Two New Steroidal Saponins from the Processed *Polygonatum kingianum*

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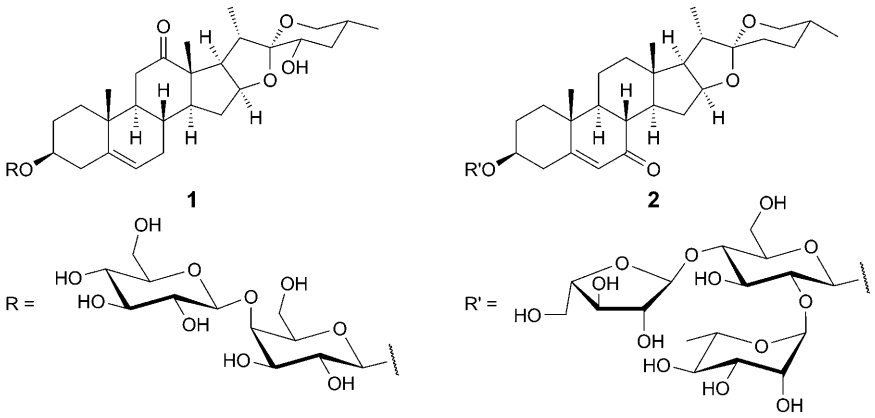
Two new spirostanol saponins, kingianoside I (**1**) and kingianoside K (**2**), corresponding to (3*β*,23*S*,25*R*)-23-hydroxy-12-oxospirost-5-en-3-yl 4-*O*-*β*-D-glucopyranosyl-*β*-D-galactopyranoside (**1**) and (3*β*,25*R*)-7-oxospirost-5-en-3-yl *α*-L-arabinofuranosyl-(1→4)-[6-deoxy-*α*-L-mannopyranosyl-(1→2)]-*β*-D-glucopyranoside (**2**), along with 13 known compounds, daucosterol, (25*R*)-kingianoside G, (25*RS*)-kingianoside A, pratioside D_1, (25*RS*)-pratioside D_1, (25*S*)-kingianoside C, kingianoside C, ginsenoside Rb_1, saponins Tb and Pb, dioscin, gracillin, and saponin Pa, were isolated from the processed rhizomes of *Polygonatum kingianum*. The structures of the new compounds were elucidated by detailed spectroscopic analyses, including 1D- and 2D-NMR techniques, and chemical methods. Compound **2** contains a novel unusual spirostanol saponin aglycone. Ginsenoside Rb_1 and saponin Tb were isolated for the first time from the genus *Polygonatum*. The 13 known compounds were detected for the first time in the processed *Polygonatum kingianum*.

Introduction. – The rhizomes of *Polygonatum kingianum* COLL. et HEMSL. (Liliaceae), one of the original plants commonly known as *Huang-jing* in traditional Chinese medicine, are used as a tonic remedy to treat lung troubles and ringworm [1]. Clinically, the processed (with yellow rice wine) products are routinely used since it is widely believed that this process would mitigate side-effects and enhance the effect of the tonic remedy.

The chemical constituents of rhizomes of several *Polygonatum* species have been studied by several groups [2–6], but no systematic study on the chemical constituents of the processed products has been reported so far. Previous phytochemical investigations on the fresh rhizomes of *P. kingianum* have resulted in the isolation of some steroidal saponins [7–9]. Our preliminary phytochemical studies on processed *P. kingianum* indicated that the levels of certain steroidal saponins were higher in processed *P. kingianum* than those in fresh *P. kingianum*, whereas the levels of some other chemical constituents were decreased. In addition, the UPLC/MS profile of the processed *P. kingianum* revealed a few constituents that have not been reported before [10]. As a result, our detailed chemical investigation on steroidal saponins of the processed *P. kingianum* led to the isolation of two new steroidal saponins, along with 13 known compounds. Compound **2**, kingianoside K, was found to possess a novel aglycone (with a C=C bond at C(5) and an oxo group in the *B* ring on the aglycone)

rarely encountered in steroidal saponins. Ginsenoside Rb_1 and saponin Tb were reported from the genus *Polygonatum* for the first time. In this article, we describe the isolation and structure elucidation of two new steroid saponins based on extensive spectral analyses, including 1D- and 2D-NMR spectral data, and chemical evidence.



