Carbohydrate Structures of Three New Saponins from the Root Bark of *Hovenia dulcis* (Rhamnaceae)

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The carbohydrate sequences of two major saponins, hovenosides D (1) and G (2) and a minor saponin, hovenoside I (3), obtained from the root barks of *Hovenia dulsis* Thunb (Rhamnaceae), have been determined mainly by g.l.c.–mass spectrometry, and the full molecular structures of these saponins have been assigned as 3-*O*-[(2-*O*-β-D-xylopyranosyl)-3-*O*-(2-*O*-β-D-xylopyranosyl-6-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl)-α-L-arabinopyranosyl]-jujubogenin, 3-*O*-[(2-*O*-β-D-xylopyranosyl)-3-*O*-(2-*O*-β-D-xylopyranosyl-β-D-glucopyranosyl)-α-L-arabinopyranosyl]jujubogenin, and 3-*O*-[(2-*O*-β-D-xylopyranosyl)-3-*O*-β-D-glucopyranosyl-α-L-arabinopyranosyl]jujubogenin respectively from additional chemical and spectroscopic evidence. Correlations among these saponins have been obtained by the action of enzymes.

PREVIOUS papers [1] have described the isolation of the new saponins hovenosides C, D, G, G', and H by droplet counter-current chromatography (d.c.c.) [2] from the methanolic extracts of the root bark of *Hovenia dulcis* Thumb [3] (Rhamnaceae) (the Japanese name is 'kenponashi,' and the seeds are used as a folk medicine), and some chemical studies of hovenoside G. This paper deals with a study of the carbohydrate moieties of hovenosides D (1), G (2), and I (3), the corresponding sapogenin of which is jujubogenin (6).

On Smith–de Mayo degradation,[4] the saponins (1)—(3) afforded the prosapogenin (5), $C_{35}H_{56}O_8$, which was hydrolysed with N-sulphuric acid to yield a secondary sapogenin, ebelin lactone (4),[5] and L-arabinose (positive plane o.r.d. curve [6]). On a second Smith–de Mayo degradation, (5) gave jujubogenin (6),[7] whose structure was confirmed by *X*-ray crystallography. In the ^{1}H n.m.r. spectrum of (5), signals at δ 5.24 (1 H, d, *J* 9 Hz), 4.70 (1 H, m), and 4.01 (2 H, br,s) are assigned respectively to protons on C-23, C-22, and C-30 of the jujubogenin moiety, and an anomeric proton signal at δ 4.36 (d, *J* 5.5 Hz) indicates the α-linkage of L-arabinose ($^4C_1$ conformation [8]) to the genin. A partial hydrolysis of hovenoside G (2), followed by repeated purification by column chromatography and preparative t.l.c., furnished a compound (7), which gave (4) and L-arabinose and D-glucose as sugar components (molar ratio 1 : 1). Compound (7) exhibits five-membered lactonic (1 768 cm^{-1}) absorption in the i.r. spectrum and strong u.v. absorption at 270, 278, and 290 nm characteristic of a conjugated triene, suggesting the existence of the ebelin lactone moiety in (7). Its per-*O*-methyl derivative (8), prepared by the Kuhn method,[9] exhibits a molecular ion (*m/e* 832) and a peak due to a terminal permethylated hexose residue (*m/e* 219 coupled with 187) in the mass spectrum. The methanolysis product of (8) was deuteriomethylated with silver oxide and trideuteriomethyl iodide in dimethylformamide to give two kinds of methylated sugar. These were identified by g.l.c.–mass spectrometry as methyl α- and β-pyranosides of 2,3,4,6-tetra-*O*-methylglucose and 3-*O*-trideuteriomethyl-2,4-di-*O*-methylarabinose [α- and β-forms are not separated from each other on g.l.c. and the ^{1}H n.m.r. spectrum of this fraction shows two anomeric proton signals at δ 4.03 (d, *J* 3.0 Hz) and 4.16 (d, *J* 4.5 Hz)]. The structure of the latter was confirmed by analysis of the mass spectrum, in which the fragment ions, CH_3O–CH=CH–OCD_3 (*m/e* 91, 90%) and CH_3O–CH=CH–CH=$\overset{+}{O}CH_3$ (chief contribution to *m/e* 101, base peak) [10] were observed. From these data, the prosapogenin (5) and compound (7) were determined to be 3-*O*-(α-L-arabinopyranosyl)jujubogenin and 3-*O*-(3-*O*-β-D-glucopyranosyl-α-L-arabinopyranosyl)ebelin lactone, respectively.

