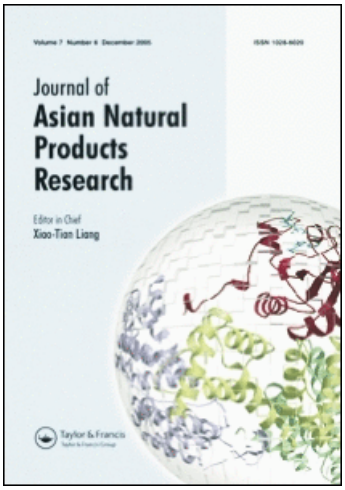

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Two new compounds from *Acanthopanax senticosus* Harms

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From the dried aerial part of *Acanthopanax senticosus*, a new coumarin glycoside, eleutheroside B_2 (**1**), and a new sesquiterpenoid, oplopanone B (**2**), were isolated. Their structures were elucidated on the basis of chemical and spectroscopic methods.

Keywords: *Acanthopanax senticosus*; coumarin glycosides; sesquiterpenoid

1. Introduction

Acanthopanax senticosus Harms has been prescribed in Chinese traditional medicine as a tonic, antirheumatic, and prophylactic for chronic bronchitis, hypertension, and ischemic heart disease [1]. The chemical constituents of this plant have been examined and the isolation of triterpene saponins [2,3], aromatic glycosides, lignans [4–6], and polysaccharides [7] has been reported. As a part of our studies on this plant, the composition of the extract of the aerial part of *A. senticosus* was examined. In the present paper, we describe the isolation and structural characterization of these compounds.

2. Results and discussion

Compound **1** was obtained as a yellow gummy material. The molecular formula was determined to be $C_{23}H_{30}O_{14}$ by HR-FAB-MS at *m/z* 530.1636 $[M+H]^+$. The IR spectrum of **1** suggested the presence of conjugated carboxyl (1720 cm^{-1}), hydroxyl groups (3509 cm^{-1}), and aromatic ring (1647–1544 cm^{-1}). In the ^1H NMR spectrum, the signals at δ 7.94 (1H, d, $J = 9.6$ Hz, H-4) and 6.38 (1H, d, $J = 9.6$ Hz, H-3) indicated the presence of two protons of the α,β-unsaturated system of the coumarin nucleus and the proton singlet at δ 7.09 revealed the presence of H-5 of the aromatic ring. The two proton signals at δ 3.89 and 3.82 (each 3H, s, OCH_3) correspond to the two methoxyls which were attached to the positions 8 and 6, respectively. The remaining signals at δ 5.06 (1H, d, $J = 7.2$ Hz, H-1′) and 4.38 (1H, brs, H-1″) suggested the presence of the anomeric protons of glucoside and rhamnoside.

The ^{13}C NMR and HSQC spectra of **1** gave 23 carbon signals for one methylene, two methyls, six quaternary carbons, including one carbonyl group at δ 160.0, and four aromatic carbons. The NMR spectral data of **1** were similar to those of eleutheroside B_1 [8], except for the appearance of an additional rhamnose. In the HMBC spectrum, the long-range correlation from H-1″ at δ 4.38 to C-6′

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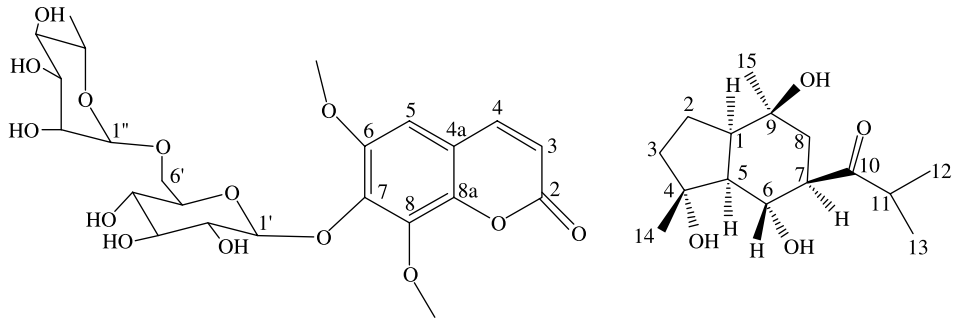

Figure 1. Structures of compounds **1** and **2**.

at δ 66.6 suggested that the additional rhamnose was linked to C-6′ of the inner glucose. Thus, the structure of **1** was determined as shown in Figure 1 and named eleutheroside B_2.

