Saponins from Roots of *Platycodon grandiflorum*. Part 2.[1] Isolation and Structure of New Triterpene Glycosides [2]

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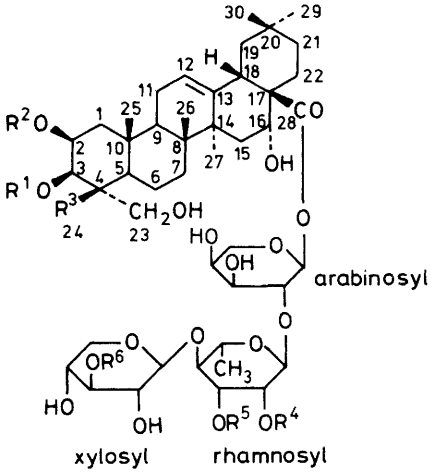
Seventeen new saponins (**2**)—(**18**) have been isolated from the roots of *Platycodon grandiflorum* A. DC. and their structures determined by comparison of their ^{13}C n.m.r. signals with those of known prosapogenins (**19**)—(**26**) and of the sugar chain at C-28 in platycodin-D (**1**). Eight of these saponins were found to have an *O*-acetyl group which migrated both readily and reversibly between the 2-*O*- and 3-*O*-positions of the rhamnose moiety in their sugar chain.

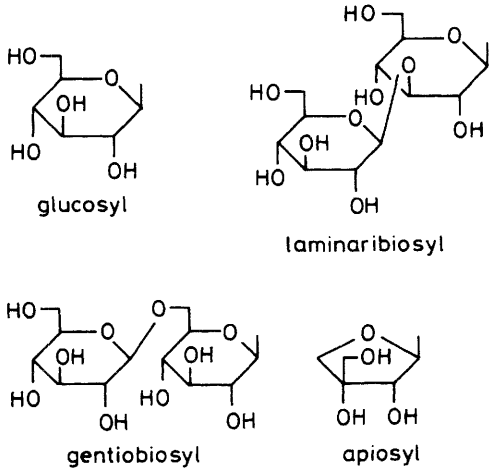
In 1975, Shibata and his co-workers[3] isolated platycodin-D (**1**) as the main saponin from the roots of *Platycodon grandiflorum* A. DC. and elucidated its entire structure except for the anomeric configuration of the arabinose moiety. In a previous paper,[1] we reported the structures of several prosapogenins (**19**)—(**26**) prepared by alkaline hydrolysis of a saponin mixture from this plant. In the present study, we isolated 17 new saponins (**2**)—(**18**) from the same saponin mixture and determined their structures by comparing their ^{13}C n.m.r. signals with those of the prosapogenins[1] and of the sugar chain at C-28 in platycodin-D (**1**), *i.e.*, an apiosyl-xylosyl-rhamnosyl-arabinosyl group.[3]

Results and Discussion

The crude saponin mixture was separated into individual saponins (**1**)—(**18**)† by repeated chromatography as shown in the Scheme. Fraction 6 was considered to contain saponins having a carboxy group at C-24 in the aglycone moiety,[4] owing to its high polarity. Methylation of the fraction with diazomethane followed by chromatography gave the two ester compounds (**16**) and (**17**), as expected. Fraction 21 was shown to be a complex mixture of (**3**)and (**10**) by t.l.c. (see R_F values in

† Saponin (**7**) was not obtained directly but prepared from (**6**) using an acetyl-migration reaction.





Compound	R^1	R^2	R^3	R^4	R^5	R^6
(**1**)	glucosyl	H	CH_2OH	H	H	apiosyl
(**2**)	glucosyl	H	CH_2OH	Ac	H	apiosyl
(**3**)	glucosyl	H	CH_2OH	H	Ac	apiosyl
(**4**)	glucosyl	H	CH_2OH	H	H	H
(**5**)	laminaribiosyl	H	CH_2OH	H	H	apiosyl
(**6**)	laminaribiosyl	H	CH_2OH	Ac	H	apiosyl
(**7**)	laminaribiosyl	H	CH_2OH	H	Ac	apiosyl
(**8**)	gentiobiosyl	H	CH_2OH	H	H	apiosyl
(**9**)	gentiobiosyl	H	CH_2OH	H	H	H
(**10**)	glucosyl	H	CH_3	H	H	apiosyl
(**11**)	glucosyl	H	CH_3	Ac	H	apiosyl
(**12**)	glucosyl	H	CH_3	H	Ac	apiosyl
(**13**)	laminaribiosyl	H	CH_3	H	H	apiosyl
(**14**)	laminaribiosyl	H	CH_3	Ac	H	apiosyl
(**15**)	laminaribiosyl	H	CH_3	H	Ac	apiosyl
(**16**)	glucosyl	H	$COOCH_3$	H	H	apiosyl
(**17**)	glucosyl	CH_3	$COOCH_3$	H	H	apiosyl
(**18**)	glucosyl	└——CO——┘		H	H	apiosyl

Table 1. Physical properties of saponins (**1**)—(**18**)

