Indian Journal of Chemistry
Vol. 47B, May 2008, pp. 773-777

Note

Two new neolignan glycosides from *Pteris multifida* Poir

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Received 2 April 2007; accepted (revised) 31 January 2008

Two new neolignan glycosides, named as multifidoside A **1** and B **2**, together with four known compounds have been isolated from the roots of *Pteris multifida* Poir. The structures of multifidoside A and B have been characterized by spectroscopic and chemical means as (7*S*, 8*S*)-$\Delta^{7'}$-2,9′-dihydroxy-5′-methoxy-7,3′-dioxy-8,4′-neolignan-4-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside and (7*S*, 8*S*)-$\Delta^{7'}$-2,9,9′-trihydroxy-7,3′-dioxy-8,4′-neolignan-4-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside. The known compounds are identified by comparing their spectral data with those of authentic samples or data reported in the literature.

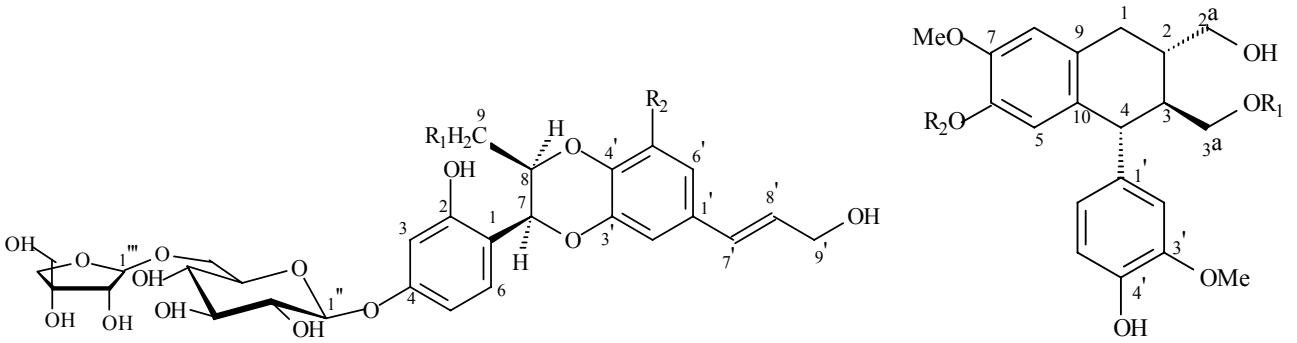
Keywords: *Pteris multifida* Poir, neolignan glycoside, (7*S*, 8*S*)-$\Delta^{7'}$-2, 9′-dihydroxy-5′-methoxy-7, 3′-dioxy-8,4′-neolignan-4-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside, (7*S*, 8*S*)-$\Delta^{7'}$-2,9, 9′-trihydroxy-7, 3′-dioxy-8, 4′-neolignan-4-*O*-β-D-apiofur anosyl-(1→6)-β-D-glucopyranoside, multifidoside A, multifidoside B

Pteris multifida Poir is widely distributed in the south and southwest districts of China (Chinese name "fengweicao")[1], which has been mainly used as a traditional Chinese folk drug for the treatment of eczema, haematemesis, enteritis, diarrhea, bacillary dysentery cold and are also known to have anticancer and antibacterial effects[2]. However, very little is known about its chemical constituents except for antimutagentic activity[3]. A previous paper reported the isolation and characterization of six compounds from EtOAc fraction obtained by partition of the EtOH extract[4]. In continuation of the phytochemical research on this plant, is now reported the isolation and structural elucidation of two new neolignan glycosides, multifidoside A, **1** and B, **2** from the *n*-BuOH fraction of the EtOH extract, along with the four known compounds (**Figure 1**), scaphopetalone **3** (Ref. 5), (-)-isolariciresinol 3α-*O*-β-apiofuranosyl-(1→2)-*O*-β-glucopyranoside **4** (Ref. 6) 6,7-dihydroxy-3'-methoxy-4',5'-methy lenedioxyisoflavone 6-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside **5** (Ref. 7) polyporusterone I, **6** (ref. 8).

