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A new glucoside from *Selaginella sinensis*

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A new glucoside, selaginoside (**1**), together with two known compounds, hinokiflavone (**2**) and 2,3-dihydroamentoflavone (**3**), were isolated from the whole plants of *Selaginella sinensis*. Their structures were elucidated by means of spectroscopic methods.

Keywords: *Selaginella sinensis*; Selaginoside

1. Instruction

Selaginella sinensis is abundantly distributed in the north part of PR China. It has been used as a folk herbal medicine for the treatment of hepatitis, cholelithiasis and other pathological conditions with the effect of heat clearing and diuresis promoting [1]. Previous photochemical studies on this species have led to the isolation and structures elucidation of biflavonoids and lignans [2]. As part of our research work, further investigating led to the isolation of a new glucoside, selaginoside (**1**), and two known compounds, hinokiflavone (**2**) and 2,3-dihydroamentoflavone (**3**) (figure 1).

2. Results and discussion

Selaginoside (**1**) was obtained as a white amorphous powder, mp 190–192°C, $[\alpha]_D^{20}$ -59.1 (c 0.65, MeOH). The IR spectrum of **1** showed the presence of hydroxyl groups (3386 cm^{-1}), double bond (1643 cm^{-1}) and the carbon–oxygen bond (1076 cm^{-1}). Its molecular formula was determined as $\text{C}_{25}\text{H}_{44}\text{O}_{15}$ by HRFAB-MS (m/z 607.2574 $[\text{M} + \text{Na}]^+$). Completed acid hydrolysis of **1** afforded xylose and glucose identified by comparison with authentic samples on TLC chromatography, and 1 xylose and 2 glucoses were further determined by means of the data of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of **1** (table 1). In addition, the aglycon moiety of **1**

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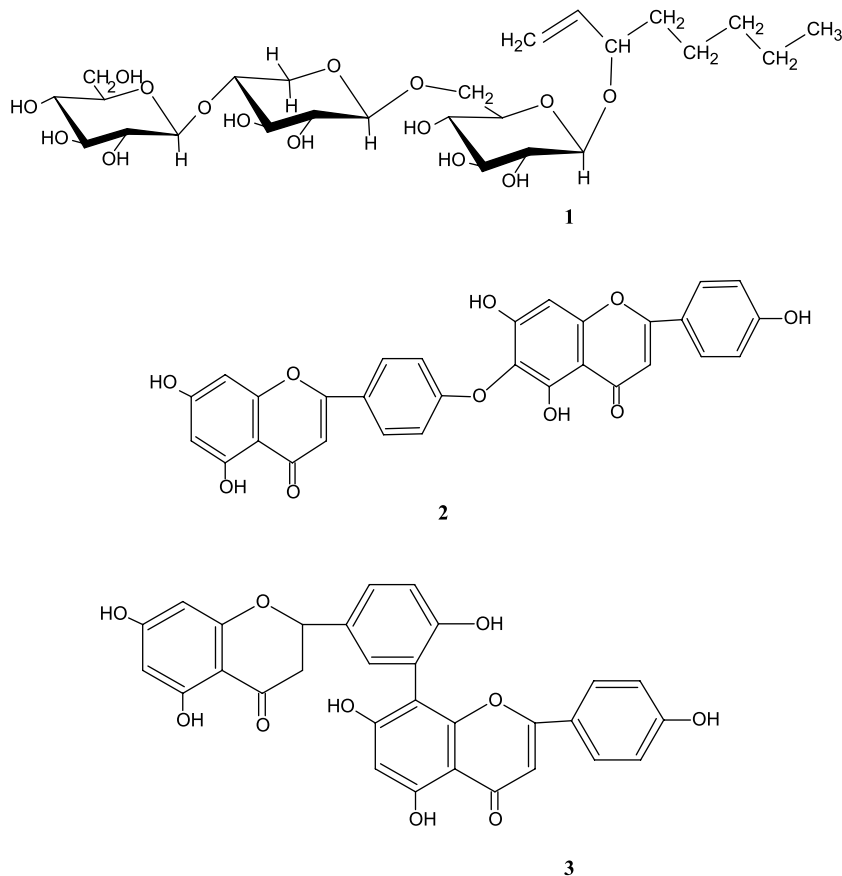


Figure 1. Structures of compounds 1–3.

