A New Cyanogenic Glycoside from *Sorbaria sorbifolia* var. *stellipila*

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A new cyanogenic glycoside, sutherlandin-5-*trans*-*p*-coumarate was isolated along with a known cardiospermin-5-(4-hydroxy) benzoate from the aerial parts of *Sorbaria sorbifolia* (L.) A. Br. var. *stellipila* MAX. (Rosaceae). The structure of the new compound was established based on spectral evidence.

Key words cyanogenic glycoside; sutherlandin-5-*trans*-*p*-coumarate; *Sorbaria sorbifolia* var. *stellipila*; Rosaceae

The stem bark of *Sorbaria sorbifolia* (L.) A. Br. var. *stellipila* MAX. (Rosaceae) has been used as a traditional Chinese drug for the treatment of bone fracture and bruise.¹⁾ This plant grows in the mountainous areas of Kangwondo, Korea.²⁾ In a previous study of *S. sorbifolia* var. *stellipila*, we reported the isolation and characterization of two cytotoxic constituents, cucurbitacins D and F,³⁾ and two lignans.⁴⁾ In continuation of our phytochemical studies of this plant, we have reinvestigated the extracts from the aerial parts of the plant, collected in Kangwondo. Previous chemical studies on this genus, several leucine-derived cyanogenic glycosides, cardiospermin-5-(4-hydroxy) benzoate, heterodendrin, and cardiospermin-5-*trans*-*p*-coumarate were reported from *S. arborea*.⁵⁾ In this paper, we report the isolation and structural elucidation of a known (**1**) and a new (**2**) cyanogenic glycoside.

Repeated column chromatography of the methanol extract yielded two cyanogenic glycosides. The structure of cardiospermin-5-(4-hydroxy) benzoate (**1**) was established by its positive-ion high resolution FAB-MS, ¹H-, ¹³C-, 2D NMR, and a heteronuclear multiple bond correlation (HMBC) experiment (Fig. 1), together with comparison of the NMR spectral data with that reported in the literature.⁵⁾

Compound **2** was assigned the molecular formula C₂₀H₂₃NO₉ (*m/z*, 422.1457, [M⁺+H]) by its positive-ion high resolution FAB-MS. The IR spectrum of **2** revealed the presence of hydroxyl (3350 cm⁻¹), nitrile (2235 cm⁻¹), and carbonyl groups (1710 cm⁻¹). The signals assigned to the sugar moiety indicated the presence of a glucose unit. In the ¹H- and ¹³C-NMR spectra, the anomeric signal was observed at δ_H 4.33 (d, *J*=7.8 Hz) and δ_C 104.3 as a β -glucopyranoside. The ¹H-NMR data showed two doublets centered at δ 7.49 and 6.81 (each 2H, *J*=8.8 Hz), assigned to the A₂B₂ system of the aromatic protons, and another two doublets at δ 7.69 and 6.41 (each 1H, *J*=16.1 Hz), which indicates a *trans*-*p*-coumaroyl moiety.⁶⁾ The ¹H- and ¹³C-NMR spectral data and HMBC experiment showed that the remaining signals were 3-oxymethyl-2-butenenitrile moiety. In the HMBC spectrum, the proton signal of H-4 (δ 4.70 and 4.60) showed ¹H–¹³C long-range correlations with anomeric carbon (δ 104.3) and C-2 (δ 97.6). The carbon signal C-1' (δ 168.1) of the cinnamoyl moiety correlated with H-5 (δ 5.00) and H-3' (δ 7.69). Finally, the whole structure was established as that of **2**. The ¹³C-NMR data of 4-(β -D-glucopyranosyloxy)-3-(oxymethyl)-2-butenenitrile moiety were nearly identical with sutherlandin reported in the literature.⁷⁾ Comparison of the NMR data of **2** with those reported compounds sutherlandin⁷⁾ and its isomer,⁸⁾ confirmed the stereochemistry about

the double bond (*E*) of butenenitrile moiety. In conclusion, the structure of **2** was determined to be 4-(β -D-glucopyranosyloxy)-3-(4-hydroxycinnamoyloxymethyl)-2-(*E*)-butenenitrile (sutherlandin-5-*trans*-*p*-coumarate).

Experimental

General Procedures IR spectrum was obtained on a JASCO FT/IR 410 spectrometer and UV spectrum was measured in MeOH on a Shimadzu UV-1601 UV-Visible spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on JEOL JMN-EX 400 and Bruker AMX-500 NMR spectrometers. HR-FAB-MS were recorded on a Tandem MS instrument.

Plant Material *Sorbaria sorbifolia* var. *stellipila* was collected in June 1997 on the Odaesan, Kangwondo, Korea. A voucher specimen is deposited in the Herbarium of College of Pharmacy, Woosuk University (WSU-97-002).

Extraction and Isolation The air-dried plant material (2 kg) was finely powdered and extracted at room temperature with MeOH for 2 weeks. The resultant MeOH extract (70 g), followed by the successive solvent partition gave CH₂Cl₂ (30 g), ethylacetate (5 g), and water soluble fractions. Ethylacetate soluble fraction was chromatographed (CC) over Sephadex LH-20 (60 g) with MeOH (150 ml) to afford four fractions (fr. 1: yield 0.8 g; fr. 2: 0.3 g; fr. 3: 1.2 g; fr. 4: 0.6 g). Rechromatography of fr. 2 over silica gel (20 g, 230–400 mesh) using *n*-hexane–EtOAc–MeOH (5 : 15 : 2, 1.2 l) to afford two fractions. Secondary fraction (220 mg) was purified on a reversed-phase Lobar-A column (Merck) using MeOH : H₂O (1 : 1) to yield **1** (50 mg) and **2** (15 mg), respectively.

