Ypsilactosides A and B, Two New C_{22}-Steroidal Lactone Glycosides from *Ypsilandra thibetica*

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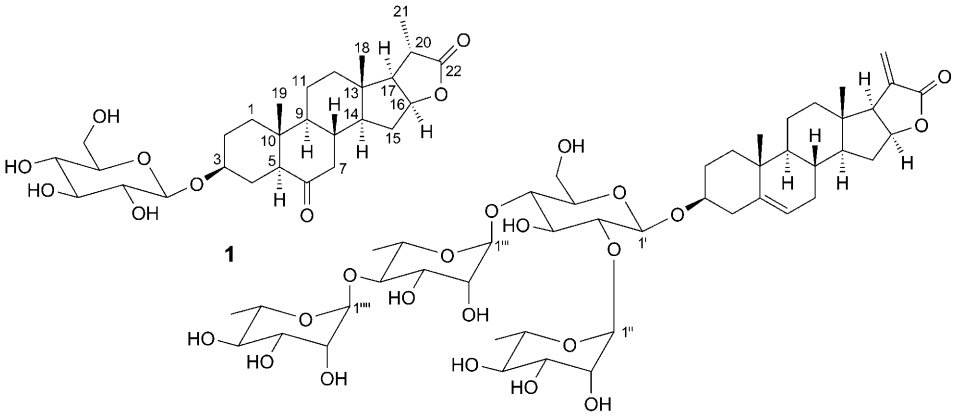
Two new C_{22}-steroidal lactone glycosides, ypsilactosides A (**1**) and B (**2**), were isolated from the EtOH extract of the whole plant of *Ypsilandra thibetica*. Their structures were established as (3β,5α,16β,20*S*)-3,16-dihydroxy-6-oxopregnane-20-carboxylic acid γ-lactone 3-(β-D-glucopyranoside) (**1**) and (3β,16β)-3,16-dihydroxypregna-5,20-diene-20-carboxylic acid γ-lactone 3-{*O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranoside} (**2**) on the basis of extensive spectroscopic analyses and chemical degradations.

Introduction. – *Ypsilandra thibetica* (Liliaceae) is a perennial plant that grows in southwestern China [1], which is used in Chinese folk medicine as hemostatic drug [2]. Our previous phytochemical investigations on *Y. thibetica* led to the isolation of two sapogenins and 16 spirostanol saponins [3][4]. In our systematic chemical study of the above species, we have reinvestigated the whole plants of *Y. thibetica* collected in Luding County of Sichuan Province and obtained two new C_{22}-steroidal lactone glycosides, ypsilactosides A (**1**) and B (**2**). Herein, we report the isolation and structural elucidation of the two new C_{22}-steroidal lactone glycosides by extensive spectroscopic analyses and chemical degradations.



1

2

Results and Discussion. – Ypsilactoside A (**1**) was obtained as a white amorphous powder, and its molecular formula was deduced to be $C_{28}H_{42}O_9$ from HR-ESI-MS at *m/z* 521.2753 ($[M-H]^-$), requiring eight degrees of unsaturation. The IR spectrum of **1** showed absorptions at 3431, 1768, and 1708 cm^{-1}, suggesting the presence of OH, C=O, and γ-lactone units, respectively. The ^{1}H-NMR spectrum of **1** (*Table 1*) displayed the following representative signals: three steroidal Me groups at δ(H) 0.60 (*s*, Me(19)), 0.67 (*s*, Me(18)), and 1.24 (*d*, $J = 7.6$ Hz, Me(21)), and one anomeric H-atom at δ(H) 5.02 (*d*, $J = 7.7$ Hz, H–C(1′)). Acid hydrolysis of **1** yielded D-glucose (identified by GC/MS by comparison with an authentic sample). The sugar unit was compatible with the negative-ion mode FAB-MS of compound **1**, which exhibited its molecular-ion peak for M^- at *m/z* 522, and a fragment-ion peak for $[M - C_6H_{10}O_5]^-$ at *m/z* 360. Thus, the glycoside part corresponds to a D-glucoside unit. The ^{13}C-NMR data (*Table 1*) revealed the presence of 28 C-atoms, 22 of which were assigned to the aglycone moiety, consisting in two tertiary Me, one secondary Me, seven CH_2, and eight CH groups (including two O-bearing ones at δ(C) 78.6 and 82.4), and four quaternary C-atoms (including a lactone group at δ(C) 181.0 and a C=O at δ(C) 209.2), while the remaining signals were due to a glucopyranosyl unit. A comparison of the ^{1}H- and ^{13}C-NMR signals of the aglycone moiety of **1** with those of solanolide (=(3β,5α,6α,16β,20*S*)-3,6,16-trihydroxypregnane-20-carboxylic acid γ-lactone) [5] indicated that the signals were similar, except for the absence of an O-bearing CH and the presence of a C=O group at δ(C) 209.2. In the HMBC spectrum (*Fig. 1*), the long-range correlations of H–C(5), CH_2(7), and H–C(8) with the C=O at δ(C) 209.2 indicated that the C=O group was attached at C(6) of the aglycone of **1**. The configurations of H–C(3), H–C(5), H–C(16), and Me(21) were assigned to be in α-orientation on the ground of the ROESY correlations of H–C(5) with H–C(9) and H–C(3), H–C(14) with H–C(16), Me(18) with H–C(20), and Me(21) with H–C(16) and H–C(17) (*Fig. 1*). The point of attachment of the sugar chain was evident from the HMBC spectrum, in which long-range correlations between C(3) at δ(C) 78.6 (*d*) and H–C(1′) at δ(H) 5.02