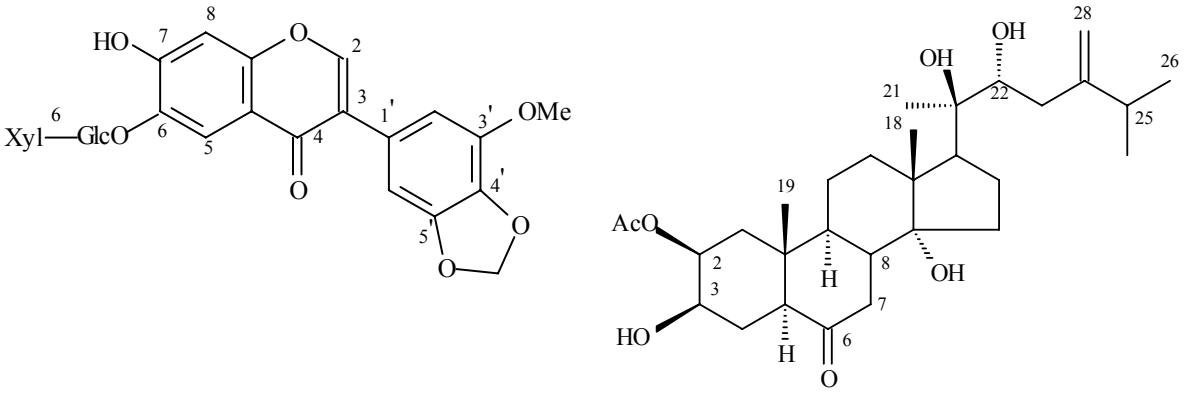
Compound **1** (**Figure 1**), to which is assigned the name multifidoside A, was obtained as white amorphous powder and has a molecular formula of $C_{28}H_{32}O_{13}$, determined by HRFAB-MS which showed a quasi-molecular formula ion peak at *m/z* 659.2289 $[M+H]^+$ (calcd. for $C_{30}H_{38}O_{15}$, 658.2211). This formula indicated 12 degrees of unsaturation. The ^{13}C NMR and DEPT spectra of **1** clearly displayed 30 carbon signals (2 × CH_3, 4×CH_2, 16 × CH, 8 × C), of which 11 could be assigned to a glucose unit (δ_C 104.5, 74.8, 77.5, 71.1, 77.2, 67.8) and an apiose unit (δ_C 111.1, 77.8, 80.4, 75.0, 65.8), and the remaining 19 carbon signals were assigned to the aglycone. The UV-Vis spectrum showed the absorption bands at 208, 266 nm. Its IR spectrum (KBr) showed the absorption bands at 3328 (hydroxyl), 1630 (olefinic C=C), 1601 and 1516 cm^{-1} (phenyl). The ^1H and ^{13}C NMR spectra of **1** showed the presence of two *meta*-coupling aromatic protons signals [δ_H 6.98 (1H, d, *J*=1.7 Hz) and 6.83 (1H, d, *J*=1.7 Hz), δ_C 110.8 and 116.8], three *asym*-coupling aromatic protons signals [δ_H 6.42 (1H, d, *J*=2.4 Hz), 6.44 (1H, dd, *J*=7.9, 2.4 Hz) and 6.96 (1H, d, *J*=7.9 Hz), δ_C 103.9, 108.7 and 116.2], one methoxyl group [δ_H 3.76 (3H, s), δ_C 55.5], a (*E*)-coniferyl alcohol signals [δ_H 4.03 (2H, br d, *J*=5.7 Hz), 6.39 (1H, d, *J*=15.3 Hz) and 6.20 (1H, dd, *J*=15.3, 5.7 Hz), δ_C 61.5, 128.8 and 126.7], (ref 9), two methenyl signals [δ_H 4.79 (1H, d, *J*=8.0 Hz) and 4.33 (1H, dq, *J*=8.0, 6.4 Hz), δ_C 79.5 and 72.9], a methyl signal [δ_H 1.19 (3H, d, *J*=6.6 Hz), δ_C 17.2], one hydroxyl signal [δ_H 9.68 (1H, s, HO-2), δ_C 154.8 (C-2)], and two anomeric protons of sugars [δ_H 4.81 (1H, d, *J*=7.5 Hz, H-1″) and 5.28 (1H, d, *J*=2.2 Hz, H-1‴), the corresponding anomeric carbon signals at δ_C 104.5 (C-1″) and 111.1 (C-1‴)]. Comparison of the ^1H and ^{13}C NMR data of **1** with those of eusiderin E (Ref. 10) indicated that **1** is a 7,3′-dioxy-8,4′-neolignan glycoside. In HMBC experiment, the correlations of δ_C 145.8 (C-4) with δ_H 4.81 (H-1″ of Glc)/6.42 (H-3)/6.44 (H-5)/6.96 (H-6); δ_C 131.2 (C-1′) with δ_H 6.39 (H-7′)/6.83 (H-6′)/6.98 (H-2′); δ_C 149.0 (C-5′) with δ_H 3.76 (-OMe)/6.83 (H-6′); and δ_C 154.8 (C-2) with δ_H 6.42 (H-3)/6.96 (H-6), suggested that the site of attachment of the disaccharide chain, (*E*)-coniferyl alcohol side-chain, the methoxyl and hydroxyl groups were at C-4, C-1′, C-5′ and C-2 of the aglycone, respectively.

