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TWO STEROIDAL GLYCOSIDES, ACULEATISIDE A AND B FROM *SOLANUM ACULEATISSIMUM**

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Key Word Index—*Solanum aculeatissimum*; Solanaceae; steroidal glycosides; aculeatiside A; aculeatiside B; nuatigenin; isonuatigenin.

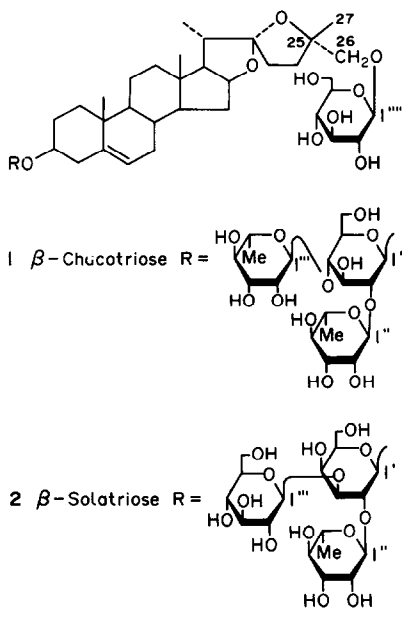
Abstract—Two new steroidal glycosides, named aculeatiside A and B, were isolated in yields of *ca* 0.1 and 3.0%, respectively, from the root of *Solanum aculeatissimum* and their structures were determined as 26-*O*-*β*-D-glucopyranosyl nuatigenin 3-*O*-*β*-chacotrioside and 26-*O*-*β*-D-glucopyranosyl nuatigenin 3-*O*-*β*-solatrioside respectively. Therefore, this plant is considered to be a useful source of pregnane derivatives.

INTRODUCTION

Solanum aculeatissimum has been used to treat bronchitis and rheumatism in China and solasodine, solasonine and solamargine are known as constituents of this plant [1, 2]. In our studies on the oriental *Solanum* plants, we have now isolated two new steroidal glycosides, named aculeatiside A and B, from the roots of *S. aculeatissimum* and elucidated their structures.

RESULTS AND DISCUSSION

The isolation and separation of aculeatiside A (**1**) and B (**2**) were carried out by a combination of CC on Amberlite XAD-2, Sephadex LH-20, alumina and Si gel followed by crystallization.



Aculeatiside A (**1**), colorless needles, mp 196–204°, $[\alpha]_D$ −96.7°, FDMS *m/z* 1069 $[M]^+$, showed strong IR absorption due to hydroxyls and gave on acid hydrolysis nuatigenin (**3**) [3], mp 206–216°, $[\alpha]_D$ −86.9°, and isonuatigenin (**4**) [3], mp 256–258°, $[\alpha]_D$ −111.6°, as the aglycone part and glucose and rhamnose as the sugar part. The permethyl ether derived from **1** by the Hakomori method [4] gave on methanolysis a mixture of methyl glycosides of 2,3,4,6-tetra-*O*-methyl-D-glucopyranose, 2,3,4-tri-*O*-methyl-L-rhamnopyranose and 3,6-di-*O*-methyl-D-glucopyranose. The ^{13}C NMR spectra of **3** and **4** were assigned as shown in Table 1. Compound **1** exhibited four peaks ascribable to the anomeric carbons

Table 1. ^{13}C NMR data (pyridine-d_5) of aculeatiside A (**1**), aculeatiside B (**2**), nuatigenin (**3**) and isonuatigenin (**4**)

Carbon No.	1	2	3	4
1	37.5	37.5	37.8	37.8
2	30.1	30.1	31.7	31.8
3	78.1	78.1	71.3	71.2
4	40.5	40.5	43.5	43.4
5	140.7	140.9	142.0	141.9
6	120.1	120.2	120.3	120.9
7	32.2	32.2	32.6*	32.6*
8	31.6	31.7	32.2	32.3
9	50.2	50.3	50.5	50.4
10	37.0	37.1	37.0	37.0
11	21.0	21.1	21.2	21.2
12	38.9	38.6	40.0	40.0
13	39.8	39.8	40.6	40.5
14	56.4	56.5	56.6	56.8
15	32.2	32.2	32.3*	32.2*
16	80.9	80.9	81.1	81.3
17	62.6	62.7	62.6	63.0
18	16.1	16.2	16.2	16.4
19	19.3	19.4	19.6	19.6
20	38.6	38.6	38.5	42.0

*Part 3 in the series "Studies on the Constituents of *Solanum* Plants". For Part 2 see Saijo, R., Murakami, K., Nohara, T., Tomimatsu, T., Sato, A. and Matsuoka, K. (1982) *Yakugaku Zasshi* **102**, 300.