Compound **2** was isolated as a colorless amorphous powder. The molecular formula was determined to be $C_{15}H_{26}O_4$ by HR-FAB-MS at *m/z* 270.1831 $[M+H]^+$. The IR spectrum of **2** suggested the presence of carbonyl (1710 cm^{-1}) and hydroxyl groups (3450 cm^{-1}). From the ^1H NMR spectrum of compound **2**, the two singlets of three protons at δ 1.27 and 1.43 were assigned to the two tertiary methyl groups. The characteristic resonances of the two secondary methyl groups appeared at δ 1.09 (3H, d, $J = 6.6$ Hz) and 1.12 (3H, d, $J = 6.6$ Hz). The methine proton attached to an oxygen-bearing carbon displayed a broad singlet at δ 4.32 (1H, brs). In the ^{13}C NMR spectrum, assignment of 15 carbon signals including three quaternary carbons among which two were oxygenated at δ 72.7–79.3, five tertiary carbons among which one was oxygenated at δ 65.0, and three secondary and four primary carbon atoms were established by the interpretation of the ^{13}C NMR and HSQC spectra (Table 1). Signals from several spin coupling units namely —C—CH_2—CH_2—CH—C—, —C—CH_2—CH—CH—CH—, and —C—CH—CH(OH)—CH— were used for the assignment of proton signals in the

Table 1. NMR spectroscopic data of compound **2** (DMSO-d_6, 150 MHz).

Atom number	^{13}C (δ)	^1H [δ, mult, J (Hz)]	HMBC (atom number of ^{13}C)	^1H–^1H COSY
1	45.7	2.20, m	C-5, 9, 15	H-2, 5
2	21.4	1.69 (2H, m)	C-1, 4	H-1
3	41.9	1.66, m, 1.76, m	C-2, 4, 14	H-2
4	79.3			
5	56.6	1.41, m	C-1, 4, 14	H-1, 6
6	65.0	4.32, brs	C-5, 8	H-5, 7
7	50.9	2.60, m	C-8, 10	H-6, 8
8	38.7	1.90, m, 1.68, m	C-6, 7, 9, 15 C-1, 6, 7, 9	H-7
9	72.7			
10	219.0			
11	40.0	2.75, m (6.6)	C-10, 12, 13	H-12, 13
12	17.8	1.09, d (6.6)	C-10, 11, 13	H-11
13	18.6	1.12, d (6.6)	C-10, 11, 12	H-11
14	26.9	1.43, s	C-3, 4	
15	19.9	1.27, s	C-1, 8, 9	

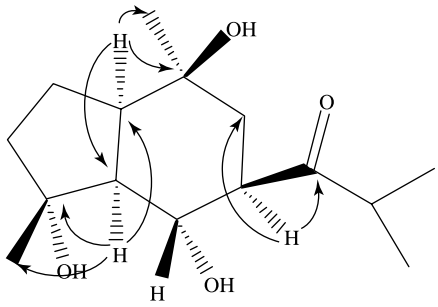

Figure 2. Key HMBC correlations observed for **2**.

^{1}H–^{1}H COSY and HSQC spectra. Inter-residue linkages and position of the attachments of the carbohydrate units were at last established by the HMBC experiment (Figure 2) as shown in Figure 1. Three hydroxyl groups should be attached at C-4,6,9 and the isobutyryl group at C-7.

The relative stereochemistry of **2** was determined using the NOESY spectrum. The correlation of H-1 (δ 2.20) with H-5 (δ 1.41) was assigned to a *cis*-configuration of the two rings. The correlation of H-5 with H-1, H-7, and H-15, and H-6 with H-14 was observed, indicating that H-1, H-5, H-7, and H-15 were at one side and H-6 and H-14 at the other side of the molecule (Figure 3). Therefore, the structure of **2** was confirmed as shown in Figure 1 and named oplopanone B.