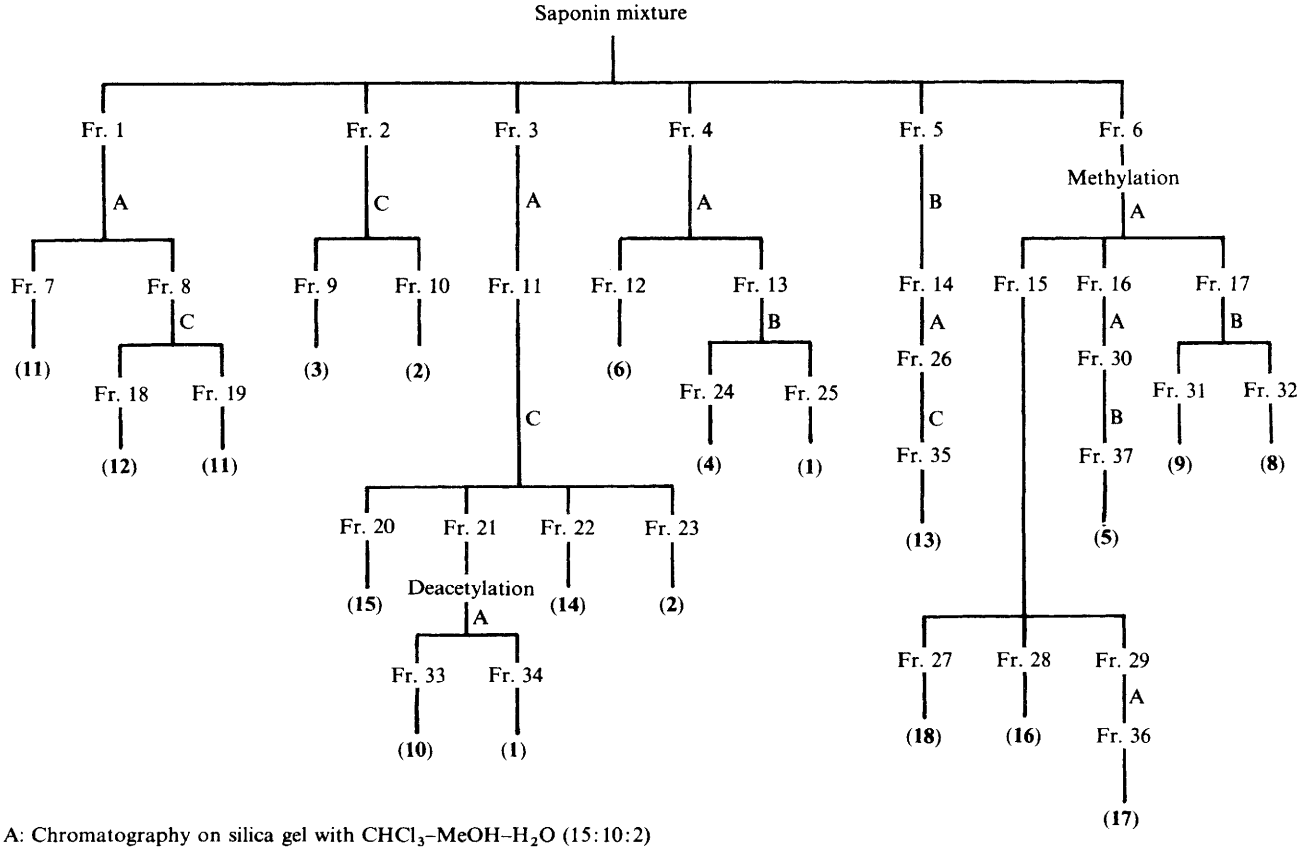
Compound	M.p. (°C)	$[\alpha]_D$ (°)[a]	Formula	R_F[b]	R_F[c]
(**1**)	228—237	−30.5	$C_{57}H_{92}O_{28}$	0.34	0.32
(**2**)	227—233	−24.8	$C_{59}H_{94}O_{29}$	0.46	0.41
(**3**)	227—231	−39.8	$C_{59}H_{94}O_{29}$	0.40	0.38
(**4**)	231—235	−22.9	$C_{52}H_{84}O_{24}$	0.34	0.34
(**5**)	227—235	−27.9	$C_{63}H_{102}O_{33}$	0.27	0.24
(**6**)	225—231	−25.0	$C_{65}H_{104}O_{34}$	0.38	0.32
(**7**)	224—232	−35.3	$C_{65}H_{104}O_{34}$	0.33	0.29
(**8**)	218—225	−24.3	$C_{63}H_{102}O_{33}$	0.26	0.21
(**9**)	223—232	−18.3	$C_{58}H_{94}O_{29}$	0.26	0.22
(**10**)	221—226	−41.5	$C_{57}H_{92}O_{27}$	0.39	0.37
(**11**)	223—227	−33.2	$C_{59}H_{94}O_{28}$	0.50	0.47
(**12**)	219—225	−41.2	$C_{59}H_{94}O_{28}$	0.46	0.43
(**13**)	229—236	−35.5	$C_{63}H_{102}O_{32}$	0.32	0.30
(**14**)	229—235	−32.0	$C_{65}H_{104}O_{33}$	0.42	0.38
(**15**)	226—233	−40.6	$C_{65}H_{104}O_{33}$	0.37	0.35
(**16**)	224—231	−19.8	$C_{58}H_{92}O_{30}$	0.45	0.36
(**17**)	223—229	−27.1	$C_{59}H_{94}O_{30}$	0.32	0.30
(**18**)	230—236	−30.2	$C_{57}H_{88}O_{29}$	0.43	0.41

[a] In methanol. [b] Solvent, $CHCl_3$–MeOH–H_2O (15:10:2), double development. [c] Solvent, EtOAc–EtOH–H_2O (15:5:4), double development.

Table 1). On alkaline treatment of the mixture, only the saponin (**3**) was converted into a more polar compound (**1**) and hence the intact saponin (**10**) was easily separated by column chromatography. The physical properties of all the saponins isolated are listed in Table 1.

Saponin (**1**) was considered to be platycodin-D[3] by t.l.c. comparisons. On subtracting the ^{13}C Fourier-transform n.m.r. spectrum of 3-*O*-β-D-glucopyranosylplatycodigenin methyl ester (**19**)[1] from that of (**1**), we obtained a signal pattern which could be reasonably attributed to the sugar chain at C-28 of platycodin-D. Signal positions of C-16, C-17, C-18, C-22, and C-28 were slightly shifted by a change from the *O*-methyl to an *O*-sugar group at C-28, while other signals due to the prosapogenin moiety remained unchanged. Thus, we tentatively assigned the ^{13}C signals of the sugar chain in (**1**) as shown in Table 2 in comparison with the data on ^{13}C chemical shifts of methyl arabinoside,[5,6] rhamnosides,[5] xylosides,[6,7] and apiosides,[8] and some *O*-acetylarabinosides,[6] on the following three rough assumptions. (i) *O*-Glycosylation of secondary hydroxy groups, except anomeric groups, in a sugar causes *ca.* 10 p.p.m. downfield shifts of the α-carbon signal but little shifts of other signals.[9] (ii) Glycosidation shifts for a sugar, *i.e.* signal shifts from methyl glycoside to secondary alcohol glycoside, are *ca.* −3 p.p.m. for the anomeric carbon but less than 1 p.p.m. for other carbons.[10] (iii) *O*-Acetylation of secondary hydroxy groups causes *ca.* 2 p.p.m. downfield and *ca.* 3 p.p.m. upfield shifts of the α- and β-carbon signals, respectively, but no shifts of other signals.[11] The order of signal recovery of anomeric carbons in the sugar chain was found to be arabinose > rhamnose > xylose > apiose in partially relaxed Fourier-transform n.m.r. spectra[12] of (**1**), being consistent[13] with the known sugar sequence of platycodin-D.[3]

We first considered the configuration of the anomeric position of L-arabinose in (**1**) to be β, because the C-5 signal of the sugar appeared to relatively higher field when the arabinose



A: Chromatography on silica gel with $CHCl_3$–MeOH–H_2O (15:10:2)
B: Chromatography on silica gel with EtOAc–EtOH–H_2O (15:5:4)
C: Droplet countercurrent chromatography with $CHCl_3$–MeOH–H_2O–Pr^{n}OH (5:6:4:1.2)

Scheme.

ring was assumed to be in a $^4C_1$ conformation.[2a] However, detailed re-examination by ^{13}C and ^1H Fourier-transform n.m.r. spectroscopy showed that the arabinose ring in (**1**) is predominantly in a $^1C_4$ conformation and its anomeric configuration is α in [$^2H_5$]pyridine at 100 °C.[14]

The ^{13}C spectrum of the saponin (**5**) indicated that it consisted of a spectrum of 3-*O*-laminaribiosylplatycodigenin methyl ester (**20**) [1] and a signal pattern of the sugar chain at C-28 of (**1**) (Table 2). Thus, the saponin was shown to have formula (**5**) and named platycodin-D_2. In a similar way, saponins (**8**), (**10**), (**13**), (**16**), (**17**), and (**18**) were assigned their structural formulae and named platycodin-D_3, polygalasin-D and -D_2, methyl platyconate-A, methyl 2-*O*-methylplatyconate-A, and platyconic acid-A lactone, respectively. The ^{13}C spectra of the saponins (**4**) and (**9**) lacked signals arising from apiose when compared with those of platycodin-D (**1**) and -D_3 (**8**), respectively, indicating that they are deapioplatycodin-D (**4**) and -D_3 (**9**). These results were also supported by the fact that alkaline treatment of each saponin yielded the corresponding prosapogenin.