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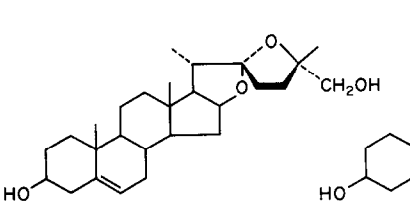
Table 1. (*contd.*)

Carbon No.	1	2	3	4
21	15.0	15.1	15.2	15.1
22	121.7	121.6	120.9	109.5
23	33.1*	33.1*	32.6*	27.8
24	33.8*	33.8*	33.8*	33.8*
25	83.8	83.8	85.6	65.9
26	77.2	77.3	70.1	69.7
27	24.3	24.3	24.1	26.9
1′	100.2	100.4	—	—
2′	79.0	74.7†	—	—
3′	76.6	85.0	—	—
4′	77.8	69.9	—	—
5′	78.1	74.9†	—	—
6′	61.4	62.2‡	—	—
1″	101.8	102.0	—	—
2″	72.5†	72.6§	—	—
3″	71.6†	72.2§	—	—
4″	73.6‡	73.9	—	—
5″	69.3§	69.3	—	—
6″	18.3‖	18.5	—	—
1‴	102.7	105.5	—	—
2‴	72.5†	76.0	—	—
3‴	72.2†	78.1	—	—
4‴	73.9‡	71.6	—	—
5‴	70.3§	77.7	—	—
6‴	18.4‖	61.7‡	—	—
1⁗	105.1	105.1	—	—
2⁗	75.1	75.2	—	—
3⁗	78.1	78.1	—	—
4⁗	72.2	71.6	—	—
5⁗	78.1	78.1	—	—
6⁗	62.4	62.4‡	—	—

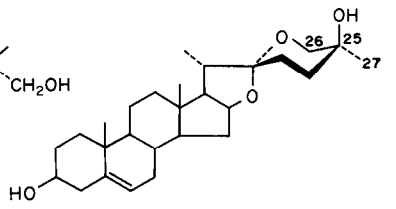
*, †, ‡, §, ‖ Data with the same sign within each column may be reversed.

of the sugar moiety and the signals due to the aglycone part were in good agreement with those of **3** except C-3 and C-26. The above evidence suggested that **1** was a nuatigenin tetraglycoside, whose sugar component consisted of two moles of glucose and two moles of rhamnose, and that the glycosyl residues were linked to the hydroxyls at C-3 and C-26 of **3** from consideration of the glycosidation shift [5, 6]. Production of isonuatigenin (**4**) was artificially derived from nuatigenin (**3**) during acid hydrolysis [3]. Furthermore, application of the Baeyer–Villiger reaction [7] on **1** using hydrogen peroxide and formic acid followed by treatment with alkali afforded a pregnane oligoside (**5**) and (*S*)-4,5-dihydroxy-4-methyl-pentanoic acid 5-*O*-β-D-glucopyranoside (**6**). Compound **5** gave on acid hydrolysis 5α-pregnane-3β,5,6β,16β,20α-pentol (**7**) [8] and glucose and rhamnose, while the structure of **6** was substantiated by the ^{13}C NMR spectrum and enzymic hydrolysis with almond emulsin to give D-glucose. Therefore, **1** must be a bisdesmoside having β-chacotriose linked at C-3 and one mole of glucose at C-26. It thus belongs to the avenacoside-type of glycoside [9, 10], and can be designated the structure 3-*O*-[α-L-rhamnopyranosyl-(1 → 2_{glu})-α-L-rhamnopyranosyl-(1 → 4_{glu})-β-D-glucopyranosyl]nuatigenin 26-*O*-β-D-glucopyranoside.