Results and Discussion. – The crude extract of the processed *P. kingianum* was chromatographed on macroporous resin, silica gel, and octadecyl silane (ODS), and further purified by semi-preparative HPLC to afford 15 compounds. Compounds **1** and **2** were found to be new spirostanol saponins, and their structures were elucidated by 1D- and 2D-NMR in combination with MS studies. The other 13 compounds are known saponins, and they were identified by comparison of their physicochemical properties and the NMR data with those reported in the literature.

Kingianoside I (**1**) was obtained as a white amorphous powder. The HR-ESI-MS (negative-ion mode) of **1** indicated a molecular formula $C_{39}H_{60}O_{15}$, which was derived from the *quasi*-molecular-ion peak at *m/z* 767.3850 ($[M-H]^-$) and confirmed by the ^{13}C-NMR data. The FAB-MS (positive-ion mode) of **1** also showed characteristic fragment ion peaks at *m/z*: 769.3 ($[M+H]^+$), 751.2 ($[M+H-18]^+$), 607.2 ($[M+H-162]^+$), 589.2 ($[M+H-162-18]^+$), 445.2 ($[M+H-162-162]^+$), 427.2 ($[M+H-162-162-18]^+$), 409.2 ($[M+H-162-162-18-18]^+$), suggesting the presence of two hexose units and two OH groups in the molecule. Compound **1** was hydrolyzed with acid to afford D-galactose and D-glucose. This was identified by comparison with authentic samples on TLC and GC analysis. Based on ^{1}H- and ^{13}C-NMR (*Table*), and 2D-NMR analyses, the structure of **1** was elucidated as (3*β*,23*S*,25*R*)-23-hydroxy-12-oxospirost-5-en-3-yl 4-*O*-*β*-D-glucopyranosyl-*β*-D-galactopyranoside.

The ^{1}H-NMR spectrum of **1** revealed the presence of two *singlet* Me signals at δ(H) 0.84 (*s*, Me(19)) and 1.26 (*s*, Me(18)), and two *doublet* Me signals at δ(H) 0.71 (*d*, $J=6.6$, Me(27)) and 1.40 (*d*, $J=6.6$, Me(21)), which were assigned to characteristic spirostanol saponin Me groups. Furthermore, the signal of an olefinic H-atom at δ(H) 5.24 (br. *s*, H–C(6)) was readily assigned, as well as signals for two anomeric H-atoms at δ(H) 4.85 (*d*, $J=7.2$) and 5.28 (*d*, $J=8.4$). The *J* values (> 7 Hz) of two anomeric H-atoms confirmed the *β*-orientation at the anomeric centers for both hexoses [11][12]. The ^{13}C-NMR spectrum of **1** showed two anomeric C-atom signals at δ(C) 102.9 and

107.2, in addition, two olefinic C-atom signals at δ(C) 140.7 and 121.4. Comparison of the ^{13}C-NMR data of **1** with those of (25*R*)-kingianoside G [9] indicated that the aglycone of **1** is the same as in (25*R*)-kingianoside G, namely (23*S*,25*R*)-3β,23-dihydroxy-12-oxospirost-5-en. The complete assignment of the glycosidic NMR signals was performed by analyses of ^{1}H,^{1}H-COSY, HSQC, and HMBC data. In the HMBC spectrum of **1** (*Fig.*), the correlations between the C-atom signal δ(C) 67.4 (C(23)) and δ(H) 1.78 (H–C(24)) and 2.03–2.10 (H–C(20)) confirmed the location of one OH group at C(23). Furthermore, the HMBC cross-peaks δ(H) 4.85 (Gal H–C(1)/δ(C) 77.7 (C(3)) and δ(H) 5.28 (Glc H–C(1)/δ(C) 80.0 (Gal C(4)) were observed, which confirmed the sugar sequence and the glycosylation position.