When hovenoside G (2) was incubated with naringinase † (a mixture of naringinase, naringin-β-1,2-rhamnosidase, and β-glucosidase), the glycoside (3) was slowly produced. This was identical with natural hovenoside I (3). On acidic hydrolysis, hovenoside I (3) furnished (4) and L-arabinose, D-xylose, and D-glucose as sugar components (molar ratio 1 : 1 : 1), while (2) afforded 2 mol. equiv. of D-xylose. This indicated that a mole of D-xylose was liberated from (2) to produce (3). Its per-*O*-methyl derivative (9) of (3), prepared by the Hakomori method,[11] exhibits fragment ions due to the terminal permethylated pentose (*m/e* 175 and 143) and hexose (*m/e* 219 and 187) residues in the mass spectrum and ^{1}H n.m.r. signals for three anomeric protons at δ 4.37 (d, *J* 5.5 Hz), 4.65 (d, *J* 7.5 Hz), and 4.69 (d, *J* 7.5 Hz), assigned respectively to α-L-arabinopyranose, β-D-glucopyranose (or xylose) in the $^4C_1$ conformation, and β-D-xylopyranose (or glucose)

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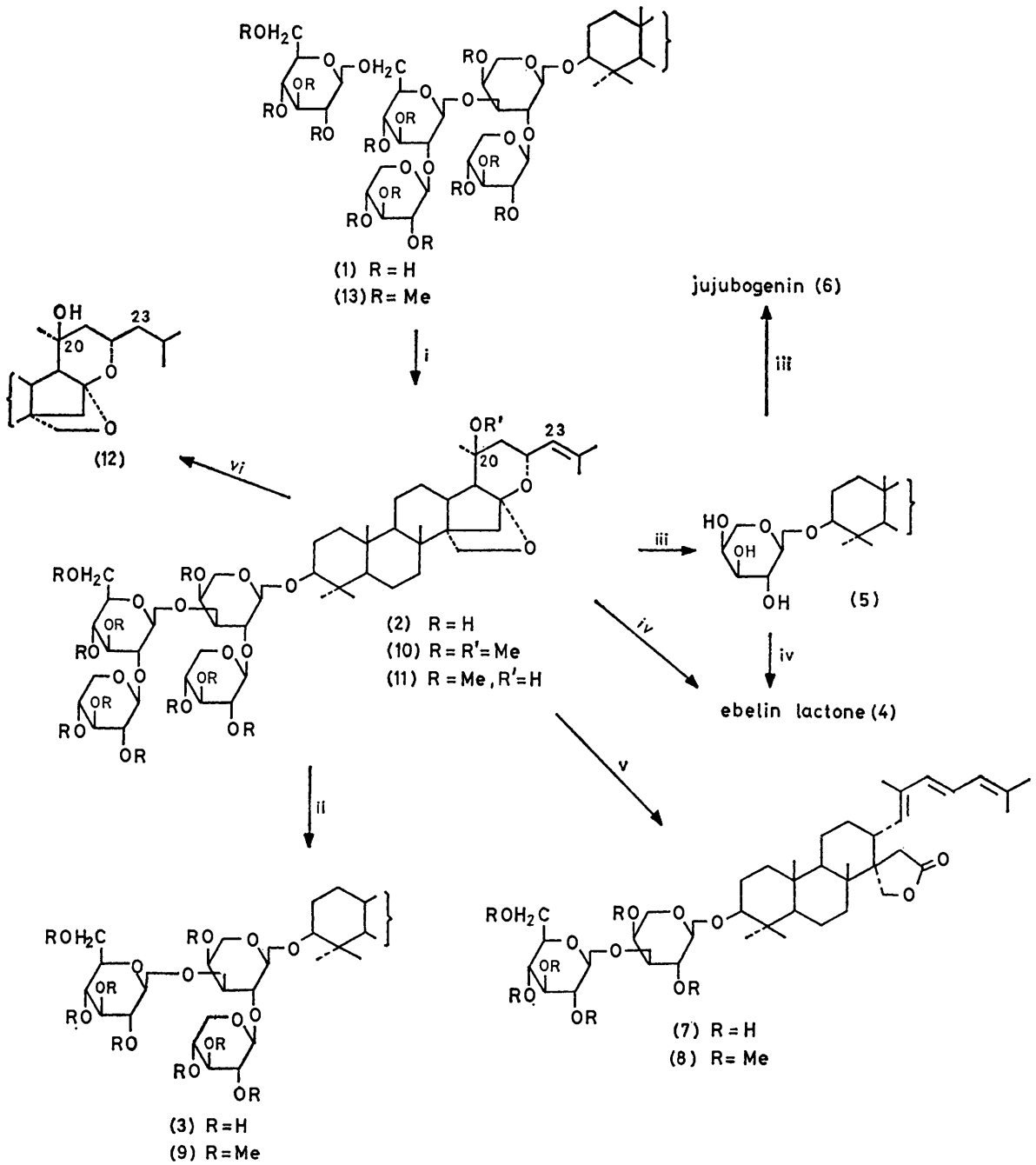
in the $^4C_1$ conformation. This conformational analysis is supported by application of Klyne's rule [12] (Table). identification of the last compounds was confirmed by the typical fragment ions, CD_3O–CH=CH–OCD_3 (*m/e*