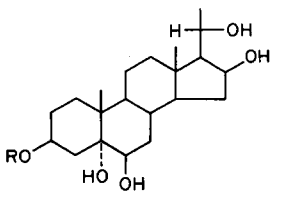
Aculeatiside B (**2**), was an amorphous powder, $[\alpha]_D$ −82.0°, which exhibited $[M+Na]^+$ at *m/z* 1085 in the FDMS and gave on acid hydrolysis compounds **3** and **4** as the aglycone components and glucose, galactose and rhamnose as the sugar components. The permethyl ether, obtained in the same manner as the permethyl ether of **1**, gave on methanolysis a mixture of methyl glycosides of 2,3,4-tri-*O*-methyl-L-rhamnopyranose, 2,3,4,6-tetra-*O*-methyl-D-glucopyranose and 4,6-di-*O*-methyl-D-galactopyranose and an additional methylated sugar, which was proved to be methyl-2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-4,6-di-*O*-methyl-α-D-galactopyranoside by the ^1H NMR spectrum of its monoacetyl



3 Nuatigenin



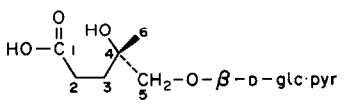
4 Isonuatigenin



5 R=β-Chacotriose

7 R=H

8 R=β-Solatriose



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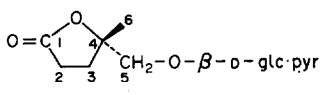

9

derivative. The Baeyer–Villiger reaction of **2** afforded a pregnane glycoside (**8**) and compound **9**, the former of which on acid hydrolysis gave galactose, glucose and rhamnose along with **7**. Compound **9** was identified as (*S*)-4-hydroxymethyl-4-methyl-γ-butyrolactone-β-D-glucopyranoside by ^{1}H and ^{13}C NMR analysis.

Consequently, the structure of **2** is represented as 3-*O*-[α-L-rhamnopyranosyl-(1 → 2$_{gal}$)-β-D-glucopyranosyl-(1 → 3$_{gal}$)-β-D-galactopyranosyl]nuatigenin 26-*O*-β-D-glucopyranoside.

Both steroidal glycosides **1** and **2** have been obtained in a good yields (*ca* 0.1 and 3.0%, respectively) in the crystalline state. The *n*-butanol layer obtained during the separation procedure contains more of **1** and **2** (7.27%). Since **3** and **4** obtained by hydrolysis of **1** and **2** can be transformed into pregnadienolone [3], it is conceivable that the title plant may be a useful source to provide pregnane derivatives.

EXPERIMENTAL

All mps were uncorr. Optical rotations were taken at 15–20° using a 1-dm cell. ^{1}H and ^{13}C NMR spectra were recorded at 100 and 50.01 MHz, respectively, using TMS as int. standard. Chemical shifts are given in δ (ppm). The FDMS were measured at ion source potentials of 8 kV for the field anode and −3 kV for the slotted cathode plate, an ion source pressure of *ca* 10^{-7} Torr and an ion source temp. between 50° and 60°. Al_2O_3 90 (70–230 mesh) and Si gel 60 (70–230 mesh) were employed for CC. Si gel 60 was used for TLC. The spots were visualized by spraying with 10% H_2SO_4 followed by heating. GC employed a glass column (3 mm × 2 m) packed with 1% neopentylglycol succinate on Chromosorb W (60–80 mesh).

Plant material. The underground parts of *Solanum aculeatissimum* Sacq. were collected in December from plants cultivated in the Medicinal Botanical Garden of Tokushima University.