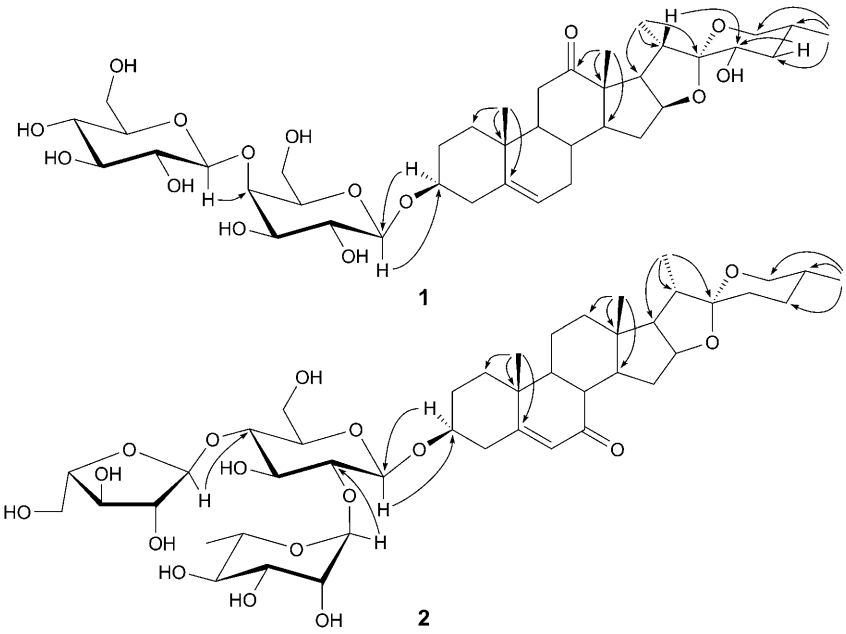


Figure. *Key HMBCs* (H → C) *for compounds* **1** *and* **2**

Kingianoside K (**2**) was obtained as a white amorphous powder. The HR-ESI-MS (positive-ion mode) of **2** exhibited the peak ($[M+Na]^+$) at *m*/*z* 891.4354 consistent with the molecular formula $C_{44}H_{68}O_{17}$. Furthermore, the FAB-MS (positive-ion mode) of **2** also showed the characteristic fragment-ion peaks at *m*/*z*: 869.4 ($[M+H]^+$), 723.2 ($[M+H-146]^+$), 591.1 ($[M+H-146-132]^+$), 429.0 ($[M+H-146-132-162]^+$), and 411.0 ($[M+H-146-132-162-18]^+$), corresponding to loss of one deoxyhexosyl, one pentosyl, and one hexosyl moiety, respectively. On the basis of extensive ^{1}H- and ^{13}C-NMR (*Table*), and 2D-NMR analyses, the structure of **2** was determined as (3β,25*R*)-7-oxospirost-5-en-3-yl α-L-arabinofuranosyl-(1 → 4)-[6-deoxy-α-L-mannopyranosyl-(1 → 2)]-β-D-glucopyranoside.

The ^{1}H-NMR spectrum of **2** showed the presence of two *singlet* Me signals at δ(H) 1.11 (*s*, Me (19)) and 0.83 (*s*, Me (18)), two *doublet* Me signals at δ(H) 0.67 (*d*, $J = 6.6$, Me (27)) and 1.13 (*d*, $J = 6.6$, Me (21)), an olefinic H-atom signal at δ(H) 5.77 (br. *s*),

Table. *^{1}H- and ^{13}C-NMR Data* ((D$_5$)Pyridine) *of Compounds* **1** *and* **2**. δ in ppm, J in Hz.