Reagents: i, snail enzyme or hesperidinase; ii, naringinase; iii, Smith–de Mayo degradation; iv, N-H_2SO_4 at 100 °C for 5 h; v, 0.1N-HCl at 100 °C for 6 h; vi, H_2,Pt_2O

The methanolysis product of (9) was deuteriomethylated without further purification to give three kinds of methylated sugar. These were identified by g.l.c.–mass spectrometry as methyl α- and β-pyranosides of 2,3,4-tri-*O*-methylxylose, 2,3,4,6-tetra-*O*-methylglucose, and 2,3-bis-*O*-trideuteriomethyl-4-*O*-methylarabinose. The

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94, 84%) and CH_3O–CH=CH–CH=$\overset{+}{O}CH_3$ (*m/e* 104, base peak). Therefore hovenoside I (3) is 3-*O*-[(2-*O*-β-D-xylopyranosyl)-3-*O*-β-D-glucopyranosyl-α-L-arabinopyranosyl]jujubogenin.

Methylation of hovenoside G (2) by the methods of Hakomori and Kuhn gave the undeca-*O*-methyl derivative (10) and the deca-*O*-methyl derivative (11), re-

spectively. The ^{1}H n.m.r. spectrum of (10) exhibits an extra signal for the tertiary OCH_3 group at δ 3.16 (3 H, s). This indicates that all carbohydrate moieties

Molecular rotations

Saponins	$[\alpha]_D$ (°)	$[M]_D$ (°)	$-\Delta[M]_D$ (°)
(6)	−36	−169.6°	
			+41.9°
(5)	−21.2	−128.0°	
			−89.3°
(3)	−24.2	−217.3°	
			−54.6°
(2)	−26.4	−271.9°	
			−80.9°
(1)	−29.9	−352.8°	

The following $[M]_D$ values were used: Me α-L-arabinopyranoside +17.3°; Me β-L-arabinopyranoside +245°; Me α-D-glucopyranoside +111°; Me β-D-glucopyranoside −66°; Me α-D-xylopyranoside +252°; Me β-D-xylopyranoside −108°.

of (2) are linked to the genin at the C-3 hydroxy group. The methanolysis product of (11) was treated as mentioned above and the reaction mixture was examined by g.l.c.–mass spectrometry. This indicated the presence of methyl α- and β-pyranosides of 2,3-di-*O*-trideuteriomethyl-4-*O*-methylarabinose, 2,3,4-tri-*O*-methylxylose, and 2-*O*-trideuteriomethyl-3,4,6-tri-*O*-methylglucose. The identification of these last compounds was confirmed by the fragment ions, $CD_3O{-}CH{=}CH{-}OCH_3$ (*m/e* 91, base peak in α- and β-forms) and $CD_3O{-}CH{=}CH{-}CH{=}\overset{+}{O}CH_3$ (*m/e* 104, 60% in α-form and 70% in β-form). In the ^{1}H n.m.r. spectrum, overlapping of two anomeric and the C-23 proton signals obscured the analysis. So (11) was hydrogenated over Adams catalyst to afford the dihydro-derivative (12).

