A New Acylated Stilbene Glycoside from *Acanthopanax brachypus*

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Received August 3, 2008, Accepted December 11, 2008

Key Words: *Acanthopanax brachypus*, Araliaceae, Acylated stilbene glycoside, Phenolic glycoside

The *Acanthopanax* genus belonging to the Araliaceae family includes 37 species around the world, are widely distributed in Korea, Japan, China and the far-eastern region of Russia. 26 species and 18 varieties grow in mainland China.[1,2] The root and stem bark of these plants have been clinically used for a long time as a tonic and sedative, as well as for the treatment of rheumatism, diabetes, chronic, bronchitis, hypertension, anti-stress and ischemic heart disease, and gastric ulcer.[3-6] As a endangered shrub in the wild due to overharvesting and loss of habitat through deforestation, *Acanthopanax brachypus* Harms is distributed in a narrow geographical area, most in the loess plateau of the northwest of China.[7-8] Research indicates that the seeds of *A. brachypus* contains many kinds of microelements indispensable to human body, can relax women's menopause syndrome and exhibit immunostimulatory and anticancer activities, and its rhizomatic extracts has also been successfully used for inhibition of the various allergic responses in China and Korea.[9-11] Nowadays, the other parts of this plant such as the roots, leaves and flowers are employed for various therapeutic purposes.[12-14] To date, however, the research mainly concentrated on the reproductive biology and ecology, there has been few studies on the chemical composition and biological activity. Only six compounds,[15,16] syringaresinol diglucoside, syringin, sucrose, *β*-sitosterol, fatty acid and olefine acid have been previously isolated from this plant. With the aim to find active principle and provide the reference for quality control and effective utilization of *Acanthopanax* species,[17-21] further phytochemical investigation led to the isolation of one new acylated stilbene glycoside, namely 3-*O*-methyl-(*E*)-resveratrol 5-*O*-*β*-*D*-apiofuranosyl-(1→6)-*β*-*D*-[2″-(*E*)-cinnamoyl]-glucopyranoside **1**, together with three known phenolic glycosides, namely (*E*)-resveratrol 3-*O*-*α*-*D*-glucopyranoside **2**, (*E*)-3-hydroxyanethole 3-*O*-*β*-*D*-glucopyranoside **3** and orcinol *O*-*β*-*D*-glucopyranoside **4**, were isolated for the first time from the stem bark of *A. brachypus*. In the present communication, we describe the isolation and structural elucidation of these compounds.

Compound **1** as a pale yellowish powder from MeOH, its positive-ion HR-FAB-MS exhibited the molecular ion at *m/z* 667.2381 $[M+H]^+$, corresponding to the molecular formula $C_{35}H_{38}O_{13}$, which indicated 17 degrees of unsaturation. The fragmention ions at *m/z* 537, 535, 405, 243 and 131 indicated that **1** contains a hexose-pentose and a cinnamoyl moiety. The UV spectrum exhibited absorptions at 220, 308 and 324 nm, suggesting the presence of a conjugated aromatic system.[22] The IR spectrum apart from hydroxyl (3429 cm^{-1}), aromatic rings (1600, 1512, 1456 cm^{-1}) and glycosidic bond (1058 cm^{-1}) absorption bands, showed an additional carbonyl absorption bands at 1698, 1632 and 970 cm^{-1}, indicating the presence of an ester group conjugated with a *trans*-double bond.[23,24] The ^{1}H NMR spectrum of **1** showed the presence of two anomeric protons, resonating at δ_H 4.91 (1H, d, J = 7.5 Hz) and 5.10 (1H, d, J = 2.4 Hz), in addition to the signals for a 1,3,5-trisubstituted aromatic ring at δ_H 6.70 (1H, br s), 6.40 (1H, br s) and 6.63 (1H, br s), one methoxy group at δ_H 3.81 (3H, s), a *para*-disubstituted aromatic ring at δ_H 7.43 (2H, d, J = 8.5 Hz, H-2′, 6′) and 6.88 (2H, d, J = 8.5 Hz, H-3′, 5′), and two *trans*-olefinic protons at δ_H 6.85/7.01 (each H, d, J = 16.0 Hz).[25] These spectra were consistent with those published for (*E*)-resveratrol[26,27] and (*E*)-resveratrol 3-*O*-*β*-*D*-glucopyranoside,[28,29] indicating that **1** had an (*E*)-resveratrol aglycon moiety. In the NMR and DEPT spectrum of **1**, the signals of one anomeric carbon (δ_C 101.3), four methines (δ_C 76.8, 74.5, 71.3 and 76.9) and one methylene (δ_C 68.2) indicated that the

