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NEW TRITERPENOID SAPONINS FROM *MUSSAENDA PUBESCENS*

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ABSTRACT.—Three new triterpenoidal saponins, mussaendosides O [**1**], P [**2**], and Q [**3**] were isolated from whole plants of *Mussaenda pubescens*. These structures were elucidated on the basis of chemical and spectral methods, such as their ^{1}H-^{1}H COSY, HMQC, HMBC, TOCSY, and NOESY nmr spectra.

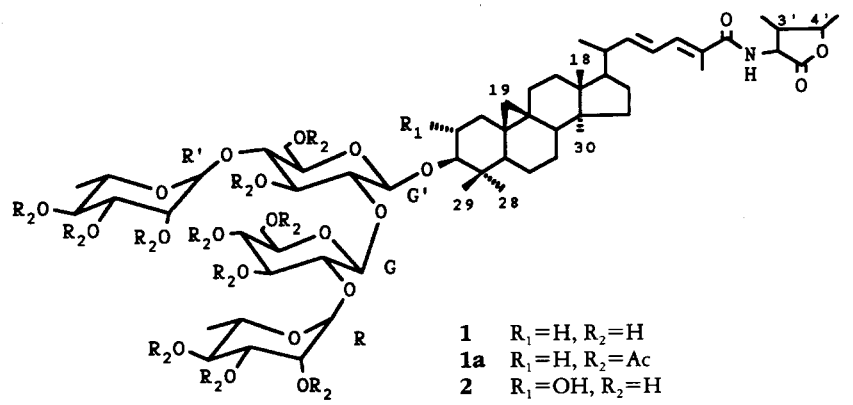
Mussaenda pubescens Ait. f. (Rubiaceae) is widely distributed in south China. It is a Chinese folk medicine used for the treatment of the common cold, laryngopharyngitis, acute gastroenteritis, and diarrhea (1). It is also used as a contraceptive in some districts of Fujian Province. The aqueous extracts of this plant and its precipitate obtained by adding 95% EtOH showed significant effects in terminating pregnancy in rats (2). In order to elucidate the structures of its active principles, we systematically studied the hydrophilic components of the whole plant collected from Guangdong Province. As result of earlier investigations, we have reported the isolation and structure determination of several new saponins, namely, mussaendosides A, B, C, M, and N, having a cycloartene-type aglycone (3–5). This paper deals with the isolation and structures of three new saponins named mussaendosides O [**1**], P [**2**], and Q [**3**].

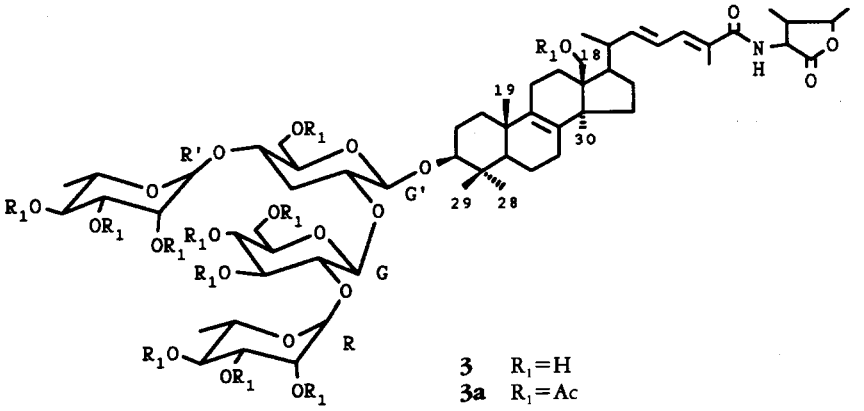
RESULTS AND DISCUSSION

The crude saponins (7 g) previously obtained from the extract of the whole plants of *M. pubescens* were chromatographed on a Si gel column eluted with $CHCl_3$/MeOH/H_2O (3–5). The fractions obtained were further chromatographed on a RP-18 Lobar column eluted with EtOH/H_2O or CH_3CN/H_2O to yield **1** (20 mg), **2** (9 mg), and **3** (20 mg).