Table 1. *^{1}H- and ^{13}C-NMR Data* (400 and 100 MHz, resp.; C_5D_5N) *of Compound* **1**. δ in ppm, *J* in Hz.

	δ(C)	δ(H)		δ(C)	δ(H)
CH_2(1)	36.7 (*t*)	1.50–1.48 (*m*), 0.99–0.98 (*m*)	CH_2(15)	32.9 (*t*)	2.03–2.00 (*m*), 1.37–1.35 (*m*)
CH_2(2)	29.5 (*t*)	2.02–1.98 (*m*), 1.54–1.51 (*m*)	H–C(16)	82.4 (*d*)	4.89 (*ddd*, $J = 7.7, 7.7, 4.5$)
H–C(3)	78.6 (*d*)	3.98–3.95 (*m*)	H–C(17)	58.8 (*d*)	1.81–1.79 (*m*)
CH_2(4)	27.0 (*t*)	2.38–2.36 (*m*), 1.71–1.67 (*m*)	Me(18)	13.7 (*q*)	0.67 (*s*)
H–C(5)	56.4 (*d*)	2.06–2.04 (*m*)	Me(19)	13.0 (*q*)	0.60 (*s*)
C(6)	209.2 (*s*)		CH_2(20)	36.3 (*d*)	2.66 (*q*, $J = 7.6$)
CH_2(7)	46.6 (*t*)	2.34–2.31 (*m*), 2.01–1.98 (*m*)	CH_2(21)	17.9 (*q*)	1.24 (*d*, $J = 7.6$)
H–C(8)	37.0 (*d*)	1.73–1.71 (*m*)	C(22)	181.0 (*s*)	
H–C(9)	53.7 (*d*)	1.10–1.07 (*m*)	H–C(1′)	102.2 (*d*)	5.02 (*d*, $J = 7.7$)
C(10)	40.8 (*s*)		H–C(2′)	75.4 (*d*)	4.04 (*dd*, $J = 7.7, 8.4$)
CH_2(11)	21.1 (*t*)	1.47–1.45 (*m*), 1.15–1.13 (*m*)	H–C(3′)	78.6 (*d*)	4.29–4.26 (*m*)
CH_2(12)	37.8 (*t*)	1.67–1.65 (*m*), 1.07–1.05 (*m*)	H–C(4′)	71.9 (*d*)	4.23–4.20 (*m*)
C(13)	42.2 (*s*)		H–C(5′)	76.7 (*d*)	3.95–3.93 (*m*)
H–C(14)	54.6 (*d*)	1.13–1.11 (*m*)	CH_2(6′)	63.0 (*t*)	4.60 (*dd*, $J = 2.2, 11.8$), 4.39 (*dd*, $J = 5.7, 11.8$)

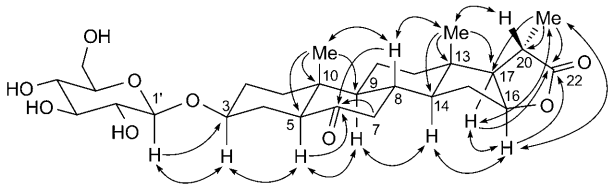


Fig. 1. *Selected HMBC* (H → C) *and Key ROESY correlations* (H ↔ H) *of* **1**

(*d*, $J = 7.7$ Hz) of the glucopyranosyl unit were observed. Therefore, the structure of ypsilactoside A (**1**) was determined to be (3*β*,5*α*,16*β*,20*S*)-3,16-dihydroxy-6-oxopregnane-20-carboxylic acid *γ*-lactone 3-(*β*-D-glucopyranoside).

