Triterpenoid Saponins from the Stem Bark of *Acanthopanax brachypus* HARMS

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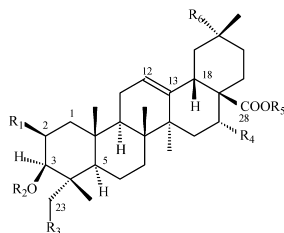
Two new triterpenoid saponins, brachyposide A (1) {3-*O*-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosyl-2β,3β,16α,23-tetrahydroxyolean-12-en-28-oic acid 28-*O*-β-D-apiofuranosyl-(1→3)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl ester} and brachyposide B (2) {3-*O*-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→3)-β-D-glucuronopyranosyl-2β,3β,23-trihydroxyolean-12-en-28-oic acid 28-*O*-β-D-xylopyranosyl-(1→4)-[β-D-apiofuranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester}, together with four known triterpenoid saponins, including tabguticoside A, nipponoside D, palmatoside E and ciwujianoside A_1, were isolated from the stem bark of *Acanthopanax brachypus*. Their structures were elucidated on the basis of spectroscopic and chemical evidence.

Key words *Acanthopanax brachypus*; Araliaceae; triterpenoid saponin; brachyposide A; brachyposide B

The *Acanthopanax* genus belonging to the Araliaceae family includes 37 species around the world, which are widely distributed in the northeast of Asia. Of these, 26 species and 18 varieties grow in mainland China, especially in the north.[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] Previous phytochemical studies on *Acanthopanax* species established the presence of triterpenoid saponins.[4—6]

An 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] Nowadays, the parts of this plant such as the roots, leaves and flowers are employed for various therapeutic purposes in China and Korea.[8] However, to date, the research has mainly concentrated on the reproductive biology and ecology, and there have been few studies on the chemical composition and biological activity. Only syringaresinol diglucoside, syringin, sucrose, β-sitosterol and fatty acids have been previously isolated from this plant.[9] Further phytochemical investigation led to the isolation of two new triterpenoid saponins: brachyposides A and B (**1** and **2**), along with tabguticoside A (**3**),[10] nipponoside D (**4**),[11] palmatoside E (**5**)[12] and ciwujianoside A_1 (**6**)[13] from the stem bark of *A. brachypus*. Among these known compounds, compounds **3** and **5** were isolated for the first time from this species.

Compound **1** was obtained as a white amorphous powder, and gave positive Liebermann-Burchard and Molish reactions. The positive FAB-MS displayed a pseudo-molecular ion peak at *m/z* 1539 $[M+Na]^+$. Combined with ^{13}C-NMR data, its molecular formula was determined as $C_{68}H_{108}O_{37}$ by (HR)-FAB-MS, *m/z* 1517.6621 $[M+H]^+$ (Calcd for $C_{68}H_{109}O_{37}$, 1517.6647). The IR spectrum exhibited absorptions at 3418 cm^{-1} (OH), 1730 cm^{-1} (ester carbonyl), and 1648 cm^{-1} (double bond). The spectral features and physicochemical properties revealed **1** to be a triterpenoid saponin. The compound displayed 68 carbon signals in ^{13}C-NMR spectrum and various distortionless enhancement by polarization transfer (DEPT) data, of which 30 were assigned to the aglycon and the remaining 45 to the sugar moieties (Table 1). The six sp^3 carbons at δ_C 15.3, 16.8, 17.9, 23.8, 27.4 and 33.3, and the two sp^2 carbons at δ_C 123.0 (CH) and 144.4 (C), coupled with information from the ^{1}H-NMR (six angular methyl proton singlets at δ_H 0.93, 1.06, 1.18, 1.39, 1.58 and 1.76, and a broad triplet-like vinyl proton signal at