The remaining eight saponins were found to possess an *O*-acetyl group by ^{13}C n.m.r. spectroscopy. Acetylsaponins (**2**) and (**3**) were interconverted in dilute alcoholic solutions (1 mg/ml), resulting in a 1:1 equilibrium mixture; they yielded the parent deacetylated compound (**1**), after a long period of time (see Experimental section). Furthermore, the ^{13}C spectra of pure (**2**) and (**3**) when taken in [$^2H_5$]pyridine at 100 °C overnight were identical, a 1:1 equilibrium mixture of the two compounds being formed. However, the ^{13}C spectra of these saponins in [$^2H_4$]methanol (*ca.* 200 mg/ml) at 60 °C show the presence of only pure compounds. Thus acetyl migration [15] seems to occur only slowly in such concentrated alcoholic solutions. Similar observations were made for the other pairs of acetylsaponins, (**6**) and (**7**), (**11**) and (**12**), and (**14**) and (**15**); their mother compounds were shown to be platycodin-D_2 (**5**), and polygalasin-D (**10**) and -D_2 (**13**), respectively, by t.l.c. and ^{13}C n.m.r. spectroscopy.

As reported previously,[16] the acetylation shift rule [11] in ^{13}C n.m.r. spectroscopy can readily point out the position of an *O*-acetyl group when the ^{13}C signals of the mother deacetylated compound are fully assigned. Therefore, we compared the spectra of these acetylsaponins with those of the parent saponins and platycodin-D peracetate. We also examined the acetylation shifts (Table 2), and found that (**2**) and (**3**), (**6**) and (**7**), (**11**) and (**12**) as well as (**14**) and (**15**) are 2-*O*- and 3-*O*-acetyl rhamnose derivatives of the parent compounds, platycodin-D (**1**) and -D_2 (**5**), and polygalasin-D (**10**) and -D_2 (**13**), respectively. Deacetylation by mild alkaline treatment confirmed these structural relationships.

At the time of our preliminary report,[2b] Shoji and his co-workers [17] also described the structures of platycodin-A and -C, which correspond to 2″-*O*-acetyl- (**2**) and 3″-*O*-acetyl-platycodin-D (**3**), respectively.

Experimental

Silica gel used for column chromatography was Kieselgel 60 (Merck) and the solvents applied were (A) $CHCl_3$–MeOH–H_2O (15:10:2) and (B) EtOAc–EtOH–H_2O (15:5:4). Each saponin was obtained as a white powder by precipitation from methanol–ether. M.p.s were determined with a Yanagimoto micro-apparatus. Optical rotations were measured with solutions in methanol. ^1H N.m.r. spectra were taken with a Varian XL-100-12A spectrometer at 100.058 MHz using [$^2H_5$]pyridine solutions in 5-mm spinning tubes at 30 and 90 °C (in parentheses) containing tetramethylsilane (TMS) as an internal reference. The concentrations were *ca.* 10 mg/ml. Fourier-transform (FT) measurement conditions were as follows: spectral width, 1 500 Hz; acquisition time, 5 s; pulse width, 3 μs (pulse flipping angle, 10°); number of data points, 15 004; number of transitions, 100. ^{13}C N.m.r. spectra were recorded on a Varian NV-14 FT n.m.r. spectrometer at 15.087 MHz using [$^2H_5$]pyridine solutions for (**1**)—(**18**) and [$^2H_4$]methanol solutions for (**2**), (**3**), (**6**), (**7**), (**11**), (**12**), (**14**), and (**15**) with TMS as an internal reference in 8-mm spinning tubes at elevated temperatures (100 °C in [$^2H_5$]pyridine and 60 °C in [$^2H_4$]methanol).[18] Typical FT measurement conditions were as follows: spectral width, 3 923 Hz; acquisition time, 0.6 s; pulse width, 10—20 μs (pulse flipping angle, 15—30°); number of data points, 4 820; number of transitions, 3 500—350 000. ^{13}C Partially-relaxed FT measurement conditions were as follows: spectral width, 3 017 Hz; acquisition time, 1.326 s; pulse delay, 0.05 s; repetition time, 5 s; number of data points, 8 191; number of transitions, 32 K. Accuracies of δ_H and δ_C are ±0.02 and ±0.1 p.p.m., respectively. Asterisked assignments may be interchanged in each compound.

Fractionation of Saponin Mixture.—The crude saponin mixture [1] (20 g) was chromatographed on silica gel (800 g) with solvent (A) and gave six fractions. Each fraction was further separated into two to three portions by chromatography with solvent (B). Fractions having similar t.l.c. properties were combined to give, in the order of increasing polarity, six larger fractions 1 (1.26 g), 2 (1.88 g), 3 (3.80 g), 4 (3.94 g), 5 (2.21 g), and 6 (4.55 g).

Platycodin-D (**1**).—Fraction 4 (1 g) was chromatographed on silica gel (100 g) with solvent (A) and gave fractions 12 (163 mg) and 13 (544 mg). Fraction 13 was re-chromatographed on silica gel (200 g) with solvent (B) and yielded fractions 24 (26 mg) and 25 (361 mg). Fraction 25 gave the saponin (**1**) (252 mg), m.p. 228—237 °C, $[\alpha]_D^{25}$ −30.5° (*c* 1.05) (Found: C, 55.8; H, 7.75. $C_{57}H_{92}O_{28}$ requires C, 55.87; H, 7.57%), identified as platycodin-D[3] (t.l.c. and ^{13}C n.m.r. spectrum). δ_H Data for 25-, 26-, 27-, 29-, and 30-H are 1.46 (1.43), 1.12 (1.06),* 1.73 (1.65), 1.14 (1.11),* and 0.99 (0.98), respectively.

2″-O-*Acetylplatycodin*-D (**2**).—Fraction 2 (550 mg) was subjected to droplet countercurrent chromatography with $CHCl_3$–MeOH–H_2O–Pr^{n}OH (5:6:4:1.2), giving fractions 9 (146 mg) and 10 (211 mg). Fraction 10 was purified by chromatography with solvent (B) and yielded the *saponin* (**2**) (165 mg), m.p. 227—233 °C, $[\alpha]_D^{26}$ −24.8° (*c* 1.01) (Found: C, 55.85; H, 7.65. $C_{59}H_{94}O_{29}$ requires C, 55.91; H, 7.48%).

