and structural elucidation of one new compound, vitrifol A (**1**), along with three known compounds, dihydrodehydrodiconifenyl alcohol (**2**),<sup>8</sup> stigmast-4-en-6 $\beta$ -ol-3-one (**3**),<sup>9</sup> and eucommiol (**4**)<sup>10</sup> from *Vitex trifolia*. To our knowledge, all compounds were isolated from this plant for the first time.

### 2. Results and discussion

Compound **1** was obtained as pale yellow oil and has the molecular formula C<sub>30</sub>H<sub>34</sub>O<sub>9</sub> as

deduced by its negative HR-ESI-MS at  $m/z$  537.2139 [M – H]<sup>–</sup>, requiring 14 degrees of unsaturation. The UV spectrum showed absorption maximum at 205 (4.84) nm, indicating the presence of an aromatic ring. The IR spectrum showed absorption bands at 3424, 1604, 1498 and 1465 cm<sup>–1</sup>, revealing the presence of hydroxyl groups and aromatic rings. The <sup>1</sup>H NMR spectrum displayed signals at  $\delta_{\text{H}}$  6.86 (1H, d,  $J = 1.8$  Hz), 6.81 (1H, m) and 6.79 (1H, d,  $J = 8.1$  Hz) for an AMX spin system of a 1,3,4-trisubstituted aromatic A-ring and four singlets (4H) at  $\delta_{\text{H}}$  6.86, 6.84 and 6.62 for two tetrasubstituted aromatic ring with four benzylic methines. The remaining <sup>1</sup>H NMR signals indicated three methoxyl substituents, a *n*-propanol and two –O–CH–CH–CH<sub>2</sub>O– spin systems. The <sup>13</sup>C NMR spectrum consisted of 30 resonances (Table 1), including 11 quaternary carbons, of which six were oxygenated aromatic; seven aromatic and four aliphatic methines, of which two were oxymethines; five methylenes, of which three were oxygenated; and three methoxyls ( $\delta_{\text{C}}$

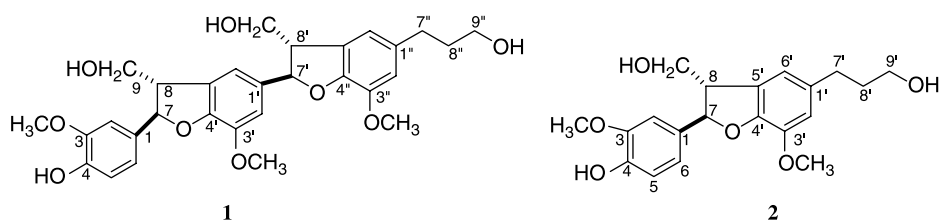
\*Corresponding author. Email: chenjj@mail.kib.ac.cn

Table 1.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectral data of compounds **1** and **2** ( $\text{CDCl}_3$ ,  $\delta$  in ppm).

No.	<b>1</b>		<b>2</b>	
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1		132.9 s		132.8 s
2	6.86 (1H, d, 1.8 Hz)	108.9 d	6.83 (1H, d, 1.5 Hz)	108.9 d
3		146.8 s		146.8 s
4		145.6 s		145.3 s
5	6.79 (1H, d, 8.1 Hz)	114.4 d	6.70 (1H, d, 8.1 Hz)	114.4 d
6	6.81 (1H, dd, 8.1, 1.8 Hz)	119.2 d	6.75 (1H, dd, 8.1, 1.5 Hz)	118.8 d
7	5.48 (1H, d, 7.5 Hz)	87.9 d	5.40 (1H, d, 6.9 Hz)	87.6 d
8	3.51–3.48 (1H, m)	53.6 d	3.43 (1H, m)	53.4 d
9	3.85 (2H, m)	63.4 t	3.52 (2H, m)	63.5 t
1'		134.7 s		135.1 s
2'	6.84 (1H, br s)	110.5 d	6.55 (1H, s)	112.0 d
3'		144.0 s		143.5 s
4'		148.2 s		145.8 s
5'		128.4 s		127.9 s
6'	6.86 (1H, br s)	114.4 d	6.57 (1H, s)	116.1 d
7'	5.49 (1H, d, 7.8 Hz)	88.3 d	2.51 (2H, t, 7.1 Hz)	31.5 t
8'	3.57–3.52 (1H, m)	53.8 d	1.73 (2H, m)	34.0 t
9'	3.76 (2H, m)	63.9 t	3.78 (2H, m)	61.3 t
1''		135.4 s		
2''	6.62 (1H, br s)	112.3 d		
3''		144.2 s		
4''		146.2 s		
5''		127.9 s		
6''	6.62 (1H, br s)	116.1 d		
7''	2.60 (2H, t, 7.5 Hz)	31.9 t		
8''	1.82 (2H, m)	34.4 t		
9''	3.61 (2H, t, 6.4 Hz)	61.8 t		
3-OMe	3.82 (s)	55.9 q	3.73 (s)	55.5 q
3'-OMe	3.80 (s)	55.9 q	3.67 (s)	55.5 q
3''-OMe	3.80 (s)	55.9 q		