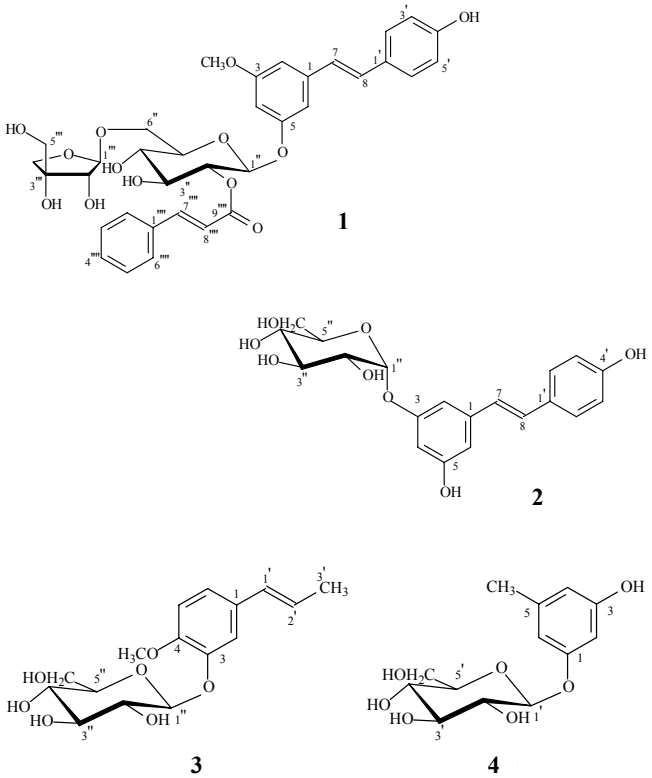

Figure 1. The structure of compounds **1-4** isolated from *Acanthopanax brachypus*.

hexose of the disaccharide moiety was *D*-glucopyranose with *β*-anomeric configuration on the basis of the coupling constant (J = 7.5 Hz) of the ^{1}H NMR signal at δ_H 4.91, and the pentose was *D*-apiofuranose with *β*-configuration based on the anomeric proton [δ_H 5.10 (1H, d, J = 2.4 Hz)] and anomeric carbon (δ_C 109.5), one methine (δ_C 78.2), two methylenes (δ_C 74.8 and 65.1) and one quaternary carbon (δ_C 80.7) signals.[30] The remaining signals at δ_H 6.30/7.23 (2H, d, J = 16.0 Hz), 7.48 (2H, d, J = 7.6 Hz), 7.31 (2H, dd, J = 7.0 and 7.6 Hz), 7.35 (1H, t, J = 7.0 Hz), and δ_C 164.8 indicated a *trans*-cinnamoyl moiety in **1**. In the FAB-MS spectrum of **1**, the significant ion peaks at *m/z* 537 $[M+H\text{-cinnamoyl}]^+$, 535 $[M+H\text{-apiosyl}]^+$, 405 $[M+H\text{-cinnamoyl-apiosyl}]^+$, 243 $[M+H\text{-cinnamoyl-apiosyl-glucosyl}]^+$, 131 $[\text{cinnamoyl}]^+$ also indicated the presence of cinnamoyl, glucosyl and apiosyl groups in **1**. This conclusion was further evidenced by the detection of *trans*-cinnamic acid, *D*-glucose and *D*-apiose (in the ratio of 1:1, determined by *co*-TLC with authentic sample and GC-MS analysis[31]) after acid hydrolysis.