On acid hydrolysis, compound **1** gave glucose and apiose respectively, which was compared with authentic sample by co-TLC, showing the presence of D-glucose and D-apiose. In addition, it was deduced from the FAB-MS spectral observation of *m/z* 507 $[M+H-132]^+$ and *m/z* 345 $[M+H-132-162]^+$ fragment ions, arising from the elimination of an apiose and a glucose unit, indicating the apiose was terminal sugars and the glucose was attached to the aglycone. Comparison of ^{13}C NMR data of the sugar moieties with literature values[11] revealed that the glucose was present in pyranoside form and the apiose was in furanoside form. The HMBC experiment of **1** showed long-range correlations (**Figure 2**) between the H-1‴ (δ_H 5.28) of apiose and the C-6″(δ_C 67.8) of glucose as well as between the H-6″ (δ_H 4.05/3.96) of glucose and the C-1‴ (δ_C 111.1) of apiose, thus suggesting the linkage of apiose-(1→6)-glucose. The relative stereochemistry of **1** was determined based on the ^{13}C NMR spectra data and the *J* values measured in the ^1H NMR spectrum. The β-configuration on C-1‴ anomeric orientation of apiose was confirmed by comparing the ^{13}C NMR spectra data of **1** with those of *α*-D-(δ_C 104.5) and β-D-apiofuranosides (δ_C 111.5), respectively[12], and the glucose had the β-configuration according to the coupling constant (*J*=7.5 Hz) of H-1″ of glucose. The coupling constants observed between H-7′ and H-8′ (*J*=15.3 Hz) suggested that the (*E*)-coniferyl alcohol side-chain had a *trans*-configuration. The signals of H-7 and H-8 in the ^1H NMR spectrum appeared at slightly lower fields (δ_H 4.79 and 4.33, respectively) with a larger coupling constant (*J*=8.0 Hz) indicating a *trans*-orientation (axial-axial) of H-7 and H-8 pair in **1** (ref. 13). Comparison of the specific optical rotation of **1** with that of the known verticillatoside B (Ref. 14), suggested **1** to have the same absolute configurations of C-7 and C-8 as *S* and *S*, respectively. On these grounds, multifidoside A was elucidated as (7*S*, 8*S*)-$\Delta^{7'}$-2,9′-dihydroxy-5′-methoxy-7,3′-dioxy-8,4′-neolignan-4-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Compound **2** was obtained as white amorphous powder, possessing a molecular formula of $C_{28}H_{36}O_{15}$ by HR FAB-MS data (*m/z* 625.2132 $[M+H]^+$, calcd for 624.2054), 14 mass units lower than that of **1**. Its UV-Vis, IR and MS spectra were very similar to those of **1**. The ^{13}C NMR and DEPT spectra clearly displayed 29 carbon signals (5 × CH_2, 17 × CH, 7 ×C). Comparing the NMR data with those of **1**, the