	1		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
CH_2(1)	1.42–1.47 (*m*), 0.86–0.88 (*m*)	37.0	0.97 (*d*, *J* = 13.8), 1.67–1.69 (*m*)	36.5
CH_2(2)	2.03–2.05 (*m*), 1.60–1.63 (*m*)	30.0	1.84 (*dd*, *J* = 10.8, 10.8), 2.09 (*d*, *J* = 9.6)	29.8
H–C(3)	3.80–3.86 (*m*)	77.7	3.89–3.92 (*m*)	77.7
CH_2(4)	2.65–2.67 (*m*), 2.32–2.35 (*m*)	39.0	2.75–2.80 (*m*), 2.91–2.93 (*m*)	38.9
C(5)		140.7		165.2
H–C(6)	5.24 (br. *s*)	121.4	5.77 (br. *s*)	126.3
CH_2(7) or C(7)	1.46[a]), 1.77–1.84 (*m*)	31.7		200.9
CH_2(8)	1.80[a])	30.8	2.40 (*d*, *J* = 4.8)	45.0
H–C(9)	1.28–1.32 (*m*)	52.3	1.35–1.40 (*m*)	49.9
C(10)		37.5		38.8
CH_2(11)	2.49 (*dd*, *J* = 15.0, 13.2), 2.26 (*dd*, *J* = 15.0, 6.0)	37.5	1.42–1.44 (*m*), 1.44[a])	21.1
C(12) or CH_2(12)		212.7	1.02–1.04 (*m*), 1.60–1.65 (*m*)	38.7
C(13)		55.5		41.2
H–C(14)	1.45[a])	56.0	1.48–1.50 (*m*)	50.0
CH_2(15)	2.09–2.13 (*m*), 1.65–1.70 (*m*)	31.7	1.71–1.77 (*m*), 3.26–3.30 (*m*)	34.4
H–C(16)	4.57–4.60 (*m*)	80.3	4.63–4.66 (*m*)	81.4
H–C(17)	2.89 (*dd*, *J* = 9.0, 7.2)	53.6	1.77[a])	61.9
Me(18)	1.26 (*s*)	16.0	0.83 (*s*)	16.5
Me(19)	0.84 (*s*)	18.7	1.11 (*s*)	17.1
H–C(20)	2.03–2.10 (*m*)	36.4	1.92–1.95 (*m*)	42.0
Me(21)	1.40 (*d*, *J* = 7.2)	13.6	1.13 (*d*, *J* = 7.2)	15.1
C(22)		111.8		109.3
H–C(23) or CH_2(23)	3.86[a])	67.4	1.63[a]), 1.65[a])	31.9
CH_2(24)	2.10[a]), 1.78[a])	38.7	1.51–1.59 (*m*)	29.3
H–C(25)	1.82[a])	31.6	1.57[a])	30.6
CH_2(26)	3.54 (*dd*, *J* = 3.0, 11.4), 3.48 (*dd*, *J* = 10.4, 10.4)	66.1	3.46–3.49 (*m*), 3.54–3.56 (*m*)	66.8
Me(27)	0.71 (*d*, *J* = 6.0)	16.9	0.67 (*d*, *J* = 4.8)	17.3
Gal				
H–C(1)	4.85 (*d*, *J* = 7.8)	102.9	4.93 (*d*, *J* = 7.8)	100.4
H–C(2)	4.38 (*dd*, *J* = 7.8, 9.6)	73.5	4.20–4.27 (*m*)	77.9
H–C(3)	4.20–4.24 (*m*)	75.4	4.27[a])	77.1
H–C(4)	4.69 (*d*, *J* = 3.0)	80.0	4.29–4.35 (*m*)	76.9
H–C(5)	3.99–4.08 (*m*)	76.0	3.79 (*d*, *J* = 7.8)	77.0
CH_2(6)	4.20–4.24 (*m*), 4.61–4.64 (*m*)	61.0	4.22[a]), 4.29[a])	62.5
Glc				
H–C(1)	5.28 (*d*, *J* = 7.8)	107.2		
H–C(2)	4.13 (*dd*, *J* = 7.8, 8.4)	75.2		
H–C(3)	4.23[a])	78.7		
H–C(4)	4.06 (*dd*, *J* = 9.6, 9.6)	72.3		
H–C(5)	4.01[a])	78.5		
CH_2(6)	4.20[a]), 4.58[a])	63.2		

Table (cont.)