Ypsilactoside B (**2**) gave a pseudo-molecular-ion peak $[M + Cl]^-$ at *m*/*z* 977.4126 in its HR-ESI-MS. Combined with ^{13}C-NMR data, its molecular formula was determined as $C_{46}H_{70}O_{20}$. The absorption bands in the IR spectrum at 1755 and 1704 cm^{-1}, and the UV maximum at 204 nm indicated the presence of an *α*,*β*-unsaturated *γ*-lactone moiety in compound **2**. The ^{1}H-NMR spectrum of **1** (*Table 2*) exhibited the signals of an exocyclic CH_2 group at *δ*(H) 6.34 and 5.51 (2 br. *s*), of an olefinic H-atom at a trisubstituted C=C bond at *δ*(H) 5.26 (*d*, $J = 4.5$ Hz), and of two tertiary Me groups at

Table 2. *^{1}H- and ^{13}C-NMR Data* (400 and 100 MHz, resp.; C_5D_5N) *of Compound* **2**. *δ* in ppm, *J* in Hz.

	δ(C)	*δ*(H)		*δ*(C)	*δ*(H)
CH_2(1)	37.5 (*t*)	1.63–1.65 (*m*), 0.92–0.89 (*m*)	H–C(1′)	100.4 (*d*)	4.93 (*d*, $J = 7.4$)
CH_2(2)	30.2 (*t*)	1.81–1.78 (*m*), 2.04–2.00 (*m*)	H–C(2′)	78.0 (*d*)	4.38–4.36 (*m*)
H–C(3)	77.8 (*d*)	3.87–3.82 (*m*)	H–C(3′)	77.9 (*d*)	4.18–4.15 (*m*)
CH_2(4)	39.0 (*t*)	2.78–2.75 (*m*), 2.70–2.65 (*m*)	H–C(4′)	77.7 (*d*)	4.21–4.20 (*m*)
C(5)	140.9 (*s*)		H–C(5′)	77.1 (*d*)	3.60–3.57 (*m*)
H–C(6)	121.5 (*d*)	5.26 (*d*, $J = 4.5$)	CH_2(6′)	61.3 (*t*)	4.18–4.16 (*m*),
CH_2(7)	32.1 (*t*)	1.82–1.78 (*m*), 1.45–1.43 (*m*)			4.02 (*dd*, $J = 2.1, 11.7$)
H–C(8)	31.6 (*d*)	1.38–1.36 (*m*)	H–C(1″)	102.2 (*d*)	6.40 (br. *s*)
H–C(9)	50.2 (*d*)	0.90–0.86 (*m*)	H–C(2″)	72.6 (*d*)	4.83–4.80 (*m*)
C(10)	37.1 (*s*)		H–C(3″)	72.9 (*d*)	4.60–4.57 (*m*)
CH_2(11)	20.6 (*t*)	1.28–1.25 (*m*), 1.43–1.37 (*m*)	H–C(4″)	74.2 (*d*)	4.34–4.32 (*m*)
CH_2(12)	38.1 (*t*)	1.67–1.65 (*m*), 1.10–1.06 (*m*)	H–C(5″)	69.6 (*d*)	4.93–4.91 (*m*)
C(13)	43.9 (*s*)		Me(6″)	18.7 (*q*)	1.57 (*d*, $J = 5.6$)
H–C(14)	54.7 (*d*)	0.99–0.94 (*m*)	H–C(1‴)	102.3 (*d*)	5.83 (br. *s*)
CH_2(15)	33.4 (*t*)	2.13–2.10 (*m*), 1.47–1.45 (*m*)	H–C(2‴)	72.9 (*d*)	4.50–4.47 (*m*)
H–C(16)	81.9 (*d*)	4.81–4.79 (*m*)	H–C(3‴)	73.4 (*d*)	4.53–4.52 (*m*)
H–C(17)	55.1 (*d*)	2.73–2.71 (*m*)	H–C(4‴)	80.4 (*d*)	4.42–4.40 (*m*)
Me(18)	14.3 (*q*)	0.47 (*s*)	H–C(5‴)	68.4 (*d*)	4.92–4.90 (*m*)
Me(19)	19.4 (*q*)	0.97 (*s*)	Me(6‴)	19.0 (*q*)	1.57 (*d*, $J = 5.6$)
C(20)	137.6 (*s*)		H–C(1⁗)	103.4 (*d*)	6.28 (br. *s*)
CH_2(21)	122.0 (*t*)	6.34, 5.51 (2 br. *s*)	H–C(2⁗)	72.6 (*d*)	4.90–4.88 (*m*)
C(22)	171.4 (*s*)		H–C(3⁗)	73.0 (*d*)	4.51–4.48 (*m*)
			H–C(4⁗)	74.1 (*d*)	4.28–4.26 (*m*)
			H–C(5⁗)	70.5 (*d*)	4.33–4.30 (*m*)
			Me(6⁗)	18.5 (*q*)	1.74 (*d*, $J = 6.2$)

