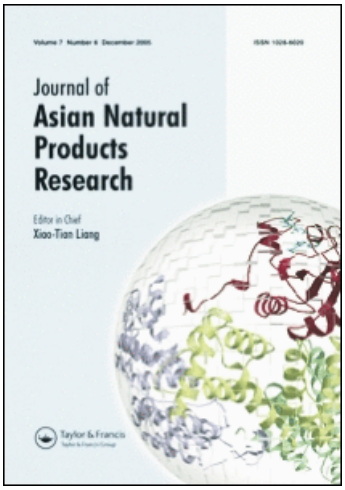

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Selaginellin C, a new natural pigment from *Selaginella pulvinata Maxim* (Hook et Grev.)

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A novel compound, selaginellin C (**1**), was isolated from *Selaginella pulvinata Maxim* (Hook et Grev.) as (*R*,*S*)-4-((1,2-dihydroxyethyl)-2′,4′-dihydroxy-3-((4-hydroxyphenyl)ethynyl)biphenyl-2-yl)((4-hydroxyphenyl)methylene)cyclohexa-2,5-dienone, along with two known compounds, selaginellin (**2**) and selaginellin A (**3**). The structure of the new compound was elucidated on the basis of 1D and 2D NMR as well as HR-ESI-MS spectroscopic analysis.

Keywords: *Selaginella pulvinata Maxim*; selaginellin; selaginellin A; selaginellin C

1. Introduction

Selaginella pulvinata Maxim (Hook et Grev.) has been used as a traditional Chinese medicine for the effectiveness in promoting blood circulation. Pharmacological investigation of the genus *Selaginella* revealed its biological activities such as anti-oxidant, antivirus, anti-inflammation, and effects on cardiovascular system protection [1–5]. A number of flavones, phenylpropanoids, alkaloids, organic acids, anthraquinones, and steroids have been identified from the genus *Selaginella*. As a continuation of our work, we report herein the isolation and structural elucidation of a new alkynyl phenol, the fourth unusual natural pigment, selaginellin C (**1**), from the 75% ethanolic extract of *S. pulvinata Maxim* (Hook et Grev.) along with two known compounds, selaginellin (**2**) and selaginellin A (**3**) (Figure 1). Compounds **2** and **3** were isolated from this plant for the first time, and selaginellin (**2**) can inhibit homocysteine-induced senescence of endothelial cells (which we will report in another article).

2. Results and discussion

Compound **1** was obtained as a brown powder. ESI-MS gave the quasi-molecular ion peak at *m/z* 559.5 $[M+H]^+$ and its molecular formula was deduced as $C_{35}H_{26}O_7$ by HR-ESI-MS at *m/z* 559.5936 $[M+H]^+$ with 23 degrees of unsaturation. Its UV spectrum showed absorption maxima at 299 and 430 nm. The IR spectrum showed the presence of hydroxyl (3426 cm^{-1}), alkynyl (2402 cm^{-1}), and aromatic ring (1510 cm^{-1}). As evident from the ^1H NMR spectrum, four phenolic active hydrogens were proved through D_2O exchange at δ 9.89 (1H, s), 9.47 (1H, s), and 9.23 (2H, s). By comparing the ^1H NMR spectral data of compound **1** with those of selaginellins A and B [6] and based on the ^1H–^1H COSY

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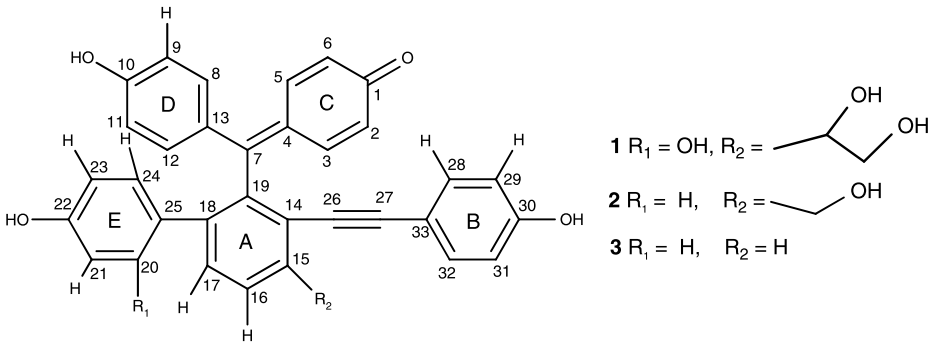