The ^{1}H n.m.r. spectrum of (12) was clear, showing four sets of anomeric proton signals at δ 4.27, 4.64, 4.72, and 4.96. A new signal at δ 4.96 (d, *J* 7.5 Hz) is assigned to that of the second β-D-xylopyranose ($^4C_1$ conformation). Thus the structure of hovenoside G (2) was determined to be 3-*O*-[(2-*O*-β-D-xylopyranosyl)-3-*O*-(2-*O*-β-D-xylopyranosyl-β-D-glucopyranosyl)-α-L-arabinopyranosyl]jujubogenin.

Generally speaking, the purification of highly polar saponins is extremely troublesome and it is also very difficult to obtain satisfactory evidence of purity.

Repeated d.c.c. and silica gel column chromatography gave pure hovenoside D (1) as a colourless powder whose purity was proved by ^{13}C n.m.r. spectroscopy.[13] D.c.c. and ^{13}C n.m.r. are very powerful weapons in this field. Acidic hydrolysis of the saponin (1) furnished (4) and L-arabinose, D-xylose, and D-glucose as sugar components (molar ratio 1 : 2 : 2). When (1) was incubated with snail intestinal juice (crude solution of β-glucuronidase) * or hesperidinase † (a mixture of hesperidinase, hesperidin-β-1,6-rhamnosidase, and β-glucosidase), the glycoside (2) was obtained almost quantitatively in a few days. The product (2) was identical with natural hovenoside G (2) in all respects including ^{13}C n.m.r. spectrum. Its per-*O*-methyl derivative (13), prepared by Hakomori's method, revealed mass fragment ions due to the terminal permethylated pentose (*m/e* 175) and hexose (*m/e* 219) residues, and gave on methanolysis four kinds of methylated sugar. They were identified by g.l.c. (with authentic samples) as methyl α- and β-pyranosides of 2,3,4,6-tetra-*O*-methylglucose, 2,3,4-tri-*O*-methylxylose, 4-*O*-methylarabinose, and 3,4-di-*O*-methylglucose. In the ^{1}H n.m.r. spectrum of (13), the anomeric proton signals appear at δ 4.25, 4.62 (2 H, br,d, *J* 7.5 Hz: accidental coincidence), 4.95, and 4.32 (d, *J* 7.5 Hz). The last anomeric proton signal is assigned to the second β-D-glucopyranose ($^4C_1$ conformation).

Consequently hovenoside D (1) is identified as 3-*O*-[(2-*O*-β-D-xylopyranosyl)-3-*O*-(2-*O*-β-D-xylopyranosyl-6-*O*-β-D-glucopyranosyl-β-D-glucopyranosyl)-α-L-arabinopyranosyl]jujubogenin.

Other saponins (C, G′, *etc.*) from the same materials whose sapogenin is different from jujubogenin are under investigation.

EXPERIMENTAL

M.p.s were measured with a Yanagimoto micro-apparatus. Unless otherwise stated, u.v. spectra were taken for solutions in ethanol, i.r. spectra for KBr discs, ^{1}H n.m.r. spectra for solutions in hexadeuterioacetone, and optical rotations for solution in methanol. G.l.c.–mass spectrometry was carried out with a Shimadzu LKB-9000 instrument [10% DEGS–Chromosorb W (60—80 mesh)]. D.c.c. experiments were carried out on home-made d.c.c. apparatus equipped with 500 columns (1.65 × 400 mm) by the ascending process [moving phase, upper layer; stationary phase, lower layer of (A) $CHCl_3$–MeOH–H_2O (35 : 65 : 40) or (B) $CHCl_3$–MeOH–H_2O (50 : 60 : 40)].