Saponin	R_1	R_2	R_3	R_4	R_5	R_6
1	OH	GlcA-[(3←1)-Xyl]-(2←1)-Gal	OH	OH	Ara-(2←1)-Rha-(4←1)-Xyl-(3←1)-Api	CH_3
2	OH	GlcA-(3←1)-Gal-(3←1)-Glc	OH	H	Glc-(2←1)-Rha-[(3←1)-Api]-(4←1)-Xyl	CH_3
3	H	Glc	OH	H	Glc-(6←1)-Glc-(4←1)-Rha	CH_3
4	H	H	OH	H	Glc-(6←1)-Glc-(4←1)-Rha	CH_2OH
5	H	Ara-(2←1)-Rha-(3←1)-Glc	H	OH	Glc-(6←1)-Glc-(4←1)-Rha	CH_3
6	H	Ara-(2←1)-Glc	H	H	Glc-(6←1)-Glc-(4←1)-Rha	CH_3

Fig. 1. Structures of Isolated Triterpenoid Glycosides **1**—**6**

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δ_H 5.58 (br s), indicated that the aglycon possessed an olean-12-ene skeleton.

Furthermore, the hydroxymethyl (δ_H 3.72, 4.39 and δ_C 65.8) and ester carbonyl (δ_C 176.4) signals were assigned to C-23 and C-28 after an extensive 2D NMR study. Also, in the ^1H- and ^{13}C-NMR spectra, three oxygenated methine carbon signals (δ_C 70.5, 83.7, 74.2) were observed, the corresponding methine proton signals at δ_H 4.81 (br s), 4.38 (d, J=3.2 Hz) and 5.16 (br s), suggesting the methine protons could be placed at 2α, 3α and 16β, respectively. Thus, the aglycon was identified as 2β,3β,16α,23-tetrahydroxyolean-12-en-28-oic acid (polygalacic acid).[14] The chemical shifts of δ_C 83.7 (C-3) and 176.4 (C-28) revealed that **1** was a 3,28-bisdesmoside. On acid hydrolysis, **1** afforded D-glucuronic acid, D-galactose, D-xylose, L-arabinose, L-rhamnose and D-apiose in the ratio of 1 : 1 : 2 : 1 : 1 : 1 as component sugars, which were identified by TLC and GC analysis after derivatization.[15] The ^1H- and ^{13}C-NMR spectra also showed seven anomeric proton signals at δ_H 6.36 (d, J=2.8 Hz), 6.15 (br s), 6.05 (d, J=4.8 Hz), 5.57 (d, J=7.6 Hz), 5.33 (d, J=7.5 Hz), 5.18 (d, J=7.8 Hz) and 4.81 (d, J=7.5 Hz), as well as one methyl doublet at δ_H 1.75 (d, J=6.1 Hz), and the corresponding carbon signals at δ_C 93.8, 101.4, 111.6, 105.8, 106.2, 106.7, 105.5 and 18.5, respectively. The assignments of all protons and carbon signals of the respective sugar components and the sequence of the oligosaccharide chain were determined by DEPT, ^1H–^1H chemical shift correlation specroscopy (^1H–^1H COSY), ^1H-detected heteronuclear multiple-bond correlation (HMBC) and nuclear Overhauser effect spectroscopy (NOESY) spectra of **1**. The linkage of the sugar units at C-3 of the aglycone was established from the following HMBC correlations: H-1 (δ_H 5.57) of galactose with C-2 (δ_C 78.1) of glucuronic acid, H-1 (δ_H 5.33) of xylose with C-3 (δ_C 85.7) of glucuronic acid, H-1 (δ_H 4.81) of glucuronic acid with C-3 (δ_C 83.7) of the aglycone. Similarly, the sugar chain at C-28 was established from the following HMBC correlations: H-1 (δ_H 6.05) of apiose with C-3 (δ_C 84.5) of xylose, H-1 (δ_H 5.18) of xylose with C-4 (δ_C 83.1) of rhamnose, H-1 (δ_H 6.15) of rhamnose with C-2 (δ_C 75.9) of arabinose, H-1 (δ_H 6.36) of arabinose with C-28 (δ_C 176.4) of the aglycone. The same conclusion with regard to the sugar sequence was also drawn from the NOESY experiment. The D-galactose, D-xylose and D-glucuronic acid were determined as β-configurations based on their $^3J_{H1-H2}$ values (J=7.5—7.8 Hz), whereas the L-rhamnose was deduced as α-configuration from the broad singlet of its anomeric proton and the ^{13}C-NMR chemical shift values of C-3 and C-5.[16] The α-anomeric configuration of the L-arabinose ($^1C_4$ config-