Mussaendoside O [**1**] was obtained as an amorphous powder. The fabms showed a quasi-molecular ion peak at *m/z* 1205, corresponding to $[M(C_{60}H_{95}NO_{22})+Na+H]^+$. On the basis of ^{1}H- and ^{13}C-nmr data, the aglycone of **1** was identified as heinsiagenin A, the same aglycone as that of mussaendoside M (5,6). Comparison of their nmr and fabms spectra revealed that **1** contained two hexose and two 6-deoxyhexose moieties, whereas mussaendoside M contained one pentose, one hexose, and two 6-deoxyhexose units. Hydrolysis of **1** yielded only L-rhamnose and D-glucose. Therefore, there were two L-rhamnose and two D-glucose units per molecule of **1**. In the ^{1}H-nmr spectrum, two anomeric proton signals were almost coincident at δ 5.83, and in the ^{13}C-nmr spectrum, two anomeric carbon signals nearly overlapped at δ 101.8. These observations made it difficult to establish the linkage sites and sequences of the four sugar units.

Peracetylation of **1** yielded **1a**. In the ^{1}H- and ^{13}C-nmr spectra of **1a**, all four anomeric proton and carbon signals were well separated. Two glucose units were defined with β-glycosyl linkages on the basis of J values of their anomeric protons (J=7.8 Hz for $H_{G\text{-}1}$ in **1** and 7.6 Hz for $H_{G'\text{-}1}$ in **1a**), and the two rhamnose units exhibited α-glycosyl linkages according to ^{13}C-nmr data. All proton and carbon signals of the aglycone and each sugar moiety in **1a** were assigned using ^{1}H-^{1}H COSY, TOCSY, HMQC, HMBC,





and NOESY nmr experiments (Table 1). Furthermore, the linkage sites and sequence of the four saccharides and the aglycone were established by NOESY (Table 2), and the result was confirmed by HMBC (Table 3). Therefore, mussaendoside O [**1**] was identified as heinsiagenin A 3-*O*-[α-L-rhamnopyranosyl(1→2)-*O*-β-D-glucopyranosyl(1→2)]-α-L-rhamnopyranosyl(1→4)-*O*-β-D-glucopyranoside.

TABLE 1. ^{1}H- and ^{13}C-Nmr Data of **1a** ($CDCl_3$), **2**, and **3** (C_5D_5N).[a,b]

Position	Compound					
	1a		**2**		**3**	
	^{1}H *J* (Hz)	^{13}C	^{1}H *J* (Hz)	^{13}C	^{1}H *J* (Hz)	^{13}C
1α	1.50 m	31.9	1.71 m	40.2	1.09 m	35.7
β	1.25 m		1.77 dd 13.2, 5.2		1.52 m	
2α	1.93 m	29.1		69.4	2.08 m	26.8
β	1.68 m		3.94 m		1.70 m	
3	3.10 dd 11.5, 4.0	90.8	3.30 d 9.0	96.3	3.26 dd 11.7, 4.0	89.7
4		41.0		42.2		39.5
5	1.29 m	47.4	1.37 m	47.4	1.09 m	50.8
6α	1.57 m	in CH_3CO	1.53 m	21.1	1.98 m	18.2
β	0.78 m		0.72 m		1.41 m	
7α	1.06 m	26.0	1.06 m	26.0	1.70 m	25.3
β	1.32 m		1.29 m		2.55 m	
8	1.51 m	48.0	1.47 dd 12.5, 5.0	47.7		133.6
9		20.0		19.4		136.0
10		26.0		25.0		36.8

TABLE 1. Continued.