By comparing ^{13}C NMR spectral data of **1** with 5-*O*-methyl-(*E*)-resveratrol 3-*O*-*β*-*D*-apiofuranosyl-(1→ 6)-*β*-*D*-glucopyranoside,[32] indicated that the cinnamoyl moiety was attached to the C-2″ of glucose as this carbon signal was shifted downfield[33-36] by 1.90 ppm, while the C-1″ and C-3″ signals shifted upfield by 1.20 and 3.40 ppm, respectively. The terminal *D*-apiosyl group connected C-6″ of the glucosyl group by a (1→6)-*O*-glycosidic linkage, because C-6″ was shifted downfield about 5 ppm. The glucosyl group connected C-5 of the aglycon through an *O*-glycosidic bond because of the downfield chemical shift of C-5. The methoxyl group was linked to C-3 as its shifted downfield. These aforementioned conclusions were also supported by the correlatons of H-2″/C-9‴, H-1‴/C-6″, H-6″/C-1‴, H-1″/C-5, H-OCH_3/C-3, H-1″/H-6, H-2″/H-4″, H-3″/H-5″ and H-OCH_3/H-2 in the HMBC and ROESY spectra (Fig. 2). On the basis of the foregoing studies, the structure of **1** was established as 3-*O*-methyl-(*E*)-resveratrol 5-*O*-*β*-*D*-apiofuranosyl-(1→6)-*β*-*D*-[2″-(*E*)-cinnamoyl]-glucopyranoside.

Compound **2** was elucidated as (*E*)-resveratrol 3-*O*-*α*-*D*-glucopyranoside by comparing its NMR data with those reported in the literature.[37,38]

Compound **3** was hydrolyzed in acid solution to give *D*-glucose detected by TLC, further characterized as (*E*)-3-hydroxyanethole 3-*O*-*β*-*D*-glucopyranoside by detailed spectroscopic analysis and comparisons of its physical and spectral data with reported values.[39]

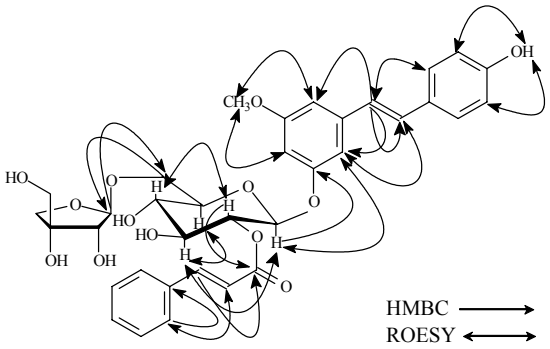

Figure 2. Significant HMBC ($^{2\text{-}3}J_{CH}$) and ROESY correlations for compound **1**.

Compound **4** exhibited NMR and melting point data identical to values in the literature,[40,41] thus it was established as orcinol *O*-*β*-*D*-glucopyranoside.

To our knowledge, compound **2, 3** and **4** were also isolated for the first time from the stem bark of *A. brachypus*.

Experimental Section

General experimental procedures. Melting points were obtained on an X-4 digital micro-melting point apparatus and

Table 1. ^{1}H and ^{13}C NMR assignments of compounds **1** in (400 and 100 MHz, J_{Hz}, in CD_3OD, TMS)[a]

No.	δ_C (DEPT)	δ_H (J_{Hz})	HMBC (H→C)
Aglycon moiety			
1	141.5 (C)		
2	107.3 (CH)	6.70 (1H, br s)	1, 3, 4, 6, α
3	160.1 (C)		
4	104.0 (CH)	6.40 (1H, br s)	2, 3, 5, 6
5	159.3 (C)		
6	107.8 (CH)	6.63 (1H, br s)	1, 2, 4, 5, α
7	126.8 (CH)	6.85 (1H, d, 16.0)	2, 6, 1′, β
8	129.8 (CH)	7.01 (1H, d, 16.0)	1, 2′, 6′, α
9	55.9 (CH_3)	3.81 (3H, s)	3
1′	131.6 (C)		
2′	128.7 (CH)	7.43 (1H, d, 8.5)	3′, 4′, β
3′	115.4 (CH)	6.88 (1H, d, 8.5)	1′, 4′
4′	158.7 (C)		
5′	115.4 (CH)	6.88 (1H, d, 8.5)	1′, 4′
6′	128.7 (CH)	7.43 (1H, d, 8.5)	4′, 5′, β
Sugar moiety			
1″	101.3 (CH)	4.91 (1H, d, 7.5)	5, 2″
2″	76.8 (CH)	4.53 (1H, dd, 9.5, 7.5)	1″, 3″, 9‴
3″	74.5(CH)	3.41 (1H, t, 9.5)	2″, 4″
4″	71.3 (CH)	3.45 (1H, m)	3″, 5″
5″	76.9 (CH)	3.58 (1H, m)	4″, 6″
6″	68.2 (CH_2)	3.98 (1H, dd, 11.5, 1.8) 3.71 (1H, dd, 11.5, 5.0)	5″, 1‴
1‴	109.5 (CH)	5.10 (1H, d, 2.4)	6″, 3‴, 4‴
2‴	78.2 (CH)	3.74 (1H, d, 2.4)	5‴
3‴	80.7 (C)		
4‴	74.8 (CH_2)	3.87/3.61 (2H, d, 9.1)	3‴, 5‴
5‴	65.1 (CH_2)	3.39/3.36 (2H, d, 10.0)	4‴
Ester moiety			
1⁗	133.8 (C)		
2⁗	130.2 (CH)	7.48 (1H, d, 7.6)	1⁗, 4⁗, 6⁗, 7⁗
3⁗	128.1 (CH)	7.31 (1H, dd, 7.6, 7.0)	1⁗, 2⁗, 5⁗
4⁗	129.2 (CH)	7.35 (1H, t, 7.0)	2⁗, 6⁗
5⁗	128.1 (CH)	7.31 (1H, dd, 7.6, 7.0)	1⁗, 3⁗
6⁗	130.2 (CH)	7.48 (1H, d, 7.6)	1⁗, 4⁗, 7⁗
7⁗	144.5 (CH)	7.23 (1H, d, 16.0)	2⁗, 8⁗, 9⁗
8⁗	117.4 (CH)	6.30 (1H, d, 16.0)	1⁗, 7⁗, 9⁗
9⁗	164.8 (C)		

