Notes

New Triterpenoid Saponins from *Gynostemma pentaphyllum*

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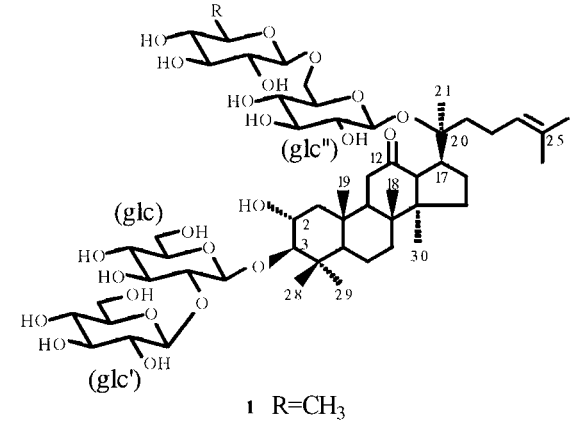
Three new triterpenoidal saponins (**1**−**3**), together with the known compound **4**, were isolated from a MeOH extract of the aerial parts of *Gynostemma pentaphyllum*. Their structures were elucidated on the basis of chemical and spectral methods, such as ^{1}H−^{1}H DQFCOSY, HMQC, HMBC, and TOCSY NMR spectra. The aglycon moiety of **1** and **2** is a new dammarane-type triterpene 12-oxo-2α,3*β*,20(*S*)-trihydroxydammar-24-ene.

Gynostemma pentaphyllum Makino (Cucurbitaceae) is a perennial liana growing wild throughout Japan, China, and Korea, once used for its sweet properties.[1] Previous investigations of this plant have shown the occurrence of dammarane-type glycosides structurally correlated to the ginseng saponins.[2−4] Because ginsenosides are the well-known, biologically active principles in Korean ginseng, *G. pentaphyllum* has received much attention. Recently we have isolated three new triterpene oligosaccharides from *G. pentaphyllum* (**1**−**3**). Structure elucidation was accomplished mainly on the basis of 2D-NMR, and ^{1}H−^{1}H and ^{1}H−^{13}C shift correlation spectroscopy.

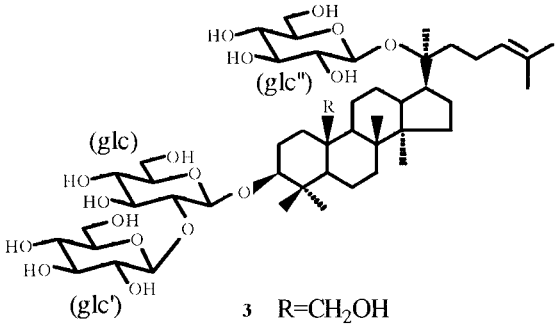
The aerial parts of *G. pentaphyllum* were extracted successively with petroleum ether, $CHCl_3$, and MeOH. The MeOH extract was partitioned with *n*-BuOH and H_2O, and the *n*-BuOH-soluble portion was subjected to Si gel column chromatography ($CHCl_3$−MeOH−H_2O, 7:3:0.1). The fractions obtained were further chromatographed on a RP-18 column eluted with MeOH−H_2O or CH_3CN−H_2O to yield **1** (35 mg), **2** (20 mg), **3** (67 mg), and **4** (85 mg). The known compound **4** was identified by comparison of its spectral data with that described in the literature.[5]

Compound **1** was obtained as an amorphous powder. The FABMS showed a quasimolecular ion peak at *m/z* 1130, corresponding to $[M(C_{54}H_{90}O_{23}) + Na + H]^+$. The ^{13}C- and DEPT ^{13}C-NMR spectra gave 54 signals, of which 24 were assigned to the saccharide portion and 30 to a triterpenoid moiety. The ^{1}H-NMR spectrum of **1** showed eight singlets assignable to tertiary methyls at 0.87−1.70, two of which were diagnostic for methyls linked to sp^2 carbons [*δ* 1.67 and 1.70], and signals at *δ* 5.39 (1H, t, *J* = 6.2 Hz) characteristic of an olefinic proton. 2α,3*β*-Dihydroxy substitutions were evident from the chemical shift, and the *J* values of the proton were ascribable to C-3 at *δ* 3.16 (1H, d, *J* = 9.0 Hz).