Position	Compound					
	1a		**2**		**3**	
	^{1}H *J* (Hz)	^{13}C	^{1}H *J* (Hz)	^{13}C	^{1}H *J* (Hz)	^{13}C
11α	2.00 m	26.5	1.94 m	26.7	2.06 m	21.4
β	1.13 m		1.08 m		2.21 m	
12α	1.65 m	32.8	1.51 m	32.9	1.64 m	26.5
β	1.65 m		1.51 m		1.98 m	
13		45.6		45.6		49.3
14		48.9		49.2		50.0
15α	1.28 m	35.6	1.25 m	35.7	1.23 m	31.0
β	1.28 m		1.25 m		1.58 m	
16α	1.26 m	28.4	1.23 m	28.7	1.69 m	28.8
β	1.76 m		1.57 m		1.49 m	
17	1.69 m	51.6	1.56 m	51.9	1.69 m	50.4
18a	1.01 s	18.3	0.95 s	18.3	3.82 m	62.2
b					3.74 d 11.5	
19en	0.33 d 3.9	29.9	0.25 d 4.1	29.5	0.89 s	19.2
ex	0.55 d 3.9		0.49 d 4.1			
20	2.24 m	41.2	2.13 m	41.2	2.90 m	41.6
21	1.04 d 6.5	19.6	0.96 d 7.0	19.8	1.35 d 6.2	21.2
22	5.94 dd 14.8, 8.8	149.3	5.62 m	147.9	5.71 m	148.9
23	6.26 dd 14.8, 11.0	123.0	6.40 dd 14.4, 11.5	123.8	6.38 dd 14.8, 11.0	123.4
24	6.90 d 11.0	135.6	7.25 d 11.5	134.8	7.26 d 11.0	134.9
25		126.6		129.0		128.4
26	1.98 s	12.8	2.17 d 1.1	13.4	2.10 br s	13.2
27		in CH_3CO		170.7		170.6
28	1.01 s	25.4	1.39 s	26.0	1.03 s	25.8
29	0.85 s	14.7	1.18 s	16.2	1.07 s	28.0
30	0.90 s	in CH_3CO	0.87 s	19.2	1.32 s	16.4
1′		175.3		175.7		175.6
2′	4.78 m	55.8	5.63 dd 7.5, 7.4	55.4	5.62 dd 7.4, 7.4	55.2
3′	3.01 m	38.6	2.90 m	38.6	2.88 m	38.4
4′	4.71 m	77.7	4.65 m	77.0	4.65 m	76.9
3′-Me	0.79 d 7.0	7.3	0.85 d 7.3	8.0	0.83 d 7.3	7.9
4′-Me	1.39 d 6.4	15.5	1.16 d 6.5	15.4	1.14 d 6.5	15.3
NH	6.18 d 4.9		9.03 d 7.6		9.03 d 7.6	
G′1	4.45 m	103.3	4.92 d 7.8	104.5	4.83 d 8.1	104.7
2	3.88 dd 7.7, 7.6	75.2	4.40 m	79.0	4.32 m	79.1
3	5.18 m	74.9	4.54 m	77.6	4.48 m	77.4
4	3.84 m	77.7	4.24 m	79.3	4.20 m	79.1
5	3.68 m	71.8	3.76 m	76.4	3.66 m	76.2
6a	4.24 br d 9.1	62.6	4.02 m	61.1	4.05 m	61.4
b	4.46 m		4.22 m		4.23 m	
G1	4.64 d 7.6	100.0	5.79 d 7.6	102.2	5.71 m	101.8
2	3.66 m	76.2	4.30 m	78.4	4.23 m	78.2
3	5.19 m	75.1	3.89 m	77.8	3.81 m	77.4
4	4.96 dd 9.7, 9.6	68.9	4.05 m	72.8	4.00 dd 9.4, 8.8	72.6
5	3.67 m	71.9	4.25 m	79.2	4.20 m	79.1
6a	4.09 br d 12.0	62.0	4.30 m	63.4	4.23 m	63.3
b	4.30 dd 12.0, 4.1		4.52 m		4.43 m	
R′1	4.80 s	99.5	5.70 s	102.7	5.71 m	102.5
2	5.03 m	70.2	4.57 br s	72.3	4.61 br s	72.3
3	5.18 m	68.6	4.58 m	72.4	4.50 m	72.4
4	5.05 m	70.7	4.26 m	73.8	4.24 m	73.7
5	3.83 m	67.8	4.82 m	70.7	4.84 m	70.4
6	1.17 d 6.2	17.2	1.68 d 6.2	18.6	1.64 d 6.1	18.4
R1	4.91 s	98.2	6.40 s	102.1	6.37 s	101.8
2	5.07 m	70.2	4.76 br s	72.2	4.72 br s	72.2
3	5.33 dd 9.8, 3.3	68.7	4.62 m	72.6	4.63 m	72.6
4	5.07 m	71.0	4.30 m	74.2	4.28 m	73.9
5	4.20 dq 9.7, 6.2	66.8	4.96 m	69.5	4.95 m	69.2
6	1.21 d 6.2	17.3	1.81 d 6.2	19.0	1.76 d 6.2	18.8
CH_3CO	1.98–2.17	20.7–20.9				
CH_3CO		169.4–175.3				

