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THE STEROIDAL GLYCOSIDES OF THE FLOWERS OF *YUCCA GLORIOSA**

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Key Word Index—*Yucca gloriosa*; Liliaceae; tigogenin glycoside; gitogenin glycosides; furostanol glycoside.

Abstract—Four steroidal compounds were isolated from the fresh flowers of *Yucca gloriosa* and their structures were elucidated as tigogenin 3-*O*-β-D-xylopyranosyl-β-lycotetraoside, gitogenin 3-*O*-β-D-xylopyranosyl-β-lycotetraoside, gitogenin 3-*O*-α-L-rhamnopyranosyl-β-lycotetraoside and proto-type of gitogenin 3-*O*-β-D-xylopyranosyl-β-lycotetraoside, on the basis of physical and chemical investigations.

INTRODUCTION

Considerable phytochemical work on the plants of the *Yucca* genus has been done and the isolation of several steroidal sapogenins [1–4] and saponins [5–9] has been reported. However, no detailed chemical investigdion appears to have been performed on *Yucca gloriosa* growing in Japan. The present communication reports the isolation and characterization of four new steroidal glycosides.

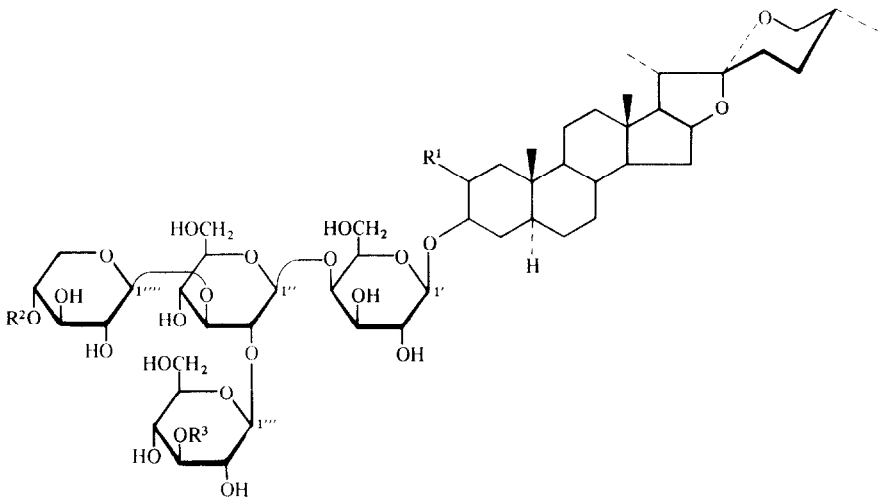
RESULTS AND DISCUSSION

The methanolic extract of the fresh flowers of *Y. gloriosa* L., on repeated chromatographic purification, gave four new steroidal glycosides, tentatively designated as YG-1 (**1**), YG-2 (**2**), YG-3 (**3**) and YG-4 (**4**).