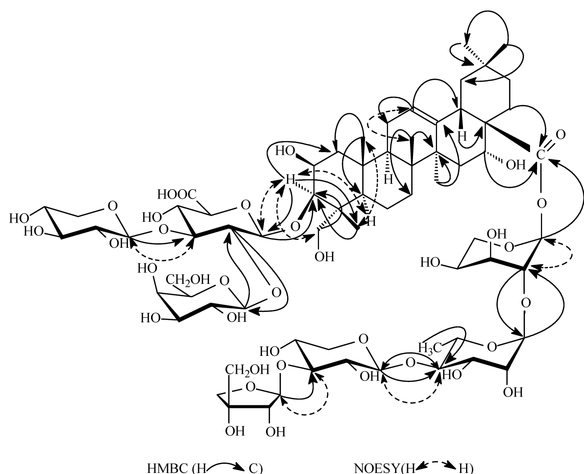

Fig. 2. Selected HMBC and NOESY Correlations of **1**

Table 1. ^{13}C-NMR (DEPT) Data of **1** and **2** in C_5D_5N (125 MHz)

No.	1	2	No.	1	2	No.	1	2
Aglycone			27	27.4, CH_3	27.1, CH_3	C-28-*O*-Sugar		
1	44.3, CH_2	44.5, CH_2	28	176.4, C	176.1, C	Ara (Glc)	Ara	Glc
2	70.5, CH	70.7, CH	29	33.3, CH_3	33.1, CH_3	1	93.8, CH	94.8, CH
3	83.7, CH	84.1, CH	30	23.8, CH_3	23.6, CH_3	2	75.9, CH	78.3, CH
4	42.9, C	42.6, C	C-3-*O*-Sugar			3	69.8, CH	78.5, CH
5	47.9, CH	47.8, CH	GlcA			4	65.8, CH	71.2, CH
6	18.2, CH_2	17.9, CH_2	1	105.5, CH	105.4, CH	5	62.5, CH_2	78.6, CH
7	33.4, CH_2	32.9, CH_2	2	78.1, CH	74.5, CH	6		62.4, CH_2
8	40.2, C	40.1, C	3	85.7, CH	86.5, CH	Rha		
9	47.8, CH	48.5, CH	4	71.6, CH	71.4, CH	1	101.4, CH	101.7, CH
10	37.2, C	37.0, C	5	77.1, CH	76.9, CH	2	71.8, CH	71.7, CH
11	24.1, CH_2	23.9, CH_2	6	171.8, C	172.1, C	3	72.3, CH	82.4, CH
12	123.0, CH	123.1, CH	Gal			4	83.1, CH	78.7, CH
13	144.4, C	144.2, C	1	105.8, CH	105.6, CH	5	68.5, CH	69.1, CH
14	42.6, C	42.1, C	2	74.5, CH	72.2, CH	6	18.5, CH_3	18.7, CH_3
15	36.3, CH_2	28.1, CH_2	3	75.4, CH	81.3, CH	Xyl		
16	74.2, CH	23.3, CH_2	4	70.6, CH	69.7, CH	1	106.7, CH	105.8, CH
17	49.9, C	47.3, C	5	76.5, CH	76.8, CH	2	74.3, CH	75.2, CH
18	41.3, CH	41.5, CH	6	61.6, CH_2	61.8, CH_2	3	84.5, CH	78.4, CH
19	47.1, CH_2	46.9, CH_2	Xyl (Glc)	Xyl	Glc	4	70.1, CH	70.9, CH
20	30.8, C	30.9, C	1	106.2, CH	104.7, CH	5	67.8, CH_2	67.4, CH_2
21	36.2, CH_2	35.7, CH_2	2	75.1, CH	75.4, CH	Api		
22	32.4, CH_2	32.6, CH_2	3	78.6, CH	77.4, CH	1	111.6, CH	111.8, CH
23	65.8, CH_2	65.4, CH_2	4	70.8, CH	70.1, CH	2	77.5, CH	77.6, CH
24	15.3, CH_3	15.1, CH_3	5	67.2, CH_2	77.6, CH	3	79.8, C	79.6, C
25	17.9, CH_3	17.6, CH_3	6		61.4, CH_2	4	74.6, CH_2	74.7, CH_2
26	16.8, CH_3	16.7, CH_3				5	64.6, CH_2	64.7, CH_2