[a] ^{1}H nmr, 600 MHz, δ in ppm, referenced to 7.26 ($CDCl_3$) and 7.56 (C_5D_5N).
[b] ^{13}C nmr, 150 MHz, δ in ppm, referenced to 77.0 ($CDCl_3$) and 135.5 (C_5D_5N).

TABLE 2. Cross-Peaks in the NOESY Spectra of **1a** ($CDCl_3$), **2** (C_5D_5N), and **3a** ($CDCl_3$).

Compound	$H_{G'-1}$/H-3	$H_{G-1}/H_{G'-2}$	H_{R-1}/H_{G-2}	$H_{R'-1}/H_{G'-4}$
1a	4.45/3.10	4.64/3.88	4.91/3.66	4.80/3.84
2	4.92/3.30	5.79/4.40	6.40/4.30	5.70/4.24
3a	4.41/3.06	4.65/3.88	4.89/3.65	4.80/3.86

Mussaendoside P [**2**] was obtained as an amorphous powder. The fabms showed a quasi-molecular ion peak at *m/z* 1221, corresponding to $[M(C_{60}H_{95}NO_{23})+Na+H]^+$, indicating the presence of one more oxygen atom in the molecule than in **1**. The ^{13}C-nmr data of its genin were very similar to those of **1** except for an oxygen-bearing methine carbon that appeared at δ 69.4. This diagnostic signal exhibited a connectivity with a proton signal at δ 3.94 in the HMQC spectrum, which in turn showed cross-peaks with H-3 (δ 3.30, d, J=9.0 Hz) in a DQF-COSY nmr experiment. These observations clearly suggested an α-hydroxy group at C-2. Furthermore, on the basis of ^{13}C-nmr, ^{1}H-^{1}H COSY, TOCSY, HMQC, HMBC, and NOESY spectra, all proton and carbon signals in its aglycone were assignable (Table 1).

Compound **2** contained four monosaccharide units, and the four anomeric signals were isolated from each other in both the ^{1}H- and ^{13}C-nmr spectra, which made it possible to determine the structure of the sugar residue directly. Hydrolysis of **2** yielded D-glucose and L-rhamnose. As in **1**, there were two units of each of these sugars in the tetrasaccharide, **2**. Assignments of all proton and carbon nmr signals of the four sugar units were made using ^{1}H-^{1}H COSY, TOCSY, and HMQC spectra (Table 1). The linkage sites and sequences of the four saccharides and the aglycone were also determined using NOESY and HMBC experiments (Tables 2 and 3). Thus, the structure of **2** was shown to be 2α-hydroxyheinsiagenin A 3-*O*-[α-L-rhamnopyranosyl(1→2)-*O*-β-D-glucopyranosyl(1→2)]-α-L-rhamnopyranosyl(1→4)-*O*-β-D-glucopyranoside.