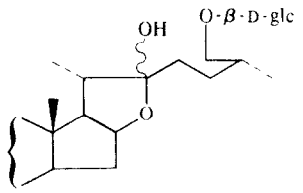
YG-1 (**1**), colourless needles, mp 273–274° (decomp.) $[\alpha]_D$ −28.0° (Py), showed a strong absorption band of hydroxy groups and characteristic absorption bands of a (25*R*)-spiroketal moiety in the IR spectrum [10]. On hydrolysis with 1M sulphuric acid –50% ethanol, **1** gave glucose, galactose, xylose and tigogenin. The FABMS spectrum of **1** showed $[M+Na]^+$ at *m/z* 1189. Accordingly, compound **1** was considered to be a pentaglycoside of tigogenin. The permethylate (**1a**) of **1** prepared by Hakomori's method [11], showed terminal permethylated pentosyl and pentosyl-hexosyl cations at *m/z* 175 and 379, respectively, in the mass spectrum. In the ^{1}H NMR spectrum of **1a**, five doublet signals with $J = 7$–8 Hz at δ4.30, 4.69, 4.72, 4.88 and 5.01 ascribable to the anomeric protons were detected, indicating that all glycosidic linkages are β. Compound **1a** was methanolized to afford methyl 2,3,4-tri-*O*-methyl-D-xylopyranoside, methyl 2,4,6-tri-*O*-methyl-D-glucopyranoside, methyl 2,3,6-tri-*O*-methyl-D-galactopyranoside and methyl 4,6-di-*O*-methyl-D-glucopyranoside. On partial hydrolysis with 0.1 M hydrochloric acid methanol **1** gave two prosapogenins, P-1 and P-2. The FABMS spectra of P-1 and P-2 showed $[M+Na]^+$ at *m/z* 1057 and 925, respectively. On hydrolysis P-1 gave galactose, glucose and xylose, P-2 gave galactose and glucose. Based on the analysis of the ^{13}C NMR spectra, the structures of P-1 and P-2 were determined to be tigogenin 3-*O*-β-D-xylopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside (tigogenin 3-*O*-β-lycotetraoside) and tigogenin 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside, respectively. P-1 was suggested to be desgalactotigonin and this was confirmed by direct comparisons with an authentic sample SN-1 obtained from *Solanum nigrum* L. [12]. From the above evidence, **1** could be represented as tigogenin 3-*O*-β-D-xylopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→3)-β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside.

YG-2 (**2**), colourless needles, mp 224–227°, $[\alpha]_D$ −43.0° (Py), showed hydroxy absorption bands and characteristic absorption bands (25*R*)-spiroketal side chain in the IR spectrum. On acid hydrolysis, **2** liberated glucose, galactose, xylose and an aglycone (**5**), which showed the M^+ at *m/z* 432 in the mass spectrum. Acetylation of **5** with Ac_2O and pyridine gave a diacetate **5a**, which showed a signal of two acetoxyl groups (δ2.00, *s*, 6H) and signals due to the proton adjacent to the acetoxyl functions (δ4.80 and 5.05, one proton each). Based on the chemical and physical properties described in the experimental section, **5** was inferred to be gitogenin [(25*R*)-5α-spirostan-2α,3β-diol] and this was confirmed by direct comparisons with an authentic sample obtained from *Solanum biflorum* Lour. [13]. The FABMS spectrum of **2** showed $[M+K]^+$ peak at *m/z* 1221 indicating that **2** is a gitogenin pentaglycoside constituted from 3 mol of hexose and 2 mol of xylose. Partial hydrolysis of **2** gave prosapogenins, Ps-1, Ps-2, Ps-3 and Ps-4, whose FABMS spectra showed $[M+K]^+$ at *m/z* 1089, 957, 795 and 633, respectively. On hydrolysis, Ps-4 gave galactose, Ps-3 and Ps-2 gave galactose and glucose whereas Ps-1 gave galactose, glucose and xylose. The ^{13}C NMR spectra of Ps-1 and Ps-2 were compared with those of P-1 and P-2. The signals due to the sugar moieties were coincident with those of prosapogenins, and the signals of the

*Part 1 in the series 'The constituents of *Yucca gloriosa*'.



	R^1	R^2	R^3
1	H	H	β-D-xyl
2	αOH	H	β-D-xyl
3	αOH	α-L-rha	H
4	αOH	H	β-D-xyl



aglycone were superimpossible on those of gitogenin except for those of C-2, C-3 and C-4, which were somewhat different due to glycosylation shifts [14–18] caused by sugar bonding to the C-3 hydroxyl of gitogenin. Based on the above result Ps-1 was suggested to be F-gitonin [19] and this was confirmed by direct comparisons with an authentic sample. The permethylate (**2a**) of **2** prepared by Hakomori's method showed terminal permethylated pentosyl and pentosyl-hexosyl cations at *m/z* 175 and 379, respectively, in its mass spectrum and five doublet signals (all $J = 7$–8 Hz) at δ 4.35, 4.73 (2H), 4.87 and 5.05 ascribable to the anomeric protons in the ^{1}H NMR spectrum, suggesting all sugar moieties to be β-linked. Methanolysis of **2a** afforded an aglycone derivative (**5b**) and a mixture of methylated sugars identical to those given by **1c**. Acetylation of **5b** with Ac_2O and pyridine gave the methylated gitogenin acetate (**5c**).

