Novel Dammarane Triterpenoid Glycosides from the Leaves of *Hovenia dulcis*. *X*-Ray Crystal Structure of Hovenolactone Monohydrate

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Saponin E,[1] isolated from the leaves of *Hoevenia dulcis*, afforded a new dammarane triterpene aglycone, hovenolactone, on treatment with naringinase. The structure of hovenolactone, including the relative configurations at C-17, C-20, and C-23, was established by chemical and spectroscopic investigations as well as by *X*-ray analysis. Saponins E and H were separated by droplet counter-current chromatography. The complete molecular configurations of both glycosides were determined to be 3-*O*-(2-*O*-α-L-rhamnopyranosyl-β-D-glucopyranosyl)-hovenolactone and 3-*O*-β-D-glucopyranosylhovenolactone, respectively, by ^{13}C n.m.r. spectroscopy.

OUR previous paper [1] described the isolation of the new saponins C_2, D, E, G, and H by droplet counter-current chromatography (d.c.c.) [2] of methanolic extracts of the leaves of *Hovenia dulcis* Thunb.[3] (Rhamnaceae), and the structural elucidation of saponins C_2, D, and G. This paper deals with the structural elucidation of a novel triterpene, hovenolactone, and a study of the carbohydrate moieties of glycosides E (1) and H (2).

RESULTS AND DISCUSSION

Structure of Hovenolactone.—Neither acidic hydrolysis nor Smith–de Mayo degradation of the glycoside (1) afforded a genuine sapogenin. When the glycoside (1) was incubated with crude (commercial) naringinase (a mixture of naringinase, naringin-β-1,2-rhamnosidase, and β-glucosidase), it was slowly converted into the prosapogenin (2), which was shown to be identical with natural saponin H (2). On further treatment with the enzyme, compound (1) afforded a genuine sapogenin, hovenolactone (3). Hovenolactone exhibits typical i.r. absorptions due to five-membered-ring lactone (1 768 cm^{-1}) and epoxide (915 and 827 cm^{-1}) moieties; these absorptions are also observed in the i.r. spectrum of the parent saponin (1).

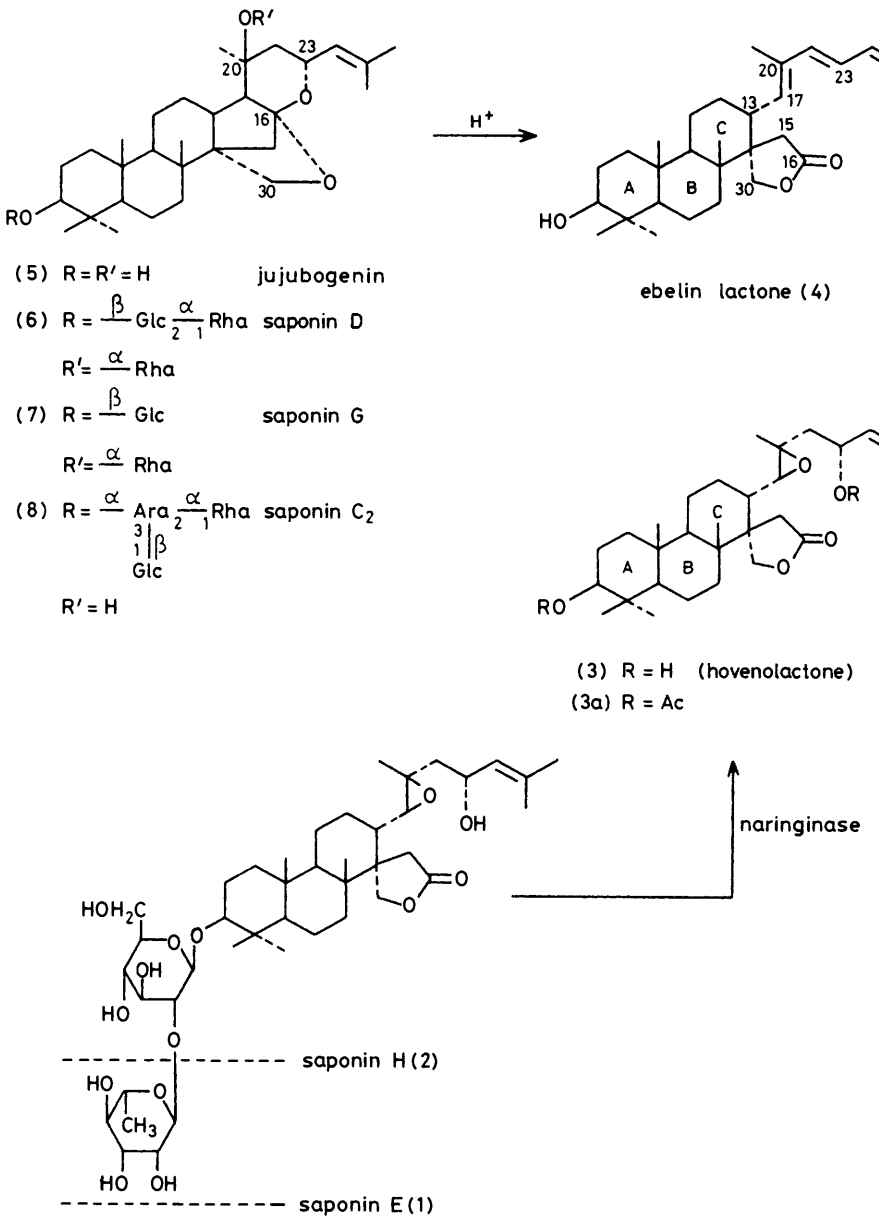
The ^1H n.m.r. spectrum of compound (3) showed signals for seven quaternary methyl groups in the region δ 0.84—1.72, two protons *geminal* to hydroxy-groups [δ 3.46 (dd, *J* 8 and 7 Hz, 3α-H) and 4.80 (ddd, *J* 9, 7, and 7 Hz, 23-H)] [these signals shifted to δ 4.44 and 5.59, respectively, in the spectrum of the diacetate (3a)], one proton *geminal* to the epoxide function [δ 2.99 (1 H, d, *J* 9 Hz, 17-H)], an oxymethylene group δ 4.54br (2 H, s, 30-H_2)], a $CH_2C{=}O$ group [δ 2.70 and 3.06 (each 1 H, AB-type pattern, *J* 18 Hz, 15-H_2)], and one olefinic proton [δ 5.68 (1 H, d, *J* 9 Hz, 24-H)].