Table 2. Selected ^{1}H-NMR Data of **1** and **2** in C_5D_5N (500 MHz, *J* in Hz)

No.	**1**	**2**
Aglycone		
2	4.81, br s	4.79, br s
3	4.38, d, 3.2	4.35, d, 3.2
12	5.58, br s	5.52, br s
16	5.16, br s	3.20
		2.86
18	3.48, dd, 14.0, 3.5	3.34, dd, 14.0, 4.0
19	1.38, dd, 13.5, 3.8	1.82
	2.76, t, 13.5	1.12
23	3.72, d, 11.0	3.71, d, 11.0
	4.39, d, 11.0	4.36, d, 11.0
24	1.39, s	1.39, s
25	1.58, s	1.57, s
26	1.18, s	1.17, s
27	1.76, s	1.28, s
29	0.93, s	0.93, s
30	1.06, s	1.05, s
C-3-*O*-Sugar		
GlcA		
1	4.81, d, 7.5	4.78, d, 7.6
2	4.35	3.88
3	4.28	4.25
4	4.45	4.42
5	4.52	4.50
Gal		
1	5.57, d, 7.6	5.51, d, 7.8
2	4.46	4.48
3	4.12	4.21
4	4.56, d, 3.1	4.50, d, 3.0
5	4.01	4.02
6	4.30	4.28
	4.52	4.51
	Xyl	Glc
1	5.33, d, 7.5	5.41, d, 7.7
2	3.94	4.02
3	4.11	4.17
4	4.12	4.24
5	3.67, t, 10.1	3.89
	4.27	
6		4.38
		4.49, dd, 12, 2
C-28-*O*-Sugar		
	Ara	Glc
1	6.36, d, 2.8	6.22, d, 7.5
2	4.65	4.26
3	3.92	4.29
4	4.28	4.27
5	4.22	3.96
	4.41	
6		4.32
		4.38, dd, 12, 2
Rha		
1	6.15, br s	6.18, br s
2	4.85	4.92
3	4.12	4.45
4	4.23	4.29
5	4.38	4.35
6	1.75, d, 6.1	1.78, d, 6.0
Xyl		
1	5.18, d, 7.8	5.28, d, 7.8
2	3.98	4.03
3	4.09	3.91
4	4.18	4.16
5	3.52	3.50
	4.21, d, 7.8	4.22, t, 7.8
Api		
1	6.05, d, 4.8	6.07, d, 5.0
2	4.76, d, 4.5	4.77, d, 4.5
4	4.03, d, 11.0	4.02, d, 11.0
	4.05, d, 11.0	4.05, d, 11.0
5	4.26, d, 9.5	4.19, d, 9.5
	4.65, d, 9.5	4.57, d, 9.5

GlcA = β-D-glucuronopyranosyl, Glc = β-D-glucopyranosyl, Ara = α-L-arabinopyranosyl, Gal = β-D-galactopyranosyl, Api = β-D-apifuranosyl, Rha = α-L-rhamnopyranosyl, Xyl = β-D-xylopyranosyl.

uration) was determined by its $^{3}J_{H1-H2}$ (2.8 Hz) and J_{C1-H1} (172 Hz) value.[17] The β-anomeric configuration of the D-apiose was determined by the comparison of the ^{13}C-NMR data for **1** with those for α and β-D-apiofuranosides, and the $^{3}J_{H1-H2}$ value of the apiose was similar to the reported data of β-D-apiofuranoside.[18] Based on the above evidence, the structure of **1** was determined to be 3-*O*-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosyl-2β,3β,16α,23-tetrahydroxyolean-12-en-28-oic acid 28-*O*-β-D-apiofuranosyl-(1→3)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl ester, and called brachyposide A (Fig. 1).