δ(H) 0.47 and 0.97, together with signals of four anomeric H-atoms at δ(H) 4.93, 5.83, 6.28, and 6.40. The ^{13}C-NMR data (*Table 2*) revealed the presence of 46 C-atoms, 22 of which were assigned to the aglycone moiety. This showed the presence of two tertiary Me, seven CH_2, six CH (including two O-bearing ones at δ(C) 77.8 and 81.9), two quaternary C-atoms, a trisubstituted C=C moiety at δ(C) 121.5 (*d*) and 140.9 (*s*), an exocyclic (terminal) C=C bond at δ(C) 122.0 (*t*) and 137.6 (*s*), and a lactone group at δ(C) 171.4. The remaining signals were due to a glucopyranosyl and three rhamnopyranosyl units. These data were in support of the aglycone of **2** being a C_{22}-steroidal lactone, which possesses a similar skeleton as the aglycone ((3β,16β,20*S*)-3,16-dihydroxypregn-5-ene-20-carboxylic acid γ-lactone) of dumoside [6] and dracaenoside A [7], except for the disappearance of a secondary Me and a CH group and the presence of an exocyclic C=C bond at δ(C) 122.0 (*t*) and 137.6 (*s*). Thus, it was supposed that the exocyclic C=C bond is located between C(20) and C(21) in compound **2**, which was confirmed by the HMBC spectrum (*Fig. 2*), exhibiting cross-peaks between δ(H) 6.34 and 5.51 (2 br. *s*) (CH_2(21)) and δ(C) 55.1 (*d*, C(17)), 137.6 (*s*, C(20)), and 171.4 (*s*, C(22)). On the basis of the above evidence, the aglycone of **2** was identified as (3β,16β)-3,16-dihydroxypregna-5,20-diene-20-carboxylic acid γ-lactone.