3″-O-*Acetylplatycodin*-D (**3**).—Fraction 9 (146 mg) was purified by chromatography with solvent (A) and gave the *saponin* (**3**) (89 mg), m.p. 227—231 °C, $[\alpha]_D^{25}$ −39.8° (*c* 1.01) (Found: C, 56.1; H, 7.65. $C_{59}H_{94}O_{29}$ requires C, 55.91; H, 7.48%).

Deapioplatycodin-D (**4**).—Fraction 24 (26 mg) gave the *saponin* (**4**) (16 mg), m.p. 231—235 °C, $[\alpha]_D^{22}$ −22.9° (*c* 1.01) (Found: C, 57.0; H, 7.9. $C_{52}H_{84}O_{24}$ requires C, 57.13; H, 7.75%); δ_H signals for 25-, 26-, 27-, 29-, and 30-H were 1.48 (1.43), 1.13 (1.06),* 1.72 (1.67), 1.13 (1.11),* and 0.99 (0.97), respectively.

Platycodin-D_2 (**5**).—Fraction 6 (4.9 g) was dissolved in MeOH (200 ml) and the solution was treated with ethereal diazomethane in the usual manner. The product was chromatographed on silica gel (200 g) with solvent (A) and afforded fractions 15 (300 ml, 1.54 g), 16 (300 ml, 613 mg), and 17 (300 ml, 773 mg). The middle fraction was re-chromatographed with the same solvent and gave fraction 30 (431 mg), which was further purified by chromatography with solvent (B). Fraction 37 thus obtained gave the *saponin* (**5**)

Table 2. ^{13}C N.m.r. chemical-shift data of saponins (**1**)—(**18**) in [$^2H_5$]pyridine and [$^2H_4$]methanol (in parentheses)

Carbon	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Sapogenin									
C-1	45.1 (45.1)	45.1 (45.1)	45.1 (45.1)	45.2	45.0 (45.2)	45.1 (45.2)	45.1 (45.0)	45.2	45.2
C-2	69.2 (70.3)	69.2 (70.3)	69.2 (70.1)	69.2	69.4 (70.1)	69.5 (70.3)	69.5 (70.1)	68.6	68.7
C-3	86.4 (86.5)	86.4 (86.5)	86.4 (86.4)	86.5	86.4 (86.6)	86.4 (86.5)	86.4 (86.7)	87.6	87.6
C-4	48.0[h] (48.3)	48.0 (48.3)	48.0 (48.3)	48.0	48.0[h] (48.4)	48.0 (48.3)	48.0 (48.3)	48.0[h]	48.1
C-5	48.0[h] (48.3)[a]	48.0 (48.6)[a]	48.0 (48.6)[a]	48.0	48.0[h] (48.4)[a]	48.0 (48.3)[a]	48.0 (48.3)[a]	46.7[h]	46.7
C-6	19.6 (19.8)	19.6 (19.8)	19.6 (19.9)	19.6	19.6 (19.9)	19.6 (19.5)	19.6 (19.7)	19.7	19.7
C-7	33.7 (34.0)	33.7 (34.2)	33.7 (34.0)	33.8	33.7 (34.2)	33.7 (34.2)	33.7 (34.1)	33.7	33.8
C-8	40.7 (41.2)	40.7 (41.2)	40.7 (41.2)	40.7	40.7 (41.3)	40.7 (41.1)	40.7 (41.1)	40.8	40.8
C-9	48.0 (47.7)[a]	48.0 (47.7)[a]	48.0 (47.7)[a]	48.0	48.0 (47.6)[a,b]	48.0 (47.6)[a]	48.0 (47.6)[a]	48.0	48.1
C-10	37.6 (37.9)	37.6 (37.9)	37.6 (37.9)	37.6	37.5 (38.0)	37.5 (37.9)	37.5 (37.9)	38.0	38.0
C-11	24.2 (24.8)	24.2 (24.8)	24.2 (24.7)	24.2	24.3 (24.8)	24.3 (24.9)	24.3 (24.8)	24.2	24.2
C-12	123.2 (123.9)	123.4 (124.0)	123.4 (123.9)	123.4	123.5 (123.9)	123.4 (123.9)	123.4 (123.8)	123.4	123.4
C-13	144.4 (144.6)	144.3 (144.6)	144.3 (144.6)	144.4	144.4 (144.8)	144.3 (144.6)	144.3 (144.7)	144.3	144.3
C-14	42.5 (43.0)	42.5 (43.0)	42.5 (43.0)	42.5	42.5 (43.1)	42.5 (43.0)	42.5 (43.0)	42.5	42.5
C-15	36.2 (36.5)	36.1 (36.4)	36.1 (36.4)	36.2	36.2 (36.6)	36.2 (36.6)	36.2 (36.5)	36.2	36.1
C-16	74.1 (74.6)	74.1 (74.7)	74.1 (74.6)	74.1	74.1 (74.8)	74.1 (74.7)	74.1 (74.6)	74.0	74.1
C-17	50.1 (50.5)	50.1 (50.5)	50.1 (50.5)	50.1	50.1 (50.7)	50.1 (50.5)	50.1 (50.5)	50.1	50.1
C-18	41.8 (42.3)	41.7 (42.3)	41.7 (42.5)	41.8	41.7 (42.4)	41.7 (42.3)	41.7 (42.5)	41.8	41.8
C-19	47.1 (47.7)	47.2 (47.7)	47.2 (47.7)	47.2	47.2 (47.7)[b]	47.2 (47.6)	47.2 (47.6)	47.2	47.2
C-20	30.8 (31.3)	30.8 (31.3)	30.8 (31.3)	30.8	30.8 (31.3)	30.8 (31.2)	30.8 (31.3)	30.8	30.8