Compound **2** was obtained as a white amorphous powder with the molecular formula $C_{70}H_{112}O_{38}$, as determined from the data of the positive (HR)-FAB-MS (*m/z* 1561.6873 $[M+H]^+$, Calcd for $C_{70}H_{113}O_{38}$, 1561.6910), ^{13}C-NMR (70 carbon signals), and various DEPT spectra. The NMR and DEPT spectra of the aglycone **2** were almost similar to those of **1**, apart from the change of the oxymethine (δ_H 5.16 and δ_C 74.2) in **1** to methene (δ_H 2.86, 3.20 and δ_C 23.3) in **2**, suggesting the hydroxyl group at C-16 in **1** was absent in the aglycone **2**. Thus, the aglycone of **2** was identified as 2β,3β,23-trihydroxyolean-12-en-28-oic acid (bayogenin).[19] Secondly, the presence of seven sugars in **2** was apparent from the seven anomeric proton signals at δ_H 4.78 (d, J=7.6 Hz), 5.51 (d, J=7.8 Hz), 5.41 (d, J=7.7 Hz), 6.22 (d, J=7.5 Hz), 6.18 (br s), 5.28 (d, J=7.8 Hz) and 6.07 (d, J=5.0 Hz), which correlated with the corresponding carbon signals at δ_C 105.4, 105.6, 104.7, 94.8, 101.7, 105.8 and 111.8, respectively. Acid hydrolysis of **2** gave D-glucuronic acid, D-glucose, D-galactose, D-xylose, L-rhamnose and D-apiose in the ratio of 1 : 2 : 1 : 1 : 1 : 1 as component sugars, which were identified by TLC and GC analysis after derivatization.[15] The assignments of all protons and carbon signals of the respective sugar components and the sequence of the oligosaccharide chain were also determined by DEPT, ^{1}H–^{1}H COSY, HMBC and NOESY spectra of **2**. The β-anomeric configurations of both D-glucoses were evident from the large $^{3}J_{H1-H2}$ (J=7.5, 7.7 Hz). The anomeric configurations of the other sugar units were identical to the corresponding ones in compound **1**. Thus, the structure of **2** was determined to be 3-*O*-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→3)-β-D-glucuronopyranosyl-2β,3β,23-trihydroxyolean-12-en-28-oic acid 28-*O*-β-D-xylopyranosyl-(1→4)-[β-D-apiofuranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl ester, and termed brachyposide B (Fig. 1).

Experimental

General Procedures Melting points were determined on X-4 digital micro-melting point apparatus and were uncorrected. Optical rotations were measured with a Perkin-Elmer 341 digital polarimeter. IR spectra were recorded with KBr pellets on a Perkin-Elmer 577 spectrometer. GC analysis was performed with a Hewlett Packard 6890 Series gas chromatograph equipped with an H_2 flame ionization detector. The FAB-MS were recorded on a VG Autospec 3000 mass spectrometer, and the NMR spectra were recorded with a Bruker AMX-500 (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR). Chemical shifts were given in δ (ppm) with tetramethyl silane (TMS) as an internal standard and coupling constants (J) were reported in Hertz (Hz). Column chromatography was performed with Silica-gel H (Qingdao Haiyang Chemical Plant, P. R. China), Diaion HP-20 (Mitsubishi Chemical, Japan), Sephadex LH-20 (Pharmacia), and macroporous resin D101 (26—60 mesh, Tianjin Haiguang Chemical Company, P. R. China). Thin-layer chromatography (TLC) employed precoated Silica-gel GF_{254} plates (Qingdao Haiyang Chemical Plant, China) and detection was achieved by 10% H_2SO_4–EtOH for saponins, and aniline-phthalate reagents for sugars.

