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NEW CUCURBITANE TRITERPENOIDS FROM *MOMORDICA CHARANTIA*

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ABSTRACT.—Three new cucurbitane triterpenoids, **1**, **3**, and **6**, have been isolated from the leaves of *Momordica charantia* along with two other known compounds, momordicines I [**8**] and II [**9**]. The structures of the new metabolites were determined by interpretation of spectral data.

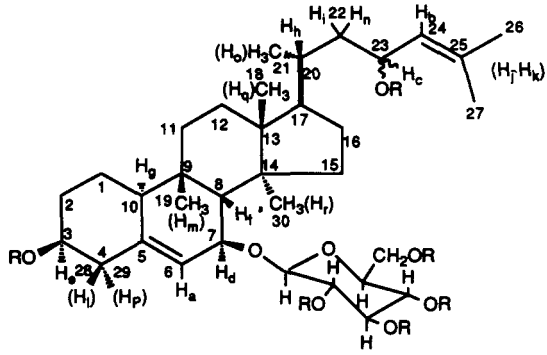
Momordica charantia L. (Cucurbitaceae), trivially called African cucumber or balsam pear (1), is widely distributed in West Africa, India, and Japan. The sample used in this study originated in Kano, a city in northern Nigeria. A related species, *Momordica balsamina* L., which is found in southern Nigeria, is uncommon in Kano. However, the two species are used both as a bitter stomachic and a purgative. *M. charantia* is available at local herbal drug stores in Kano city.

The leaves of *M. charantia* contain antibacterial and insecticidal principles (2–4). A number of cucurbitane triterpenoids, named momordicosides and momordicines, respectively (5,6), have previously been isolated from the fruits and leaves of *M. charantia*. This paper details the isolation and structure elucidation of three new compounds **1**, **3**, and **6** obtained from the leaves of *M. charantia*.

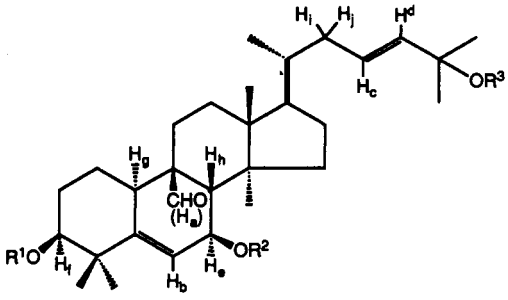
RESULTS AND DISCUSSION

The MeOH extract of the dried leaves of *M. charantia* was redissolved in 90% MeOH and extracted successively with *n*-hexane, CCl_4, and $CHCl_3$. Extensive chromatography of the $CHCl_3$-soluble fraction over Si gel and Lobar RP-8 columns gave compounds **1**, **3**, and **6** together with the known momordicines I [**8**] and II [**9**] (5).

Compound **1**, $[\alpha]_D$ +89.0° (MeOH), was obtained as an amorphous powder, and



1 R=H
2 R=Ac

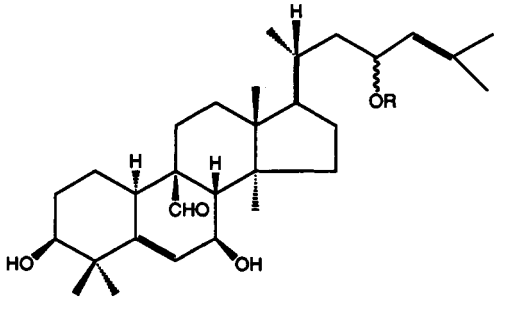


3 $R^1=R^2=R^3=H$
4 $R^1=R^2=Ac$, $R^3=H$
5 $R^1=R^3=H$, $R^2=\beta$-D-glucopyranosyl
6 $R^1=R^2=H$, $R^3=Me$
7 $R^1=R^2=Ac$, $R^3=Me$