Consequently, the structure of YG-2 (**2**) was assigned as 3-*O*-β-D-xylopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→3)-β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl-(1→4)-β-D-galactopyranosyl gitogenin.

YG-3 (**3**), colourless needles, mp 242–248°, $[\alpha]_D$ −54.3° ($CHCl_3$–MeOH 1:1), showed hydroxy absorptions and characteristic absorptions (25*R*)-spiroketal side chain in the IR spectrum. Acid hydrolysis of **3** gave glucose, galactose, xylose, rhamnose and gitogenin. The FABMS spectrum of **3** showed a peak due to $[M+K]^+$ at *m/z* 1235 indicating that **3** is a gitogenin pentaglycoside constituted from three mol of hexose and one mol each of rhamnose and xylose. The permethylate (**3a**) of **3** prepared by Hakomori's method, showed terminal permethylated methylpentosyl and hexosyl cations at *m/z* 189 and 219, respectively, in its mass spectrum. The ^{1}H NMR spectrum of **3a** exhibited signals ascribable to five anomeric protons at δ 4.36 (1H, *d*, $J = 8$ Hz), 4.75 (1H, *d*, $J = 7$ Hz), 4.88 (1H *br s*), 4.90 (1H, *d*, $J = 8$ Hz) and 5.05 (1H, *d*, $J = 8$ Hz), which indicated the presence of four β-linkages and one α-linkage. On methanolysis, **3a** yielded methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside, methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside, methyl 2,3,6-tri-*O*-methyl-D-galactopyranoside, methyl 2,3-di-*O*-methyl-D-xylopyranoside and methyl 4,6-di-*O*-methyl-D-glucopyranoside. On enzymic hydrolysis with crude hesperidinase, **3** liberated a glycoside and rhamnose. The former was identical with Ps-1 (F-gitonin) in terms with physical data and ^{13}C NMR spectrum. Moreover, the ^{13}C NMR spectrum of **3** showed the significant glycosylation shift at the xylopyranosyl C-4. Therefore, YG-3 (**3**) was deduced to be gitogenin 3-*O*-α-L-rhamnopyranosyl-(1→4)-β-D-xylopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside.

YG-4 (**4**), amorphous powder, $[\alpha]_D$ +21.0° (Py), showed absorptions due to hydroxyls, but no spiroketal side chain absorptions in the IR spectrum, and was positive to the Ehrlich reagent [20] suggesting that it is a furostanol glycoside. The FABMS spectrum of **4** showed a peak due to $[M+K]^+$ at *m/z* 1401. On enzymic hydrolysis with β-glucosidase, **4** gave D-glucose and a glycoside, which was identical with YG-2 (**2**) in terms with physical data and ^{13}C NMR spectrum. Therefore, YG-4 (**4**) was deduced to be furostanol glycoside corresponding to YG-2, 3-*O*-β-D-xylopyranosyl-(1→3)-β-D-glucopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→4)-β-D-galactopyranosyl (22ξ, 25*R*)-furost-5α-spirostan-2α,3β,22,26-tetraol 26-*O*-β-D-glucopyranoside.