Purification of Saponins.—In the previous paper [1] we have described the isolation of hovenosides by d.c.c. In that work only *hovenoside G* (2) was obtained as pure crystals, $[\alpha]_D$ −26.4° (*c* 1.00) (Found: C, 55.2; H, 8.0. $C_{51}H_{82}O_{21}\cdot 4H_2O$ requires C, 55.5; H, 8.2%). The hovenoside D fraction was chromatographed on silica gel [lower layer of $CHCl_3$–MeOH–H_2O (7 : 3 : 1)] to afford pure *hovenoside D* (1) as a white powder from aqueous butanol, m.p. 205—210°, $[\alpha]_D$ −29.6° (*c* 0.50), $\nu_{max.}$ 3 400 and 1 100—1 000 cm^{-1}; no u.v. absorption above 210 nm (Found: C, 55.95; H, 7.9. $C_{57}H_{92}O_{26}\cdot 2H_2O$ requires C, 55.7; H, 7.85%). On a prepacked column (Merck Kieselgel 60), the so-called hovenoside H fraction was separated into three pure compounds, hovenosides H_1, H_2, and I (3). *Hovenoside I* (3) was obtained from methanol as colourless needles, m.p. 272—274°, $[\alpha]_D$ −24.2° (*c* 0.50), $\nu_{max.}$ 3 400 and 1 100—1 000 cm^{-1}; no u.v. absorption above 210 nm (Found: C, 56.95; H, 8.45. $C_{46}H_{74}O_{17}\cdot 4H_2O$ requires C, 56.9; H, 8.5%).

Acidic Hydrolysis of Saponins.—Hovenoside D (1) (5 mg) was dissolved in dioxan (1 ml), 2N-H_2SO_4 (2 ml), and water (1 ml) and heated under reflux for 5 h. The solution was diluted with water and extracted with ether. From this layer, ebelin lactone (4) was obtained. The aqueous layer of the hydrolysate was neutralized with ion-exchange resin (IR-45) and evaporated. Trimethylsilylation followed by

* Suc Helix Pomatia, Industrie Biogique Francaise F.F. 1828–6–70.

† Tanabe Pharm. Ind. Co., Ltd., CW 0290M.

[13] O. Inoue, Y. Ogihara, and K. Yamasaki, *J. Chem. Research*, 1978(*S*), 144.

g.l.c. [2% OV-1 on Chromosorb W (60—80 mesh) (3 mm × 2 m); column temperature 160°; N_2 gas flow rate 70 ml min^{-1}] showed the presence of arabinose, glucose, and xylose in the ratio 1 : 2 : 2. In the case of hovenosides G (2) and I (3), arabinose, glucose, and xylose were identified in the ratios 1 : 1 : 2 and 1 : 1 : 1, respectively.

Smith–de Mayo Degradation of Hovenoside G (2).—To a cooled solution of hovenoside G (2) (500 mg) in water (50 ml) was gradually added sodium periodate (1 g) with stirring, and the mixture was stirred at room temperature for 4 days, then extracted with butan-1-ol. The organic layer was washed with water and evaporated to dryness below 60 °C under reduced pressure. The residue was dissolved in aqueous 5% KOH (25 ml) and heated under reflux in argon for 2 h. The mixture was acidified to pH 3 by careful addition of 10% H_3PO_4 and extracted with butanol. The butanol layer was washed with water and evaporated to dryness and the residue was purified on a silica gel column [methanol–chloroform (1 : 5)] to give the prosapogenin (5), 3-O-(α-L-*arabinopyranosyl*)*jujubogenin*, obtained from methanol–chloroform (1 : 2.5) as colourless needles (45 mg), m.p. 237—241°, $[\alpha]_D$ −21.2° (*c* 0.50), δ[$CDCl_3$–CD_3OD (2.5 : 1)] 4.36 (1 H, d, *J* 5.5 Hz) (Found; C, 67.8; H, 9.3. $C_{35}H_{56}O_8 \cdot H_2O$ requires C, 67.5; H, 9.4%). Hovenosides D (1) and I (3) also gave (5) by the same procedure.

Isolation of L-*Arabinose*.—The prosapogenin (5) (30 mg) was hydrolysed in the same way as before and the resulting sugar portion was purified by d.c.c. [solvent system (A)] to give 4.2 mg of L-arabinose (positive plane o.r.d. curve in water).