its molecular formula was determined as $C_{36}H_{60}O_8 \cdot 3/2H_2O$ based on elemental analysis and fabms. The ^1H nmr of **1** showed the presence of five tertiary methyl groups at δ 0.74 (H_3-30), 0.98 (H_3-18), 1.14 (H_3-29), 1.40 (H_3-19), and 1.44 (H_3-28) (each 3H, s), a secondary methyl group at δ 1.16 (3H, d, $J=6.3$ Hz, H_3-21), and two methyl groups on olefinic carbons at δ 1.72 and 1.73 (each 3H, d, $J=1.1$ Hz, H_3-26 and H_3-27). In addition, the ^1H nmr showed the presence of three secondary carbinyl groups at δ 3.81 (1H, m, H-3), 4.58 (1H, br d, $J=5.0$ Hz, H-7), and 4.83 (1H, m, H-23), two trisubstituted olefinic bonds at δ 5.63 (1H, br d, $J=8.1$ Hz, H-24) and 6.06 (1H, br d, $J=5.0$ Hz, H-6), and a hexopyranose moiety indicated by one anomeric proton signal at δ 5.09 (1H, d, $J=7.8$ Hz, H-1′).

The ^{13}C-nmr spectrum of **1** (Table 1) showed signals due to eight methyl groups, seven methylene groups, four methine groups and four quaternary carbon atoms, two trisubstituted olefinic bonds at δ 121.09, 131.83 (each d), 130.84, and 148.30 (each s), a hexopyranose moiety, and three secondary carbinyl groups at δ 65.31, 72.55, and 76.06 (each d), respectively. Acetylation of compound **1** gave the hexaacetate **2**. Methanolysis of **1** gave methyl-1-*O*-glucoside which was identified by glc as its trimethylsilyl ether. Based on these data and on the co-occurrence of momordicines I [**8**] and II [**9**] in the plant material presently studied, compound **1** was assumed to be a trihydroxycucurbitadiene monoglucoside.

The structure of the aglycone and the position of the glycosidic linkage of **1** were further elucidated as follows. In the ^1H-COSY spectrum (Figure 1) of **1**, H_a crossed peaks with both H_d and the signal at δ 2.44 (1H, m, H_g), and H_d crossed peaks with



8 R=H
9 R=β-D-glucopyranosyl

TABLE 1. ^{13}C-nmr Data[a] of Compounds **1**, **3**, and **6** (measured in C_5D_5N solution).

Carbon	Compound		
	1	**3**	**6**
C-1	21.72 (t)	21.76 (t)	21.75 (t)
C-2	30.12 (t)	29.94 (t)	29.91 (t)
C-3	76.06 (d)	75.68 (d)	75.67 (d)
C-4	41.95 (s)	41.79 (s)	41.79 (s)
C-5	148.30 (s)	145.73 (s)	145.73 (s)
C-6	121.09 (d)	124.29[b] (d)	124.29 (d)
C-7	72.55 (d)	65.73 (d)	65.72 (d)
C-8	48.14 (d)	50.66 (d)	50.59 (d)
C-9	34.41 (s)	50.61 (s)	50.64 (s)
C-10	39.29 (d)	36.90 (d)	36.89 (d)
C-11	28.23 (t)	22.71 (t)	22.71 (t)
C-12	32.89 (t)	29.44 (t)	29.46 (t)
C-13	46.43 (s)	45.76 (s)	45.79 (s)
C-14	48.46 (s)	48.28 (s)	48.28 (s)
C-15	34.82 (t)	34.96 (t)	34.96 (t)
C-16	30.65 (t)	27.75 (t)	27.76 (t)
C-17	51.34 (d)	50.15 (d)	50.14 (d)
C-18	15.64 (q)	15.05 (q)	15.05 (q)
C-19	29.33 (q)	207.81 (d)	207.76 (d)
C-20	32.99 (d)	36.58 (d)	36.36 (d)
C-21	19.31 (q)	18.96 (q)	18.97 (q)
C-22	45.51 (t)	39.56 (t)	39.72 (t)
C-23	65.31 (d)	124.23[b] (d)	128.41 (d)
C-24	131.83 (d)	141.73 (d)	137.68 (d)
C-25	130.84 (s)	69.72 (s)	74.83 (s)
C-26	25.79 (q)	30.85 (q)	26.47 (q)
C-27	18.10[b] (q)	30.85 (q)	26.08 (q)
C-28	26.34 (q)	26.24 (q)	26.23 (q)
C-29	28.38 (q)	27.39 (q)	27.36 (q)
C-30	18.07[b] (q)	18.20 (q)	18.19 (q)
OMe			50.21 (q)
C-1′	101.20 (d)		
C-2′	75.16 (d)		
C-3′	78.77 (d)		
C-4′	71.93 (d)		
C-5′	78.50 (d)		
C-6′	62.88 (t)		