EXPERIMENTAL

Mps: uncorr. Chemical shifts are given on a δ (ppm) scale with TMS as an internal standard. CC was carried out with Sephadex

Table 1. ^{13}C NMR spectral data of YG-1, YG-2, YG-3 and PS-1 (C_5D_5N)

C	YG-1(1)	YG-2(2)	C	YG-1(1)	YG-2(2)	YG-3(3)	PS-1
1	37.2	45.5	gal −1′	102.4	103.2	103.2	102.9
2	29.8	70.7	−2′	73.0	72.4	73.8	72.5
3	77.5	84.2	−3′	74.9	75.0	75.1	75.5
4	34.8	33.9	−4′	79.5	79.1	79.2	79.3
5	44.7	44.6	−5′	75.4	75.6	75.6	75.9
6	28.9	28.1	−6′	60.6	60.5	60.5	60.6
7	32.4	32.1	glc −1″	103.8	103.7	103.2	104.5
8	35.2	34.6	−2″	80.6	80.5	81.1	81.1
9	54.4	54.4	−3″	86.7[a]	87.0	86.8	87.1
10	35.8	36.8	−4″	70.3	70.4	70.4	70.3
11	21.3	21.4	−5″	78.2[b]	78.3[a]	78.3[a]	78.1[a]
12	40.1	40.2	−6″	62.1	62.8	62.6	62.4
13	40.8	40.8	glc −1‴	104.7	104.3	104.6	104.6
14	56.4	56.4	−2‴	74.9	74.9	75.4	75.0
15	32.1	32.4	−3‴	86.8[a]	87.0	78.0[a]	78.3[a]
16	81.1	81.1	−4‴	70.6	70.6	71.3	71.3
17	63.0	63.0	−5‴	77.4[b]	77.7[a]	77.3[a]	78.6[a]
18	16.6	16.6	−6‴	62.9	62.8	62.8	62.6
19	12.3	13.4	xyl −1⁗	104.7	104.7	104.6	104.9
20	42.0	42.0	−2⁗	75.2	75.3	75.1	75.7
21	15.0	15.0	−3⁗	77.5[b]	77.7[a]	75.9	77.5[a]
22	109.1	109.2	−4⁗	70.6	70.7	76.0	70.7
23	31.8	31.8	−5⁗	67.0	66.8	64.0	67.2
24	29.2	29.3	xyl −1′′′′′	105.9	105.9	99.7	
25	30.6	30.5	(rha) −2′′′′′	75.2	75.1	72.3	
26	66.8	66.8	−3′′′′′	77.4[b]	77.5[a]	72.4	
27	17.3	17.3	−4′′′′′	69.1	69.3	74.7	
			−5′′′′′	67.1	67.1	69.8	
			(−6‴)			18.5	

[a,b] Signals may be interchanged in each vertical column.

LH-20 (Pharmacia), silica gel (Merck) and MCI-gel CHP 20P (Mitsubishi). TLC was performed on precoated Kieselgel 60 F_{254} plates (Merck) and detection was achieved by spraying 10% H_2SO_4 followed by heating. GLC was performed on a column of 1.5% neopenthylglycol succinate with N_2 gas carrier-gas (17 ml/min) initial 130° programme at 4°/min to final 190°.

Extraction and isolation of saponins. The fresh flowers (3.85 kg) of *Yucca gloriosa* L., collected at the campus of this Faculty in December, were extracted with hot MeOH (10 l × 3). The methanolic extract was evapd to give residue (588 g), which was partitioned between *n*-BuOH and H_2O (1 l of each). The BuOH soluble fraction was concd *in vacuo* to afford a residue (90 g), which was subjected to CC over silica gel (solv. $CHCl_3$–MeOH–H_2O 90:10:1 → 14:6:1) to afford Fr. 1–Fr. 10. Frs. 4 and 6 were rechromatographed over Sephadex LH-20 (MeOH and 80% MeOH) and silca gel to afford YG-1 (**1**) (1.23 g), YG-2 (**2**) (1.54 g) and YG-3 (**3**) (352 mg). Chromatography of Fr. 8 on MCI-gel CHP 20P (10 → 90% MeOH) gave YG-4 (**4**) (76 mg).