was concluded as a liner enol with the data of DEPT, ^{13}C -NMR spectra of **1** (table 1) and there were four unsaturations in this molecule. In ^{13}C -NMR spectrum, the aglycon signals were observed at δ 115.3 (C-1), 140.7 (C-2), 80.7 (C-3), 35.1 (C-4), 24.9 (C-5), 32.2 (C-6), 22.8 (C-7) and 14.2 (C-8). These data agree well with those of β -D-glucopyranosid, 1-ethenylhexyl O- α -L-arabinopyranosyl-(1 \rightarrow 6)-O- $[\beta$ -D-glucopyranosyl-(1 \rightarrow 2)] reported in the literature [3]. The ^1H -NMR spectrum also contained the characteristic signals of aglycon moiety of **1** located at δ 5.15 (1H, *d*, $J = 10.5$ Hz, H-1), 6.13 (1H, *ddd*, $J = 6.5, 10.5, 17.5$ Hz, H-2) and 4.48 (1H, *dt*, $J = 6.0, 6.5$ Hz, H-3). For the sugars, the anomeric proton signals at δ 4.88 (1H, *d*, $J = 7.5$ Hz), 4.96 (1H, *d*, $J = 7.5$ Hz) and 5.04 (1H, *d*, $J = 8.5$ Hz) were assigned to H-1', H-1'' and H-1''' of glucose (inner), xylose and glucose respectively. The carbon signals of sugars were determined by means of ^{13}C -NMR and HMQC-TOCSY experiments (table 1). The connections of groups in the compound were determined by HMBC experiment. In HMBC spectra, the signal of H-1''' at δ 5.04 gave a cross-peak with the signal at δ 78.0 (C-4''), the signal of H-1'' at δ 4.96 gave a cross-peak with the signal at δ 69.8 (C-6') and the signal of H-1' at δ 4.88 gave a cross-peak with the signal at δ 80.7 (C-3), suggesting that the C-1''' of glucose was linked with C-4'' of xylose, C-1'' of xylose was linked with C-6' of glucose, and C-1' of glucose was linked with C-3 of aglycon. Thus, the structure of seliginoside (**1**) was determined as 1-octylenol-3-O- β -D-glucopyranosyl-

Table 1. ^{13}C and ^1H NMR spectral data of compound **1** (δ in ppm, J in Hz).

Position	$^{13}\text{C}^a$	DEPT ^a	$^1\text{H}^b$	Position	$^{13}\text{C}^a$	DEPT ^a	$^1\text{H}^b$
Aglycon				Sugar			
1	115.3	CH ₂	5.15 (H, <i>d</i> , $J = 10.5$ Hz)	Glc-(inner)			
		CHb	5.42 (H,d,J = 17.5)	C-1'	103.6	CH	4.88 (1H, <i>d</i> , $J = 7.5$ Hz)
2	140.7	CH	6.13 (1H, <i>ddd</i> , $J = 6.5, 10.5, 17.5$ Hz)	C-2'	75.3	CH	
3	80.7	CH	4.48 (1H, <i>dt</i> , $J = 6.0, 6.5$ Hz)	C-3'	78.6	CH	
4	35.1	CH ₂	1.66 (2H, <i>brd</i>)	C-4'	71.7	CH	
5	24.8	CH ₂	1.42 (2H, <i>brs</i>)	C-5'	77.3	CH	
6	32.2	CH ₂	1.13 (4H, <i>brs</i>)	C-6'	69.8	CH ₂	
7	22.8	CH ₂		Xyl-			
8	14.2	CH ₃	0.75 (3H, <i>t</i> , $J = 7.0$ Hz)	C-1''	105.5	CH	4.96 (1H, <i>d</i> , $J = 7.5$ Hz)
				C-2''	74.7	CH	
				C-3''	76.2	CH	
				C-4''	78.0	CH	
				C-5''	64.7	CH ₂	
				Glc-			
				C-1'''	103.7	CH	5.04 (1H, <i>d</i> , $J = 8.5$ Hz)
				C-2'''	74.3	CH	
				C-3'''	78.9	CH	
				C-4'''	71.6	CH	
				C-5'''	78.2	CH	
				C-6'''	62.6	CH ₂	3.62 (H, <i>dd</i> , $J = 11.0, 1.0$ Hz) 4.40(H,dd,J = 5,11)

^a Recorded at 125 MHz in pyridine-*d*₅.^b Recorded at 500 MHz in pyridine-*d*₅.

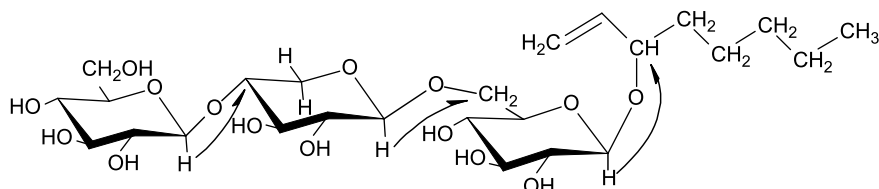


Figure 2. Selected HBMC correlations of compound 1.

(1 → 6)-β-D-xylcopyranosyl-(1 → 4)-β-D-glucopyranoside. The correlations of HMBC were shown in figure 2.