Irradiation of the 23-H proton at δ 4.80 resulted in decoupling of the signals of the neighbouring methylene and olefinic protons: protons of the C-22 methylene group gave an AB system [δ 2.39 (d, *J* 14 Hz)], while the C-24 olefinic proton signal at δ 5.68 collapsed to a singlet. Following irradiation of the C-24 olefinic proton, the 23-H signal became a triplet (*J* 7 Hz). These results suggested the presence of a side chain $CH_2CH(OH)$-$CH{=}CMe_2$ in compound (3).

The ^{13}C n.m.r. spectrum of compound (3) in [$^2H_5$]-pyridine was compared with that of ebelin lactone (4) [4] obtained by acidic hydrolysis of saponin C_2 (8).[1] The signal assignments of ebelin lactone (4) were fairly straightforward, being made by comparison with the literature data for dihydroebelin lactone acetate.[5] The ^{13}C n.m.r. signals of the atoms in the A-, B-, C-, and γ-lactone-rings were almost identical for compounds (3) and (4); the assignments are summarized in Table 1 and show the considerable differences in the chemical shifts of their side-chain atoms; *e.g.* the signals at δ_C 130.3 and 132.7 p.p.m. for compound (3) were assigned to the olefinic carbons C-24 and C-25, and the signals at δ_C 63.7 (d) and 57.7 p.p.m. (s) were assigned to the epoxide carbons C-17 and C-20. In addition, the signals at δ_C 77.8 (d), 69.5 (t), and 65.4 p.p.m. (d) were assigned to three sp^3-carbon atoms bearing oxygen (C-3, C-30, and C-23, respectively) by means of the off-resonance-decoupled spectrum.

Confirmation of the full structure of hovenolactone (3) was given by *X*-ray crystallography (Figure).