The ^{13}C-NMR spectrum of **1** suggested a dammarane-type triterpene skeleton with a carbonyl function. By comparison of its ^{13}C-NMR spectra with those of Gyp-XLIII[6] **1** showed the absence of a 12-oxymethine signal, and an additional quaternary carbonyl carbon signal (*δ* 210.9) was observed. From biogenetic considerations and NMR data, the carbonyl group was placed at C-12.



1 R=CH_3
2 R=H



3 R=CH_2OH
4 R=CHO

This assignment was confirmed by the following observations: the quaternary carbonyl signal (*δ* 210.9, C-12) showed long-range connectivities with H-13 (*δ* 3.53, d, *J* = 9.2 Hz, 1H) and H-11 (*δ* 2.31, m, 2H). Glycosidation of the alcoholic function at C-3 and C-20 was indicated by the significant downfield shift observed for these carbon resonances in **1**, relative to the corresponding signals in model compounds reported in the literature.[6]

Hydrolysis of **1** yielded D-glucose and L-rhamnose. According to its ^{1}H- and ^{13}C-NMR spectra, **1** contained three units of D-glucose and one of L-rhamnose. Chemical shifts, the multiplicity of the signals, the absolute values of the coupling constants, and their magnitude in the ^{1}H-NMR spectrum, as well as the ^{13}C-NMR data, indicated a *β*-configuration at the anomeric positions for the glucosyl units and an α-configuration for the rhamnosyl unit. ^{13}C-NMR data allowed assignment of the pyranose form to D-glucose and L-rhamnose. All ^{1}H- and

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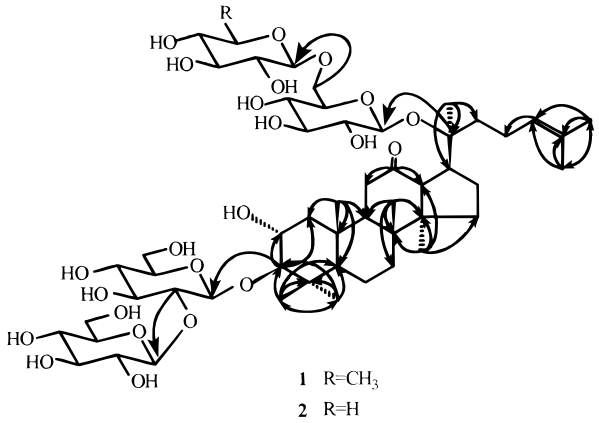

1 R=CH_3
2 R=H

Figure 1. $^{13}C-^{1}H$ long-range correlations from HMBC experiments (J = 6 Hz) for **1**−**2**.

^{13}C-NMR signals of the four sugar units were assigned using $^{1}H-^{1}H$ DQFCOSY, HMQC, HMBC, and TOCSY spectra. The linkage sites and sequences of the four saccharides and of the aglycon were deduced from an HMBC experiment. Correlations were observed between H_{G-1} of glucose (glc); $H_{G'-1}$ of glucose (glc′); $H_{G''-1}$ of glucose (glc″), and H_{R-1} of rhamnose and $C_{G''-6}$ (Figure 1). Thus, the structure of **1** was shown to be 12-oxo-2α,3*β*,20(*S*)-trihydroxydammar-24-ene-3-*O*-[*β*-D-glucopyranosyl(1→2)-*β*-D-glucopyranosyl]-20-*O*-[α-L-rhamnopyranosyl (1→6)-*β*-D-glucopyranoside].

The FABMS of **2** displayed a quasimolecular ion peak at *m*/*z* 1116 $[M + Na + H]^+$, establishing a molecular formula of $C_{53}H_{88}O_{23}$. Comparison of the ^{1}H- and ^{13}C-NMR spectra between **1** and **2** indicated an identical aglycon moiety. The major difference between **1** and **2** was that the rhamnosyl group in **1** was replaced by an pentosyl group. Hydrolysis of **2** yielded D-xylose and D-glucose. The *β*-xylosyl linkage was defined on the basis of *J* values of its anomeric proton (J = 7.3 Hz). The linkage sites and sequences of the four saccharides and of the aglycon were also determined using an HMBC experiment (Figure 1). Based on the above results, the structure of **2** was elucidated as 12-oxo-2α,3*β*,20(*S*)-trihydroxydammar-24-ene-3-*O*-[*β*-D-glucopyranosyl(1→2)-*β*-D-glucopyranosyl]-20-*O*-[*β*-D-xylopyranosyl(1→6)-*β*-D-glucopyranoside].