Isolation of aculeatiside A (**1**) *and B* (**2**). The fresh sliced materials (715 g) were extracted with refluxing MeOH (1.5 l. × 3). After evaporation of solvent, the MeOH extractives (70 g) were defatted with *n*-hexane to give a residue, which was partitioned between *n*-BuOH (2 l.) and H_2O (2 l.). The organic layer was concd to 20% vol. to afford a ppt (36 g). The filtrate (16 g) was chromatographed on Si gel using $CHCl_3$–MeOH–H_2O (8:2:0.2→7:3:0.5) to furnish aculeatiside A (**1**), 638 mg (0.1% based on the fresh root) as colorless needles, while a part (3.12 g) of the ppt was separated by Al_2O_3 CC using the upper layer of EtOAc–pyridine–H_2O (3:1:3) as solvent to afford aculeatiside B (**2**), 1.88 g (3%), as an amorphous powder.

Aculeatiside A (**1**). Colorless needles from dil. MeOH, mp 196–204° (decomp.), $[\alpha]_D^{22}$ −96.7° (pyridine; *c* 1.08), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 919, 870, 840, 818 (spiroketal). FDMS (*m/z*): 1069 [M + Na]$^+$. ^{1}H NMR (pyridine-d_5): δ 0.81 (3H, *s*, Me-18), 1.05 (3H, *s*, Me-19), 1.08 (3H, *d*, *J* = 6 Hz, Me-21), 1.40 (3H, *s*, Me-27), 1.62 (3H, *d*, *J* = 6 Hz, rha-Me-5), 1.76 (3H, *d*, *J* = 6 Hz, rha-Me-5).

Acid hydrolysis of **1**. A soln of **1** (360 mg) in 2 N HCl–MeOH (10 ml) was refluxed for 2.5 hr. After cooling the mixture was neutralized with 5% KOH–MeOH, concentrated, and *n*-BuOH and H_2O added. The BuOH layer was evaporated *in vacuo* to dryness to give a residue, which was separated by Si gel CC with $CHCl_3$–MeOH (100:1 → 30:1) to afford nuatigenin (**3**) (18 mg) and isonuatigenin (**4**) (42 mg). While the aq. layer was examined by Si gel TLC to detect glucose and rhamnose ($CHCl_3$–MeOH–Me_2CO–H_2O, 3:3:3:1).

Nuatigenin (**3**). R_f 0.71 ($CHCl_3$–MeOH, 10:1), colorless needles, mp 212–216°, $[\alpha]_D^{19}$ −86.9° ($CHCl_3$; *c* 0.61) (lit. 210–214°, $[\alpha]_D^{23}$ −93° [3]), IR ν_{max}^{KBr} cm^{-1}: 3350 (OH), 920, 874, 860, 836, 804. EIMS (*m/z*): 430 [M]$^+$, 412 [$C_{27}H_{40}O_3$]$^+$, 399 [$C_{26}H_{39}O_3$]$^+$, 381 [$C_{26}H_{37}O_2$]$^+$, 300 [$C_{21}H_{32}O$]$^+$, 282 [$C_{21}H_{30}$]$^+$, 271 [$C_{19}H_{27}O$]$^+$, 253 [$C_{19}H_{25}$]$^+$, 155 [$C_9H_{15}O_2$]$^+$. Nuatigenin (**3**) was acetylated in the usual manner to afford the diacetate, colorless needles, mp 156–176°, $[\alpha]_D^{22}$ −105.6° ($CHCl_3$; *c* 0.89) (lit. 156–159°, $[\alpha]_D^{22}$ −95° [3]). EIMS (*m/z*): 496 [M − H_2O]$^+$, 454 [$C_{29}H_{42}O_4$]$^+$, 441 [$C_{28}H_{41}O_4$]$^+$, 381 [$C_{26}H_{37}O_2$]$^+$, 313 [$C_{21}H_{29}O_2$]$^+$, 253 [$C_{19}H_{25}$]$^+$, 197 [$C_{11}H_{17}O_3$]$^+$, 185 [$C_{10}H_{17}O_3$]$^+$. ^{1}H NMR ($CDCl_3$): δ 0.76 (3H, *s*, Me-18), 0.96 (3H, *d*, *J* = 6 Hz, Me-21), 1.02 (3H, *s*, Me-19), 1.16 (3H, *s*, Me-27), 2.00, 2.06 (2 × OAc), 3.89, 4.15 (each 1H, *d*, *J* = 11 Hz, H_2-26), 4.20–4.72 (2H, *m*, H-3 and H-16), 5.33 (1H, *m*, H-6).