Mussaendoside Q [**3**], an amorphous powder, exhibited a quasi-molecular ion peak at *m/z* 1220, corresponding to $[M(C_{60}H_{95}NO_{23})+Na]^+$ in the fabms spectrum. By comparison of its ^{1}H- and ^{13}C-nmr spectra with those of **1** and **2**, it was apparent that **3** had a lanostene-type sapogenin. Further analyses showed that the side-chain of **3** was identical with that of **1** and the only difference occurred in their triterpene skeleton functions. The ^{1}H-nmr spectrum of **3** showed the absence of two characteristic cyclopropane-methylene signals, present in both **1** and **2**. Moreover, two additional quaternary olefinic carbon signals (δ 133.6 and 136.0) were observed in the ^{13}C-nmr spectrum of **3**. From biogenetic considerations and nmr data, the tetra-substituted double bond was located at C-8–C-9. This assignment was confirmed by the following observations: (a) the quaternary methyl signal (δ 0.89, H_3-19) showed long-range connectivities with C-1 (δ 35.7), C-10 (δ 36.8), and a quaternary carbon at δ 136.0 (C-9); (b) the quaternary methyl signal (δ 1.03, H_3-30) showed long-range couplings with C-15 (δ 31.0), C-13 (δ 49.3), C-14 (δ 50.0), and a quaternary olefinic carbon at δ 133.6 (C-8). In an HMBC experiment, long-range connectivities of all other methyls with their neighboring carbons were also observed, but no additional methyl signal was found for H-18 (Figure 1). In an HMQC experiment of **3**, a CH_2 signal at δ_C 62.2 correlated with

TABLE 3. Cross-Peaks in the HMBC Spectra of **1a** ($CDCl_3$) and **2** (C_5D_5N).

Compound	C-3	$H_{G'-1}$	C_{G-1}	$H_{G'-2}$	$C_{R'-1}$	$H_{G'-4}$	C_{R-1}	H_{G-2}
1a	90.8	4.45	100.0	3.88	99.5	3.84	98.2	3.66
2	96.3	4.92	102.2	4.40	102.7	4.24	102.1	4.30

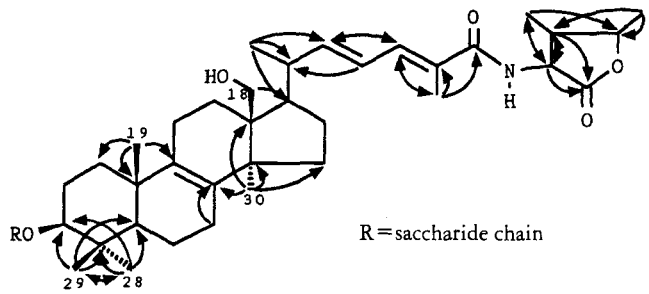


FIGURE 1. ^{13}C-^{1}H long-range nmr correlations in **3**.

two protons at δ_H 3.82 and 3.74. The latter two protons were coupled only to each other (J=11.5 Hz), which indicated the existence of a quaternary hydroxymethyl substituent. A ROESY experiment exhibited a cross-peak between H-20 (δ 2.90) and one of the methylene protons at δ 3.74, while, in the HMBC experiment, the methylene proton at δ 3.82 exhibited long-range coupling with C-17 (δ 50.4). All the above evidence confirmed the presence of a hydroxyl group at C-18 in **3**. Furthermore, all proton and carbon signals of its aglycone were assigned using ^{1}H-^{1}H COSY, TOCSY, HMQC, HMBC, and ROESY nmr spectra (Table 1).

Hydrolysis of **3** yielded D-glucose and L-rhamnose. According to its ^{1}H- and ^{13}C-nmr spectra, **3** also contained two units of D-glucose and two of L-rhamnose. All ^{1}H- and ^{13}C-nmr signals of its sugar moieties were also assigned using the nmr experiments described above (Table 1). The anomeric signals in the ^{1}H- and ^{13}C-nmr spectra of **3** were overlapped and similar to those seen in the spectra of **1**. Two anomeric protons appeared at δ 5.71, and two anomeric carbons appeared at δ 101.8.