Compound **3**, an amorphous powder, exhibited a quasimolecular ion peak at *m*/*z* 969, corresponding to $[M(C_{48}H_{82}O_{18}) + Na]^+$ in the FABMS. Its ^{1}H- and ^{13}C-NMR spectra were similar to those of **4**. The only difference between **3** and **4** was that a CH_3 group signal in the aglycon of **4** was replaced by a CH_2OH. On the basis of ^{1}H- and ^{13}C-NMR data, the aglycon of **3** was identified as 3*β*,20(*S*),19-trihydroxydammar-24-ene, the same aglycon as that of Gyp-LXIII.[7] Therefore, **3** was identified as 3*β*,19,20(*S*)-trihydroxydammar-24-ene-3-*O*-[*β*-D-glucopyranosyl(1→2)-*β*-D-glucopyranosyl]-20-*O*-*β*-D-glucopyranoside. The structure was confirmed by $^{1}H-^{1}H$ DQFCOSY, HMQC, HMBC, and TOCSY NMR experiments.

Experimental Section

General Experimental Procedures. Optical rotations were measured in MeOH with a Perkin-Elmer model 141 polarimeter. IR were measured with Perkin-Elmer 559B apparatus. NMR spectra were obtained on Bruker AMX-400 spectrometer in C_5D_5N solution. Chemical shifts are reported in ppm. ^{1}H-NMR chemical shifts were referenced to the residual solvent signal (*δ* 7.56). ^{13}C-NMR spectra were referenced to the center peak of the solvent at *δ* 135.5. FABMS were run on a VG Quattro GC/MS/MS using glycerin plus NaCl as matrix.

Plant Material. *Gynostemma pentaphyllum* was collected at Hangzhou, Zhejiang province, People's Republic of China in June 1994. A voucher sample of the plant is deposited at the herbarium of the Department of Phytochemistry, Shanghai Institute of Materia Medica, Academia Sinica, Shanghai, People's Republic of China.

Extraction and Isolation. The aerial parts of *G. pentaphyllum* (0.5 kg) were extracted successively with petroleum ether, $CHCl_3$, and MeOH. The MeOH extract was partitioned with *n*-BuOH and H_2O to afford the *n*-BuOH-soluble portion (30 g), which was subjected to Si gel column chromatography ($CHCl_3-MeOH-H_2O$, 7:3:0.1). The fractions obtained were further chromatographed on a Rp-18 lobar column eluted with MeOH−H_2O (500 mL, 1:1) or CH_3CN-H_2O (650 mL, 2:3) to yield **1** (35 mg), **2** (20 mg), **3** (67 mg), and **4** (85 mg).