Partial Hydrolysis of Hovenoside G (2).—Hovenoside G (2) (2 g) was dissolved in dioxan–0.1N-HCl (1 : 3; 60 ml) and heated under reflux for 6 h. The mixture was diluted with water and extracted with butan-1-ol. The organic layer was washed and evaporated to dryness and the residue chromatographed on silica gel [methanol–chloroform (1 : 5)]. Further purification (preparative t.l.c.) gave compound (7) (20 mg), 3-O-(3-O-β-D-*glucopyranosyl*-α-L-*arabinopyranosyl*)*ebelin lactone*, as a white powder, m.p. 198—203° (decomp.), $\nu_{max.}$ 1 768 cm^{-1}, $\lambda_{max.}$ 270, 278 (ε 11 850), and 290 nm (Found: C, 62.8; H, 8.55. $C_{41}H_{64}O_{12} \cdot 2H_2O$ requires C, 62.75; H, 8.75%). Compound (7) was hydrolysed in the usual way. From the organic layer, (4) was obtained, and L-arabinose and D-glucose were detected on g.l.c. in the ratio 1 : 1.

Methylation of Compound (7) *and Saponins by the Kuhn Method*.—Compound (7) (85 mg) was methylated in dimethylformamide (2 ml) with freshly prepared silver oxide (430 mg) and methyl iodide (3 ml) at 100 °C for 15 h according to the Kuhn method. The precipitate was filtered off, and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel [n-hexane–acetone (5 : 1)] to give the per-*O*-methylpyranoside (8) (10 mg), white powder, m.p. 111—113°, *m/e* 832 (M^+), 454 (ebelin lactone moiety; $C_{30}H_{46}O_3^+$), and 219 (terminal permethylated hexose residue).

Hovenoside G (2) (2 g) was methylated in the same way to give the *deca*-O-*methyl derivative* (11) (113 mg), colourless needles from n-hexane–acetone, m.p. 150—152°, $[\alpha]_D$ −33.0° (*c* 1.00), $\nu_{max.}$(CCl_4) 3 440w cm^{-1} (Found: C, 61.3; H, 8.65. $C_{61}H_{102}O_{21} \cdot H_2O$ requires C, 61.55; H, 8.8%).

Hydrogenation of Compound (11).—Compound (11) (90 mg) was hydrogenated over Adams catalyst in ethanol at room temperature overnight (uptake 1 mol. equiv.). After removal of catalyst, the filtrate was concentrated to dryness and the residue purified on silica gel [n-hexane–acetone (5 : 1)] to afford the *dihydro-derivative* (12) (21 mg), colourless needles from n-hexane–acetone, m.p. 127—130°, δ 4.27 (1 H, d, *J* 5.5 Hz), 4.64 (1 H, d, *J* 7.5 Hz), 4.72 (1 H, d, *J* 7.5 Hz), and 4.96 (1 H, d, *J* 7.5 Hz) (Found: C, 61.7; H, 9.1. $C_{61}H_{104}O_{21} \cdot H_2O$ requires C, 61.5; H, 8.95%).

Permethylation of Saponins by the Hakomori Method.—To a stirred solution of hovenoside I (3) (110 mg) in dimethyl sulphoxide (10 ml) under argon was added a solution (20 ml) of methylsulphinylmethanide and the mixture was stirred at room temperature for 5 h. Methyl iodide (10 ml) was then added and the reaction was continued for 24 h. The mixture was poured into water and extracted with chloroform. The organic layer was washed with aqueous 5% $Na_2S_2O_3$ and water and evaporated. The residue was chromatographed on silica gel [n-hexane–acetone (5 : 1)] to give the *nona*-O-*methyl derivative* (9) (27 mg), colourless needles, m.p. 135—137°; no OH i.r. absorption (CCl_4); δ($CDCl_3$) 3.16 (3 H, s, 20*S*-OCH_3), 4.37 (1 H, d, *J* 5.5 Hz), 4.65 (1 H, d, *J* 7.5 Hz), and 4.69 (1 H, d, *J* 7.5 Hz) (Found: C, 63.6; H, 8.8. $C_{55}H_{92}O_{17} \cdot H_2O$ requires C, 63.3; H, 9.1%).