Isonuatigenin (**4**). R_f 0.67 ($CHCl_3$–MeOH, 10:1), colorless needles, mp 256–258°, $[\alpha]_D^{22}$ −111.6° ($CHCl_3$; *c* 1.00) (lit. 248–251°, $[\alpha]_D^{23}$ −123° [3]). IR ν_{max}^{KBr} cm^{-1}: 3350 (OH). EIMS (*m/z*): 430 [M]$^+$, 412 [$C_{27}H_{40}O_3$]$^+$, 399 [$C_{26}H_{39}O_3$]$^+$, 381 [$C_{26}H_{27}O_2$]$^+$, 300 [$C_{21}H_{32}O$]$^+$, 282 [$C_{21}H_{30}$]$^+$, 271 [$C_{19}H_{27}O$]$^+$, 253 [$C_{19}H_{25}$]$^+$, 155 [$C_9H_{15}O_2$]$^+$. ^{1}H NMR ($CDCl_3$ + CD_3OD): δ 0.82 (3H, *s*, Me-18), 1.04 (3H, *s*, Me-19), 1.05 (3H, *d*, *J* = 6 Hz, Me-21), 1.11 (3H, *s*, Me-27), 3.27, 3.67 (each 1H, *d*, *J* = 12 Hz, H_2-26), 5.30 (1H, *m*, H-6). Isonuatigenin (**4**) was acetylated in the usual manner to afford the monoacetate, colorless needles, mp 197–208°, $[\alpha]_D^{22}$ −129.0° ($CHCl_3$; *c* 0.85) (lit. 215.5–218.5°, $[\alpha]_D^{22}$ −140° [3]). ^{1}H NMR ($CDCl_3$): δ 0.79 (3H, *s*, Me-18), 1.02 (3H, *d*, *J* = 6 Hz, Me-21), 1.03 (3H, *s*, Me-19), 1.10 (3H, *s*, Me-27), 2.00 (3H, *s*, OAc), 3.20 (1H, *dd*, *J* = 2, 10 Hz, H-26β), 3.68 (1H, *d*, *J* = 10 Hz, H-26α), 4.24–4.68 (2H, *m*, H-3 and H-16), 5.31 (1H, *m*, H-6).

Methylation of **1**. NaH (150 mg) in DMF (4 ml) was stirred for 10 min, then **1** (109 mg) and MeI (3 ml) were added, the mixture was stirred overnight and then poured into ice–water. Extraction with $CHCl_3$ and usual work-up gave a crude product, which was chromatographed on Si gel (*n*-hexane–Me_2CO, 5:1 → 4:1) to provide the permethyl ether of **1** as an amorphous powder (117 mg), $[\alpha]_D^{22}$ −68.6° ($CHCl_3$; *c* 1.05), IR: no OH. EIMS (*m/z*): 777 [$C_{43}H_{69}O_{12}$]$^+$, 631 [$C_{37}H_{59}O_8$]$^+$, 413 [$C_{27}H_{41}O_3$]$^+$, 412 [$C_{27}H_{40}O_3$]$^+$, 381 [$C_{26}H_{37}O_2$]$^+$, 282 [$C_{21}H_{30}$]$^+$, 253 [$C_{19}H_{25}$]$^+$, 189 [methylpentose·3Me]$^+$, 157 [189 − MeOH]$^+$ ^{1}H NMR ($CDCl_3$): δ 0.77 (3H, *s*, Me-18), 0.96 (3H, *d*, *J* = 6 Hz, Me-21), 1.02 (3H, *s*, Me-19), 1.22 (3H, *s*, Me-27), 1.29, 1.44 (each 3H, *s*, 2 × methylpentosyl-Me), 3.34–3.60 (OMe), 4.28, 4.36 (each 1H, *d*, *J* = 8 Hz, 2 × hexosyl anomeric proton), 4.96, 5.20 (each 1H, *br s*, 2 × methylpentosyl anomeric proton), 5.32 (1H, *m*, H-6).