Compound 1: amorphous powder; $[\alpha]^{18.5}_{D}$ −6.01° (*c* 0.0200, MeOH); IR υ_{max} (KBr) 3420, 2920, 1690, 1620, 1100−950 cm^{-1}; ^{1}H NMR (C_5D_5N, 400 MHz) *δ* 2.12 (1H, m, H-1), 1.10 (1H, t, J = 12.6 Hz, H-1′), 4.00 (1H, m, H-2), 3.16 (1H, d, J = 9.0 Hz, H-3), 0.76 (1H, br d, J = 9.8 Hz, H-5), 1.45 (1H, m, H-6), 1.37 (1H, m, H-6′), 1.37 (1H, m, H-7), 1.22 (1H, m, H-7′), 1.78 (1H, m, H-9), 2.10 (2H, m, H_2-11), 3.50 (1H, d, J = 7.2 Hz, H-13), 1.89 (1H, m, H-15), 1.11 (1H, m, H-15′), 2.24 (1H, m, H-16), 1.89 (1H, m, H-16′), 2.90 (1H, m, H-17), 1.24 (3H, s, Me-18), 0.87 (3H, s, Me-19), 1.52 (3H, s, Me-21), 2.12 (1H, m, H-22), 2.01 (1H, m, H-22′), 2.43 (1H, m, H-23), 2.24 (1H, m, H-23′), 5.39 (1H, t, J = 7.3 Hz, H-24), 1.70 (3H, s, H-26), 1.67 (3H, s, H-27), 1.28 (3H, s, H-28), 1.18 (3H, s, H-29), 0.87 (3H, s, H-30); 3-*O*-Glc (inner) 4.91 (1H, d, J = 7.5 Hz, H-1), 4.27 (1H, m, H-2), 4.27 (1H, m, H-3), 4.08 (1H, m, H-4), 4.01 (1H, m, H-5), 4.56 (1H, m, H-6), 4.25 (1H, m, H-6′); 3-*O*-Glc′ (terminal) 5.50 (1H, d, J = 7.6 Hz, H-1), 4.11 (1H, m, H-2), 3.92 (1H, m, H-3), 4.26 (1H, m, H-4), 4.27 (1H, m, H-5), 4.45 (1H, dd, J = 11.5, 3.5 Hz, H-6), 4.51 (1H, m, H-6′); 20-*O*-Glc″ (inner) 5.11 (1H, d, J = 7.6 Hz, H-1), 3.95 (1H, m, H-2), 4.16 (1H, m, H-3), 3.96 (1H, m, H-4), 3.93 (1H, m, H-5), 4.65 (1H, d, J = 8.4 Hz, H-6), 3.99 (1H, m, H-6′); 20-*O*-Rham 5.47 (1H, s, H-1), 4.58 (1H, m, H-2), 4.49 (1H, m, H-3), 4.21 (1H, m, H-4), 4.26 (1H, m, H-5), 1.62 (3H, d, J = 5.5 Hz, Me-6); ^{13}C NMR (C_5N_5D, 100 MHz) *δ* 47.5 (t, C-1), 66.5 (d, C-2), 95.3 (d, C-3), 41.0 (s, C-4), 56.5 (d, C-5), 18.6 (t, C-6), 34.8 (t, C-7), 40.8 (s, C-8), 55.0 (d, C-9), 38.3 (s, C-10), 40.1 (t, C-11), 210.9 (s, C-12), 56.0 (d, C-13), 56.0 (s, C-14), 32.1 (t, C-15), 24.8 (t, C-16), 42.6 (d, C-17), 15.9 (q, C-18), 17.5 (q, C-19), 81.4 (s, C-20), 22.3 (q, C-21), 40.4 (t, C-22), 24.0 (t, C-23), 125.9 (d, C-24), 130.8 (s, C-25), 25.8 (q, C-26), 17.9 (q, C-27), 28.2 (q, C-28), 17.5 (q, C-29), 17.7 (q, C-30); 3-*O*-Glc (inner) 104.4 (d, C-1), 82.4 (d, C-2), 79.1 (d, C-3), 71.3 (d, C-4), 78.4 (d, C-5), 62.4 (t, C-6); 3-*O*-Glc′ (terminal) 105.6 (d, C-1), 76.7 (d, C-2), 78.3 (d, C-3), 71.9 (d, C-4), 78.1 (d, C-5), 63.0 (t, C-6); 20-*O*-Glc″ (inner) 98.3 (d, C-1), 75.6 (d, C-2), 79.1 (d, C-3), 71.9 (d, C-4), 76.5 (d, C-5), 68.5 (t, C-6); 20-*O*-Rham (terminal) 102.2 (d, C-1), 72.3 (d, C-2), 72.8 (d, C-3), 74.1 (d, C-4), 69.7 (d, C-5), 18.6 (q, C-6). FABMS *m*/*z* 1130 $[M + Na + H]^+$; anal. calcd for $C_{54}H_{90}O_{23}\cdot 4\,H_2O$: C, 55.00; H, 8.38. Found: C, 55.18; H, 8.60.