[a]Proton attachments determined via DEPT are shown in parentheses.
[b]The assignments in the same vertical column may be reversed.

the signal at δ 2.51 (1H, br s, H_f). As a result, H_a, H_d, H_f, and H_g were assigned as H-6, H-7, H-8, and H-10, and the presence of a trisubstituted double bond at C-5 and a secondary carbinyl group at C-7 was thus established. The location of a glycosidic linkage at C-7 was inferred from both the ^{1}H-nmr spectrum of hexaacetate **2** derivative of **1** and nOe experiments. The resonance frequency of H_d did not shift downfield on acetylation, whereas H_c and H_e moved downfield relative to **1** (δ 4.83 vs. 5.67 and 3.81 vs. 4.74). On separate irradiation of H_d and H_f, difference nOe's were observed for the anomeric proton at δ 5.09 (1H, d, $J = 7.8$ Hz), confirming the location of the glucose moiety. The configuration of the glycosidic linkage of **1** was determined as β based on the coupling constant ($J = 7.8$ Hz) of the anomeric proton.

In the ^{1}H-COSY spectrum of **1**, the methyl protons H_j and H_k crossed peaks with

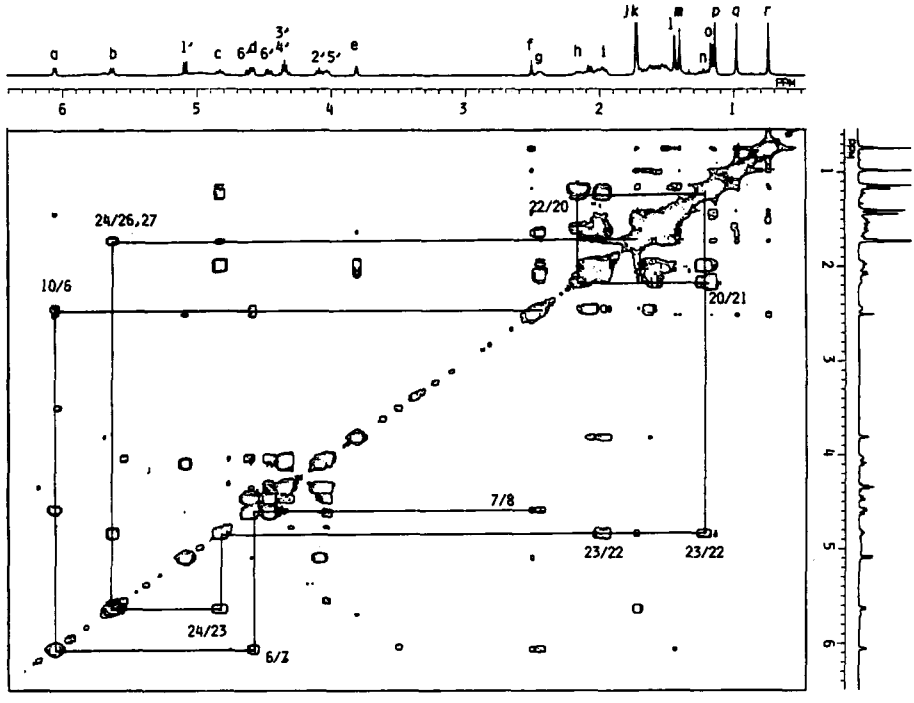


FIGURE 1. ^{1}H-COSY spectrum of compound **1**.