Cardiospermin-5-(4-hydroxy) benzoate (**1**): HR-FAB-MS (*m*-nitrobenzyl alcohol as matrix) *m/z*: 396.1303 [M⁺+1, Calcd for C₁₈H₂₂NO₉, 396.1295]. ¹³C-NMR (CD₃OD) δ 167.6 (C-1'), 163.9 (C-5'), 139.1 (C-3), 133.1 (C-3', 7'), 121.7 (C-2'), 119.5 (C-4), 117.4 (C-1), 116.3 (C-4', 6'), 102.1 (C-1''), 78.5 (C-5''), 77.8 (C-3''), 74.7 (C-2''), 71.4 (C-4''), 67.6 (C-2), 64.4 (C-5), 62.7 (C-6''). ¹H-NMR data were in good agreement with those reported in the literature,³⁾ while ¹³C-NMR data have not yet been reported. * Chemical shift values in the same column are interchangeable.

Fig. 1

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Table 1. NMR Data for Compound 2 (CD₃OD)

C	DEPT ^{a)}	¹³ C ^{a)}	¹ H ^{b)}	HMBC (¹ H→ ¹³ C) ^{c)}
1	C	116.5	—	—
2	CH	97.6	5.73 (1H, s)	4-C, 5-C
3	C	159.8	—	—
4	CH ₂	68.4	4.70 (1H, d, <i>J</i> =13.2 Hz) 4.60 (1H, d, <i>J</i> =13.2 Hz)	2-C, 3-C, 5-C, 1''-C 2-C, 3-C, 5-C, 1''-C
5	CH ₂	64.4	5.00 (2H, s)	2-C, 3-C, 1'-C
1'	C	168.1	—	—
2'	CH	114.2	6.41 (1H, d, <i>J</i> =16.1 Hz)	4'-C, 1'-C
3'	CH	147.6	7.69 (1H, d, <i>J</i> =16.1 Hz)	1'-C, 5'-C, 9'-C
4'	C	127.0	—	—
5'	CH	131.4	7.49 (1H, d, <i>J</i> =8.8 Hz)	3'-C, 7'-C
6'	CH	116.9	6.81 (1H, d, <i>J</i> =8.8 Hz)	4'-C
7'	C	161.6	—	—
8'	CH	116.9	6.81 (1H, d, <i>J</i> =8.8 Hz)	4'-C
9'	CH	131.4	7.49 (1H, d, <i>J</i> =8.8 Hz)	3'-C, 7'-C
1''	CH	104.3	4.33 (1H, d, <i>J</i> =7.8 Hz)	4-C
2''	CH	74.9	—	—
3''	CH	78.0*	—	—
4''	CH	71.4	—	—
5''	CH	78.2*	—	—
6''	CH ₂	62.5	—	—

a) 100 MHz, CD₃OD. b) 400 MHz, CD₃OD. c) 500 MHz, CD₃OD. *Chemical shift values in the same column are interchangeable.

Sutherlandin-5-*trans*-*p*-coumarate (2): white needle crystals, $[\alpha]_D^{18} +27.8^\circ$ (*c*=0.09, MeOH), mp 88—89 °C, IR (Nujol) $\nu_{\max}$ cm⁻¹: 3350, 2235, 1710. UV (MeOH) $\lambda_{\max}$ nm: 315, 211. HR-FAB-MS (*m*-nitrobenzyl alcohol as matrix) *m/z*: 422.1457 [*M*⁺+1, Calcd for C₂₀H₂₄NO₉ 422.1451]. ¹H- and ¹³C-NMR see Table 1.

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References and Notes

- 1) "The Dictionary of Chinese Drugs," Vol. 3, Shanghai Science and Technology Press and Shougakukan, Tokyo, 1985, p. 1813.
- 2) Lee T. B., "Illustrated Flora of Korea," Hyang Moon Sa, Seoul, 1989, p. 426.
- 3) Kim D. K., Choi S. H., Lee J. O., Ryu S. Y., Park D. K., Shin D. H., Jung J. H., Pyo S. K., Lee K. R., Zee O. P., *Arch. Pharm. Res.*, **20**, 85—87 (1997).
- 4) Kim D. K., Eun J. S., Lim J. P., Lee K. R., Zee O. P., *Yakhak Hoeji*, **43**, 285—288 (1999).
- 5) Nahrstedt A., Scheid H., *Phytochemistry*, **20**, 1309—1310 (1981).
- 6) Takeda Y., Masuda T., Honda G., Takaishi Y., Ito M., Ashurmetov O. A., Khodzhimatov O. K., Otsuka H., *Chem. Pharm. Bull.*, **47**, 1338—1340 (1999).
- 7) Swenson W. K., Dunn J. E., Conn E. E., *Phytochemistry*, **26**, 1835—1836 (1987).
- 8) Braekman J. C., Daloze D., Pasteels J. M., *Biochem. System. Ecol.*, **10**, 355—364 (1982).