Compound 2: amorphous powder; $[\alpha]^{18.5}_D$ −2.32° (*c* 0.0302, MeOH); IR υ_{max} (KBr): 3410, 2900, 1690, 1620, 1100−950 cm^{-1}; ^1H NMR (C_5D_5N, 400 MHz) δ 2.12 (1H, m, H-1), 1.02 (1H, t, J = 12.6 Hz, H-1′), 4.32 (1H, m, H-2), 3.16 (1H, d, J = 9.1 Hz, H-3), 0.77 (1H, m, H-5), 1.45 (1H, m, H-6), 1.34 (1H, m, H-6′), 1.34 (1H, m, H-7), 1.21 (1H, m, H-7′), 1.76 (1H, dd, J = 11.5, 4.7 Hz, H-9), 2.31 (2H, m, H_2-11), 3.53 (1H, d, J = 9.2 Hz, H-13), 1.90 (1H, m, H-15), 1.19 (1H, m, H-15′), 2.23 (1H, m, H-16), 1.90 (1H, m, H-16′), 2.92 (1H, m, H-17), 1.26 (3H, s, Me-18), 0.87 (3 H, s, Me-19), 1.54 (3H, s, Me-21), 2.18 (1H, m, H-22), 1.99 (1H, m, H-22′), 2.40 (1H, m, H-23), 2.17 (1H, m, H-23′), 5.41 (1H, t, J = 7.4 Hz, H-24), 1.65 (3H, s, H-26), 1.65 (3H, s, H-27), 1.29 (3H, s, H-28), 1.18 (3H, s, H-29), 0.86 (3H, s, H-30); 3-*O*-Glc (inner) 4.91 (1H, d, J = 7.4 Hz, H-1), 4.38 (1H, m, H-2), 4.11 (1H, m, H-3), 4.15 (1H, m, H-4), 4.19 (1H, m, H-5), 4.67 (1H, dd, J = 11.4, 1.6 Hz, H-6), 4.37 (1H, m, H-6′); 3-*O*-Glc′ (terminal) 5.49 (1H, d, J = 7.5 Hz, H-1), 4.21 (1H, m, H-2), 4.35 (1H, m, H-3), 4.32 (1H, m, H-4), 4.04 (1H, m, H-5), 4.61 (1H, dd, J = 11.8, 3.3 Hz, H-6), 4.53 (1H, dd, J = 11.8, 4.5, H-6′); 20-*O*-Glc″ (inner): 5.11 (1H, d, J = 7.5 Hz, H-1), 4.00 (1H, m, H-2), 4.22 (1H, m, H-3), 4.11 (1H, m, H-4), 4.02 (1H, m, H-5), 4.78 (1H, dd, J = 11.4, 1.2 Hz, H-6), 4.39 (1H, m, H-6′); 20-*O*-Xyl 4.97 (1H, d, J = 7.3 Hz, H-1), 4.11 (1H, m, H-2), 4.22 (1H, m, H-3), 4.28 (1H, m, H-4), 4.43 (1H, m, H-5), 3.77 (1H, dd, J = 11.4, 9.0 Hz, H-5′); ^{13}C NMR (C_5N_5D, 100 MHz) δ 47.5 (t, C-1), 66.5 (d, C-2), 95.3 (d, C-3), 41.0 (s, C-4), 56.5 (d, C-5), 18.6 (t, C-6), 34.7 (t, C-7), 40.9 (s, C-8), 54.8 (d, C-9), 38.3 (s, C-10), 40.3 (t, C-11), 212.0 (s, C-12), 56.2 (d, C-13), 56.0 (s, C-14), 32.3 (t, C-15), 24.6 (t, C-16), 42.6 (d, C-17), 16.0 (q, C-18), 17.5 (q, C-19), 81.5 (s, C-20), 22.3 (q, C-21), 40.6 (t, C-22), 24.0 (t, C-23), 125.9 (d, C-24), 130.8 (s, C-25), 25.8 (q, C-26), 17.9 (q, C-27), 28.2 (q, C-28), 17.5 (q, C-29), 17.0 (q, C-30); 3-*O*-Glc (inner) 104.4 (d, C-1), 82.4 (d, C-2), 78.2 (d, C-3), 71.9 (d, C-4), 78.2 (d, C-5), 63.0 (t, C-6); 3-*O*-Glc′ (terminal) 105.7 (d, C-1), 76.7 (d, C-2), 78.2 (d, C-3), 71.9 (d, C-4), 78.2 (d, C-5), 62.4 (t, C-6); 20-*O*-Glc″ (inner) 98.4 (d, C-1), 75.6 (d, C-2), 79.0 (d, C-3), 71.3 (d, C-4), 76.7 (d, C-5), 70.2 (t, C-6); 20-*O*-Rham (terminal) 105.7 (d, C-1), 74.7 (d, C-2), 77.9 (d, C-3), 71.1 (d, C-4), 66.9 (t, C-5), 18.6 (q, C-6); FABMS *m/z* 1116[M + Na + H]$^+$; anal. calcd for $C_{53}H_{88}O_{23}\cdot 3\ H_2O$: C, 55.49; H, 8.26. Found: C, 55.28; H, 8.10.