Methanolysis of the permethyl ether of **1**. A soln of the permethyl ether of **1** (12 mg) in 2 N HCl–MeOH (1 ml) was refluxed for 2 hr. After cooling the mixture was neutralized with 3% KOH–MeOH, filtered and the filtrate was passed through Sephadex LH-20 (MeOH). The methylated sugars in the eluate were identified as the methylglycosides of 2,3,4,6-tetra-*O*-methyl-D-glucopyranose, 2,3,4-tri-*O*-methyl-L-rhamnopyranose and 3,6-di-*O*-methyl-D-glucopyranose by direct comparison on Si gel TLC (EtOAc–EtOH, 25:1) and GC with authentic samples.

Baeyer–Villiger reaction of **1**. A mixture of **1** (500 mg), $(CH_2)_2Cl_2$ (10 ml), 90% HCOOH (13 ml), 30% H_2O_2 (0.5 ml) was heated at 55° for 30 min, and then evaporated to give a residue, which was subsequently treated with 3% KOH–MeOH (15 ml) at 50° for 20 min, neutralized with 5% HCl–MeOH and desalted by passing through Sephadex LH-20 with MeOH to give the products. They were chromatographed on a Si gel column to give (*S*)-4,5-dihydroxy-4-methylpentanoic acid 5-*O*-β-D-glucopyranoside (**6**, 48 mg) and a pregnane derivative (**5**, 185 mg). Compound **6**, a syrup, R_f 0.41 ($CHCl_3$–MeOH–H_2O, 7:3:0.5), $[\alpha]_D^{23}$ −25.5° (MeOH; *c* 1.10). ^{13}C NMR (pyridine-d_5): δ 182.9, 35.9, 31.2, 72.9, 77.9, 24.3 (C_{1-6}), 104.9, 75.2, 78.0, 71.7, 78.0, 62.8

(glucosyl $C_{1'-6'}$). Compound **6** (38 mg) was incubated with almond emulsin at 40° for 4 hr to yield D-glucose, $[\alpha]_D^{24}$ + 49.9° (MeOH; *c* 1.11). Compound **5**, an amorphous solid, $[\alpha]_D^{23}$ − 63.2° (MeOH; *c* 0.95), IR ν_{max}^{KBr} cm^{-1}: 3350 (OH). ^1H NMR (CD_3OD): δ 0.84 (3H, *s*, Me-18), 1.11 (3H, *s*, Me-19), 1.20 (9H, *d*, 2 × rhamnosyl-Me and Me-21). Acid hydrolysis of **5** (120 mg) with 2 N HCl–MeOH (5 ml) in a water bath for 2 hr followed by purification using Si gel CC with $CHCl_3$–MeOH–H_2O (10:2:0.2) gave 5α-pregnane-3β,5,6β,16β,20α-pentol (**7**), colorless needles, mp 251–253°, $[\alpha]_D^{24}$ − 5.4° (MeOH; *c* 0.93) (lit. mp 250–252° [8]), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH).

Aculeatiside B (**2**). An amorphous powder, $[\alpha]_D^{21}$ − 82.0° (pyridine; *c* 1.02), IR ν_{max}^{KBr} cm^{-1}: 3350 (OH). FDMS (*m/z*): 1085 $[M + Na]^+$.

Acid hydrolysis of **2**. Compound **2** (10 mg) was acid hydrolysed with 2 N HCl–MeOH (2 ml) in the same manner as described for **1** to give a mixture of sapogenols, nuatigenin and isonuatigenin, and a sugar part consisting of methylgalactopyranoside [R_f 0.38 (α), 0.35(β) on TLC, $CHCl_3$–MeOH–H_2O (7:3:0.5)], methylglucopyranoside [R_f 0.40(α)] and methylrhamnopyranoside [R_f 0.66(α), 0.60(β)].