Crystal Data. Hovenolactone monohydrate, $C_{30}H_{48}O_5 \cdot H_2O$, $M = 506.7$, orthorhombic, space group $P2_12_12$, $a = 14.474(7)$, $b = 28.584(14)$, $c = 6.749(3)$ Å, $U = 2\,792.2$ Å^3, $Z = 4$, $D_C = 1.205$ g cm^{-3}. A prismatic crystal of approximate dimensions $0.3 \times 0.08 \times 0.06$ mm, grown from methanol solution, was mounted on a Philips PW 1100 diffractometer. The intensity data of 2 132 reflections were measured within the range $6 < 2\theta < 140°$ using Cu-K_α radiation monochromated by a graphite plate. The structure was solved by direct methods and refined by least-squares with block-diagonal matrix approximations. 37 Out of 50 hydrogen atoms were located on difference electron-density maps and their positions were refined with isotropic thermal parameters. The final *R*-value for 2 132 reflections was 0.08, taking into account the hydrogen-atom contributions. The absolute configuration of the molecule was assumed, from biogenetic considerations, to be the same as that of ebelin lactone. The atomic co-ordinates are listed in Table 2 and the bond lengths in Table 3.



The structure factors and the bond angles are deposited as a Supplementary Publication [SUP No. 23372 (11 pp.)].*

Structure of Saponins E and H.—On acidic hydrolysis, saponin E(1), $C_{42}H_{68}O_{14}$, gave the sugars L-rhamnose and D-glucose (molar ratio 1 : 1). With crude naringinase, saponin E afforded hovenolactone (3) and saponin H (2). The ^1H n.m.r. spectrum of compound (1) exhibits signals for two anomeric, carbohydrate protons at δ 5.43 (1 H, d, *J* 9 Hz) and 6.43br (1 H, s), assigned to β-D-glucopyranose ($^4C_1$ conformation) and α-L-rhamnopyranose ($^1C_4$ conformation), respectively. Complete methylation of compound (1) by Hakomori's method [6] yielded the per-*O*-methyl ether. The methanolysis product of this per-*O*-methyl ether was worked up to give two kinds of methylated sugar. These were identified (g.l.c.) as the methyl α- and β-pyranosides of both 3,4,6-tri-*O*-methylglucose and 2,3,4-tri-*O*-methylrhamnose.

The i.r. spectrum of saponin E (1) indicated the presence of a five-membered-ring lactone (absorption at 1 768 cm^{-1}).

In our previous paper [1] we discussed the structural elucidation of the dammarane-type saponins D (6) and G (7) by ^{13}C n.m.r. spectroscopy. This work enabled us to propose that the saponins E (1) and H (2) are C-3 glycosides since the C-3 signal, observed as a doublet in the off-resonance-decoupled spectra, was at δ_C 88.5/88.6 p.p.m. in the spectra of the saponins, and at δ_C 77.8 p.p.m. in that of the corresponding aglycone, hovenolac-

* For details of the Supplementary Publications Scheme see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

TABLE 1

^{13}C Chemical shifts {δ/p.p.m. from $SiMe_4$; solvent [$^2H_5$]pyridine [$CDCl_3$ for compound (3a)]}

Carbon	(1)	(2)	(3) [a]	(3a)	(4) [b]	(5) [b]
1	38.8	38.5	38.7 (t)	37.8	38.7	38.5
2	26.8	26.5	28.1 (t)	23.5	28.0	27.9
3	88.5	88.6	77.8 (d)	80.4	77.8	78.0
4	39.5	39.5	39.4 (s)	38.2	39.4	39.5
5	55.5	55.3	55.2 (d)	55.2	55.2	56.0
6	18.1	18.1	18.1 (t)	18.0	18.1	18.4
7	34.1	34.0	34.0 (t)	33.9	34.5	36.1
8	40.2	40.2	40.2 (s)	40.0	40.2	37.6
9	52.5	52.5	52.5 (d)	52.4	52.7	53.0
10	36.8	36.8	37.2 (s)	37.0	37.3	37.6
11	19.8	19.7	19.8 (t)	19.8	20.1	21.7
12	25.3	25.3	25.4 (t)	25.1	28.6	28.6
13	39.7	39.7	39.7 (d)	39.2	39.5	37.0
14	51.4	51.4	51.4 (s)	51.3	52.0	53.7
15	34.1	34.0	34.0 (t)	33.6	35.0	37.0
16	177.0	176.9	177.0 (s)	176.7	176.7	110.6
17	63.7	63.7	63.7 (d)	62.9	131.6 [c]	53.7
18	18.1	18.1	18.3 (q)	18.6	18.3	18.4
19	16.1	16.0	16.0 (q)	16.0	16.1	16.3
20	57.7	57.7	57.7 (s)	56.8	135.2 [d]	68.6
21	17.9	17.8	17.9 (q)	17.3	13.3	30.0
22	47.5	47.5	47.5 (t)	44.2	134.9 [c]	45.2
23	65.4	65.4	65.4 (d)	68.5	124.7 [c]	68.7
24	130.2	130.2	130.3 (d)	123.5	126.3 [c]	126.8
25	132.8	132.8	132.7 (s)	138.0	137.0 [d]	134.3
26	25.8	25.8	25.8 (q)	25.8	26.1	25.8
27	17.9	17.8	17.9 (q)	17.8	18.3	18.8
28	27.9	28.1	28.6 (q)	28.0	28.6	28.6
29	16.9	16.7	16.2 (q)	16.5	16.2	16.3
30	69.5	69.5	69.5 (t)	69.1	69.6	65.9
Glucose 1	105.3	106.7				
Glucose 2	79.7	75.6				
Glucose 3	77.7	78.5				
Glucose 4	72.2	71.8				
Glucose 5	78.1	78.1				
Glucose 6	62.9	63.1				
Rhamnose 1	101.6					
Rhamnose 2	72.2					
Rhamnose 3	72.2					
Rhamnose 4	74.0					
Rhamnose 5	69.5					
Rhamnose 6	18.6					