Compound 3: amorphous powder; $[\alpha]^{29.5}_D$ +8.57° (*c* 0.0385, MeOH); IR υ_{max} (KBr): 3400, 2950, 1630, 1100−950 cm^{-1}; ^1H NMR (C_5D_5N, 400 MHz) δ 2.51 (1H, d, J = 12.8 Hz, H-1), 0.81 (1H, t, J = 12.8 Hz, H-1′), 2.30 (1H, m, H-2), 2.16 (1H, m, H-2′), 3.40 (1H, dd, J = 11.3, 3.9 Hz, H-3), 0.91 (1H, d, J = 8.9 Hz, H-5), 1.45 (1H, m, H-6), 1.34 (1H, m, H-6′), 1.34 (1H, m, H-7), 1.21 (1H, m, H-7′), 1.76 (1H, dd, J = 11.5, 4.7 Hz, H-9), 2.31 (2H, m, H_2-11), 3.53 (1H, d, J = 9.2 Hz, H-13), 1.90 (1H, m, H-15), 1.19 (1H, m, H-15′), 2.23 (1H, m, H-16), 1.90 (1H, m, H-16′), 2.92 (1H, m, H-17), 1.26 (3H, s, Me-18), 0.87 (3H, s, Me-19), 1.54 (3H, s, Me-21), 2.18 (1H, m, H-22), 1.99 (1H, m, H-22′), 2.40 (1H, m, H-23), 2.17 (1H, m, H-23′), 5.41 (1H, t, J = 7.4 Hz, H-24), 1.65 (3H, s, H-26), 1.65 (3H, s, H-27), 1.29 (3H, s, H-28), 1.18 (3H, s, H-29), 0.86 (3H, s, H-30); 3-*O*-Glc (inner) 4.91 (1H, d, J = 7.4 Hz, H-1), 4.38 (1H, m, H-2), 4.11 (1H, m, H-3), 4.15 (1H, m, H-4), 4.19 (1H, m, H-5), 4.67 (1H, dd, J = 11.4, 1.6 Hz, H-6), 4.37 (1H, m, H-6′); 3-*O*-Glc′ (terminal) 5.49 (1H, d, J = 7.5 Hz, H-1), 4.21 (1H, m, H-2), 4.35 (1H, m, H-3), 4.32 (1H, m, H-4), 4.04 (1H, m, H-5), 4.61 (1H, dd, J = 11.8, 3.3 Hz, H-6), 4.53 (1H, dd, J = 11.8, 4.5, H-6′); 20-*O*-Glc″ (inner) 5.11 (1H, d, J = 7.5 Hz, H-1), 4.00 (1H, m, H-2), 4.22 (1H, m, H-3), 4.11 (1H, m, H-4), 4.02 (1H, m, H-5), 4.78 (1H, dd, J = 11.4, 1.2 Hz, H-6), 4.39 (1H, m, H-6′); ^{13}C NMR (C_5N_5D, 100 MHz) δ 34.6 (t, C-1), 27.6 (t, C-2), 89.4 (d, C-3), 39.7 (s, C-4), 57.1 (d, C-5), 18.3 (t, C-6), 36.2 (t, C-7), 41.0 (s, C-8), 53.0 (d, C-9), 42.1 (s, C-10), 25.0 (t, C-11), 25.8 (t, C-12), 43.2 (d, C-13), 51.1 (s, C-14), 32.0 (t, C-15), 28.8 (t, C-16), 48.4 (d, C-17), 16.1 (q, C-18), 61.5 (q, C-19), 82.4 (s, C-20), 21.4 (q, C-21), 40.3 (t, C-22), 23.2 (t, C-23), 126.2 (d, C-24), 130.6 (s, C-25), 25.9 (q, C-26), 17.9 (q, C-27), 28.8 (q, C-28), 16.9 (q, C-29), 17.5 (q, C-30); 3-*O*-Glc (inner) 105.1 (d, C-1), 83.4 (d, C-2), 78.0 (d, C-3), 71.7 (d, C-4), 78.2 (d, C-5), 62.7 (t, C-6); 3-*O*-Glc′ (terminal) 106.0 (d, C-1), 77.1 (d, C-2), 78.0 (d, C-3), 71.7 (d, C-4), 78.2 (d, C-5), 62.8 (t, C-6); 20-*O*-Glc″ (inner) 98.6 (d, C-1), 75.8 (d, C-2), 79.0 (d, C-3), 72.0 (d, C-4), 78.0 (d, C-5), 63.2 (t, C-6); FABMS *m/z* 969[M + Na + H]$^+$; anal. calcd for $C_{48}H_{82}O_{18}\cdot 3\ H_2O$: C, 57.58; H, 8.86. Found: C, 57.42; H, 8.60.

