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The chemical constituents from *Schisandra propinqua* var. *intermedia*

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Abstract

A new cinnamic acid monoterpenoid ester, intermedin C (**1**), was isolated from the aerial parts of *Schisandra propinqua* var. *intermedia*. The structure of **1** was elucidated by spectroscopic methods including extensive ^{1}D and ^{2}D NMR techniques.

Keywords: *Schisandra propinqua*; Monoterpenoid; Intermedin C

Phytochemical investigation on the aerial parts of *Schisandra propinqua* (Wall) Hook. Thoms. var. *intermedia* A. C. Sm. resulted in the isolation of a new cinnamic acid monoterpenoid ester, intermedin C (**1**), along with 18 known compounds. The structure of compound **1** was elucidated by spectroscopic methods including extensive ^{1}D and ^{2}D NMR techniques.

The air-dried and powdered aerial parts of *S. propinqua* var. *intermedia* (8.3 kg) collected from Honghe district in Yunnan province of China were extracted three times with 70% aq. acetone at r.t. The concentrated syrup was suspended in H_2O and then extracted with EtOAc. The EtOAc extract (80 g) was subjected to repeated silica gel column and reverse chromatography and finally purified on sephadex LH-20 to give **1** (the yield of compound **1** was 0.0024‰).

Compound **1**, $[\alpha]_D^{24} + 22.6$ (*c* 0.34, $CHCl_3$), was obtained as yellow oil. Its molecular formula $C_{19}H_{26}O_4$ was determined by HR-ESI-MS (*m/z* 341.1728, $[M + Na]^+$), in combination with ^{1}H and ^{13}C NMR data (Table 1), indicating seven degrees of unsaturation.

The signals at δ 134.2 (s, C-1′), 130.5 (d, C-4′), 128.9 × 2 (d, C-3′, 5′), and 128.2 × 2 (d, C-2′, 6′) in the ^{13}C NMR spectrum, and the signals at δ 7.54 (dd, 2H, $J = 2.8$, 6.6 Hz, H-2′, 6′), and 7.39 (3H, overlapped, H-3′, 5′, 4′) in the ^{1}H NMR spectrum, indicated the presence of a monosubstituted phenyl ring [1]. The signal at δ 145.6 (d, C-7′), 117.8 (d, C-8′) and 167.3 (s, C-9′) suggested the existence of an α,β-unsaturated ester group, which was further confirmed by the HMBC correlations (Fig. 1) from δ 7.72 (d, 1H, $J = 16.0$ Hz, H-7′) and 6.48 (d, 1H, $J = 16.0$ Hz, H-8′) to C-9′. In

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Table 1
^{1}H (500 MHz) and ^{13}C NMR (125 MHz) data of compound 1 ($CDCl_3$, δ ppm, J_{Hz}).

No.	δ_H	δ_C	No.	δ_H	δ_C
1	5.21 (dd, 0.7, 17.0, Ha)	112.0 (t)	9	1.24 (s)	26.5 (q)
	5.05 (dd, 0.7, 10.7, Hb)		10	1.27 (s)	27.9 (q)
2	5.88 (dd, 10.7, 17.0)	144.9 (d)	1′		134.2 (s)
3		73.0 (s)	2′, 6′	7.54 (dd, 2.8, 6.6)	128.2 × 2 (d)
4	1.52–1.61 (m)	38.3 (t)	3′, 5′	7.39 (overlapped)	128.9 × 2 (d)
5	1.69–1.83 (m)	24.0 (t)	4′	7.39 (overlapped)	130.5 (d)
6	4.95 (dd, 2.6, 10.1)	80.2 (d)	7′	7.72 (d, 16.0)	145.6 (d)
7		72.6 (s)	8′	6.48 (d, 16.0)	117.8 (d)
8	1.24 (s)	25.3 (q)	9′		167.3 (s)

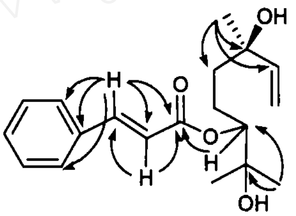

Fig. 1. Key HMBC correlations of compound **1**.

addition, the HMBC correlations between H-7′ and C-1′, C-2′, and C-6′ indicated the α,β-unsaturated ester group was attached to the phenyl ring directly. In other words, there was a cinnamic acid ester group in the molecule, which was further confirmed by the significant peak at *m/z* 131 (C_6H_5–CH=CH–CO^+) in the positive FAB-MS. Moreover, the coupling constant between H-7′ and H-8′ (J = 16.0 Hz) suggested the two olefinic protons located at *trans*-orientation [2].

Except for the signals belonging to the cinnamic acid ester group, the remains of the signals in the ^{13}C NMR spectrum were in good accordance with those of 3,7-dimethyl-oct-1-ene-3,6,7-triol, which possessed an acyclic monoterpenoid skeleton [3]. The correlations in the HMBC and ^{1}H–^{1}H COSY spectra further confirmed the existence of the monoterpenoid. In addition, the HMBC correlation from δ 4.95 (dd, 1H, J = 2.6, 10.1 Hz, H-6) to C-9′ indicated that 6-OH of the monoterpenoid formed ester with cinnamic acid. Thus, the structure of 1 (Fig. 2) was determined and named as intermedin C.

The known compounds were determined to be kadsulignan L [4], schisantherin I [5], schisantherin P [6], kadsulignan A [7], meso-dihydroguaiaretic acid [8], pinoresinol [9], 7,9,9′-trihydroxy-3,4,3′-trimethoxy-7′-ene-8,4′-oxyneo lignan [10], turmeronol A [11], bisacurone [12], 1β,6α-dihydroxyeudesm-4 (15)-ene [13], 5α-hydroxy-8,9-dihydrocarvone [14], (1*R*, 4*S*, 6*R*) *p*-menthenediol [15], 2,3-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-propan-1-one [16], 1-(4-hydroxy-3-methoxyphenyl) propan-1,2-diol [17], curcumin [18], hexadecanoic acid-2,3-dihydroxy-propyl ester [19], 2-hydroxy-1-linoleic acid-propaneyl ester [20] and β-sitosterol [21], by comparison of their spectral data with those of literature values. Except for kadsulignan L and β-sitosterol, other compounds were all isolated from this plant for the first time. In addition, kadsulignan A was isolated from the genus *Schisandra* for the first time.

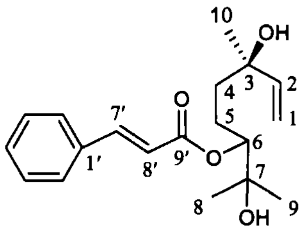

Fig. 2. The structure of compound **1**.

Compound **1** demonstrated weak anti-HIV-1 activity with EC_{50} value of 20.18 μg/mL, and a therapeutic index (TI) of 2.60.

Acknowledgments

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