[a]Assigniments were confirmed by 1D and 2D NMR methods.

uncorrected. Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter. UV spectra were recorded on a Shimadzu UV-300 spectrophotometer. IR spectra were recorded on IMPACT-400 FTIR spectrometer with KBr pellets. ^{1}H (400 MHz), ^{13}C (100 MHz) and 2D NMR spectra were determined on a Bruker DRX-400 spectrometer using tetramethylsilane as the internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Mass spectra were obtained on VG Auto Spec-3000 mass spectrometer. GC-MS: GC6890N-MSD5973N; HP-5 MS fused silica capillary column (30 m × 0.25 mm, film thinkness 0.25 μm). Column chromatography was carried out on silica gel (100-200, 200-300 mesh) and Sephadex LH-20 (25-100 μm). Thin-layer chromatography (TLC) was performed on precoated sillica gel plates (GF_{254}), and spots were visualized under UV light (254 and 365 nm) by spraying proper colored reagent.

Plant materials. The stem bark of *A. brachypus* were collected in August of 2007, from Qingyang of Gansu Province, and were identified by Prof. Xiao-qiang Guo, Department of Life-Sciences, Longdong University. A voucher specimen (10732) was deposited in the Herbarium of the Department of Life-Sciences, Longdong University, People's Republic of China.

Extraction and isolation. The air-dried and pulverized stem barks of *A. brachypus* (5.0 kg) were extracted three times with 95% EtOH (15 L×7 d, each time) at room temperature, and then the extracts were combined and concentrated under reduced pressure at 60 °C to yield 242 g of a brown viscous residue. The EtOH extract was suspended in water and partitioned successively with *n*-hexane, EtOAc and *n*-BuOH. The EtOAc-soluble extract (188 g) was subjected to silica-gel column and eluated with *n*-hexane, $CHCl_3$, $CHCl_3$-Me_2CO (from 5:1 to 1:5, v/v), Me_2CO and Me_2CO-MeOH (from 10:1 to 1:10, v/v) linear gradient, the eluted fractions were examined by analytical TLC and similar fractions were pooled together to give 18 main fractions (A_1-A_{18}). Fraction A_5 was rechromatographed over silica-gel column eluting with $CHCl_3$-MeOH (4:1, v/v) and further purified by preparative TLC (MeOH/$CHCl_3$/*n*-hexane, 1:5:2, v/v) to afford compound **4** (24 mg). Fraction A_8 was chromatographed over silica-gel column with a gradient mixture of $CHCl_3$-MeOH (from 8:1 to 1:8, v/v) to give two subtraction (A_{81} and A_{82}). Subfraction A_{81} was chromatographed on Sephadex LH-20 with MeOH-H_2O (1:1, v/v) to afford compound **3** (40 mg). Subfraction A_{82} was rechromatographed on silica-gel column with EtOAc-MeOH (5:2, v/v) to afford compound **2** (16 mg). Fraction A_{13} was further purified on silica-gel column eluting stepwise with $CHCl_3$-MeOH (from 5:1 to 1:8, v/v), and then on Sephadex LH-20 eluting with MeOH to obtain compound **1** (31 mg).