1 R_1=H R_2=OMe **2** R_1=OH R_2=H **3** R_1=H R_2=Me **4** R_1=Glc—Api R_2=H



5 **6**

Figure 1 — The structure of compounds **1-6**

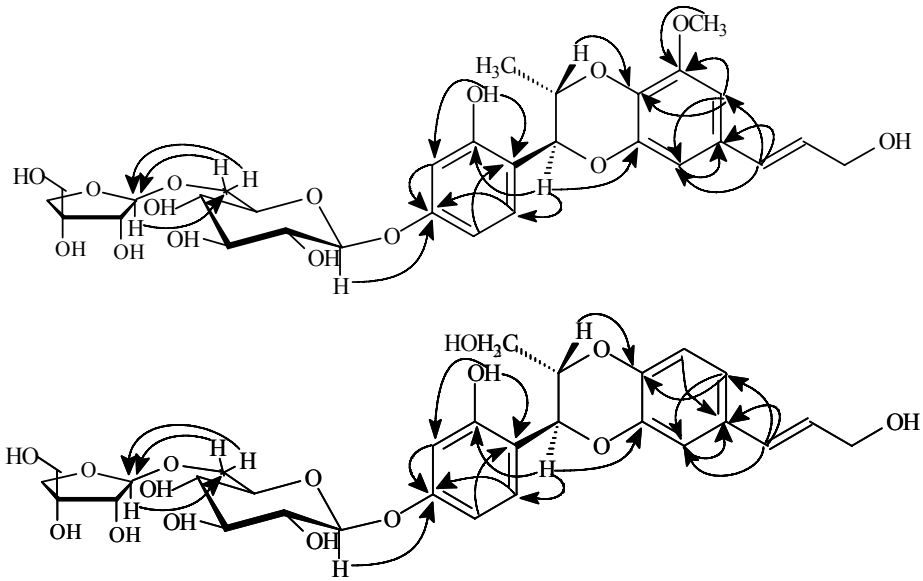


Figure 2 — The key HMBC correlations of compounds **1** and **2**

NMR signals of the sugar moiety were almost the same as those of **1**, except that an extra hydroxyl proton signal at δ_H 5.18 (HO-9) and an aromatic proton singlet at δ_H 6.82 (1H, d, *J*=8.2 Hz, H-5′) was present in ^{1}H NMR spectrum of **2**, and a methyl carbon signal (δ_C 17.2) disappeared and a methylene carbon signal (δ_C 60.8) appeared in the ^{13}C NMR and DEPT spectra of **2**. All these data indicated that a hydroxyl group is linked to C-9 and a methoxyl group disappeared from C-5′ of **1** (**Table I**). It was further supported by the upfield shift signal of C-5′ (from δ_C 149.0 to 117.3) and downfield shift signal of C-9 (from δ_C 17.2 to 60.8) in ^{13}C NMR spectra of **2** (**Table I**). The absolute configurations of C-7 and C-8 were determined as *S* and *S*, respectively, by comparison of the specific optical rotation of **2** with that of **1**. These data suggested **2** to be the analogue of **1**. Therefore, the structure of **2** was characterized as (7*S*, 8*S*)-$\Delta^{7'}$-2,9,9′-trihydroxy-7,3′-dioxy-8,4′-neolignan-5-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

The known compounds were identified by comparing their spectral data with reported values in the literature or their melting points and R_f values with authentic samples.

Experimental Section

General Procedures

Melting points were observed with a Chinese X-4 melting point apparatus and are uncorrected. Optical rotations were measured with Perkin-Elmer 241 digital polarimeter. UV-Vis and IR (KBr disks) spectra were obtained on Shimadzu UV-300 (double beam) and Alpha-Centauri FT-TR spectrometer. ^{1}H and ^{13}C NMR (DEPT) spectra were recorded on Bruker AM-400 NMR spectrometer. Mass spectra were obtained on ZAB-HS and MAT-112 mass spectrometer, respectively. Separation and purification were performed by column chromatography over silica gel (100-200, 200-300 mesh). TLC was performed on silica gel GF_{254} plates. The spots were visualized by UV (254 nm) and EtOH-H_2SO_4.