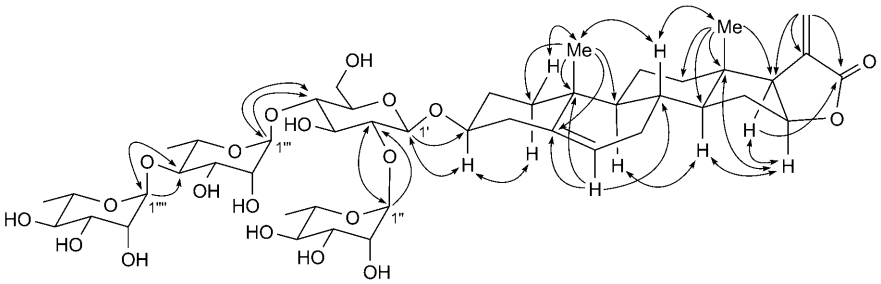


Fig. 2. *Selected HMBC* (H → C) *and Key ROESY correlations* (H ↔ H) *of* **2**

In the ^{1}H- and ^{13}C-NMR spectra of **2**, signals for four anomeric H-atoms at δ(H) 4.93 (*d*, J = 7.4 Hz), 5.83 (br. *s*), 6.28 (br. *s*), and 6.40 (br. *s*) with their corresponding anomeric C-atoms at δ(C) 100.4, 102.3, 103.4, and 102.2, respectively, appeared (*Table 2*). The sugars obtained on acid hydrolysis of **2** were identified as D-glucose and L-rhamnose on the basis of GC analysis. The ^{1}H-NMR coupling constant (^3J(1′,2′) > 7 Hz) for the anomeric H-atom revealed that the glucose unit has a β-configuration, while the three rhamnose units have α-configuration on the basis of the chemical-shift values of C(3″) (δ(C) 72.9 (*d*)), C(5″) (δ(C) 69.6 (*d*)), C(3‴) (δ(C) 73.4 (*d*)), C(5‴) (δ(C) 68.4 (*d*)), C(3⁗) (δ(C) 73.0 (*d*)), and C(5⁗) (δ(C) 70.5 (*d*)), which were compared with those of the corresponding C-atoms of methyl α- and β-rhamnopyranoside [8][9]. The linkage sites and sequences were determined by analyzing the 2D-NMR spectrum of **2**. In the HMBC spectrum, the long-range correlations δ(H) 4.93 (*d*, J = 7.4, H–C(1′))/δ(C) 77.8 (*d*, C(3)), δ(H) 6.40 (br. *s*, H–C(1″))/δ(C) 78.0 (*d*, C(2′)), δ(H) 5.83 (br. *s*, H–C(1‴))/δ(C) 77.7 (*d*, C(4′)), and δ(H) 6.28 (br. *s*, H–C(1⁗))/δ(C) 80.4 (*d*, C(4‴)) revealed that the glucopyranosyl unit was linked to C(3) of the aglycone, a terminal rhamnopyranosyl unit to C(2′) of the glucopyranosyl unit, an inner

rhamnopyranosyl unit to C(4′) of the glucopyranosyl unit, and another terminal rhamnopyranosyl unit to C(4‴) of the inner rhamnopyranosyl unit. Consequently, the structure of ypsilactoside B (**2**) was determined to be (3*β*,16*β*)-3,16-dihydroxypregna-5,20-diene-20-carboxylic acid *γ*-lactone 3-*O*-*α*-L-rhamnopyranosyl-(1 → 4)-*O*-*α*-L-rhamnopyranosyl-(1 → 4)-*O*-[*α*-L-rhamnopyranosyl-(1 → 2)]-*β*-D-glucopyranoside.

This work was supported by the *Natural Science Foundation of Yunnan Province* (No. 2009CC019), the *West Light Foundation of the Chinese Academy of Sciences* (No. 2908025712W1) with an award to *H.-Y. L.* and a fund (No. 540806321211) of the State Key Laboratory of Phytochemistry and Plant Resources in West China, the *Germplasm Bank of Wild Species*, and the *CAS Innovation Program of Kunming Institute of Botany.*

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Marine Chemical Inc.*, China) or SiO_2 *H* (10–40 μm; *Qingdao Marine Chemical Inc.*), and *Sephadex LH-20* (*GE Healthcare*). TLC: SiO_2 plates; detection by spraying with 10% H_2SO_4 in EtOH, followed by heating. Semi-prep. HPLC: *Agilent-1100* apparatus; *Zorbax-SB-C-18* column (9.4 mm × 25 cm; *Agilent*). GC: *Shimadzu-GC-2010* instrument; H_2 flame ionization detector. Optical rotations: *Jasco-DIP-370* digital polarimeter. UV Spectra: *Shimadzu-UV-2401-PC* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Bio-Rad-FTS-135* spectrometer; KBr pellets; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-AM-400* instrument (400 and 100 MHz, resp.); δ in ppm rel. to $SiMe_4$ as internal standard, *J* in Hz. FAB-MS: *VG-Auto-Spec-3000* mass spectrometer; in *m*/*z*. HR-ESI-MS: *API-Qstar-Pulsar* LC/TOF instrument; in *m*/*z*.

Plant Material. The whole plants of *Y. thibetica* were collected in November 2006 from Luding County, Sichuan Province, P. R. China, and identified by Prof. *Xin-Qi Chen*, Institute of Botany, Chinese Academy of Sciences, Beijing. A voucher specimen (No. HY0002) was deposited with the State Key Laboratory of Phytochemistry and Plant Resources in West China.