H_b, H_b crossed peaks with H_c, H_c crossed peaks with both the signal at δ 1.95 (1H, m) (H_i) and 1.25 (1H, m) (H_n), H_n crossed peaks with the signal at δ 2.16 (1H, m) (H_h). H_h was coupled to the methyl hydrogen atoms (H_o). Taken together these data supported the location of a secondary hydroxyl group at C-23 and the proposed structure for the side chain carbons. The methyl protons (H_l and H_p) crossed peaks, supporting the location of two methyl groups at C-4. Separate irradiation of the resonance frequency of H_l and H_p gave difference nOe's for H_e. Considering the coupling pattern of H_e, a secondary hydroxyl group with axial configuration must be located at C-3. All data taken together, compound **1** was assumed to be 3β,7β,23-trihydroxycucurbita-5,24-diene-7-*O*-β-D-glucoside [**1**]. This assumption was further substantiated by the results of extensive nOe experiments (Figure 2).

Compound **3**, [α]D +58.0° (MeOH), was obtained as an amorphous powder. The molecular formula was determined as $C_{30}H_{48}O_4 \cdot H_2O$ based on fabms, eims, and ele-

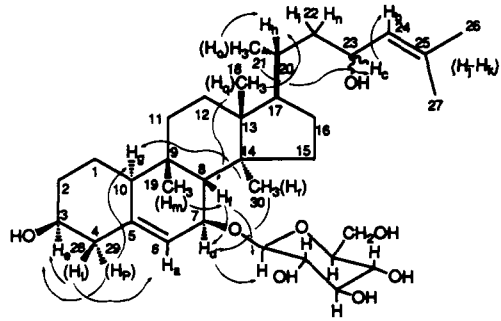


FIGURE 2. Difference nOe of compound **1**.

mental analyses. The ^{1}H- [and ^{13}C-] nmr spectra of **3** showed the presence of an aldehyde group at δ 10.66 (1H, s, H-19, H_a) [δ 207.81 (d)], two secondary carbinyl groups at δ 4.38 (1H, br d, J = 5.5 Hz, H-7, H_e) and 3.84 (1H, m, H-3, H_f) [δ 65.73 and 75.68 (each d)], a trisubstituted double bond at δ 6.28 (1H, br d, J = 4.1 Hz, H-6, H_b) [δ 124.29 (d) and 145.73 (s)], a trans disubstituted double bond at δ 5.93 (1H, m, H-23, H_c) and 5.91 (1H, d, J = 15.4 Hz, H-24, H_d) [δ 124.23 (d) and 141.73 (d)], and seven methyl groups at δ 0.85, 0.88, 1.19, 1.49, 1.546, 1.551 (each 3H, s), and 0.99 (3H, d, J = 6.3 Hz) [δ 15.50, 18.20, 18.96, 26.24, 27.39, 30.85, and 30.85 (each q)]. In addition to the above mentioned signals, the ^{13}C-nmr spectrum (Table 1) further showed signals due to seven methylene groups, four methine groups, four quaternary carbon atoms, and a tertiary carbinyl group at δ 69.72 (s).

These spectral data of **3** are very similar to those reported (5) for momordicine I [**8**] except that one of the two trisubstituted olefinic bonds and the signal at C-23 (the carbon having a hydroxy group) in **8** were absent and, instead, a trans disubstituted olefinic bond and a hydroxylated quaternary carbon atom at C-25 were observed. Thus, the structure of compound **3** was assumed to be 3β,7β,25-trihydroxycucurbita-5,(23*E*)-dien-19-al [**3**]. The substitution pattern of C-10, C-6, C-7, and C-8 was confirmed by following the cross peaks: H_g [δ 2.69 (1H, m), H-10]↦H_b (6-H)↦H_e (H-7)↦H_h [δ 2.39 (1H, br s, H-8)] in the ^{1}H-COSY spectrum of **3**. The chemical shift and coupling pattern of H_f resonance are consistent with those of momordicine I [**8**]. H_f also crossed peaks with the signals at δ 1.19 and 1.49 (each 3H, s) assigned as H_3-29 and H_3-28 in the ^{1}H-NOESY spectrum of **3**. Thus, the stereochemistry of the hydroxyl group located at C-3 must be β. The location of an aldehyde group at C-9β was supported by observation of the cross peaks between H_a and H_h in the ^{1}H-NOESY spectrum.