Methylation of **2**. Compound **2** (214 mg) was methylated according to Hakomori's method as described for **1** to give the permethyl ether (122 mg), colorless needles from dil. MeOH, mp 170–174°, $[\alpha]_D^{19}$ − 34.2° ($CHCl_3$; *c* 0.79). EIMS (*m/z*): 468 [M − solatriose·9Me]$^+$, 413 [M − solatriose·9Me − hexose·4Me]$^+$, 399 $[C_{26}H_{39}O_3]^+$, 381 $[C_{26}H_{37}O_2]^+$, 282 $[C_{21}H_{30}]^+$, 253 $[C_{19}H_{25}]^+$, 189 [methylpentose·Me-3]$^+$, 187 [hexose·4Me − MeOH]$^+$, 157 (methylpentose·3Me − MeOH]$^+$. ^1H NMR ($CDCl_3$): δ 0.78 (3H, *s*, Me-18), 0.96 (3H, *d*, *J* = 6 Hz, Me-21), 1.03 (3H, *s*, Me-19), 1.24 (3H, *s*, Me-27), 1.27 (3H, *s*, methylpentosyl-Me), 4.28, 4.33, 4.36 (each 1H, *d*, *J* = 6 Hz, 3 × hexosyl anomeric proton), 5.18 (1H, *br s*, methylpentosyl anomeric proton).

Methanolysis of the permethyl ether of **2**. The permethyl ether (100 mg) of **2** was methanolysed with 2 N HCl–MeOH (3 ml) to give methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside, methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside, methyl-4,6-di-*O*-methyl-galactopyranoside and methyl-2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-4,6-di-*O*-methyl-α-D-galactopyranoside (by TLC and GC), the last of which was acetylated to give a monoacetate, ^1H NMR ($CDCl_3$): δ 2.21 (3H, *s*, OAc), 3.47–3.60 (21H, *m*, 7 × OMe), 4.39 (1H, *d*, *J* = 8 Hz, glucosyl anomeric proton), 4.86 (1H, *d*, *J* = 4 Hz, galactosyl anomeric proton), 5.28 (1H, *dd*, *J* = 4, 12 Hz, galactosyl H-2) and on further methanolysis to give methyl-2,3,4,6-tetra-*O*-methyl-D-glucopyranoside and methyl-4,6-di-*O*-methyl-D-galactopyranoside (TLC and GC).

Baeyer–Villiger reaction of **2**. Compound **2** (360 mg) was treated with $(CH_2)_2Cl_2$ (7.5 ml), 90% HCOOH (10 ml), 30% H_2O_2 (0.3 ml) as described for **1** to yield a pregnane derivative (**8**, 169 mg) and (*S*)-4-hydroxymethyl-4-methyl-γ-butylolactone-β-D-glucopyranoside (**9**, 35 mg). Compound **8**, an amorphous powder, $[\alpha]_D^{21}$ − 28.0° (MeOH; *c* 0.93), IR ν_{max}^{KBr} cm^{-1}: 3350 (OH). ^1H NMR (CD_3OD): δ 0.86 (3H, *s*, Me-18), 1.17 (3H, *s*, Me-19), 1.29 (3H, *d*, *J* = 6 Hz, rhamnosyl-Me), 1.25 (3H, *d*, *J* = 7 Hz, Me-21). Acid hydrolysis of **8** gave **7**, mp 251–253°, $[\alpha]_D^{28}$ − 5.4° (MeOH; *c* 0.93), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH). Compound **9**, a colorless syrup, $[\alpha]_D^{22}$ − 25.5° (MeOH; *c* 1.10). ^{13}C NMR (pyridine-d_5): δ 177.2, 30.7, 29.8, 85.1, 75.5, 23.6 (C_{1-6}), 105.2, 75.0, 78.6, 71.5, 78.6, 62.7 (glucosyl $C_{1'-6'}$). Compound **9** was acetylated to give an acetate, a colorless syrup, $[\alpha]_D^{28}$ − 22.0° (MeOH; *c* 2.46). EIMS (*m/z*): 461 $[M + 1]^+$, 361 [hexose·4Ac + CH_2O]$^+$, 331 [hexose·4Ac]$^+$, 99 $[C_5H_7O_2]^+$. ^1H NMR ($CDCl_3$): δ 3.50, 3.87 (each 1H, *d*, *J* = 11 Hz, H_2-5), 4.55 (1H, *d*, *J* = 8 Hz, glucosyl anomeric proton).

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