Properties of YG-1, 2, 3 and 4. YG-1 (**1**). Colourless needles from dil. MeOH, mp 273–274° (dec.), $[\alpha]_D^{21}$ −28.0° (pyridine; *c* 1.0), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 980, 920, 900, 860 [intensity 900 > 920, (25*R*)-spiroketal]. FAB-MS (*m/z*): 1189 $[M+Na]^+$. YG-2 (**2**), colourless needles from dil. MeOH, mp 224–227°, $[\alpha]_D^{27}$ −43.0° (pyridine; *c* 1.0), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 980, 920, 900, 860 (900 > 920, 25*R*-spiroketal), FABMS (*m/z*): 1221 $[M+K]^+$. YG-3 (**3**), colourless needles from dil. MeOH, mp 242–248° (dec.), $[\alpha]_D^{20}$ −54.3° ($CHCl_3$–MeOH 1:1; *c* 1.1), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 980, 920, 900, 860 (900 > 920, 25*R*-spiroketal), FABMS (*m/z*): 1235 $[M+K]^+$. YG-4 (**4**), amorphous powder, $[\alpha]_D^{19}$ +21.0° (pyridine; *c* 1.0), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), FABMS (*m/z*): 1401 $[M+k]^+$. Ehrlich reagt: positive.

Acid hydrolysis of **1–3**. A soln of **1** (22 mg) in 1 M H_2SO_4–50% EtOH was refluxed for 2 hr and the reaction mixture was diluted with H_2O. The ppt. was collected by filtration and purified by recrystallization from MeOH to afford colourless needles (10 mg), mp 198–200°, $[\alpha]_D^{19}$ −48.0° ($CHCl_3$; *c* 0.5), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 980, 920, 900, 860 (900 > 920). This was identified as tigogenin by direct comparisons with an authentic sample. The aq. hydrolysate was neutralized and concd *in vacuo*. The residue was examined by TLC, D-xylose, D-galactose and D-glucose were detected (solv. $CHCl_3$–MeOH–Me_2CO–H_2O = 3:3:3:1, R_f 0.47, 0.30 and 0.32, respectively). **2** (100 mg) and **3** (10 mg) were hydrolysed with 1 M H_2SO_4–50% EtOH as described above, to afford an aglycone (**5**) (25 mg), colourless needles, mp 268–270° (dec.), $[\alpha]_D^{22}$ −59.5° ($CHCl_3$; *c* 0.4), EIMS (*m/z*): 432 (M^+, $C_{27}H_{44}O_4^+$), 417, 318, 289, 139 ($C_9H_{15}O^+$), IR ν_{max}^{KBr} cm^{-1}: 990, 960, 930, 905, 870 [intensity 905 > 930, (25*R*)-spiroketal]. ^1H NMR ($CDCl_3$): 0.76 (3H, *s*, 18-Me), 0.77 (3H, *d*, *J* = 6 Hz, 27-Me), 0.86 (3H, *s*, 19-Me), 0.96 (3H, *d*, *J* = 6.6 Hz, 21-Me), 3.30-3.64 (4H, *m*), 4.38 (1H, *m*, 16-H). Compound **5** was acetylated in the usual manner to afford the diacetate (**5a**), colourless needles, mp 238–240°, $[\alpha]_D^{21}$ −91.9° ($CHCl_3$; *c* 0.56). ^1H NMR ($CDCl_3$): 0.76 (3H, *s*), 0.78 (3H, *d*, *J* = 6.3 Hz), 0.92 (3H, *s*), 0.96 (3H, *d*, *J* = 6.8 Hz), 2.00 (6H, *s*, OAc × 2), 3.30-3.45 (2H, *m*, 26-H_2), 4.38 (1H, *m*, 16-H), 4.86 (1H, *ddd*, *J* = 6, 10, 10, Hz, 3-H), 5.04 (H, *ddd*, *J* = 5, 10, 10 Hz, 2-H). This compound was identified as gitogenin by direct comparison with

an authentic sample. The hydrolysate from **2** provided the same sugar components as in **1**, while the hydrolysate from **3** revealed rhamnose (R_f 0.52) in addition.