[a] Multiplicities given in parentheses. [b] The assignments of these signals have been revised: *cf.* ref. 1 and O. Inoue, Y. Ogihara, and K. Yamasaki, *J. Chem. Res.*, 1978, (*S*) 144. [c,d] Assignments may be reversed.

tone (3). From the complete similarity of the ^{13}C n.m.r. spectra of the sugar moieties of saponins E (1) and D (6), saponin E was identified as 3-*O*-(2-*O*-α-L-rhamnopyranosyl-β-D-glucopyranosyl) hovenolactone.

The natural glycoside saponin H (2), $C_{36}H_{58}O_{10}$, was identical with the prosapogenin obtained on enzymic treatment of saponin E. On acidic hydrolysis, saponin H gave D-glucose. The ^{1}H n.m.r. spectrum of compound (2) exhibits a signal for the carbohydrate anomeric proton at δ 5.42 (1 H, d, *J* 9 Hz) a value typical of β-D-glucopyranose ($^4C_1$ conformation). From these data, saponin H was identified as 3-*O*-β-D-glucopyranosyl hovenolactone.

EXPERIMENTAL

M.p.s were measured with a Yanagimoto microapparatus. Unless otherwise stated, u.v. spectra were recorded for solutions in methanol, optical rotations for solutions in methanol, i.r. spectra for KBr discs, and n.m.r. spectra for solutions in [$^2H_5$]pyridine. ^{1}H N.m.r. spectra were recorded at 100 MHz using a JEOL Model JNM-MH-100 spectrometer employing Me_4Si as internal standard. ^{13}C N.m.r. spectra (Table 1) were recorded at 25.0 MHz on a JEOL Model JNM-FX-100 spectrometer using [$^2H_5$]pyridine solutions containing Me_4Si as an internal reference in 5 mm i.d. tubes at room temperature.

The isolation and purification of the saponins (1) and (2) has already been reported.[1]

Physical Properties of Saponins E (1) *and H* (2).—*Glycoside E* (1): needles, m.p. 167—169.5 °C; $[\alpha]_D$ −26.5° (*c*, 0.32); $\nu_{max.}$ (KBr) 3 400 and 1 768 cm^{-1}; $\lambda_{max.}$ no absorption above 210 nm; δ_H 5.43 (1 H, d, *J* 9 Hz, glucopyranose 1-H) and 6.43br (1 H, s, rhamnopyranose 1-H) (Found: C, 60.35; H, 8.7. $C_{42}H_{68}O_{14}\cdot 2H_2O$ requires C, 60.55; H, 8.7%).

Glycoside H (2): needles, m.p. 171—172 °C; $[\alpha]_D$ −14.3° (*c*, 0.35); $\nu_{max.}$ (KBr) 3 400 and 1 768 cm^{-1}; $\lambda_{max.}$ no absorption above 210 nm; δ_H 5.42 (1 H, d, *J* 9 Hz, glucopyranose 1-H) (Found: C, 64.8; H, 8.95. $C_{36}H_{58}O_{10}\cdot H_2O$ requires C, 64.65; H, 9.05%).