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

Extraction and Isolation The air-dried and pulverized stem bark of *A. brachypus* (30.0 kg) was extracted three times with 75% aqueous 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 give 1460 g of brown viscous residue. The residue was disolved in MeOH (1.5 l) and precipitated in acetone (3 l). The dry precipitate was suspended in H_2O, and further extracted with *n*-BuOH to retain the saponins which have less than nine sugar units.[20] The *n*-BuOH-soluble fraction (156 g) was subjected to column chromatography by a combination of D101 macroporous resin, eluted gradiently with H_2O, EtOH (10→95%) to give five fractions (Fr. A—E). Fraction A (22.3 g) was subjected to a silica gel column with a $CHCl_3$–MeOH gradient system (1 : 0→0 : 1), affording 8 subfractions. Subfractions 3 (1.1 g) and 7 (1.1 g) were respectively purified by repeated octadecyl silane (ODS) column chromatography (MeOH–H_2O) to afford compounds **4** (39.4 mg) and **3** (16.4 mg). Fraction C (17.5 g) was separated on Sephadex LH-20 column with MeOH, and further recrystallized with MeOH to provide compounds **5** (18.1 mg) and **6** (22.4 mg). Fraction E (14.7 g) was separated on Sephadex LH-20 column with MeOH, and further purified on ODS column with MeOH–H_2O to provide compounds **1** (10.8 mg) and **2** (13.2 mg).

Brachyposide A (**1**): White amorphous powder. $[\alpha]_D^{20}$ −36.5° (c=0.22, MeOH). IR (KBr) ν_{max} cm^{-1}: 3418, 2937, 1730, 1648, 1422, 1074. ^{1}H-NMR

(pyridine-d_5, 500 MHz) and ^{13}C-NMR (pyridine-d_5, 125 MHz): see Tables 1 and 2. (HR)-FAB-MS (positive) *m*/*z*: 1517.6621 $[M+H]^+$ (Calcd for $C_{68}H_{109}O_{37}$, 1517.6647).

Brachyposide B (**2**): White amorphous powder. $[\alpha]_D^{20}$ $-18.6°$ (c=0.18, MeOH). IR (KBr) ν_{max} cm^{-1}: 3422, 2938, 1727, 1652, 1423, 1072. ^{1}H-NMR (pyridine-d_5, 500 MHz) and ^{13}C-NMR (pyridine-d_5, 125 MHz): see Tables 1 and 2. (HR)-FAB-MS (positive) *m*/*z*: 1561.6873 $[M+H]^+$ (Calcd for $C_{70}H_{113}O_{38}$, 1561.6910).

Acid Hydrolysis of Compounds 1 and 2 and Determination of the Absolute Configuration of the Monosaccharide A solution of compounds **1** or **2** (5.0 mg) in 2 mol/l HCl–dioxane (1 : 1, 1 ml) was refluxed in a water bath at 90 °C for 2 h. After dioxane was removed, the solution was extracted with EtOAc (1 ml×3). The aqueous layer was neutralized by passing through an Amberlite MB-3 resin column eluted with H_2O, then concentrated and dried to furnish a monosaccharide residue. Then, the sugars were detected by TLC analysis [$CHCl_3$–CH_3OH–H_2O–HOAc (15 : 6 : 2 : 3), detection solution: aniline-phthalic acid] against the standard samples. The residue was dissolved in pyridine (0.2 ml), and then a pyridine solution (0.3 ml) of L-cysteine methyl ester hydrochloride (5 mg) was added to the solution. The mixture was kept at 60 °C for 1.5 h, dried *in vacuo*, and trimethylsilylated with hexamethyl-disilazane-trimethylchlorosilane (HMDS-TMCS) (0.1 ml) at 60 °C for 1 h. After being partitioned between *n*-hexane (0.5 ml) and H_2O (0.5 ml), 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 thickness 0.25 μm), column temperature at 230 °C, injection temperature at 250 °C, N_2 as carrier gas. The sugars were confirmed by comparison of the retention times of their derivatives with standard samples [retention time, D-glucuronic acid (20.1 min), D-glucose (24.7 min), D-galactose (26.6 min), D-xylose (17.5 min), L-rhamnose (19.3 min), L-arabinose (18.8 min) and D-apiose (12.8 min)]. The presence of D-glucuronic acid, D-galactose, D-xylose, L-arabinose, L-rhamnose and D-apiose in **1**, D-glucuronic acid, D-galactose, D-xylose, D-glucose, L-rhamnose and D-apiose in **2** were detected.

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