	1		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
Rha				
H–C(1)			6.29 (br. *s*)	101.8
H–C(2)			4.76 (*m*)	72.4
H–C(3)			4.54–4.56 (*m*)	72.8
H–C(4)			4.35[a])	74.1
H–C(5)			4.94 (*d*, *J* = 7.8)	69.5
Me(6)			1.73 (*d*, *J* = 7.2)	18.7
Ara				
H–C(1)			5.91 (*s*)	109.6
H–C(2)			4.84–4.89 (*m*)	82.7
H–C(3)			4.85[a])	77.9
H–C(4)			4.86[a])	86.8
CH_2(5)			4.17[a]), 4.27[a])	61.5

[a]) Overlapped with other signals.

and three anomeric H-atom signals at δ(H) 4.93 (*d*, *J* = 7.8), 6.29 (br. *s*), and 5.91 (*s*). The ^{13}C-NMR spectrum of **2** displayed three anomeric C-atom signals at δ(C) 100.4, 101.8, and 109.6, two olefinic C-atom signals at δ(C) 165.2 and 126.3, and a ketone C-atom signal at δ(C) 200.9. The complete assignment of the glycosidic NMR signals was confirmed by analyses of ^{1}H,^{1}H-COSY, HSQC, and HMBC data. Evaluation of spin-spin couplings and chemical shifts allowed the identification of one β-glucopyranosyl (Glc), one α-rhamnopyranosyl (Rha), and one α-arabinofuranosyl unit (Ara). In the HMBC spectrum, the C-atom signal at δ(C) 165.2 showed long-range correlations with H-atom signals at δ(H) 2.75–2.80 (H–C(4)) and 1.11 (Me(19)), indicating a C=C bond between C(5) and C(6) on the aglycone. Furthermore, the C-atom signal at δ(C) 200.9 showed long-range correlations with the H-atom signals at δ(H) 1.49 (H–C(14)) and 2.40 (H–C(8)). This demonstrated that the oxo group is at C(7). The chemical structure of the steroidal saponin with a C=C bond at C(5) and an oxo group within ring *B* in the aglycone is rare in natural products. The HMBC cross-peaks δ(H) 4.93 (Glc H–C(1))/δ(C) 77.7 (C(3)), δ(H) 5.91 (Ara H–C(1))/δ(C) 76.9 (Glc C(4)), and δ(H) 6.29 (Rha H–C(1))/δ(C) 77.9 (Glc C(2)) were observed, which confirmed the sugar sequence and the glycosylation position.

Comparison of the physicochemical properties and NMR data with those reported in the literature allowed us to identify the 13 known compounds as daucosterol [13], (25*R*)-kingianoside G [9], (25*RS*)-kingianoside A [9], pratioside D1 [4], (25*RS*)-pratioside D1 [9], (25*S*)-kingianoside C [7], kingianoside C [7], ginsenoside Rb_1 [14], saponins Tb [15] and Pb [5], dioscin [5], gracillin [5], and saponin Pa [5]. Ginsenoside Rb_1 and saponin Tb are reported for the first time from the genus *Polygonatum*. All 13 known compounds are reported from the processed *P. kingianum* for the first time.