Hydrolysis of Saponin E (1) *with Crude Naringinase.*—The glycoside (1) (185 mg) in AcONa–AcOH buffer (pH 5.6) (5 ml) was incubated with commercial naringinase (300 mg) at 38 °C for 7 d and the hydrolysate was then extracted with chloroform. The organic layer was concentrated to dryness and the residue (117 mg) was chromatographed on silica gel [$CHCl_3$–MeOH (25 : 1) as eluant] to give a prosapogenin (2) (20 mg) and hovenolactone (3) (50 mg). Compound (2)

TABLE 2

Atomic co-ordinates (×10^4 for heavier atoms and ×10^3 for hydrogen atoms) and equivalent isotropic temperature factors (Å^2)

	Hovenolactone monohydrate			
Atom	*x*	*y*	*z*	$B_{equiv.}$
C(1)	8 053(5)	8 509(2)	6 107(12)	3.97 (0.10)
C(2)	8 558(5)	8 967(3)	5 615(14)	4.60 (0.12)
C(3)	7 940(6)	9 295(3)	4 451(15)	5.78 (0.13)
C(4)	7 018(6)	9 410(2)	5 502(13)	3.70 (0.11)
C(5)	6 548(5)	8 940(2)	6 125(11)	3.01 (0.10)
C(6)	5 600(5)	8 987(2)	7 040(12)	3.74 (0.10)
C(7)	5 088(5)	8 519(3)	7 077(12)	3.88 (0.10)
C(8)	5 618(4)	8 128(2)	8 186(10)	2.98 (0.08)
C(9)	6 624(4)	8 108(2)	7 372(10)	3.05 (0.09)
C(10)	7 155(5)	8 583(2)	7 302(11)	2.85 (0.09)
C(11)	7 172(4)	7 708(2)	8 305(11)	3.96 (0.10)
C(12)	6 697(5)	7 236(2)	8 040(14)	4.83 (0.11)
C(13)	5 704(5)	7 246(2)	8 830(11)	3.98 (0.09)
C(14)	5 135(5)	7 642(2)	7 833(10)	3.21 (0.08)
C(15)	4 116(5)	7 638(3)	8 519(12)	4.21 (0.10)
C(16)	3 556(5)	7 656(3)	6 656(14)	4.43 (0.12)
C(17)	5 286(5)	6 757(2)	8 674(13)	5.04 (0.11)
C(18)	5 585(5)	8 234(3)	10 449(12)	3.64 (0.11)
C(19)	7 421(5)	8 758(3)	9 411(12)	3.50 (0.11)
C(20)	5 399(5)	6 400(3)	10 261(13)	4.97 (0.11)
C(21)	5 899(8)	6 491(3)	12 121(14)	5.80 (0.16)
C(22)	5 254(5)	5 895(2)	9 641(15)	5.57 (0.12)
C(23)	6 175(5)	5 622(2)	9 435(11)	3.13 (0.10)
C(24)	6 695(6)	5 791(2)	7 678(12)	4.29 (0.10)
C(25)	7 594(6)	5 919(2)	7 687(15)	5.14 (0.13)
C(26)	8 045(8)	6 094(4)	5 872(19)	10.27 (0.20)
C(27)	8 217(7)	5 929(5)	9 468(21)	5.15 (0.24)
C(28)	6 408(7)	9 657(3)	3 912(18)	7.04 (0.16)
C(29)	7 158(7)	9 752(3)	7 247(16)	4.29 (0.16)
C(30)	5 017(5)	7 534(3)	5 563(11)	3.64 (0.11)
O(1)	8 466(5)	9 722(2)	4 066(14)	10.07 (0.14)
O(2)	4 072(4)	7 615(2)	5 049(9)	3.73 (0.09)
O(3)	2 721(4)	7 717(4)	6 563(13)	8.83 (0.17)
O(4)	4 527(4)	6 657(2)	10 026(12)	9.63 (0.11)
O(5)	5 931(4)	5 132(2)	9 238(10)	4.51 (0.09)
W	4 938(45)	4 976(21)	3 785(25)	25.24 (0.62)

TABLE 2 (*continued*)