The structure of the side chain was substantiated from the following observations. H_c resonance crossed peaks with H_d, H_i [δ 2.24 (1H, m)], and H_j [δ 1.85 (1H, m)] in the ^{1}H-COSY spectrum of **3**. In the ^{1}H-^{13}C long range-COSY spectrum, H_c crossed peaks with the quaternary carbon C-25. Acetylation of compound **3** gave the diacetate **4**, mp 101–104°. The diacetate **4** was found identical with aglycone diacetate of previously isolated momordicoside L [**5**] (6).

Compound **6**, [α]D +48.9° (MeOH) was obtained as an amorphous powder. Its molecular formula, $C_{31}H_{50}O_4 \cdot {}^3/_2H_2O$, was determined on the basis of ms and elemental analyses and found to be 14 mass units more than that of compound **3**. The spectral characteristics of **3** and **6** (see Experimental and Table 1) are very similar except for the appearance of a methoxy group signal in the latter. Acetylation of compound **6** gave the diacetate **7**. Thus, compound **6** is the methyl ether of compound **3**. This structural assignment was supported by ^{13}C signals of C-23 and C-24, which moved ca. 4 ppm downfield and ca. 4 ppm upfield, respectively, in **6** relative to **3**.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Ir spectra were measured with a Hitachi 215 spectrophotometer. Optical rotations were determined with a Union Giken PM-201 digital polarimeter. Nmr spectra were measured with a JEOL FX-200 or JEOL GSX-400 spectrometer. Mass spectra were obtained with a JEOL D-300 mass spectrometer (eims, 70 eV; fabms, gun high voltage, 3.0 kV; matrix, thioglycerol). Kiesel gel 60 (0.040–0.063 mm; Merck) was used for cc, and Kiesel gel 60 F_{254} precoated plates (0.25 mm or 0.5 mm; Merck) were used for tlc and preparative layer chromatography.

PLANT MATERIAL.—The plant material was collected in Sharada, Kano, Nigeria in April 1987 by Mallam Isa Isyaku and identified as *M. charantia* by Dr. Y. Karatela and Mr. Ali Garko. A voucher specimen was deposited in the herbarium of Bayero University, Kano, Nigeria.

ISOLATION PROCEDURES.—The MeOH extract of the dried leaves (420 g) of *M. charantia* was concentrated in vacuo. The residue was dissolved in 90% MeOH (330 ml), and the solution was extracted with *n*-hexane (300 ml × 3). To the 90% MeOH layer, H_2O (54 ml) was added, and the resulting 80% MeOH

solution was extracted with CCl_4 (300 ml × 3). The 80% MeOH layer was converted to 65% MeOH by addition of H_2O (112 ml), and the solution was extracted with $CHCl_3$ (300 ml × 3). The organic extracts were dried and evaporated in vacuo to give the following residues: 3 g from *n*-hexane layer; 3 g from CCl_4 layer, and 18 g from $CHCl_3$ layer. The 65% MeOH layer was concentrated in vacuo to give a residue (37 g). A portion (17.5 g) of the residue from $CHCl_3$ extract was chromatographed on Si gel (750 g) and eluted with $CHCl_3$-MeOH mixtures containing increasing MeOH content in this order: $CHCl_3$ (2 liters), $CHCl_3$-MeOH (19:1) (2.5 liters), $CHCl_3$-MeOH (9:1) (3.5 liters), $CHCl_3$-MeOH (17:3) (4 liters), $CHCl_3$-MeOH (4:1) (3 liters). Fraction of 200 ml were collected.