Partial hydrolysis of **1** *and* **2**. Compound **1** (250 mg) was heated at 80° with 0.1 M HCl–MeOH (10 ml) for 1 hr. The reaction mixture was neutralized with 3% KOH–MeOH and evapd to dryness *in vacuo*. The residue was chromatographed on silica gel (solv. $CHCl_3$–MeOH–H_2O, 40:10:1) to afford two prosapogenins P-1 (70 mg) and P-2 (35 mg). P-1, colourless needles, mp 230–233°, $[\alpha]_D^{19}$ −18.1° (pyridine; *c* 0.5), FABMS *m/z*: 1057 $[M+Na]^+$, ^{13}C NMR (C_5D_5N): sugar moiety: 102.4, 73.1, 75.0[a]*, 79.8, 75.5, 60.6 (galactosyl C-1′-C-6′), 104.7, 81.3, 86.9, 70.4, 78.0[b], 62.5 (glucosyl C-1″–C-6″), 104.9, 75.2[a], 77.8[b], 70.8, 78.5[b], 61.9 (glucosyl C-1‴–C-6‴), 105.0, 75.3, 77.5[b], 70.7, 67.3 (xylosyl C-1⁗–C-5⁗). This spectrum was superimposable on that of an authentic sample of SN-1 [12]. P-2, colourless needles, mp 214–217°, $[\alpha]_D^{19}$ −38.5° (pyridine; *c* 1.5), FABMS *m/z*: 925 $[M+Na]^+$, ^{13}C NMR (C_5D_5N): sugar moiety: 102.3, 73.1, 75.5, 80.8, 76.6, 60.4 (galactosyl C-1′-C-6′), 105.0, 85.9, 77.4, 70.3, 78.3[a], 61.6 (glucosyl C-1″–C-6″), 106.8, 75.0, 78.0[a], 71.7, 78.8[a], 63.1 (glucosyl C-1‴–C-6‴). Partial hydrolysis of **2** (500 mg) as carried out with 0.25 M HCl–MeOH (50 ml) gave a mixture of prosapogenins and gitogenin, which was purified by CC ($CHCl_3$–MeOH–H_2O, 4:1:0.1) to afford Ps-1 (72 mg), Ps-2 (31 mg), Ps-3 (28 mg) and Ps-4 (15 mg). Ps-1, colourless needles, mp 262–265°, $[\alpha]_D^{26}$ −60.0° ($CHCl_3$–MeOH, 1:1, *c* 0.6), FABMS *m/z*: 1089 $[M+K]^+$. It was found identical to F-gitonin by co-TLC and superimposable IR spectra. Ps-2, colourless needles, mp 220–227°, $[\alpha]_D^{26}$ +1.0° (pyridine; *c* 1.0), FABMS *m/z*: 957 $[M+K]^+$. Ps-3, colourless needles, mp 220–223°, $[\alpha]_D^{21}$ −30.0° (pyridine, *c* 1.0), FABMS *m/z*: 795 $[M+K]^+$. Ps-4, colourless needles, mp 220–222°, FABMS *m/z*: 633 $[M+K]^+$.