Compound **3** was acetylated to afford the peracetate, **3a**. Four anomeric signals were evident in the ^{1}H- and ^{13}C-nmr spectra of compound **3a**. Using the same methods as for **1a**, the structure of its saccharide moiety was shown to be identical with those of **1** and **2**. Therefore, mussaendoside Q [**3**] was elucidated as *N*-(2*S*,3*R*,4*R*-3-methyl-4-pentanolid-2-yl)-18-hydroxylanosta-8(9),22*E*,24*E*-trien-27-amide-3-*O*-[α-L-rhamnopyranosyl(1→2)-*O*-β-D-glucopyranosyl(1→2)]-α-L-rhamnopyranosyl(1→4)-*O*-β-D-glucopyranoside.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv spectra were recorded on a Shimadzu UV-250 instrument using MeOH as solvent. Nmr spectra were obtained on Bruker AMX-600, Bruker AM-400, and Varian Gemini 300 spectrometers. Chemical shifts are reported in ppm. Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter. Mass spectra were determined on a VG Quattro GC/MS/MS or a Varian MAT 212 instrument.

PLANT MATERIAL.—Whole plants of *M. pubescens* were collected in Zhaoqing, Guangdong Province, People's Republic of China. The plant was identified by Dr. Jian-yu Chen of Guangdong Medical College. A voucher specimen is deposited in the herbarium of the Department of Phytochemistry, Shanghai Institute of Materia Medica.

EXTRACTION AND ISOLATION.—The previously obtained crude saponins (7 g) of *M. pubescens* were subjected to cc on Si gel, eluted with $CHCl_3$/MeOH/H_2O (5). From fractions eluted with the solvent system $CHCl_3$-MeOH-H_2O (7:3:0.5), a mixture (500 mg) was obtained, which was separated on repeated RP-18 Lobar cc. Elution with EtOH-H_2O (1.1:1) gave **3** (20 mg) and a mixture of **1** and **2** (70 mg). The mixture was further separated on a RP-18 Lobar column, eluted with CH_3CN-H_2O (1:1) to give **1** (20 mg) and **2** (9 mg).

Compound **1**.—Amorphous powder; $[\alpha]^{15}D$ +2.4° (c=0.06, pyridine); fabms m/z 1205 $[M+Na+H]^+$; uv (MeOH) λ max 265 nm; ^{1}H nmr [400 MHz, δ relative to 7.56 (C_5D_5N)] 9.20 (1H, d, J=7.7 Hz, NH),

7.26 (1H, br d, J=11.0 Hz, H-24), 6.49 (1H, s, $H_{R\text{-}1}$), 6.40 (1H, dd, J=14.8 and 11.0 Hz, H-23), 5.84 (1H, d, J=7.8 Hz, $H_{G\text{-}1}$), 5.82 (1H, s, $H_{R'\text{-}1}$), 5.70 (1H, dd, J=7.5 and 7.4 Hz, H-2′), 5.61 (1H, dd, J=14.8 and 9.0 Hz, H-22), 4.90 (1H, d, J=7.8 Hz, $H_{G'\text{-}1}$), 3.47 (1H, dd, J=10.0 and 4.0 Hz, H-3), 2.90 (1H, m, H-3′), 2.20 (3H, br s, Me-26), 1.87 (3H, d, J=6.0 Hz, $Me_{R\text{-}6}$), 1.68 (3H, d, J=6.1 Hz, $Me_{R'\text{-}6}$), 1.40 (3H, s, Me-30), 1.16 (3H, d, J=7.1 Hz, Me-4′), 1.15 (3H, s, Me-28), 0.98 (6H, m, Me-21 and Me-29), 0.88 (3H, s, Me-18), 0.86 (3H, d, J=7.4 Hz, Me-3′), 0.47 (1H, d, J=3.5 Hz, H-19a), 0.19 (1H, d, J=3.5 Hz, H-19b); ^{13}C nmr (75 MHz, δ relative to 135.4 (C_5D_5N)] C-1 to C-30: 31.8, 29.4, 89.4, 41.1, 47.3, 20.9, 26.1, 47.7, 19.7, 26.0, 26.3, 32.8, 45.4, 48.9, 35.5, 28.5, 51.7, 18.2, 29.4, 41.1, 19.6, 147.7, 123.3, 134.6, 128.8, 13.2, 170.5, 19.2, 25.7, 15.1; C-1′ to C-4′: 175.5, 55.2, 38.4, 76.8; Me-3′: 7.9; Me-4′: 15.3; G′-1 to G′-6: 104.4, 78.8, 77.3, 79.2, 76.2, 61.3; G-1 to G-6: 101.8, 78.1, 79.1, 72.5, 77.5, 63.2; R′-1 to R′-6: 102.4, 72.2, 72.3, 73.7, 70.3, 18.4; R-1 to R-6: 101.8, 72.1, 72.4, 74.0, 69.3, 18.9.