Fractions 33–37 gave a residue (2.46 g) which was rechromatographed on Si gel (200 g) and eluted with $CHCl_3$/MeOH with increasing MeOH content. A portion (1.16 g) of the 10% MeOH eluate (1.48 g) was separated on a Lobar column (LiChroprep RP-8) using MeOH/H_2O as eluent. Collecting 8-ml fractions, MeOH-H_2O (7:3) (1 liter) and MeOH-H_2O (4:1) (500 ml) were passed through the column in that order. Fractions 24–60 gave momordicin II [**9**] (806 mg) on evaporation in vacuo, and fractions 121–150 gave compound **1** (136 mg) on evaporation.

Fractions 10–15 gave a residue (1.34 g) on evaporation. The residue was rechromatographed on Si gel (140 g) column with MeOH/$CHCl_3$ mixtures of increasing MeOH content. The $CHCl_3$-MeOH (49:1) eluent gave a residue (218 mg) which was purified by preparative layer chromatography [Si gel, $CHCl_3$-MeOH (93:7) developed three times] and gave compound **6** (84 mg); $CHCl_3$-MeOH (97:3) eluent gave a residue (590 mg) which was recrystallized from $CHCl_3$ to give momordicin I [**8**] (185 mg). The residue from mother liquor was separated on Lobar column (LiChroprep RP-8) [solvent MeOH-H_2O (8:2)] to give compound **3** (86 mg). Momordicines I [**8**] and II [**9**] were identical with authentic samples.

COMPOUND **1**.—Amorphous powder: $[\alpha]^{26}D$ +89.0° (c = 0.43, MeOH); ir ν max (KBr) 3450 (br), 1650, 1475, 1460, 1390, 1080, 1045, 1020, 990, 945 cm^{-1}; ^1H nmr (400 MHz, C_5D_5N) δ 0.74 (3H, s, H_3-30), 0.98 (3H, s, H_3-18), 1.14 (3H, s, H_3-29), 1.16 (3H, d, J = 6.3 Hz, H_3-21), 1.25 (1H, m, H_1-22), 1.40 (3H, s, H_3-19), 1.44 (3H, s, H_3-28), 1.72 and 1.73 (each 3H, d, J = 1.1 Hz, H_3-26), 1.95 (1H, m, H_1-22), 2.16 (1H, m, H-20), 2.44 (1H, m, H-10), 2.51 (br s, H-8), 3.81 (1H, m, H-3), 4.03 (1H, m, H-5′), 4.09 (1H, t, J = 7.8 Hz, H-2′), 4.33–4.36 (2H, H-3′ and H-4′), 4.46 (1H, dd, J = 11.9 and 5.3 Hz, H-6′), 4.58 (1H, br d, J = 5.0 Hz, H-7), 4.62 (1H, dd, J = 2.4 and 11.9 Hz, H-6′), 4.83 (1H, m, H-23), 5.09 (1H, d, J = 7.8 Hz, H-1′), 5.63 (1H, br d, J = 8.1 Hz, H-24), 6.06 (1H, br d, J = 5.0 Hz, H-6); ^{13}C nmr see Table 1; eims *m/z* 422.3513 $[M - Gluc - H_2O]^+$ (calcd for $C_{30}H_{46}O_1$, 422.3548); fabms *m/z* $[M + Na]^+$ 643 (+NaI), $[M + K]^+$ 659 (+KI). *Anal.* found C 66.41, H 10.11%; calcd for $C_{36}H_{60}O_8 \cdot 2/3\ H_2O$, C 66.73, H 9.80%.