Figure 1. Structures of compounds **1**–**3**.

spectrum, the protons at δ 6.98 (H-3, 5, 8, 12, 4H, d, $J = 9.0$ Hz) and 6.56 (H-2, 6, 9, 11, 4H, d, $J = 9.0$ Hz) should have eight aromatic protons of rings C and D, because the delocalization of π-electrons over the two rings makes them close to equivalent [7]. Especially, in dimethylsulfoxide-d_6 (DMSO), the extensive delocalization takes place and the aromatic rings of quinonic groups are free to rotate, which make the aromatic protons attached to either ring C or D chemically equivalent [8]. The carbon signals at δ 100.8 (C-27) and 84.1 (C-26) showed the presence of an acetylene bond. The ^{1}H NMR spectrum indicated the presence of another *para*-benzene moiety [δ 6.89 (H-28, 32, 2H, d, $J = 8.5$ Hz) and 6.71 (H-29, 31, 2H, d, $J = 8.5$ Hz)]. In the HMBC spectrum, the correlations between H-28, 32, H-29, 31 and C-27 showed that the C≡C bond was connected to ring B (Figure 2). Two aliphatic methylenes at δ 64.4 (C-34) and 61.4 (C-35) should be linked to hydroxyl groups, respectively, by chemical shifts. In the HMBC spectrum, there were correlations between H-35 and C-15, C-26, and also between H-16 and C-14, C-35. These indicated that the substitution of vicinal diol should be at C-15 of ring A. The other three aromatic protons [δ 7.65 (H-24, d, $J = 8.0$ Hz), 6.73 (H-23, dd, $J = 8.0, 2.0$ Hz), 6.64 (H-21, d, $J = 2.0$ Hz)] should belong to ring E based on the ^{1}H–^{1}H COSY and HMBC spectra. The correlations between H-24, H-23 and C-18, and also

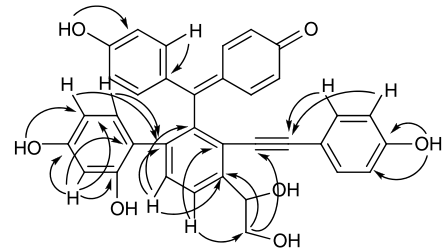

Figure 2. Key HMBC correlations of compound **1**.

between H-21 and C-23, C-22, C-20, C-25, showed that ring E was connected to ring A at C-18 position.

Thus, the structure of compound **1** was established to be (*R*,*S*)-4-((1,2-dihydroxyethyl)-2′,4′-dihydroxy-3-((4-hydroxyphenyl)ethynyl)biphenyl-2-yl)((4-hydroxyphenyl)methylene)cyclohexa-2,5-dienone, and named selaginellin C.

For the known compounds, selaginellin (**2**) and selaginellin A (**3**), isolated from *S. pulvinata Maxim* (Hook et Grev.) for the first time, were identified by 1D and 2D NMR spectroscopic analysis as well as by the comparison of their spectral data with those reported [6,9].

3. Experimental

3.1 General experimental procedures

Melting points were measured using a Buchi-540 melting point apparatus (uncorrected). UV spectra were performed on a Shimadzu UV-2450 instrument

Table 1. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectral data of compounds **1**–**3** (DMSO-d_6).

Position	δ_H, J (Hz)	δ_C		
		Selaginellin C	Selaginellin	Selaginellin A
1		155.8	185.6	185.5
2	6.56 d (9.0)	114.3	115.6	139.6
3	6.98 d (9.0)	129.7	133.0	127.7
4		132.7	129.5	130.5
5	6.98 d (9.0)	129.7	132.7	127.9
6	6.56 d (9.0)	114.3	114.5	138.4
7		151.4	159.1	158.7
8	6.98 d (9.0)	129.7	129.7	132.9
9	6.56 d (9.0)	114.3	115.0	115.0
10		155.8	156.4	159.2
11	6.56 d (9.0)	114.3	115.0	115.0
12	6.98 d (9.0)	129.7	129.7	132.9
13		132.7	142.4	129.0
14		118.0	121.0	124.0
15		141.8	142.4	130.0
16	7.50 d (8.0)	125.7	127.0	129.3
17	7.75 d (8.0)	118.6	129.5	129.9
18		139.2	140.4	142.4
19		132.9	140.2	140.3
20		155.8	129.5	129.4
21	6.64 d (2.0)	112.0	114.7	114.7
22		158.0	156.4	156.5
23	6.73 dd (8.0, 2.0)	114.7	114.7	114.7
24	7.65 d (8.0)	120.7	129.5	129.4
25		129.8	130.6	130.5
26		84.1	83.7	86.5
27		100.8	98.6	93.5
28	6.89 d (8.5)	132.2	132.7	132.8
29	6.71 d (8.5)	115.7	115.6	115.5
30		158.0	158.1	158.0
31	6.71 d (8.5)	115.7	115.6	115.5
32	6.89 d (8.5)	132.2	132.7	132.8
33		113.0	112.2	112.0
34	5.20 t (5.6)	64.3	61.3	
35	4.63 d (5.6)	61.4		
1/10-OH	9.23			
22-OH	9.47			
24-OH	9.23			
30-OH	9.89			