Extraction and Isolation. The whole plants of *Y. thibetica* (10 kg) were extracted with 70% EtOH (3 × 50 l) under reflux for a total of 6 h, and the combined extract was concentrated. Then, the concentrated extract was passed through *YWD-3F* macroporous resin and eluted successively with H_2O, 40% EtOH, 70% EtOH, and 95% EtOH, resp. The evaporated 70% EtOH fractions (70 g) were fractionated by CC (SiO_2, $CHCl_3$/MeOH/H_2O 10:1:0 → 7:3:0.5): *Fractions 1–4*. *Fr. 1* (12 g) was repeatedly subjected to CC (SiO_2, $CHCl_3$/MeOH 9:1): **1** (15 mg). *Fr. 2* (10 g) was subjected to MPLC (*Rp-18*, MeOH/H_2O 8:2 → 7:3): *Fr. 2.1–2.3*. *Fr. 2.2* was further purified by semi-prep. HPLC (MeCN/H_2O 35:65; flow rate 3 ml/min): **2** (12 mg).

Ypsilactoside A (*= (3β,5α,16β,20*S*)-3,16-Dihydroxy-6-oxopregnane-20-carboxylic Acid γ-Lactone 3-(β-*D*-Glucopyranoside) = (3β,5α,16β,20*S*)-3-(β-*D*-Glucopyranosyloxy)-16-hydroxy-6-oxopregnane-20-carboxylic Acid γ-Lactone*; **1**): White amorphous powder. $[\alpha]_D^{25} = -98.1$ ($c = 0.53$, pyridine). IR (KBr): 3431, 2938, 2847, 1768, 1708, 1035, 884. ^1H- and ^{13}C-NMR: *Table 1*. FAB-MS (neg.): 522 (100, M^-), 360 (6, $[M-C_6H_{10}O_5]^-$). HR-ESI-MS: 521.2753 ($[M-H]^-$, $C_{28}H_{41}O_9^-$; calc. 521.2750).

Ypsilactoside B (*= (3β,16β)-3,16-Dihydroxypregna-5,20-diene-20-carboxylic Acid γ-Lactone 3-*O*-α-L-Rhamnopyranosyl-(1 → 4)-*O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranoside = (3β,16β)-3-[*O*-6-Deoxy-α-L-mannopyranosyl-(1 → 4)-*O*-6-deoxy-α-L-mannopyranosyl-(1 → 4)-*O*-[6-deoxy-α-L-mannopyranosyl-(1 → 2)]-β-D-glucopyranosyl)oxy]-16-hydroxypregna-5,20-diene-20-carboxylic Acid γ-Lactone*; **2**): White amorphous powder. $[\alpha]_D^{18} = -78.0$ ($c = 0.29$, pyridine). UV (MeOH): 204. IR (KBr): 3424, 2934, 1755, 1704, 1629, 1452, 1383, 1132, 1096, 1042, 984, 912, 885, 825, 804. ^1H- and ^{13}C-NMR: *Table 2*. ESI-MS (neg.): 941 ($[M-H]^-$). HR-ESI-MS: 977.4126 ($[M+Cl]^-$, $C_{46}H_{70}ClO_{20}^-$; calc. 977.4148).

Acid Hydrolysis of Compounds **1** *and* **2** *and GC Analysis.* Compound **1** or **2** (4 mg each) was refluxed with 4M CF_3COOH/dioxane 1:1 (2 ml) in a water bath for 4 h. The mixture was neutralized with 1M NaOH and filtered. The filtrate was extracted with $CHCl_3$ and H_2O. The H_2O-soluble fraction was concentrated. The dried sugar residue was dissolved in pyridine (1 ml) and treated with chloro(trime-

thyl)silane (0.5 ml) and stirred at 60° for 5 min. After drying the soln. with a stream of N_2, the residue was extracted with Et_2O (1 ml). The Et_2O layer was analyzed by GC (*SGE-AC-10* quartz cap. column (0.25 μm; 30 m × 0.32 mm); column temp. 180–280°; programmed increase 3°/min; carrier gas N_2 (2 ml/min); injector and detector temp. 250°; injection volume 2 μl; split ratio 1/50). Peaks of the hydrolysate were detected by comparison with retention times of authentic samples of D-glucose and L-rhamnose after treatment with chloro(trimethyl)silane in pyridine. The absolute configurations of the sugar residues were determined to be L-rhamnose (t_R 7.67 min) and D-glucose (t_R 14.22 min).

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Received March 31, 2010