HEXAACETATE **2**.—Compound **1** (10 mg) was treated with a mixture of Ac_2O (0.5 ml) and pyridine (0.5 ml) overnight at room temperature. Excess MeOH was added to the mixture and the solvent was removed in vacuo. The residue was purified by preparative layer chromatography (solvent Et_2O, developed twice) to give hexaacetate **2** (13.7 mg) as an amorphous powder: Ir ν max ($CHCl_3$) 1760, 1730, 1455, 1380, 1260, 1250–1210, 1140, 1040, 990, 945 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 0.70, 0.87, 0.92 (each 3H, s), 0.90 (3H, d, J = 5.1 Hz, H_3-21), 1.05, 1.12, 1.70, 1.74 (each 3H, s), 2.015, 2.022, 2.03, 2.09 (each 3H, s, 4 × OAc), 2.05 (6H, s, 2 × OAc), 3.67 (1H, m, H-5′), 3.98 (1H, d, J = 5.5 Hz, H-7), 4.21 (2H), 4.62 (1H, d, J = 8.1 Hz, H-1′), 4.74 (1H, t-like, J = 2.2 Hz, H-3), 4.98–5.30 (4H), 5.67 (1H, m, H-23), 5.69 (1H, br d, J = 5.5 Hz, H-6); fabms *m/z* $[M + Na]^+$ (+NaI) 895 $[M + K]^+$ (+KI) 911.

METHANOLYSIS OF COMPOUND **1**.—Compound **1** (1 mg) was dissolved in 1 N methanolic HCl (0.5 ml), and the solution was heated (60–70°) for 1.5 h. After being neutralized with Ag_2CO_3, the precipitate was centrifuged off. The supernatant was treated with H_2S gas, and the resulting precipitate was also centrifuged off. The supernatant was concentrated and dried in vacuo. The residue was trimethylsilylated and subjected to glc (column HiCap, i.d. 0.2 mm × 50 ml; liquid phase CBP-1; carrier gas He at 50 ml/min; column temperature 210°; injection temperature 290°; detection fid; detection temperature 290°). The chromatogram showed two peaks (Rt 16.7 and 17.6 min) that were completely identical with those from glucose.

Compound **3**.—Amorphous powder; $[\alpha]^{26}D$ +58.0° (c = 0.48, MeOH); ir ν max (KBr) 3400 (br), 1715, 1660, 1470, 1460, 1385, 1155, 1090, 1050, 1020, 980 cm^{-1}; ^1H nmr (400 MHz, C_5D_5N) δ 0.85 (3H, s, H_3-30), 0.88 (3H, s, H_3-18), 0.99 (3H, d, J = 6.3 Hz, H_3-21), 1.19 (3H, s, H_3-29), 1.24 (1H, m, H_1-16), 1.49 (3H, s, H_3-28), 1.546, 1.551 (each 3H, br s, H_3-26 and H_3-27), 1.76 (1H, m, H_1-1), 1.85 (1H, m, H_1-22), 2.09 (2H, m, H_1-1, H_1-2), 2.24 (1H, m, H_1-22), 2.39 (1H, br s, H-8), 2.69 (1H, m, H-10), 3.84 (1H, m, H-3), 4.38 (1H, br d, J = 5.5 Hz, H-7), 5.91 (1H, d, J = 15.4 Hz, H-24), 5.93 (1H, m, H-23), 6.28 (1H, br d, J = 4.1 Hz, H-6), 10.66 (1H, s, H_1-19); ^{13}C nmr see Table 1; eims *m/z* $[M]^+$ 472.3519 (calcd for $C_{30}H_{48}O_4$, 472.3552) fabms *m/z* $[M + Na]^+$ (+NaI) 495, $[M + K]^+$ (+KI) 511. *Anal.* found C 73.89, H 10.52%; calcd for $C_{30}H_{48}O_4 \cdot H_2O$, C 73.43, H 10.27%.