Atom	*x*	*y*	*z*	$B_{equiv.}$
HC(1)	787(5)	838(2)	499(11)	3.78 (1.58)
H'C(1)	854(5)	825(2)	697(12)	4.66 (1.74)
HC(2)	914(5)	892(2)	455(11)	3.75 (1.57)
H'C(2)	875(5)	914(3)	697(12)	4.76 (1.81)
HC(5)	642(4)	880(2)	482(10)	2.65 (1.31)
HC(6)	563(5)	908(2)	844(12)	3.87 (1.63)
H'C(6)	518(7)	929(3)	623(14)	6.94 (2.38)
HC(7)	498(5)	842(2)	534(10)	4.05 (1.56)
H'C(7)	445(5)	856(3)	757(12)	5.09 (1.80)
HC(9)	662(5)	805(3)	578(12)	4.54 (1.73)
HC(11)	728(4)	779(2)	971(11)	3.61 (1.58)
H'C(11)	776(6)	767(3)	726(14)	6.12 (2.13)
HC(12)	668(5)	716(3)	638(14)	5.78 (2.04)
H'C(12)	697(6)	687(3)	852(13)	6.48 (2.18)
HC(13)	571(5)	735(2)	1 023(11)	3.90 (1.60)
HC(15)	388(6)	786(3)	945(15)	6.53 (2.23)
H'C(15)	399(6)	734(3)	924(13)	5.57 (1.95)
HC(17)	523(5)	665(3)	715(11)	4.74 (1.77)
HC(19)	791(6)	901(2)	943(13)	4.93 (1.87)
H'C(19)	688(6)	887(3)	1 058(13)	6.06 (2.07)
H''C(19)	776(6)	847(3)	1 026(13)	5.96 (2.07)
HC(18)	564(5)	860(3)	1 080(12)	4.79 (1.80)
H'C(18)	620(5)	806(2)	1 143(11)	4.72 (1.78)
H''C(18)	509(6)	813(3)	1 118(14)	7.08 (2.25)
HC(21)	616(6)	672(3)	1 226(14)	6.23 (2.24)
H'C(21)	659(9)	617(5)	1 227(22)	13.80 (4.11)
HC(22)	487(4)	577(2)	1 049(9)	2.66 (1.30)
HC(23)	668(5)	569(2)	1 068(12)	4.51 (1.74)
HC(26)	832(5)	588(3)	530(13)	4.95 (1.84)
H'C(26)	833(6)	646(3)	593(13)	6.26 (2.07)
H''C(26)	761(5)	607(3)	462(13)	5.20 (1.90)
HC(29)	764(6)	970(3)	820(13)	5.81 (2.04)
H'C(29)	667(7)	975(3)	874(17)	9.46 (3.02)
H''C(29)	712(7)	1 019(3)	679(14)	7.95 (2.45)
HC(28)	588(5)	974(3)	447(13)	4.90 (1.82)
HC(30)	543(6)	776(3)	451(13)	6.05 (2.10)
H'C(30)	523(6)	717(3)	523(15)	8.10 (2.54)

was identified as being natural glycoside H (2) by ^{13}C n.m.r. and i.r. spectroscopy and t.l.c.

Hovenolactone (3) was recrystallized from methanol as needles, m.p. 226—228 °C; $[\alpha]_D$ +12.3° (*c*, 0.57); $\nu_{max.}$ (KBr) 3 400, 1 768, 915, and 827 cm^{-1}; $\lambda_{max.}$ no absorption above 210 nm; *m/z* 473 (M^+ − 15), 470 (M^+ − 18), 137, 109, and 81; δ 0.84 (3 H, s), 0.91 (3 H, s), 1.03 (3 H, s), 1.24 (3 H, s), 1.50 (3 H, s), 1.68 (3 H, s), 1.72 (3 H, s), 2.39 (1 H, dd, J_{22a-23} 7 and $J_{22a-22b}$ 14 Hz, 22-H_a), 2.70 and 3.06 (total 2 H, ABq, *J* 18 Hz, 15-H_2), 2.99 (1 H, d, *J* 9 Hz, 17-H), 3.46 (1 H, dd, *J* 8 and 7 Hz, 3-H), 4.54br (2 H, s, 30-H_2), 4.80 (1 H, ddd, J_{23-24} 9, J_{23-22a} 7, and J_{23-22b} 7 Hz, 23-H), and 5.68 (1 H, d, J_{24-23} 9 Hz, 24-H) (Found: C, 72.4; H, 10.0. $C_{30}H_{48}O_5 \cdot 0.5H_2O$ requires C, 72.4; H, 9.9%).