C-21	36.2 (36.5)	36.1 (36.4)	36.1 (36.4)	36.1	36.2 (36.6)	36.2 (36.6)	36.2 (36.5)	36.2	36.1
C-22	31.3 (31.7)	31.3 (31.7)	31.3 (31.6)	31.4	31.4 (31.7)	31.3 (31.4)	31.3 (31.6)	31.5	31.4
C-23	63.8 (64.1)	63.9 (64.1)	63.9 (63.8)	63.9	63.8 (63.8)	63.8 (63.9)	63.8 (64.0)	63.7	63.7
C-24	66.3 (65.5)	66.4 (65.4)	66.4 (65.5)	66.3	66.0 (65.3)	65.8 (65.4)	65.8 (65.5)	67.7	67.7
C-25	18.2 (18.4)	18.2 (18.4)	18.2 (18.4)	18.2	18.2 (18.4)	18.1 (18.3)	18.1 (18.4)	18.8	18.8
C-26	17.6 (18.0)	17.7 (18.0)	17.7 (18.0)	17.7	17.7 (18.0)	17.7 (18.0)	17.7 (18.0)	17.7	17.7
C-27	27.3 (27.4)	27.3 (27.4)	27.3 (27.4)	27.3	27.3 (27.4)	27.2 (27.4)	27.2 (27.4)	27.2	27.3
C-28	175.8 (177.1)	175.9 (177.0)	175.9 (177.0)	175.8	175.8 (177.2)	175.8 (177.1)	175.8 (177.1)	175.8	175.9
C-29	33.1 (33.3)	33.1 (33.3)	33.1 (33.3)	33.1	33.1 (33.3)	33.0 (33.3)	33.0 (33.4)	33.1	33.1
C-30	25.2 (25.4)	25.2 (25.3)	25.2 (25.4)	25.2	25.2 (25.3)	25.2 (25.3)	25.2 (25.3)	25.2	25.2
2-OCH_3									
24-OCH_3									
Glucose (inner)									
C-1	105.9 (105.9)	105.9 (105.9)	105.9 (105.8)	106.0	105.4 (105.6)[c]	105.4 (105.4)	105.4 (105.5)	105.9	105.9
C-2	75.2 (75.3)	75.3 (75.2)	75.3 (75.3)	75.3	74.1 (74.8)	74.1 (74.5)	74.1 (74.6)	75.0	75.3
C-3	78.6 (78.3)	78.6 (78.3)	78.6 (78.0)	78.6	88.6 (88.6)	88.6 (88.4)	88.6 (88.4)	77.9	78.0
C-4	72.0 (71.5)	72.0 (71.5)	72.0 (71.5)	72.1	70.1 (70.1)	70.1 (69.9)	70.1 (70.1)	72.0	72.1
C-5	78.2 (78.1)	78.1 (78.0)	78.1 (78.0)	78.2	77.9 (78.2)[d]	77.9 (78.0)	77.9 (78.0)	76.5	76.6
C-6	62.9 (62.6)	62.9 (62.6)	62.9 (62.6)	63.0	62.7 (62.7)	62.8 (62.7)	62.8 (62.7)	70.3	70.3
Glucose (terminal)									
C-1					105.4 (105.3)[c]	105.4 (105.4)	105.4 (105.5)	104.8	104.9
C-2					75.3 (75.6)[g]	75.3 (75.3)[b]	75.3 (75.3)[b]	75.0	75.0
C-3					78.3 (78.4)	78.2 (78.4)	78.2 (78.0)	78.6	78.7
C-4					72.0 (71.8)	72.0 (71.6)	72.0 (71.7)	71.9[a]	72.1
C-5					78.2 (78.2)[d]	78.2 (78.0)	78.2 (78.0)	77.9	78.0
C-6					62.8 (62.9)	62.8 (62.7)	62.8 (62.7)	63.0	63.0
Arabinose									
C-1	93.7 (94.2)	93.6 (94.2)	93.6 (94.0)	93.7	93.7 (94.4)	93.5 (94.1)	93.5 (94.1)	93.7	93.7
C-2	75.6 (75.8)	76.3 (76.2)	76.3 (76.4)	75.7	75.7 (75.9)	76.3 (76.3)	76.3 (76.5)	75.6	75.8
C-3	70.4[i] (71.2)[i]	70.3[i] (71.1)[i]	70.3[i] (71.1)[i]	70.2[i]	70.4 (71.4)	70.1 (71.2)	70.1 (71.0)	70.3[i]	70.3[i]
C-4	65.9[i] (66.9)[b,i]	65.8[i] (66.9)[b,i]	65.8 (66.7)[i]	65.9[i]	66.0 (67.0)[e]	65.8 (66.8)[c]	65.8 (66.7)[c]	66.0[i]	65.9[i]
C-5	62.9 (64.1)	62.9 (64.1)	62.9 (64.1)	63.0	63.1 (64.3)	62.8 (64.1)	62.8 (64.0)	63.0	63.0
Rhamnose									
C-1	101.0 (101.3)	98.4 (98.6)	101.6 (101.4)	101.1	101.1 (101.5)	98.3 (98.6)	101.4 (101.4)	101.0	101.1
C-2	72.0 (72.2)	73.6 (73.9)	70.3 (70.1)	72.1	72.0 (72.4)	73.6 (73.9)	70.1 (70.1)	72.0	72.1
C-3	72.4 (72.4)	70.3 (70.5)	75.3 (75.3)	72.5	72.5 (72.7)	70.1 (70.5)	75.3 (75.5)[b]	72.4	72.5
C-4	83.7 (83.8)	83.4 (83.4)	77.6 (78.0)	83.7	83.7 (83.9)	83.5 (83.3)	77.9 (78.0)	83.8	83.6
C-5	68.6 (69.1)[c]	68.7 (69.1)[c]	68.7 (69.2)[b]	68.7	68.7 (69.1)[f]	68.6 (69.1)[d]	68.6 (69.1)[d]	68.6	68.7
C-6	18.1 (18.1)	18.3 (18.1)	18.3 (18.4)	18.2	18.2 (18.2)	18.1 (18.1)	18.1 (18.4)	18.1	18.2
CH_3CO		20.7 (20.9)	21.1 (21.4)			20.7 (20.9)	21.1 (21.4)		
CH_3CO		170.6 (172.3)	170.6 (172.6)			170.3 (172.3)	170.5 (172.6)		