Permethylation of **1**–**3**. Compound **1** (227 mg), **2** (160 mg) and **3** (100 mg) were separately permethylated by Hakomori's method [11]. The products from **1**, **2** and **3** were purified by CC (hexane–Me_2CO 5:1) to yield **1a** (150 mg), **2a** (132 mg) and **3a** (17 mg), respectively. Compound **1a**, white powder, $[\alpha]_D^{19}$ −40.0° ($CHCl_3$, *c* 0.25), ^1H NMR ($CDCl_3$): 0.76 (3H, *s*), 0.78 (3H, *d*, *J* = 6 Hz), 0.82 (3H, *s*), 0.96 (3H, *d*, *J* = 6.5 Hz), 3.35–3.62 (OMe × 14), 4.30 (1H, *d*, *J* = 7.5 Hz), 4.69 (1H, *d*, *J* = 7 Hz), 4.72 (1H, *d*, *J* = 7.5 Hz), 4.88 (1H, *d*, *J* = 7.3 Hz), 5.01 (1H, *d*, *J* = 7.5 Hz). EI-MS *m/z*: 551, 391, 379 ($C_{17}H_{31}O_9^+$), 187, 175 ($C_8H_{15}O_4^+$), 143, 111. Compound **2a**, white powder, $[\alpha]_D^{21}$ −50.0° ($CHCl_3$, *c* 1.0), ^1H NMR ($CDCl_3$): 0.76 (3H, *s*), 0.78 (3H, *d*, *J* = 7 Hz), 0.85 (3H, *s*), 0.98 (3H, *d*, *J* = 6.8 Hz), 3.3–3.65 (OMe × 15), 4.35 (1H, *d*, *J* = 7.3 Hz), 4.73 (2H, *d*, *J* = 7.3 Hz), 4.88 (1H, *d*, *J* = 7.3 Hz), 5.05 (1H, *d*, *J* = 7.8 Hz). EIMS *m/z*: 743, 551, 487, 429, 379 ($C_{17}H_{31}O_9^+$), 201, 187, 175 ($C_8H_{15}O_4^+$), 155, 143, 111, 101, 88. Compound **3a**, syrup, $[\alpha]_D^{19}$ −55.7° ($CHCl_3$, *c* 1.37), ^1H NMR ($CDCl_3$): 0.76 (3H, *s*), 0.78 (3H, *d*, *J* = 6 Hz), 0.84 (3H, *s*), 0.96 (3H, *d*, *J* = 7 Hz), 1.27 (3H, *d*, *J* = 6 Hz, rha-Me), 3.35–3.65 (OMe × 15), 4.36 (1H, *d*, *J* = 8 Hz), 4.75 (1H, *d*, *J* = 7 Hz), 4.88 (1H, *br s*, rha 1-H), 4.90 (1H, *d*, *J* = 8 Hz), 5.05 (1H, *d*, *J* = 8 Hz. EIMS *m/z*: 429, 391, 349, 219, ($C_{10}H_{19}O_5^+$) 189 ($C_9H_{17}O_4^+$), 187, 155, 111, 88.

Methanolysis of **1a**, **2a** *and* **3a**. Compounds **1a** (10 mg), **2a** (80 mg) and **3a** (10 mg) were separately refluxed with 1 M HCl–MeOH. The neutralized and concd methanolysate from **1a** was subjected to CC over silica gel (hexane–Me_2CO 10:1) to afford tigogenin and the methylated sugars (**a**–**d**). Compounds **c** and **d** were identified by TLC and GLC, with the aid of authentic samples, as methyl 2,3,4-tri-*O*-methyl-D-xylopyranoside and methyl 4,6-di-*O*-methyl-D-glucopyranoside. Compound **b** was characterized as methyl 2,4,6-tri-*O*-methyl-α-D-glucopyranoside [acetate of **b**; MS *m/z*: 247 ($C_{11}H_{19}O_6^+$), 187 ($C_9H_{15}O_4^+$), 116 ($C_5H_8O_3^+$), 101 ($C_5H_9O_2^+$), 88, 75, 74, 71. ^1H NMR ($CDCl_3$): 2.12 (3H, *s*, OAc), 3.30 (1H, *dd*, *J* = 3.4, 9.5 Hz, 2-H), 3.41 (6H, *s*, OMe × 2), 3.42, 3.43 (each 3H, *s*, OMe), 4.88 (1H, *d*, *J* = 3.4 Hz, 1-H), 5.36 (1H, *t*, *J* = 9.5 Hz, 3-H)]. Compound **c** was identified as methyl 2,3,6-tri-*O*-methyl-α-D-galactopyranoside [acetate of **c**; MS *m/z* 247, 187, 101, 88, 75, 74. ^1H NMR ($CDCl_3$): 2.14 (3H, *s*, OAc), 3.36, 3.41, 3.42, 3.45 (each 3H, *s*, OMe), 4.93 (1H, *d*, *J* = 3.2 Hz, 1-H), 5.49 (1H, *dd*, *J* = 1.2, 2.0 Hz, 4-H]. The methanolysate from **2a** gave gitogenin monomethylether (**5b**, 32 mg), colourless needless mp 216–218°, $[\alpha]_D^{23}$ −100.0° ($CHCl_3$; *c* 0.2), and the same methylated sugars from **1a**. Compound **5b** was acetylated with Ac_2O–pyridine (each 1 ml) in the usual manner to give the corresponding monoacetate (**5c**, 7 mg) colourless needles, mp 201–204°, $[\alpha]_D^{23}$ −117.8° ($CHCl_3$; *c* 0.9), ^1H NMR ($CDCl_3$): 0.77 (3H, *s*), 0.78 (3H, *d*, *J* = 6.3 Hz), 0.86 (3H, *s*), 0.96 (3H, *d*, *J* = 6.5 Hz), 2.06 (3H, *s*, OAc), 3.37 (3H, *s*, OMe), 3.26–3.51 (3H, *m*), 4.38 (1H, *m*, 16-H), 4.68 (1H, *ddd*, *J* = 6, 10, 10 Hz, 3-H).