Plant Material

The roots of *P. multifida* Poir. were collected in August 2002, from Pingjiang district of Hunan Province, China. It was identified by Prof. Lian Yun-Shan (Department of Biology, Northwest Normal University). A voucher specimen (No.107083) of the plant is deposited in the Herbarium of the Botany Department, Northwest Normal University, Lanzhou, 730070, China.

Extraction and Isolation

The air-dried and powered roots of *P. multifida* Poir. (5.0 kg) were soaked in 95% EtOH (15 L, 7 d×3) at RT. After removing the solvent, the crude extract (250 g) was suspended in warm water and partitioned successively with petroleum ether (60-90°C), $CHCl_3$, EtOAc and *n*-BuOH, concentrated under reduced pressure. The *n*-BuOH-soluble fraction was concentrated under reduced pressure to give 78.5

Table I — ^{1}H and ^{13}C NMR spectral data of compounds **1** and **2** (400 and 100 MHz, J_{Hz}, DMSO-d_6, TMS)*

	1				**2**			
No	δ_H	δ_C	DEPT	HMBC(H→C)	δ_H	δ_C	DEPT	HMBC(H→C)
1		131.2	C	3,6,5,7,HO-2		131.1	C	3,6,5,7,HO-2
2		154.8	C	3,6,7,HO-2		155.0	C	3,6,7,HO-2
3	2.42 (1H,d,2.4)	103.9	CH	HO-2,5	6.473 (1H,d,2.4)	104.0	CH	HO-2,5
4		145.8	C	1″,3,5,6		145.9	C	1″,3,5,6
5	6.44 (1H,dd,7.9,2.4)	108.7	CH	3,6	6.45 (1H,dd,7.9,2.4)	108.5	CH	3,6
6	6.96 (1H,d,7.9)	116.2	CH	5,7	6.96 (1H,d,7.9)	116.7	CH	5,7
7	4.79 (1H,d,8.0)	79.5	CH	8,6	4.76 (1H,d,8.0)	80.2	CH	8,6
8	4.33 (1H,dq,8.0,6.4)	72.9	CH	7,9	4.30 (1H,8.0,6.4)	73.8	CH	7,9
9	1.19 (3H,d,6.6)	17.2	CH_3	8	3.76 (2H,br d,11.2)	60.8	CH_2	8,OH-9
1′		131.2	C	2′,6′,7′		131.3	C	2′,6′,7′,5′
2′	6.98 (1H,d,1.7)	110.8	CH	7′,6′	6.93 (1H,d,1.7)	110.9	CH	7′,6′
3′		143.6	C	2′,7		143.4	C	2′,7,5′
4′		135.5	C	6′,8		136.7	C	6′,8,5′
5′		149.0	C	CH_3O-,6′	6.82 (1H,d,8.2)	117.3	CH	6′
6′	6.83 (1H,d,1.7)	116.8	CH	2′,7′	6.88 (1H,dd,1.7,8.2)	118.2	CH	2′,5′
7′	6.39 (1H,d,15.3)	128.8	CH	2′,6′	6.38 (1H,d,15.3)	128.6	CH	2′,6′
8′	7.20 (1H,dd,15.3,5.7)	126.7	CH	9′	6.19 (1H,dd,15.3,5.7)	126.5	CH	9′
9′	4.03 (2H,brd,5.7)	61.5	CH_2	8′,HO-9′	4.02 (2H,brd,5.7)	61.6	CH_2	8′,HO-9′
HO-2	9.68 (1H,s)				9.70 (1H,s)			
HO-9					5.18 (1H,s)			
MeO-5′	3.76 (1H,s)	55.5	CH_3					
Glc-1″	4.81 (1H,d, 7.5)	104.5	CH		4.82 (1H,d, 7.5)	104.6	CH	
2″	3.82 (1H,dd,9.1,7.4)	74.8	CH		3.82 (1H,d,9.1,7.4)	74.7	CH	
3″	3.77 (1H,dd,9.1,8.5)	77.5	CH		3.78 (1H,d,9.1,8.5)	77.5	CH	
4″	3.94 (1H,dd,9.9,8.5)	71.1	CH		3.94 (1H,dd,9.9,8.5)	71.0	CH	
5″	3.82 (1H,ddd,9.9,6.0,1.6)	77.2	CH		3.81(1H,dd,9.9,6.0,1.6)	77.1	CH	
6″	4.05 (1H,dd,11.3,1.6) 3.96 (1H,dd,11.3,6.0)	67.8	CH_2	1‴	4.06 (1H,dd,11.3,1.6) 3.94 (1H,dd,11.3,6.0)	68.0	CH_2	1‴
Api-1‴	5.28 (1H,d, 2.2)	111.1	CH	6″	5.27 (1H,d, 2.2)	111.0	CH	6″
2‴	4.29 (1H,d, 2.2)	77.8	CH		3.98 (1H,d, 2.2)	77.9	CH	
3‴		86.4	C			86.4	C	
4‴	3.75 (1H,d, 9.4) 3.96 (1H,d, 9.4)	75.0	CH_2		3.77 (1H,d, 9.4) 3.95 (1H,d, 9.4)	75.1	CH_2	
5‴	3.69 (2H,s)	65.8	CH_2		3.68 (2H,s)	65.7	CH_2	