Carbon	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
Sapogenin									
C-1	44.2	44.3 (44.4)	44.3 (44.6)	44.3	44.4 (44.8)	44.4 (44.8)	45.8	43.3	41.6
C-2	70.2	70.3 (70.2)	70.3 (70.1)	70.1	70.1 (69.8)	70.1 (69.9)	69.8	80.1	82.8
C-3	83.9	84.0 (84.3)	84.0 (84.2)	83.7	83.9 (84.4)	83.9 (84.5)	84.4	85.1	89.8
C-4	42.8	42.8 (43.0)	42.8 (43.0)	42.9	42.8 (43.0)	42.8 (42.9)	56.1	55.2	53.9
C-5	48.4	48.5 (48.5)[a]	48.5 (48.5)[a]	48.3	48.3 (48.6)[a]	48.3 (48.6)[a]	50.1	50.5	52.5
C-6	18.1	18.1 (18.1)	18.1 (18.0)	18.1	18.1 (18.1)	18.1 (18.1)	20.5	20.6	19.5
C-7	33.4	33.5 (33.3)	33.5 (33.7)	33.5	33.5 (33.5)	33.5 (33.8)	33.7	34.0	33.6
C-8	40.6	40.6 (41.0)	40.6 (41.0)	40.6	40.6 (41.0)	40.6 (41.0)	40.3	40.6	40.7
C-9	48.0	48.0 (47.7)[a]	48.0 (47.6)[a]	48.0	48.0 (47.6)[a]	48.0 (47.6)[a]	47.6	47.6	48.5
C-10	37.2	37.2 (37.6)	37.2 (37.6)	37.2	37.2 (37.6)	37.2 (37.6)	37.4	38.0	37.9
C-11	24.2	24.2 (24.4)	24.2 (24.4)	24.2	24.3 (24.6)	24.3 (24.7)	24.4	24.4	24.7
C-12	123.4	123.4 (123.8)	123.4 (123.8)	123.4	123.4 (124.0)	123.4 (123.8)	123.0	123.4	122.3
C-13	144.4	144.4 (144.6)	144.4 (144.6)	144.4	144.4 (144.6)	144.4 (144.7)	144.4	144.5	145.0
C-14	42.4	42.5 (43.0)	42.5 (43.1)	42.5	42.5 (43.0)	42.5 (43.1)	42.4	42.5	42.5
C-15	36.2	36.2 (36.5)	36.2 (36.3)	36.2	36.1 (36.4)	36.1 (36.4)	36.1	36.2[a]	36.0
C-16	74.1	74.1 (74.6)	74.1 (74.7)	74.2	74.2 (74.8)	74.2 (74.7)	74.1	74.1	73.9
C-17	50.0	50.1 (50.5)	50.1 (50.5)	50.1		50.1 (50.5)	50.1	50.1	50.0
C-18	41.6	41.6 (42.1)	41.6 (42.2)	41.6		41.6 (42.1)	41.6	41.7	41.6
C-19	47.2	47.2 (47.7)	47.2 (47.6)	47.2		47.2 (47.6)	47.2	47.2	47.2
C-20	30.8	30.8 (31.2)	30.8 (31.2)	30.8		30.8 (31.2)	30.8	30.8	30.7
C-21	36.2	36.2 (36.5)	36.2 (36.3)	36.2	36.1 (36.4)	36.1 (36.4)	36.1	36.3[a]	36.0
C-22	31.3	31.3 (31.7)	31.3 (31.6)	31.3	31.4 (31.6)	31.4 (31.5)	31.4	31.4	31.3
C-23	66.8	66.8 (66.7)	66.8 (66.6)	66.8	66.5 (66.7)	66.5 (66.7)	64.5	64.1	57.5
C-24	14.8	14.8 (14.8)	14.8 (14.8)	14.8	14.8 (14.8)	14.8 (14.8)	175.5	173.6	177.7
C-25	17.8	17.8 (18.1)	17.8 (18.0)	17.8	17.8 (18.1)	17.8 (18.1)	15.8	16.5	18.1
C-26	17.5	17.5 (17.8)	17.5 (17.8)	17.5	17.5 (18.1)	17.5 (17.8)	17.6	17.8	17.4
C-27	27.3	27.4 (27.5)	27.4 (27.5)	27.3	27.3 (27.5)	27.3 (27.5)	27.2	27.3	27.4
C-28	175.8	175.9 (177.0)	175.9 (177.0)	175.8	175.9 (177.0)	175.9 (177.0)	175.8	175.8	175.8
C-29	33.1	33.1 (33.3)	33.1 (33.3)	33.1	33.1 (33.3)	33.1 (33.3)	33.1	33.0	33.0
C-30	25.2	25.3 (25.4)	25.3 (25.4)	25.3	25.3 (25.4)	25.3 (25.4)	25.2	25.2	25.2
C-30								58.7	
2-OCH_3							51.3	50.5	
24-OCH_3									
Glucose (inner)									
C-1	105.2	105.2 (105.3)	105.2 (105.3)	104.9	104.9 (105.1)	104.9 (105.2)	106.3	106.6	105.1
C-2	75.5	75.4 (75.4)	75.4 (75.5)	74.2	74.2 (74.8)	74.2 (75.0	75.3	75.7	75.0
C-3	78.5	78.5 (78.0)	78.5 (78.0)	88.7	88.7 (88.3)	88.7 (88.3)	78.5	78.4	78.2
C-4	72.0	72.0 (71.3)	72.0 (71.3)	70.1	70.1 (69.8)	70.1 (70.1)	72.0	72.1	71.8
C-5	77.9	77.9 (78.0)	77.9 (78.0)	77.7	77.7 (78.0)	77.7 (78.0)	78.1	78.1	78.2
C-6	63.0	63.0 (62.5)	63.0 (62.5)	62.9	62.8 (62.6)	62.8 (62.6)	63.0	63.3	62.9
Glucose (terminal)									
C-1				105.5	105.5 (105.1)	105.5 (105.2)			
C-2				75.3	75.3 (75.1)[b]	75.3 (75.0)[b]			
C-3				78.2	78.4 (78.0)	78.4 (78.0)			
C-4				72.0	72.0 (71.6)	72.0 (71.6)			
C-5				78.2	78.2 (78.0)	78.2 (78.0)			
C-6				62.9	62.8 (62.6)	62.8 (62.6)			
Arabinose									
C-1	93.7	93.5 (94.1)	93.5 (94.0)	93.7	93.5 (94.0)	93.5 (94.0)	93.7	93.7	93.7
C-2	75.7	76.3 (76.3)	76.3 (76.3)	75.7	76.3 (76.2)	76.3 (76.4)	75.7	75.7	75.7
C-3	70.2	70.3 (71.0)	70.3 (71.1)	70.2[i]	70.2 (71.0)	70.2 (71.0)	70.1[i]	70.1[i]	70.2[i]
C-4	65.8	65.8 (66.7)	65.8 (66.6)	65.8[i]	75.8 (66.7)	65.8 (66.7)	65.8[i]	65.8[i]	65.9[i]
C-5	63.0	63.0 (63.8)	63.0 (63.3)	62.9	62.8 (63.9)	62.8 (64.0)	63.0	63.0	62.9
Rhamnose									
C-1	101.1	98.4 (98.5)	101.5 (101.4)	101.1	98.4 (98.6)	101.5 (101.4)	101.1	101.2	101.1
C-2	72.0	73.6 (73.9)	70.3 (70.1)	72.0	73.6 (73.9)	70.2 (70.1)	72.0	72.1	72.0
C-3	72.4	70.3 (70.6)	75.4 (75.5)	72.5	70.2 (70.5)	75.3 (75.5)[b]	72.4	72.4	72.4
C-4	83.7	83.4 (83.3)	77.6 (78.0)	83.7	83.4 (83.3)	77.7 (78.0)	83.6	83.6	83.6
C-5	68.6	68.7 (69.0)[b]	68.7 (69.2)[b]	68.7	68.7 (69.1)[c]	68.7 (69.3)[c]	68.7	68.7	68.6
C-6	18.1	18.3 (18.1)	18.3 (18.3)	18.1	18.4 (18.1)	18.4 (18.4)	18.1	18.1	18.3
CH_3CO		20.7 (21.0)	21.1 (21.4)		20.7 (20.9)	21.1 (21.4)			
CH_3CO		170.4 (172.3)	170.6 (172.5)		170.4 (172.3)	170.6 (172.6)			