DIACETATE **4**.—Compound **3** (12 mg) was acetylated with a mixture of Ac_2O and pyridine as above. The product was purified by preparative layer chromatography to give diacetate **4** (9.8 mg) which was crystallized on addition of MeOH as colorless needles: mp 101–104°, ir ν max ($CHCl_3$) 3450 (br), 1735, 1720, 1610, 1470, 1380, 1260, 1220, 1190, 1020, 990, 940, 920 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 0.83, 0.89 (each 3H, s), 0.91 (3H, d, J = 5.5 Hz, H_3-21), 1.14, 1.18 (each 3H, s), 1.32 (6H, s, H_3-26, H_3-27), 2.04, 2.05 (each 3H, s, 2 × OAc), 4.48 (1H, t-like, J = 2.5 Hz, H-3), 5.22 (1H, br d, J = 5.5 Hz, H-7), 5.60 (2H, H-23, H-24), 5.88 (1H, br d, J = 5.5 Hz, H-6), 9.85 (1H, s, H-19); eims *m/z* $[M - HOAc - H_2O]^+$ 478.3462 (calcd for $C_{32}H_{48}O_3$, 478.3447); fabms *m/z* $[M + Na]^+$ (+NaI) 579, $[M + K]^+$ (+KI) 595.

COMPOUND **6**.—Amorphous powder: $[\alpha]^{26}D$ +48.9° (c = 0.45, MeOH); ir ν max (KBr) 3425 (br), 1715, 1660, 1470, 1380, 1000, 980 cm^{-1}; ^1H nmr (400 MHz, C_5D_5N) δ 0.88 (3H, s, H_3-30), 0.90 (3H, s, H_3-18), 0.99 (3H, d, J = 5.8 Hz, H_3-21), 1.18 (3H, s, H_3-29), 1.33 (6H, s, H_3-26, H_3-27), 1.48 (3H, s, H_3-28), 3.22 (1H, m, H_1-22), 2.39 (1H, br s, H-8), 2.72 (1H, m, H-10), 3.22 (3H, s, OMe), 3.83 (1H, m, H-3), 4.38 (1H, br d, J = 5.2 Hz, H-7), 5.55 (1H, d, J = 15.7 Hz, H-24), 5.63 (1H, m, H-23), 6.28 (1H, br d, J = 5.2 Hz, H-6), 10.65 (1H, s, H-19); ^{13}C nmr see Table 1; eims *m/z* $[M - H_2O]^+$ 468.3615 (calcd for $C_{31}H_{48}O_3$, 468.3603); fabms *m/z* $[M + Na]^+$ (NaI) 593, $[M + K]^+$ (+KI) 609. *Anal.* found C 72.68, H 9.98%; calcd for $C_{31}H_{50}O_4 \cdot 3/2\ H_2O$, C 72.47, H 10.39%.

DIACETATE **7**.—Compound **6** (11.2 mg) was acetylated with a mixture of Ac_2O and pyridine as above. The product was purified by preparative tlc [solvent $CHCl_3$-MeOH (97:3)] to give diacetate **7** (8.8 mg): ir ν max ($CHCl_3$) 1740, 1725, 1640, 1610, 1480, 1385, 1260, 1225, 1080, 1030, 950 cm^{-1}; ^1H nmr (200 MHz, $CDCl_3$) δ 0.82, 0.89 (each 3H, s), 0.93 (3H, d, J = 5.9 Hz, H_3-21), 1.14, 1.18 (each 3H, s), 1.26 (6H, s, H_3-26, H_3-27), 2.04, 2.05 (each 3H, s, 2 × OAc), 3.16 (3H, s, OMe), 4.84 (1H, t-like, J = 2.5 Hz, H-3), 5.22 (1H, br d, J = 5.1 Hz, H-7), 5.40 (1H, d, J = 16.1 Hz, H-24), 5.49 (1H, m, H-23), 5.88 (1H, br d, J = 4.0 Hz, H-6), 9.85 (1H, s, H-19); eims *m/z* $[M - HOAc]^+$ 510.3682 (calcd for $C_{33}H_{50}O_4$, 510.3709); fabms *m/z* $[M + Na]^+$ (+NaI) 593, $[M + K]^+$ (+KI) 609.

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