Hovenolactone (3) (22 mg) was acetylated in the usual way with pyridine and acetic anhydride to give the *diacetate* (3a) (14 mg), m.p. 118—120 °C; $[\alpha]_D$ +16.9° (*c*, 0.24 in $CHCl_3$); $\nu_{max.}$ (KBr) 1 775, 1 732, and 1 725 cm^{-1}; *m/z* 512 (M^+ − AcOH), 446, 137, 109 (100%), and 81; δ_H ($CDCl_3$) 0.85 (total 6 H, s), 0.96 (3 H, s), 1.29 (3 H, s), 1.71 (3 H, s), 1.73 (3 H, s), 1.75 (3 H, s), 2.02 (3 H, s), 2.05 (3 H, s), 2.45 and 2.71 (total 2 H, ABq, *J* 18 Hz, 15-H_2), 2.47 (1 H, d, *J* 9 Hz, 17-H), 4.25 and 4.41 (total 2 H, ABq, *J* 10 Hz, 30-H_2), 4.44 (1 H, dd, *J* 8 and 9 Hz, 3-H), 5.05 (1 H, d, J_{24-23} 9 Hz, 24-H), and 5.59 (1 H, ddd, J_{23-24} 9, J_{23-22b} 7, and J_{23-22a} 7 Hz, 23-H) (Found: C, 71.2; H, 9.25. $C_{34}H_{52}O_7$ requires C, 71.3; H, 9.15%).

Complete Acidic Hydrolysis of Saponins E (1) *and H* (2).—*Glycoside E* (1) (5 mg) and H (2) (5 mg) were each dissolved in a mixture of dioxan (1 ml), 2N-H_2SO_4 (2 ml), and water (1 ml) and the solutions were heated under reflux for 2 h. The solutions were diluted with water and extracted with diethyl ether (5 ml). The aqueous layer of the hydrolysate was neutralized with ion-exchange resin (IR-45) and evaporated to dryness. Trimethylsilylation followed by g.l.c. [2% OV-17 in Chromosorb W (60—80 mesh); column temperature 150 °C; N_2 flow rate 60 ml/min] showed the presence of glucose and rhamnose (molar ratio 1 : 1) from the glycoside E (1) and the presence of glucose from the glycoside H (2).

TABLE 3

Bond lengths and their e.s.d.'s in parentheses.

	Hovenolactone monohydrate Length (std)		Length (std)
C(1)–C(2)	1.536(10)	C(15)–C(16)	1.497(12)
C(1)–C(10)	1.545(10)	C(15)–HC(15)	0.964(92)
C(1)–HC(1)	0.886(70)	C(15)–H'C(15)	1.004(81)
C(1)–H'C(1)	1.184(74)	C(16)–O(2)	1.322(11)
C(2)–C(3)	1.515(12)	C(16)–O(3)	1.223(10)
C(2)–HC(2)	1.116(71)	C(17)–C(20)	1.488(11)
C(2)–H'C(2)	1.075(81)	C(17)–O(4)	1.456(10)
C(3)–C(4)	1.547(12)	C(17)–HC(17)	1.073(76)
C(3)–O(1)	1.461(10)	C(19)–HC(19)	1.044(76)
C(4)–C(5)	1.565(10)	C(19)–H'C(19)	1.159(87)
C(4)–C(29)	1.543(13)	C(19)–H''C(19)	1.125(80)
C(4)–C(28)	1.558(14)	C(18)–HC(18)	1.065(74)
C(5)–C(6)	1.512(11)	C(18)–H'C(18)	1.219(74)
C(5)–C(10)	1.563(9)	C(18)–H''C(18)	0.910(93)
C(5)–HC(5)	0.990(66)	C(20)–C(21)	1.472(13)
C(6)–C(7)	1.530(10)	C(20)–C(22)	1.516(10)
C(6)–HC(6)	0.982(78)	C(20)–O(4)	1.469(9)
C(6)–H'C(6)	1.182(90)	C(21)–HC(21)	0.769(84)
C(7)–C(8)	1.549(10)	C(21)–H'C(21)	1.362(**)
C(7)–HC(7)	1.219(70)	C(22)–C(23)	1.552(10)
C(7)–H'C(7)	0.984(77)	C(22)–HC(22)	0.881(62)
C(8)–C(9)	1.556(9)	C(23)–C(24)	1.484(11)
C(8)–C(14)	1.574(9)	C(23)–O(5)	1.451(8)
C(8)–C(18)	1.558(10)	C(23)–HC(23)	1.136(77)
C(9)–C(10)	1.560(9)	C(24)–C(25)	1.352(11)
C(9)–C(11)	1.528(9)	C(25)–C(26)	1.476(16)
C(9)–HC(9)	1.088(83)	C(25)–C(27)	1.502(16)
C(10)–C(19)	1.557(11)	C(26)–HC(26)	0.825(76)
C(11)–C(12)	1.525(10)	C(26)–H'C(26)	1.133(81)
C(11)–HC(11)	0.990(76)	C(26)–H''C(26)	1.059(84)
C(11)–H'C(11)	1.108(88)	C(29)–HC(29)	0.963(83)
C(12)–C(13)	1.534(10)	C(29)–H'C(29)	1.233(**)
C(12)–HC(12)	1.138(93)	C(29)–H''C(29)	1.279(85)
C(12)–H'C(12)	1.169(80)	C(28)–HC(28)	0.886(76)
C(13)–C(14)	1.553(9)	C(30)–O(2)	1.430(9)
C(13)–C(17)	1.527(9)	C(30)–HC(30)	1.134(86)
C(13)–HC(13)	0.987(77)	C(30)–H'C(30)	1.113(92)
C(14)–C(15)	1.546(10)		
C(14)–C(30)	1.572(10)		