3-*O*-Methyl-(*E*)-resveratrol 5-*O*-*β*-*D*-apiofuranosyl-(1→6)-*β*-*D*-[2″-(*E*)-cinnamoyl]-glucopyranoside (1): Pale yellowish powder (MeOH), mp. 232-233 °C, $[\alpha]_D^{22}$ -32.9° (*c* 0.14, MeOH); UV λ_{max}^{MeOH} (log ε): 220 (4.24), 308 (4.46) and 324 (4.56) nm; IR ν_{max}^{KBr} : 3429, 1698, 1632, 1600, 1512, 1456, 1278, 1140, 1058, 970 cm^{-1}; HR-FAB-MS (positive mode) *m/z*: 667.2381 $[M+H]^+$ (calculated for $C_{35}H_{39}O_{13}$, 667.2391); FAB-MS (positive mode) *m/z*: 667 $[M+H]^+$, 537 $[M+H-130]^+$, 535 $[M+H-132]^+$, 405 $[M+H-130-132]^+$, 243 $[M+H-130-132-162]^+$, 131 $[cinnamoyl]^+$; ^{1}H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) data see Table 1.

(*E*)-Resveratrol 3-*O*-*α*-*D*-glucopyranoside (2): White acicular crystals (MeOH), mp. 202-205 °C; HR-FAB-MS (positive mode) *m/z*: 391.1384 $[M+H]^+$ (calculated for $C_{20}H_{23}O_8$, 391.1393); FAB-MS (positive mode) *m/z*: 391 $[M+H]^+$, 229 $[M+H-162]^+$; ^{1}H NMR (400 MHz, CD_3OD) δ_H: 7.38 (2H, d, J = 8.6 Hz, H-2' and 6'), 6.99 (1H, d, J = 16.1 Hz, H-8), 6.85 (1H, d, J = 16.1 Hz, H-7), 6.78 (2H, d, J = 8.6 Hz, H-3' and 5'), 6.71 (1H, br s, H-2), 6.57 (1H, br s, H-6), 6.39 (1H, br s, H-4), 5.33 (1H, d, J = 3.5 Hz, H-1"), 3.68-3.22 (6H, m, H-2", 3", 4", 5", 6"a, 6"b); ^{13}C NMR (100 MHz, CD_3OD) δ_C: 159.4 (C-3), 158.8 (C-5), 158.3 (C-4'), 140.6 (C-1), 128.8 (C-8), 128.5 (C-1′), 127.9 (C-2' and 6′), 126.1 (C-7), 115.5 (C-3' and 5'), 107.5 (C-6), 105.2 (C-4), 103.4 (C-2), 98.3 (C-1"), 73.8 (C-5"), 73.3 (C-3"), 72.4 (C-2"), 70.3 (C-4"), 61.2 (C-6").

(*E*)-3-Hydroxyanethole 3-*O*-*β*-*D*-glucopyranoside (3): White amorphous powder (MeOH), $[\alpha]_D^{22}$ -26.5° (*c* 0.35, MeOH); lit.[39]: -28° (*c* 0.40, MeOH); HR-FAB-MS (positive mode) *m/z*: 327.1439 $[M+H]^+$ (calculated for $C_{16}H_{23}O_7$, 327.1444), 165 $[M+H-162]^+$; ^{1}H NMR (400 MHz, CD_3OD) δ_H: 7.32 (1H, d, J = 1.5 Hz, H-2), 7.08 (1H, dd, J = 8.0 and 1.5 Hz, H-6), 6.92 (1H, d, J = 8.0 Hz, H-5), 6.40 (1H, d, J = 16.0 Hz, H-1'), 6.23 (1H, dq, J = 16.0 and 6.1 Hz, H-2′), 4.92 (1H, d, J = 7.5 Hz, H-1″), 3.84 (1H, dd, J = 11.9 and 1.8 Hz, H-6″a), 3.75 (3H, s, CH_3O), 3.61 (1H, dd, J = 4.6 and 11.9 Hz, H-6″b), 3.38 (1H, dd, J = 7.5 and 9.0 Hz, H-2″), 3.34 (1H, m, H-3″), 3.26 (1H, m, H-4″), 3.24 (1H, m, H-5″), 1.68 (3H, d, J = 6.1 Hz, H-3′); ^{13}C NMR (100 MHz, CD_3OD) δ_C: 149.8 (C-4), 148.6 (C-3), 132.1 (C-1), 131.8 (C-1′), 124.5 (C-2′), 121.6 (C-6), 114.5 (C-2), 113.5 (C-5), 102.1 (C-1″), 78.6 (C-3″), 77.8 (C-5″), 74.5 (C-2″), 71.3 (C-4″), 61.9 (C-6″), 56.4 (OCH_3), 18.6 (C-3′); Significant HMBC ($^{2\text{-}3}J_{CH}$) and ROESY correlations: H-2/C-3, C-4, C-6 and C-1′; H-5/C-1, C-3 and C-4; H-6/C-2, C-4 and C-1′; H-1′/C-2, C-6, C-2′ and C-3′; H-2′/C-1, C-1′ and C-3′; H-3′/C-1′ and C-2′; H-OCH_3/C-4; H-1″/C-3; H-1″/H-2 and H-3″; H-2/H-2′; H-5/H-OCH_3.