Acidic Hydrolysis of 1−3. MeOH solutions of each glycoside (**1**, **2**, and **3**) together with standard sugar samples were applied at points about 1 cm from the bottom of HPTLC Si gel plates and hydrolyzed with HCl vapor for 2 h at 50 °C. The plate was then heated at 60 °C for 2 h to remove residual HCl, and developed using $CHCl_3$−CH_3OH−H_2O (8:2:0.1) as the eluent. The plate was sprayed with 10% H_2SO_4 (in EtOH), and then heated to 110 °C .

Compound 4: amorphous powder; $[\alpha]^{25}_D$ +10.6° (*c* 3.2, MeOH); IR υ_{max} (KBr) 3400, 2900, 1690, 1380, 1100−950 cm^{-1}; ^1H-NMR (C_5D_5N, 400 MHz) δ 5.33 (1H, d, J = 7.6 Hz), 5.27 (1H, t, H-24), 5.06 (1H, d, J = 7.6 Hz), 4.91 (1H, d, J = 7.4 Hz), 3.31 (1H, dd, H-3), 1.65 (6H, s), 1.46 (3H, s), 1.31 (3H, s), 1.06 (3H, s), 0.96 (3H, s), 0.89 (3H, s); ^{13}C NMR (C_5N_5D, 100 MHz) δ 33.4 (t, C-1), 27.7 (t, C-2), 87.7 (d, C-3), 40.1 (s, C-4), 54.6 (d, C-5), 17.8 (t, C-6), 34.8 (t, C-7), 40.3 (s, C-8), 52.9 (d, C-9), 52.9 (s, C-10), 22.5 (t, C-11), 25.4 (t, C-12), 42.1 (d, C-13), 50.4 (s, C-14), 32.0 (t, C-15), 27.9 (t, C-16), 48.3 (d, C-17), 15.9 (q, C-18), 206.1 (d, C-19), 82.2 (s, C-20), 21.4 (q, C-21), 40.3 (t, C-22), 23.1 (t, C-23), 126.0 (d, C-24), 130.9 (s, C-25), 25.8 (q, C-26), 17.9 (q, C-27), 26.6 (q, C-28), 16.8 (q, C-29), 17.2 (q, C-30); 3-*O*-Glc (inner) 105.0 (d, C-1), 83.4 (d, C-2), 78.0 (d, C-3), 71.9 (d, C-4), 78.2 (d, C-5), 62.8 (t, C-6); 3-*O*-Glc (terminal) 106.1 (d, C-1), 77.0 (d, C-2), 78.0 (d, C-3), 71.7 (d, C-4), 78.2 (d, C-5), 62.8 (t, C-6); 20-*O*-Glc (inner) 98.5 (d, C-1), 75.6 (d, C-2), 79.1 (d, C-3), 71.5 (d, C-4), 77.0 (d, C-5), 62.9 (t, C-6).

References and Notes

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