56.0). By comparing the IR, UV and NMR spectral data for **1** with the literature,<sup>11</sup> it showed that compound **1** was a dimer of dihydrobenzofuran neolignan. In the HMBC spectrum (Figure 2), the observed cross-peaks of H-7' ( $\delta_{\text{H}}$  5.49, 1H, d,  $J = 7.8$  Hz) with C-1', C-2', C-6', C-8', C-9', C-4'', H-7 ( $\delta_{\text{H}}$  5.48,

1H, d,  $J = 7.5$  Hz) with C-1, C-2, C-6, C-8, C-9 and C-4', H-2' ( $\delta_{\text{H}}$  6.84, 1H, br s), H-6' ( $\delta_{\text{H}}$  6.86, 1H, br s) with C-7', as well as the cross-peaks of H-2 ( $\delta_{\text{H}}$  6.86, 1H, d,  $J = 1.8$  Hz) and H-6 ( $\delta_{\text{H}}$  6.81, 1H, m) with C-7, suggested that one dihydrobenzofuran moiety was connected to 1,3,4-trisubstituted aromatic ring (A) and the

Figure 1. Structures of compounds **1–2**.



### 3.3 Extraction and isolation

The n-BuOH extract (240 g) was subjected to silica gel column chromatography (10 × 150 cm, 200–300 mesh, 1500 g) eluting with CHCl<sub>3</sub>/MeOH/H<sub>2</sub>O (from 9:1:0.1 to 7:3:0.3) to provide fractions A–J. Fraction A (10 g) was chromatographed on silica gel (4.5 × 60 cm, 200–300 mesh, 200 g) column with an elution of CHCl<sub>3</sub>/Me<sub>2</sub>CO (from 9:1 to 7:3) to obtain fractions A<sub>1</sub>–A<sub>3</sub>. Fraction A<sub>3</sub> (3 g) was chromatographed on silica gel column (3 × 60 cm, 200–300 mesh, 90 g) eluting with CHCl<sub>3</sub>/Me<sub>2</sub>CO (8:2), followed by recrystallizing in CHCl<sub>3</sub> to yield compound **3** (120 mg). Fraction B (15 g) was submitted to a silica gel column (4.5 × 60 cm, 200–300 mesh, 300 g) using gradient elution of CHCl<sub>3</sub>/Me<sub>2</sub>CO (from 8:2 to 1:1) to obtain fractions B<sub>1</sub>–B<sub>5</sub>. Fraction B<sub>3</sub> (4 g) was performed on silica gel column (4.5 × 60 cm, silica gel H, 120 g) eluting with CHCl<sub>3</sub>/EtOAc (7:3) to produce the mixture of compounds **1** and **2**. The mixture was repeatedly purified over silica gel (silica gel H) eluting with petroleum ether/EtOAc (2.5:7.5) to afford compounds **1** (10 mg) and **2** (20 mg). Fraction J (30 g) was decolorized on MCI gel CHP-20 (1.5 × 30 cm) with an elution of MeOH/H<sub>2</sub>O (90:10) to yield a pale yellow gum (15 g), which was subjected to silica gel, RP-18 (1.5 × 35 cm), and Sephadex LH-20 (1.5 × 60 cm) column subsequently to give compound **4** (727 mg).

#### 3.3.1 Vitrifol A (I)

Pale yellow oil.  $[\alpha]_D^{28} = +5.95$  ( $c = 0.20$ , MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ): 205 (4.84), 282 (3.80), 357 (2.51) nm; IR (KBr)  $\nu_{\max}$ : 3424, 2924, 2853, 1604, 1517, 1498, 1465, 1377, 1303, 1286, 1139, 1123, 1037, 982, 946, 852, 813, 744 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR spectral data (see Table 1); negative

ESI-MS:  $m/z$  537 [M – H]<sup>-</sup>; negative HR-ESI-MS  $m/z$ : 537.2139 [M – H]<sup>-</sup> (calcd for C<sub>30</sub>H<sub>33</sub>O<sub>9</sub>, 537.2124).

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