Orcinol *O*-*β*-*D*-glucopyranoside (4): White amorphous powder (MeOH), mp. 131-132 °C, lit.[42]: 132-133 °C; FAB-MS (positive mode) *m/z*: 287 $[M+H]^+$, 125 $[M+H-162]^+$; ^{1}H NMR (400 MHz, CD_3OD) δ_H: 6.38 (1H, br s, H-2), 6.26 (1H, br s, H-4), 6.25 (1H, br s, H-6), 4.91 (1H, d, J = 7.4 Hz, H-1'), 3.78 (1H, dd, J = 11.8 and 1.6 Hz, H-6'a), 3.59 (1H, dd, J = 4.5 and 11.8 Hz, H-6'b), 3.48 (1H, m, H-4'), 3.46 (1H, dd, J = 7.4 and 9.0 Hz, H-2'), 3.42 (1H, m, H-3'), 3.22 (1H, m, H-5'), 2.16 (3H, s, CH_3); ^{13}C NMR (100 MHz, CD_3OD) δ_C: 159.1 (C-1), 158.2 (C-3), 141.2 (C-5), 111.2 (C-6), 109.8 (C-4), 103.4 (C-2), 101.8 (C-1′), 78.3 (C-3′), 78.1 (C-5′), 74.9 (C-2′), 71.8 (C-4′), 62.7 (C-6′), 21.8 (CH_3).

Acid hydrolysis of compounds 1 and determination of the absolute configuration of the monosaccharide. Compounds **1** (10 mg) were dissolved in MeOH (10 mL) and 2N HCl (5 mL), respectively. The mixtures were refluxed with magnetic stirring in a water bath at 90 °C for 2 h. After cooling, the reaction mixture was diluted with 5 mL of H_2O, then extracted twice with EtOAc. The EtOAc phase was evaporated, and *trans*-cinnamic acid was identified by TLC with standard samples. The aqueous layer were neutralized by passing through an ion-exchange resin (Amberlite MB-3) column eluted with

H_2O, then concentrated and dried to furnish a monosaccharide residue. The residue was trimethylsilylated with 1-(trimethylsilyl)-imidazole at ambient temperature for 2 h. After the excess reagent was decomposed with H_2O, the mixture was partitioned between *n*-hexane (2 mL) and H_2O (2 mL), and the *n*-hexane extract was concentrated and analyzed by GC under the following conditions: HP-5 MS fused silica capillary column (30 m × 0.25 mm, film thinkness 0.25 μm), column temperature at 230 °C, injection temperature at 250 °C, N_2 as carrier gas. In the acid hydrolysate of **1**, *D*-glucose and *D*-apiose were confirmed by comparison of the retention times of their derivatives with those of *D*-glucose (22.8 min), *L*-glucose (21.9 min), *D*-apiose (11.6 min), *L*-apiose (10.1 min), respectively.

Acknowledgments. This work was financially suported by the Postgraduates' Innovative Education Program (NWU Graduate Cross-discipline Funds, No. 08YJC20) of Northwest University, P. R. China. The authors are grateful to Prof. Qi-xiu Zhu and Prof. Fan-zhi Zhao of the Analytical Center of Lanzhou University for NMR and MS measurements.

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