Hovenoside G (2) (500 mg) was methylated and the product worked up as for (3) to give the *undeca*-O-*methyl derivative* (10) (198 mg), colourless needles, m.p. 120—123°, $[\alpha]_D$ −31.3° (*c* 1.00), *m/e* 379 (permethylated disaccharide residue), δ($CDCl_3$) 3.16 (3 H, s) and 5.24 (1 H, d, *J* 9 Hz, olefinic) (Found: C, 62.6; H, 9.05. $C_{62}H_{104}O_{21}$ requires C, 62.8; H, 8.85%).

Hovenoside D (1) (30 mg) was methylated and the product worked up as for (3) to give the *tetradeca*-O-*methyl derivative* (13) (10 mg), a colourless syrup, *m/e* 219, 187, 175, and 143, δ 4.17 (3 H, s), 4.25 (1 H, d, *J* 5.5 Hz), 4.32 (1 H, d, *J* 7.5 Hz), 4.62 (2 H, d, *J* 7.5 Hz), 4.95 (1 H, d, *J* 7.5 Hz), and 5.10 (1 H, d, *J* 9 Hz).

Methanolysis of Permethylated Saponins, followed by Deuteriomethylation.—A solution of the sample (5—10 mg) in 5% HCl–methanol was refluxed for 2 h and evaporated (hydrogen chloride removed under reduced pressure). The residue was deuteriomethylated in dimethylformamide (0.8 ml) with freshly prepared silver oxide (130 mg) and trideuteriomethyl iodide (0.4 ml) at 100 °C for 15 h. The precipitate was filtered off and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel (2 g) [n-hexane–acetone (5 : 1)] to afford a sample for g.l.c.–mass spectrometry [conditions for g.l.c.: 10% DEGS on Chromosorb W (3 mm × 2 m); column temperature 160°].

(*a*) In the sample from compound (8), methyl α- and β-pyranosides of 2,3,4,6-tetra-*O*-methylglucose and 3-*O*-trideuteriomethyl-2,4-di-*O*-methylarabinose [*m/e* 179 (5%), 178 (4%), 101 (100%), and 91 (90%)] were identified.

(*b*) In the sample from compound (9), methyl α- and β-pyranosides of 2,3,4-tri-*O*-methylxylose, 2,3,4,6-tetra-*O*-methylglucose, and 2,3-bis-*O*-trideuteriomethyl-4-*O*-methylarabinose [*m/e* 182 (2%), 181 (4%), 104 (100%), and 94 (84%)] were identified.

(*c*) In the sample from compound (10), methyl α- and β-pyranosides of 2,3-bis-*O*-trideuteriomethyl-4-*O*-methylarabinose, 2,3,4-tri-*O*-methylxylose, and 2-*O*-trideuteriomethyl-3,4,6-tri-*O*-methylglucose [*m/e* 222 (0.6%), 208 (0.2%), 104 (60%), and 91 (100%) in α-form; 222 (0.16%), 208 (0.5%), 104 (70%), and 91 (100%) in β-form] were identified.

(*d*) In the case of compound (13), methylated sugars, obtained by methanolysis, were identified as methyl α- and β-pyranosides of 2,3,4,6-tetra-*O*-methylglucose, 2,3,4-tri-*O*-methylxylose, 4-*O*-methylarabinose, and 3,4-di-*O*-methylglucose on g.l.c. by comparison with authentic samples.

Hydrolysis of Saponins with Crude Enzymes.—(*a*) Hovenoside D (1) (60 mg) in distilled water (50 ml) was incubated with commercial snail juice (1 ml) at 30 °C for 24 h and the hydrolysate was extracted with butan-1-ol saturated with water. The organic layer was concentrated to dryness and subjected to d.c.c. with solvent system (A) to give crystalline hovenoside G (2) (22 mg).

(*b*) Hovenoside D (1) (50 mg) in citrate–phosphate buffer solution (pH 3.9) (50 ml) was treated with commercial hesperidinase (55 mg) at 30 °C for 3 days and the product worked up as above to afford pure (2) (13 mg).

(*c*) Hovenoside G (2) (120 mg) in acetate buffer solution (pH 5.1) (50 ml) was incubated with commercial naringinase (300 mg) at 30 °C for 7 days and the product worked up as usual, but with solvent system (B), to furnish pure crystals of hovenoside I (3) (20 mg) and starting material (80 mg).

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