g of residues, which was isolated on a silica gel column eluting with $CHCl_3$-MeOH (8:0→1:5) in increasing polarity and combined by monitoring with TLC to give three fractions (A, B and C). Fraction A (3.9 g) was further fractionated over silica gel column and eluted with $CHCl_3$-MeOH (4:1) to obtain **6** (21 mg). Fraction B (2.6 g) was purified by a silica gel column using $CHCl_3$- MeOH (3:1→1:1) as elution gradient to afford **1** (15 mg) and **2** (12 mg). Fraction C (3.1 g) was rechromatographed over a silica gel column eluting with EtOAc-MeOH (3:1→2:1) to yield **3** (9 mg) and subfraction. Subfraction was further purified by preparative TLC (silica gel) and developed with $CHCl_3$-MeOH (1:1) as development to provide compound **4** (13 mg) and **5** (11 mg).

Compound **1**: White amorphous powder (MeOH), m.p. 216-18°C; $[\alpha]_D^{20}$ -11.2° (c=0.45, MeOH); HRFAB-MS: *m/z* 639.2289 $[M+H]^+$ (calcd. for $C_{30}H_{38}O_{15}$, 638.2211); UV-Vis λ_{max}^{MeOH} (nm): 208, 266; IR (KBr): 3328 (OH), 1630 (olefinic C=C), 1601, 1516 cm^{-1} (phenyl); FAB-MS: *m/z* 639 [M+H], 507

$[M+H-132]^+$ and 345 $[M+H-162-132]^+$; for ^1H and ^{13}C NMR data see **Table I**.

Compound **2**: White amorphous powder (MeOH), m.p. 212-15°C; $[\alpha]_D^{20}$ -10.8° (c=0.45, MeOH); HRFAB-MS: *m/z* 625.2048 $[M+H]^+$ (calcd. for $C_{29}H_{36}O_{15}$, 624.2054); UV-Vis λ_{max}^{MeOH} (nm): 209, 266; IR (KBr): 3327(OH), 1628 (olefinic C=C), 1602, 1515 cm^{-1} (phenyl); FAB-MS: *m/z* 625 $[M+H]^+$, 493 $[M+H-132]^+$ and 331 $[M+H-162-132]^+$; for ^1H and ^{13}C NMR data see **Table I**.

Acknowledgements

Author are grateful to Prof. Zheng Shang-zhen (College of Chemistry and Chemical Engineering, Northwest Normal University) for experimental assistance, and to the Educational Foundation of Gansu Province of China (Grant No. 2003039-04) for financial support.

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