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Experimental Part

General. Macroporous resin *SP825* (*Mitsubishi Chemical*, Japan), silica gel (SiO_2; *Qingdao Haiyang Chemical Co., Ltd.*, P. R. China), and *ODS* silica gel (120 Å, 50 μm, *YMC*) were used for chromatography. HPLC was performed on *Agilent 1100* system (pump, quaternary pump. detector, *RID* and *DAD*, USA), *Apollo* C_{18} (*Alltech*, 8.0 mm i.d. × 250, *ODS*, 10 μm, USA), and *YMC-Pack ODS-A* C_{18} (*YMC*, 4.6 mm i.d. × 250 mm, *ODS*, 5 μm, Japan). Gas chromatographic (GC) analysis: *Agilent 6890* gas chromatograph, equipped with a H_2 flame ionization detector; *HP-5* cap. column (30 m × 0.25 mm × 0.25 μm; *Agilent*, USA). Optical rotations: *Perkin-Elmer 343* polarimeter. NMR Spectra: *Varian* ^{UNITY}*INOVA 600* (at 599.8 (^{1}H) and 150.8 MHz (^{13}C)); chemical shifts given in δ [ppm] with TMS as internal standard. FAB-MS: *Micromass Zabspec*. HR-ESI-MS: *9.4 T Q-FT-MS Apex Qe* (*Bruker Co.*).

Plant Material. The material was collected from Fenggang County of Guizhou Province, P. R. China, in December 2006, and was identified as rhizomes of *Polygonatum kingianum* COLL. *et* HEMSL. by *L.-J. Z.* of the Tianjing University of Traditional Chinese Medicine. The samples were processed according to the procedures of the Chinese pharmacopoeia. A voucher specimen (No. 061201) was deposited with the Herbarium of Beijing Institute of Radiation Medicine, Beijing.

Extraction and Isolation. The decoction pieces of processed *Polygonatum kingianum* (5.5 kg) were extracted for three times with 45% acetone. The combined extract was concentrated under reduced pressure to give 72.0 g of residue. The extract was fractionated by CC on a macroporous resin (*SP825*) with a gradient mixture of Me_2CO/H_2O (10:90, 40:60, and 80:20) to give three fractions, *Frs. A–C*. *Fr. A* was further purified on a macroporous resin (*SP825*) column with a gradient mixture of Me_2CO/H_2O (25:75, 30:70, and 60:40) to give three fractions, *Frs.* A_1 (1.8 g), A_2 (0.9 g), and A_3 (4.0 g). *Fr.* A_1 (1.8 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH/H_2O 12:1:0.01 → 2:1:0.01) to yield daucosterol (*Frs.* A_1*-36–*A_1*-42*; 49.4 mg), and *Frs.* A_1*-162–*A_1*-212* were separated by semi-prep. HPLC with MeCN/H_2O 32:68, to give compound **1** (37.4 mg) and (25*R*)-kongianoside G (48.5 mg). *Fr.* A_2 (0.9 g) was submitted to CC (SiO_2; $CHCl_3$/MeOH/H_2O 6:1:0.01 → 2:1:0.01) to afford ginsenoside Rb_1 (*Frs.* A_2*-46–*A_2*-58*; 15.4 mg). *Fr. B* (3.0 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH/H_2O 10:1:0.01 → 2:1:0.01) to yield (25*RS*)-kingianoside A (*Frs. B-41–B-45*; 22.4 mg) and (25*RS*)-pratioside D_1 (*Frs. B-76–B-83*; 36.7 mg), and *Frs. B-72–B-75* were separated by semi-prep. HPLC with MeCN/H_2O 30:70 to give pratioside D_1 (8.3 mg); *Frs. B-85–B-92* were further separated by semi-prep. HPLC with MeCN/H_2O 22:78 to give (25*S*)-kingianoside C (5.3 mg) and kingianoside C (6.7 mg). *Fr. C* (2.4 g) was subjected to CC (*ODS* SiO_2; MeCN/H_2O 45:55, 48:52, and 52:48) to give saponin Pb (*Frs. C-173* and *C-174*; 26.3 mg) and dioscin (*Frs. C-192–C-196*; 10.3 mg); *Frs. C-76–C-84* were further separated by semi-prep. HPLC with MeCN/H_2O 46:54 to afford compound **2** (10.4 mg) and saponin Tb (18.3 mg). Finally, *Frs. C-181–C-186* were further purified by semi-prep. HPLC with MeCN/H_2O 49:51 to yield gracillin (8.3 mg) and saponin Pa (16.7 mg).