Permethylation of Saponins by Hakomori's Method and Methanolysis.—(*a*) To a stirred solution of saponin E (1) (10 mg) in dimethyl sulphoxide (3 ml) under argon was added a solution (5 ml) of sodium methylsulphinylmethanide and the mixture was stirred at room temperature for 5 h. Methyl iodide (3 ml) was then added and the reaction was continued for 24 h. The mixture was poured into water and extracted with chloroform (10 ml). The organic layer was washed with water and evaporated to dryness. The residue was chromatographed on silica gel [n-hexane–acetone (6 : 1) as eluant] to give the per-*O*-methyl ether (4 mg). A solution of the per-*O*-methyl ether (4 mg) in 5% HCl–MeOH was refluxed for 2 h and evaporated to dryness to afford a sample which [g.l.c. analysis 10% DEGS on Chromosorb W (3 mm × 2 m); column temperature 160 °C] showed the presence of methyl α- and β-pyranosides of 3,4,6-tri-*O*-methylglucose and 2,3,4-tri-*O*-methylrhamnose.

(*b*) Saponin H (2) 7 mg) was methylated and the product was worked up as in method (*a*) to give the per-*O*-methyl ether of saponin H, a solution of which (3 mg) in 5% HCl–

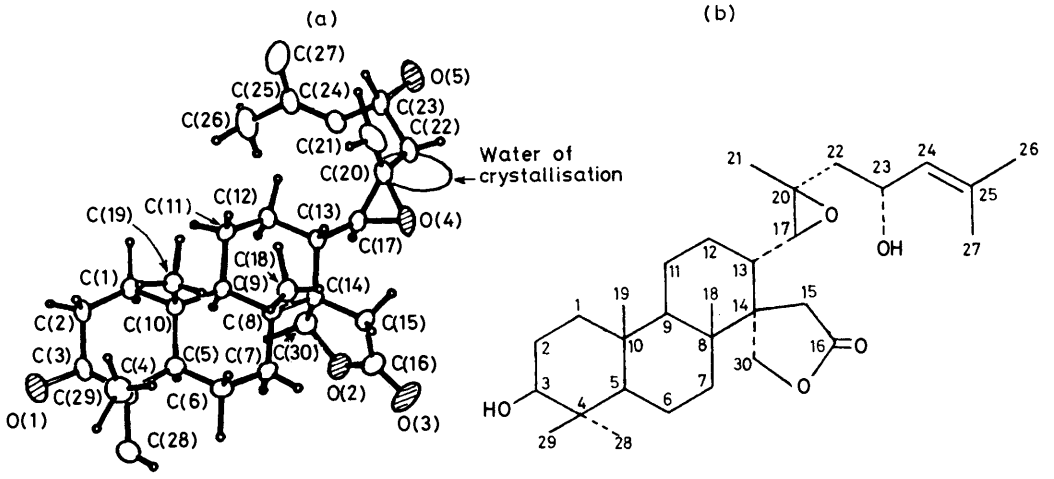


FIGURE (a) *X*-Ray crystal structure of hovenolactone monohydrate. (b) Systematic numbering scheme

MeOH was methanolysed to give a compound, identified by g.l.c. analysis as a mixture of methyl α- and β-2,3,4,6-tetra-*O*-methylglucopyranoside.

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