Table 2 (*cont.*)

Carbon	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Xylose									
C-1	106.6 (106.6)	106.4 (106.4)	105.4 (105.5)	106.7	106.6 (106.7)	106.5 (106.4)	105.4 (105.5)	106.6	106.7
C-2	75.0 (75.3)	75.0 (75.2)	75.0 (75.3)	75.7	75.0 (75.3)[g]	75.0 (75.1)[b]	75.0 (75.1)[b]	75.0	75.8
C-3	85.6 (86.0)	85.7 (85.9)	85.7 (85.5)	78.4	85.7 (86.1)	85.5 (85.8)	85.5 (85.5)	85.6	78.4
C-4	69.5 (70.0)[c]	69.5 (69.9)[c]	69.5 (70.1)[b]	71.0	69.5 (70.1)[f]	69.5 (69.9)[d]	69.5 (70.1)[d]	69.5	71.0
C-5	66.8 (67.2)[b]	66.7 (67.2)[b]	66.7 (66.7)	67.3	66.8 (67.4)[e]	66.8 (67.1)[c]	66.8 (66.7)[c]	66.8	67.3
Apiose									
C-1	111.2 (111.2)	111.2 (111.2)	111.2 (111.2)		111.2 (111.4)	111.2 (111.2)	111.2 (111.3)	111.3	
C-2	77.9 (78.1)	77.9 (78.0)	77.9 (78.0)		77.9 (77.9)[d]	77.9 (78.0)	77.9 (78.0)	77.9	
C-3	80.0 (80.4)	80.0 (80.3)	80.0 (80.4)		80.0 (80.5)	79.9 (80.4)	79.9 (80.4)	80.0	
C-4	75.0 (75.3)	75.0 (75.2)	75.0 (75.3)		75.0 (75.6)[g]	75.0 (75.3)[b]	75.0 (75.3)[b]	75.0	
C-5	65.7 (65.5)	65.8 (65.4)	65.7 (65.5)		65.7 (65.7)	65.8 (65.4)	65.8 (65.5)	65.7	

[a–g] Assignments may be interchanged in each vertical column. [h] Assignments of C-4 and C-5 in the corresponding prosapogenin methyl ester were reversed in refs. 2*a* and *b*.

(84 mg), m.p. 227—235 °C, $[\alpha]_D^{25}$ −27.9° (*c* 1.02) (Found: C, 54.3; H, 7.55. $C_{62}H_{102}O_{33}$ requires C, 54.53; H, 7.41%); δ_H signals for 25-, 26-, 27-, 29-, and 30-H were 1.46 (1.42), 1.12 (1.06),* 1.73 (1.64), 1.14 (1.10),* and 0.99 (0.97), respectively.

2″-O-*Acetylplatycodin*-D_2 (**6**).—Fraction 12 (163 mg) was chromatographed on silica gel (30 g) with solvent (B) and yielded the *saponin* (**6**) (124 mg), m.p. 225—231 °C, $[\alpha]_D^{26}$ −25.0° (*c* 1.03) (Found: C, 54.4; H, 7.4. $C_{65}H_{104}O_{34}$ requires C, 54.61; H, 7.33%).

3″-O-*Acetylplatycodin*-D_2 (**7**).—A solution of compound (**6**) (400 mg) in MeOH (200 ml) was set aside at room temperature for 4 days. After removal of the solvent, the residue was chromatographed on silica gel (100 g) with solvent (A). The initial eluate gave starting material (**6**) (234 mg) and the final afforded the *saponin* (**7**) (156 mg), m.p. 224—232 °C, $[\alpha]_D^{25}$ −35.3° (*c* 1.01) (Found: C, 52.7; H, 7.2. $C_{65}H_{104}O_{34}\cdot 3H_2O$ requires C, 52.62; H, 7.47%).

Platycodin-D_3 (**8**).—Fraction 17 (773 mg) was chromatographed on silica gel (100 g) with solvent (B) and gave fractions 31 (149 mg) and 32 (412 mg). The latter fraction yielded the *saponin* (**8**) (355 mg), m.p. 218—225 °C, $[\alpha]_D^{22}$ −24.3° (*c* 1.04) (Found: C, 54.65; H. 7.75. $C_{63}H_{102}O_{33}$ requires C, 54.53; H, 7.41%); δ_H signals for 25-, 26-, 27-, 29-, and 30-H were 1.47 (1.38), 1.09 (1.04),* 1.70 (1.64), 1.13 (1.11),* and 1.01 (0.99), respectively.

Deapioplatycodin-D_2 (**9**).—Fraction 31 (149 mg) was purified by chromatography with solvent (B) and gave the *saponin* (**9**) (108 mg), m.p. 223—232 °C, $[\alpha]_D^{23}$ −18.3° (*c* 1.01) (Found: C, 55.65; H, 7.65. $C_{58}H_{94}O_{29}$ requires C, 55.49; H, 7.75%).

Polygalacin-D (**10**).—Fraction 3 (1.5 g) was chromatographed on silica gel (200 g) with solvent (A) to separate the middle portion, fraction 11 (715 mg), which was subjected to droplet countercurrent chromatography with $CHCl_3$–MeOH–H_2O–Pr^nOH (5:6:4:1.2) and afforded fractions 20 (23 mg), 21 (162 mg), 22 (106 mg), and 23 [127 mg, saponin (**2**)].

Fraction 21 (162 mg) was dissolved in 2% KOH–MeOH (10 ml) and left at room temperature for 30 min. The reaction mixture was worked up as usual and gave a product (145 mg), which was separated by chromatography with solvent (A) into fractions 33 (43 mg) and 34 (92 mg). Fraction 33 gave the *saponin* (**10**) (28 mg), m.p. 221—226 °C, $[\alpha]_D^{25}$ −41.5° (*c* 1.03) (Found: C, 56.4; H, 7.75. $C_{57}H_{92}O_{27}$ requires C, 56.61; H, 7.67%). Fraction 34 yielded the saponin (**1**) (63 mg) (^{13}C n.m.r. spectrum).

2″-O-*Acetylpolygalacin*-D (**11**).—Fraction 1 (720 mg) was chromatographed on silica gel (100 g) with solvent (A) and gave fractions 7 (98 mg) and 8 (440 mg). Fraction 7 was purified by chromatography with solvent (B) and produced the *saponin* (**11**) (64 mg), m.p. 223—227 °C, $[\alpha]_D^{26}$ −33.2° (*c* 1.04) (Found: C, 55.95; H, 7.65. $C_{59}H_{94}O_{28}\cdot H_2O$ requires C, 55.82; H, 7.62%).

3″-O-*Acetylpolygalacin*-D (**12**).—Fraction 8 (440 mg) was subjected to droplet countercurrent chromatography as before and gave fractions 18 (112 mg) and 19 [188 mg, saponin (**11**)]. The former fraction gave the *saponin* (**12**) (96 mg), m.p. 219—225 °C, $[\alpha]_D^{26}$ −41.2° (*c* 0.74) (Found: C, 55.05; H, 7.7. $C_{59}H_{94}O_{28}\cdot 2H_2O$ requires C, 55.04; H, 7.67%).

Polygalacin-D_2 (**13**).—Fraction 5 (2 g) was chromatographed on silica gel (200 g) with solvent (B). After elution with 550 ml of the solvent, fraction 14 (160 ml, 889 mg) was obtained. This fraction was again chromatographed with solvent (A) and gave a middle fraction 26 (413 mg), which was subjected to droplet countercurrent chromatography and yielded fraction 35 (181 mg) which was rich in (**13**). Purification of this fraction by silica gel chromatography gave the *saponin* (**13**) (145 mg), m.p. 229—236 °C, $[\alpha]_D^{25}$ −35.5° (*c* 1.03) (Found: C, 55.1; H, 7.65. $C_{63}H_{102}O_{32}$ requires C, 55.17; H, 7.50%).