From the methanolysate of **3a**, methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside, methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside, methyl 2,3,6-tri-*O*-methyl-D-galactopyranoside and methyl 4,6-di-*O*-methyl-D-glucopyranoside were identified. In addition, methyl 2,3-di-*O*-methyl-α-D-xylopyranoside was characterized [acetate; MS *m/z*: 203 ($C_9H_{15}O_5^+$), 143 ($C_7H_{11}O_3^+$), 101, 71. ^1H NMR ($CDCl_3$): 2.08 (3H, *s*, OAc), 3.43, 3.53, 3.55 (each 3H, *s*, OMe), 4.83 (1H, *d*, *J* = 3.4 Hz, 1-H), 4.84 (1H, *m*, 4-H)].

Enzymic hydrolysis of **3**. Compound **3** (15 mg) was dissolved in $CHCl_3$–MeOH (1:1, 1 ml), added AcOH–NaOAc buffer (pH 4.5, 2 ml) and crude hesperidinase (10 mg), and then incubated at 80° for 2 hr. The reaction mixture was evapd to dryness *in vacuo*. The residue was chromatographed over silica gel (solv. $CHCl_3$–MeOH–H_2O, 7:3:0.5) to give a glycoside (8 mg), colourless needles, mp 262–267°, $[\alpha]_D^{20}$ −56.0° ($CHCl_3$–MeOH, 1:1, *c* 0.4), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 980, 920, 900, 860 (900 > 920). It was found identical to Ps-1 by co-TLC (solv. $CHCl_3$–MeOH–H_2O 7:3:0.5 and $CHCl_3$–MeOH–EtOAc–H_2O 3:3:4:0.5), superimposable IR and ^{13}C NMR spectra.

Enzymic hydrolysis of **4**. A solution of **4** (31 mg) in H_2O was incubated with almond emulsin (20 mg) at 37° overnight. The reaction mixture was extracted with BuOH and the organic layer was concd *in vacuo* to afford a residue, which was subjected to CC over silica gel (solv. $CHCl_3$–MeOH–H_2O 14:6:1), yielding a glycoside (20 mg), colourless needles from dil. MeOH, mp 228–230°, $[\alpha]_D^{23}$ −36.0° (pyridine; *c* 1.0), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 980, 920, 900, 860 (900 > 920). It was identified with YG-2 (**2**) by co-TLC, IR and ^{13}C NMR spectra.

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*^{13}C NMR data: [a, b] assignments are interchangeable between carbons marked with similar sign in a compound.

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