Compound **2**.—Amorphous powder; $[\alpha]^{15}D$ +7.0° (c=0.05, pyridine); fabms m/z 1221 $[M+Na+H]^+$; uv (MeOH) λ max 265 nm, ^{1}H and ^{13}C nmr, see Table 1.

Compound **3**.—Amorphous powder; $[\alpha]^{16}D$ +10.7° (c=0.29, pyridine); fabms m/z 1220 $[M+Na]^+$; uv (MeOH) λ max 265 nm; ^{1}H and ^{13}C nmr, see Table 1.

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°. The plate was then heated at 60° for 2 h to remove residual HCl, and developed using $CHCl_3$-CH_3OH-H_2O (8:2:0.1) as eluent. The plate was sprayed with 10% H_2SO_4 (in EtOH), and then heated at 110°.

ACETYLATION OF **1** AND **3**.—10 mg of **1** and **3** were kept at room temperature in Ac_2O-pyridine (1:1) for 48 h, worked up in the usual manner, and purified by Lobar RP-18 cc (EtOH-H_2O, 9:1), to yield the corresponding peracetates, **1a** (10 mg) and **3a** (10 mg).

Compound **1a**.—Amorphous powder; $[\alpha]^{14}D$ +34° (c=0.23, $CHCl_3$); ^{1}H and ^{13}C nmr, see Table 1.

Compound **3a**.—Amorphous powder; $[\alpha]^{14}D$ +25° (c=0.14, $CHCl_3$); ^{1}H nmr [600 MHz, δ relative to 7.26 ($CDCl_3$)] 6.89 (1H, d, J=10.6 Hz, H-24), 6.26 (1H, dd, J=14.9 and 10.6 Hz, H-23), 6.18 (1H, d, J=4.9 Hz, NH), 5.87 (1H, dd, J=14.9 and 8.7 Hz, H-22), 4.79 (1H, dd, J=6.9 and 5.0 Hz, H-2′), 4.71 (1H, m, H-4′), 4.11 (1H, d, J=11.5 Hz, H-18a), 3.87 (1H, m, H-18b), 3.06 (1H, dd, J=11.7 and 4.0 Hz, H-3), 3.01 (1H, m, H-3′), 2.21 (1H, m, H-20), 1.39 (3H, d, J=6.4 Hz, Me-4′), 1.15 (3H, d, J=6.4 Hz, Me-21), 1.05 (3H, s, Me-28), 0.98 (3H, s, Me-19), 0.92 (3H, s, Me-30), 0.82 (3H, s, Me-29), 0.79 (3H, d, J=7.2 Hz, Me-3′); G-1 to G-6: 4.65 (d, J=7.7 Hz), 3.65 (m), 5.19 (m), 4.95 (dd, J=9.7 and 9.7 Hz), 3.66 (m), 4.31 (dd, J=12.0 and 4.0 Hz), 4.08 (br d, J=12.0 Hz); G′-1 to G′-6: 4.41 (d, J=6.9 Hz), 3.88 (m), 5.18 (m), 3.86 (m), 3.65 (m), 4.45 (br d, J=12.0 Hz), 4.25 (dd, J=12.0 and 4.0 Hz); R-1 to R-6: 4.89 (s), 5.05 (m), 5.34 (dd, J=9.8 and 3.4 Hz), 5.06 (m), 4.20 (m), 1.21 (d, J=6.3 Hz); R′-1 to R′-6: 4.80 (s), 5.02 (d, J=3.1 Hz), 5.19 (m), 5.04 (m), 3.83 (m), 1.18 (d, J=6.2 Hz).

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