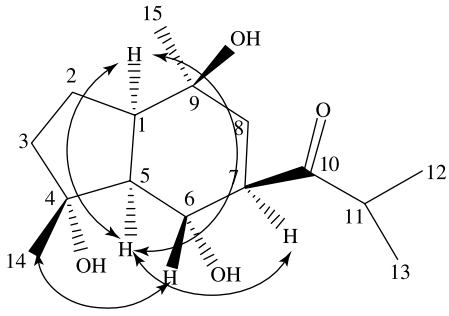

Figure 3. Key NOESY correlations observed for **2**.

3. Experimental

3.1 General experimental procedures

Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The UV spectra were measured on a Shimadzu UV-1601. IR spectra were taken on a Bruker IFS-55 infrared spectrophotometer. The NMR data were recorded on a Bruker AV-600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) in DMSO-d_6 with TMS as an internal standard. The HR-FAB-MS data were obtained on the Micross Mass Autospec-UltimaE TOF mass spectrophotometer. Chromatography was performed on silica gel (200–300 mesh; Qingdao Haiyang Chemical Factory, Qingdao, China), Sephadex LH-20 (Pharmacia, Piscataway, NJ, USA), and reversed-phase HPLC (Shimadzu LC-10A vp, Kyoto, Japan).

3.2 Plant material

The aerial parts of *A. senticosus*, cultivated in the Liaoning Province of China, were bought from the Cooperation of Traditional Chinese Medicine of Shenyang, China, in June, 2005. A voucher specimen (No. 6098) was identified by Prof. Qi-shi Sun and has been deposited in the School of Traditional Chinese Medicine of Shenyang Pharmaceutical University, China.

3.3 Extraction and isolation

The aerial parts (20 kg) of *A. senticosus* were extracted thrice with hot 65% EtOH, every time for 2 h, and the combined solution was concentrated *in vacuo* to a syrup (1000 g), followed by suspension in water. The suspension was extracted with petroleum ether, ethyl acetate, and *n*-butanol successively. The *n*-butanol fraction (150 g) was further chromatographed over a D101 macroporous resin column eluted with H_2O, 30, 70, and 95% EtOH gradually. The fraction (60 g) eluted with 30% EtOH was subjected to silica gel column chromatography (eluted with $CHCl_3$ and MeOH in increasing polarity) to obtain nine fractions

(I–IX). Fraction IV was purified by Sephadex LH-20 column chromatography (CH_3OH) and preparative HPLC (CH_3OH–H_2O, 35:100, flow rate 4 ml/min, wavelength 210 nm) to obtain compounds **1** (10 mg) and **2** (15 mg).

3.3.1 *Eleutheroside B_2 (**1**)*

A yellow gummy material; $[\alpha]_D^{25}$ +10.6 (MeOH). IR (KBr) ν_{max} (cm^{-1}): 3509, 1720, 1647, 1544; UV λ (nm): 223, 266, 289; ^{1}H NMR (DMSO-d_6) δ: 7.94 (1H, d, $J = 9.6$ Hz, H-4), 6.38 (1H, d, $J = 9.6$ Hz, H-3), 7.09 (1H, s, H-5), 5.06 (1H, d, $J = 7.2$ Hz, H-1′), 4.38 (1H, brs, H-1″), 3.89 (3H, s, OCH_3-8), 3.82 (3H, s, OCH_3-6); ^{13}C NMR (DMSO-d_6) δ: 159.9 (C-2), 114.8 (C-3), 144.5 (C-4), 105.5 (C-5), 149.6 (C-6), 142.4 (C-7), 141.6 (C-8), 114.8 (C-5a), 105.4 (C-8a); Glu: 102.5, 74.1, 76.4, 70.0, 75.8, 66.6; Rha: 100.7, 70.3, 70.6, 71.8, 68.3, 17.8; HR-FAB-MS *m/z*: 530.1647 $[M+H]^+$ (calcd for $C_{23}H_{30}O_{14}$, 530.1636).

3.3.2 *Oplopanone B (**2**)*

A colorless amorphous powder; $[\alpha]_D^{25}$ −20.6 (MeOH). IR (KBr) ν_{max} (cm^{-1}): 3450, 1710; UV λ (nm): 223, 266; NMR (DMSO-d_6) spectral data, see Table 1; HR-FAB-MS *m/z*: 270.1843 $[M+H]^+$ (calcd for $C_{15}H_{26}O_4$, 270.1831).

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