Note: Coupling constants (J) in Hz are given in parentheses. The assignments were based on DEPT, ^{1}H–^{1}H COSY, HMQC, and HMBC experiments.

(Shimadzu Corporation, Tokyo, Japan). IR spectra were obtained on a Nicolet Avatar (Nicolet Instrument Corporation, Madison, WI, USA) 360 FT-IR instrument as a film on KBr disk. NMR spectra were recorded using Varian (Varian, Inc. Corporate, CA, USA) INOVA-400 and INOVA-500 spectrometers with TMS as the internal standard. MS spectra were measured using an LCQ-Advantage (Thermo Electron. Corporation, CA, USA) mass spectrometer. HR-MS spectra were recorded using a Micromass Zabspec (Micromass UK Ltd, Manchester, UK) HR-MS spectrometer.

3.2 Plant material

Herbs of *S. pulvinata Maxim* (Hook et Grev.) were collected in Zhangjiajie of

Hunan Province, China, and identified by Associate Prof. Jin-Ping Li (Central South University, Changsha, China). A voucher specimen has been deposited at the School of Pharmaceutical Sciences, Central South University (No. JB-001).

3.3 Extraction and isolation

The whole herb of *S. pulvinata Maxim* (Hook et Grev.) (18.0 kg) was extracted with 75% EtOH and the solvent was removed to obtain a concentrated solution. The filtrate of the solution was successively partitioned with petroleum ether (PE) and ethyl acetate (EtOAc) to afford three parts: PE- (28.8 g), EtOAc- (105.3 g), and H_2O-soluble parts. The H_2O-soluble part was chromatographed over a polyamide column with EtOH–H_2O gradient elution (30, 60, 95%). The 30% EtOH portion was subjected to column chromatography on silica gel eluting with $CHCl_3$–MeOH (in gradient) and preparative HPLC (70% MeOH) to yield selaginellin (**2**, 100 mg) and selaginellin A (**3**, 40 mg). The 60% EtOH portion was further purified on silica gel column chromatography eluting with $CHCl_3$–MeOH (in gradient) and preparative HPLC [YMC-Pack ODS-A (250 × 30 mm), 1% HAc–MeOH (100:45), flow rate 30.0 ml/min, retention time 60 min] to yield compound **1** (140 mg).

3.3.1 Compound *1*

A brown powder; carbonization temperature 252°C; UV λ_{max}^{MeOH} (nm): 299, 430. IR (KBr) ν_{max} (cm^{-1}): 3426, 2402, 1510. ^1H and ^{13}C NMR spectral data: see Table 1; ESI-MS: *m/z* 559.5 $[M+H]^+$, HR-ESI-MS: *m/z* 559.5936 $[M+H]^+$ (calcd for $C_{35}H_{27}O_7$, 559.5847).

3.3.2 Compound *2*

A red powder; UV λ_{max}^{MeOH} (nm): 226, 255, 432; IR (KBr) ν_{max} (cm^{-1}): 3318, 2925, 2193, 1595, 1509, 1467, 1271, 1163; ^{13}C NMR (100 MHz, DMSO-d_6): see Table 1; ESI-MS: *m/z* 513.1 $[M+H]^+$.

3.3.3 Compound *3*

A red powder; UV λ_{max}^{MeOH} (nm): 217, 280, 426; IR (KBr) ν_{max} (cm^{-1}): 3420, 2924, 2854, 1608, 1593, 1509, 1467, 1160, 835; ^{13}C NMR (100 MHz, DMSO-d_6): see Table 1; ESI-MS: *m/z* 483.1 $[M+H]^+$.

Acknowledgements

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