3. Experimental

3.1 General experimental procedures

Melting points were recorded on a AAE042 melting apparatus and were uncorrected. ¹H-NMR, ¹³C-NMR, DEPT and HMQC-TOCSY spectra were recorded on a INOVA-500 spectrometer using tetramethylsilane as internal standard. FAB-MS were recorded on a AutoSpec Ultima-Tof spectrometer. IR spectrum was taken on a Nicolet Impact 400 spectrometer and recorded in KBr pellets. Column chromatography was performed with silica gel (160–200 mesh, Qingdao Hhaiyang Chemical Co., LTD, China).

3.2 Plant material

The plant material of *Selaginella sinensis* was collected from Hebei Province, China in September 1999, and a voucher specimen (LD-99023), identified by Prof. Rui-Chao Lin, is deposited in the Museum for Material Medica, National Institute for the Control of Pharmaceutical and Biological Products, Beijing, China.

3.3 Extraction and isolation

The dried whole plants of *Selaginella sinensis* (10 kg) were extracted with hot 95% EtOH. After removal of the solvent by evaporation, the EtOH extract was successively extracted with CHCl₃, EtOAc, Bu-OH to give three fractions. The EtOAc fraction (126 g) was subjected to silica gel column chromatography and eluted with CHCl₃-MeOH (100:1–100:50) to yield compounds 2 (30 mg) and compound 3 (18 mg). The Bu-OH fraction (237 g) was subjected to silica gel column chromatography and eluted with CHCl₃-MeOH (10:1–10:5) to yield compound 1 (41 mg).

Selaginolide (1): C₂₅H₄₄O₁₅, white powder; mp 190–192°C; UV λ_{max} (MeOH) nm (logε): 268.8 (2.78); IR (KBr) ν_{max} (cm⁻¹): 1643 (C=C), 3386 (–OH), 1076, 1038 (C–O); HRFAB-MS *m/z* 607.2574 [M + Na]⁺ (calcd for C₂₅H₄₄O₁₅ + Na, 607.2578), ¹H-NMR and ¹³C-NMR data are shown in table 1.

Hinokiflavone (2): C₃₀H₁₈O₁₀, yellow powder; ¹H-NMR (500 MHz, DMSO-*d*₆) δ: 7.83 (2H, *d*, *J* = 8.8 Hz, H-2''', H-6'''), 7.78 (2H, *d*, *J* = 8.5 Hz, H-2', H-6'), 7.01 (2H, *d*, *J* = 8.5 Hz, H-3', H-5'), 6.86 (2H, *d*, *J* = 8.8 Hz, H-3''', 5'''), 6.55 (1H, *s*, H-3), 6.44

(1H, *s*, H-3''), 6.36 (1H, *d*, *J* = 1.9 Hz, H-8), 6.36 (1H, *s*, H-8''), 6.11 (1H, *d*, *J* = 1.9 Hz, H-6); FAB-MS *m/z*: 539 [M + H]⁺(32), 268 (57), 285 (14) [4].

2,3-Dihydroamentoflavone (**3**): C₃₀H₂₀O₁₀, yellow powder; ¹H-NMR (500 MHz, C₅D₅N-d₅) δ: 7.48 (2H, *d*, *J* = 9 Hz, H-2''', H-6'''), 7.36 (1H, *d*, *J* = 9 Hz, H-2'), 7.35 (1H, *d*, *J* = 2 Hz, H-6'), 6.98 (1H, *d*, *J* = 9, H-5'), 6.71 (2H, *d*, *J* = 9, H-3''', H-5'''), 6.52 (1H, *s*, H-3''), 6.30 (1H, *s*, H-6''), 5.82 (1H, *d*, *J* = 2 Hz, H-8), 5.80 (1H, *d*, *J* = 2 Hz, H-6), 5.33 (1H, *dd*, *J* = 13, 3 Hz, H-2), 3.10 (1H, *dd*, *J* = 13, 17 Hz, H-3), 2.67(1H, *dd*, *J* = 3, 17 Hz, H-3); FAB-MS *m/z*: 541 [M + H]⁺(19), 268 (67), 153 (25) [4].

References

- [1] *Xinhua Bencao Gangyao*, Jiangsu Provincial Research Institute of Botany, Shanghai, PR China (1990).
- [2] Z. Dai, G.L. Wang, Q.Y. Hou. *Chin. Tradi. Herb. Drugs*, **32**, 784 (2001).
- [3] T. Ikeda, T. Miyase, A. Ueno. *Natural Medicines*, **48**, 32 (1994).
- [4] K.R. Markham, C. Sheppard, H. Geiger. *Phytochemistry*, **26**, 3335 (1987).