2″-O-*Acetylpolygalacin*-D_2 (**14**).—Fraction 22 (106 mg) gave the *saponin* (**14**) (84 mg), m.p. 229—235 °C, $[\alpha]_D^{25}$ −32.0° (*c* 1.04) (Found: C, 55.15; H, 7.65. $C_{65}H_{104}O_{33}$ requires C, 55.23; H, 7.42%).

3″-O-*Acetylpolygalacin*-D_2 (**15**).—Fraction 20 (23 mg) yielded the *saponin* (**15**) (15 mg), m.p. 226—233 °C, $[\alpha]_D^{25}$ −40.6° (*c* 1.08) (Found: C, 54.95; H, 7.55. $C_{65}H_{104}O_{33}$ requires C, 55.23; H, 7.42%).

Methyl Platyconate-A (**16**).—Fraction 15 (2.07 g) was chromatographed on silica gel (200 g) with solvent (B) and gave fractions 27 (543 mg), 28 (756 mg), and 29 (206 mg). Fraction 28 was purified by chromatography with solvent (A), giving the *saponin* (**16**) (387 mg), m.p. 224—231 °C, $[\alpha]_D^{22}$ −19.8° (*c* 0.99) (Found: C, 55.15; H, 7.55. $C_{58}H_{92}O_{30}$ requires C, 54.88; H, 7.31%); δ_H signals for 25-, 26-, 27-, 29-, 30-H, and 24-OMe were

Table 2 (*cont.*)

Carbon	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
Xylose									
C-1	106.6	106.5 (106.3)	105.4 (105.3)	106.6	106.5 (106.3)	105.5 (105.4)	106.5	106.5	106.5
C-2	75.0	75.0 (75.1)	75.0 (75.1)	75.0	75.0 (75.1)[b]	75.0 (75.0)[b]	75.0	75.0	75.0
C-3	85.5	85.6 (85.5)	85.6 (85.8)	85.6	85.5 (85.8)	85.5 (85.3)	85.5	85.5	85.6
C-4	69.5	69.5 (70.0)[b]	69.5 (70.1)[b]	89.5	69.6 (69.8)[c]	69.6 (70.1)[c]	69.5	69.5	69.5
C-5	66.8	66.8 (66.7)	66.8 (66.6)	66.8	66.9 (66.7)	66.9 (66.7)	66.8	66.8	66.8
Apiose									
C-1	111.2	111.3 (111.2)	111.3 (111.2)	111.3	111.3 (111.2)	111.3 (111.3)	111.2	111.3	111.2
C-2	77.9	77.9 (78.0)	77.9 (78.0)	77.9	77.9 (78.0)	77.9 (78.0)	77.9	77.9	77.9
C-3	80.0	80.0 (80.3)	80.0 (80.4)	80.0	80.0 (80.3)	80.0 (80.4)	80.0	80.1	80.0
C-4	75.0	75.0 (75.1)	75.0 (75.1)	75.0	75.0 (75.4)[b]	75.0 (75.5)[b]	75.0	75.0	75.0
C-5	65.8	65.8 (65.4)	65.8 (65.5)	65.8	65.8 (65.4)	65.8 (65.5)	65.8	65.8	65.7

1.35 (1.33), 1.12 (1.07), 1.75 (1.65), 1.15 (1.12), 1.00 (0.98), and 3.61 (3.61), respectively.

Methyl 2-O-*Methylplatyconate*-A (**17**).—Fraction 29 (206 mg) was chromatographed on silica gel (50 g) with solvent (A). Elution of 230 ml of the solvent gave fraction 36 (146 mg), which was rich in (**17**). This was further chromatographed with solvent (B) and gave the *saponin* (**17**) (82 mg), m.p. 223—229 °C, $[\alpha]_D^{23}$ −27.1° (*c* 1.02) (Found: C, 53.5; H, 7.45. $C_{59}H_{94}O_{30}\cdot 2H_2O$ requires C, 53.71; H, 7.43%); δ_H signals for 25-, 26-, 27-, 29-, 30-H, 2-OMe, and 24-OMe were 1.39 (1.37), 1.18 (1.13), 1.77 (1.67), 1.15 (1.12), 1.00 (0.98), 3.68 (3.62),* and 3.62 (3.61),* respectively.

Platyconic Acid-A *Lactone* (**18**).—Fraction 27 (543 mg) was purified by chromatography with solvent (A) and gave the *saponin* (**18**) (357 mg), m.p. 230—236 °C, $[\alpha]_D^{22}$ −30.2° (*c* 1.04) (Found: C, 55.45; H, 7.35. $C_{57}H_{88}O_{29}$ requires C, 55.33; H, 7.17%); δ_H signals for 25-, 26-, 27-, 29-, and 30-H were 1.32 (1.30), 1.07 (1.03), 1.70 (1.63), 1.15 (1.12), and 1.00 (0.98), respectively.

Conversion of Saponins into the Corresponding Prosapogenin Methyl Esters.—A solution of the saponin (**1**) (400 mg) in 2% KOH–MeOH (50 ml) was kept at room temperature for 5 days. Water (50 ml) was added to the reaction mixture, which was neutralized with 5% HCl and extracted with butan-1-ol (5 × 30 ml). The organic layer was washed with water, dried, and evaporated under reduced pressure, leaving a residue (201 mg). The residue was purified by chromatography with $CHCl_3$–MeOH–H_2O (8:2:0.2) and gave prosapogenin methyl ester (**19**) (154 mg), identical with an authentic sample[1] (t.l.c. and ^{13}C n.m.r. spectrum).

Similarly, the saponins (**4**), (**5**), (**8**) and (**9**), (**10**), (**13**), (**17**), and (**18**) gave the corresponding prosapogenin methyl esters (**19**)—(**23**), (**25**), and (**26**), respectively. The saponin (**16**) remained unchanged under the above conditions, but the reaction proceeded upon refluxing for 3 h to yield prosapogenin dimethyl ester (**24**).

Mutual Conversion between 2″-O- and 3″-O-Acetylsaponins.—The saponin (**2**) (200 mg) was dissolved in MeOH (200 ml) and left at room temperature for 10 days. After removal of the solvent, the residue was found to be a 1:1 mixture of (**2**) and (**3**) (t.l.c. and ^{13}C n.m.r. spectrum in CD_3OD). The mixture was dissolved again in MeOH (200 ml) and kept at room temperature for a further 15 days. The residue gave the saponin (**1**) containing a small amount of (**2**) and (**3**) (t.l.c. and ^{13}C n.m.r. spectrum). The saponin (**3**) showed the same behaviour as above in a methanolic solution, and similar conversions were also observed between (**6**) and (**7**), (**11**) and (**12**), and (**14**) and (**15**).

Deacetylation of Acetylsaponins.—Acetylsaponins (**2**), (**6**), (**11**), and (**14**) (150 mg each) were dissolved in 2% KOH–MeOH (20 ml) and left for 30 min at room temperature. The reaction mixture was worked up as usual, giving platycodin-D (**1**) and -D_2 (**5**), and polygalacin-D (**10**) and -D_2 (**13**), respectively (^{13}C n.m.r. spectrum).

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