Kingianoside I (=(*3β,23*S,*25*R)*-23-Hydroxy-12-oxospirost-5-en-3-yl 4-*O*-β-*D*-Glucopyranosyl-β-*D*-galactopyranoside*; **1**). White amorphous powder. $[\alpha]_D^{20} = -43.6$ ($c = 0.046$, pyridine). ^{1}H- and ^{13}C-NMR: *Table*. FAB-MS (pos.): 769.3 ($[M + H]^+$), 751.2 ($[M + H - 18]^+$), 607.2 ($[M + H - 162]^+$), 589.2 ($[M + H - 162 - 18]^+$), 445.2 ($[M + H - 162 - 162]^+$), 427.2 ($[M + H - 162 - 162 - 18]^+$), 409.2 ($[M + H - 162 - 162 - 18 - 18]^+$). HR-ESI-MS (neg.): 767.3850 ($[M - H]^-$, $C_{39}H_{59}O_{15}^-$; calc. 767.3859).

Kingianoside K (=(*3β,25*R)*-7-Oxospirost-5-en-3-yl α-*L*-Arabinofuranosyl-(1 → 4)-[6-deoxy-α-*L*-mannopyranosyl-(1 → 2)]-β-*D*-glucopyranoside*; **2**). White amorphous powder. $[\alpha]_D^{20} = -113.8$ ($c =$ 0.065, pyridine). ^{1}H- and ^{13}C-NMR: *Table*. FAB-MS (pos.): 869.4 ($[M + H]^+$), 723.2 ($[M + H - 146]^+$), 591.1 ($[M + H - 146 - 132]^+$), 429.0 ($[M + H - 146 - 132 - 162]^+$), 411.0 ($[M + H - 146 - 132 - 162 - 18]^+$). HR-ESI-MS (pos.): 891.4354 ($[M + Na]^+$, $C_{44}H_{68}NaO_{17}^+$; calc. 891.4359).

Acid Hydrolysis. Each of **1** and **2** (*ca.* 2.0 mg) was treated in 1M HCl (dioxane/H_2O 1:1; 2 ml) at 100° for 1.5 h. The mixture was neutralized with silver carbonate, and the solvent was thoroughly driven out

under N_2 overnight. The residue was extracted with $CHCl_3$ and H_2O. Then, in monosaccharide mixture, glucose and galactose of **1**, and glucose, rhamnose, and arabinose of **2** were detected by TLC on a cellulose plate with BuOH/AcOEt/C_5H_5N/H_2O 6 : 1 : 5 : 4 for development and aniline-*o*-phthalic acid for detection, comparing with the authentic samples: glucose (R_f 0.46), rhamnose (R_f 0.69), arabinose (R_f 0.48), and galactose (R_f 0.39). Furthermore, the sugar residue in pyridine (1 ml) was added to L-cysteine methyl ester hydrochloride (3.0 mg) and kept at 60° for 1 h. Then, HMDS-TMCS (hexamethyldisilazane-trimethylchlorosilane; 0.6 ml) was added to the mixture, and the mixture was kept at 60° for 0.5 h. The supernatant (1.0 ml) was analyzed by GC under the following conditions: *Agilent Technologies 6890* GC was the equipment carrying H_2 flame ionization detector and *HP-5* cap. column (30 m × 0.25 mm × 0.25 μm); column temp.: 180°/250°; programmed increase: 3°/min; carrier gas: N_2 (1 ml/min); injection and detector temp.: 250°; injection volume: 4.0 μl, split ratio: 1 : 50. The retention times of the derivatives for the standards were: t_R: 17.949 min (D-glucose derivative), 18.388 min (L-glucose derivative), 18.571 min (D-galactose derivative), 19.181 min (L-galactose derivative), 13.728 min (D-arabinose derivative), 13.001 min (L-arabinose derivative), and 14.532 min (L-rhamnose derivative). The retention times of the derivatives of D-glucose and D-galactose for compound **1** were 17.940 and 18.567 min, resp. The derivatives of D-glucose, L-rhamnose, and L-arabinose for compound **2** were observed at 17.941, 14.528, and 13.006 min, resp.

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