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Studies on the Constituents of *Hedera rhombea* BEAN. IV.[1] On the Hederagenin Glycosides. (2)[2]

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On the basis of chemical and physicochemical evidence, the structures of two new hederagenin bisdesmosides, named Kizuta saponins K_8 (X) and K_{11} (I), which were isolated from the stem and bark of *Hedera rhombea* BEAN (Araliaceae), were established to be as follows: X, 3-*O*-α-L-arabinopyranosyl-hederagenin 28-*O*-α-L-rhamnopyranosyl-(1→4)-6-*O*-acetyl-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester; I, 3-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl-hederagenin 28-*O*-α-L-rhamnopyranosyl(1→4)-6-*O*-acetyl-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester. A glucoside mixture (XIII) was considered to be a mixture of the β-D-glucopyranosides of campesterol (trace), stigmasterol and β-sitosterol based on chemical and physicochemical evidence.

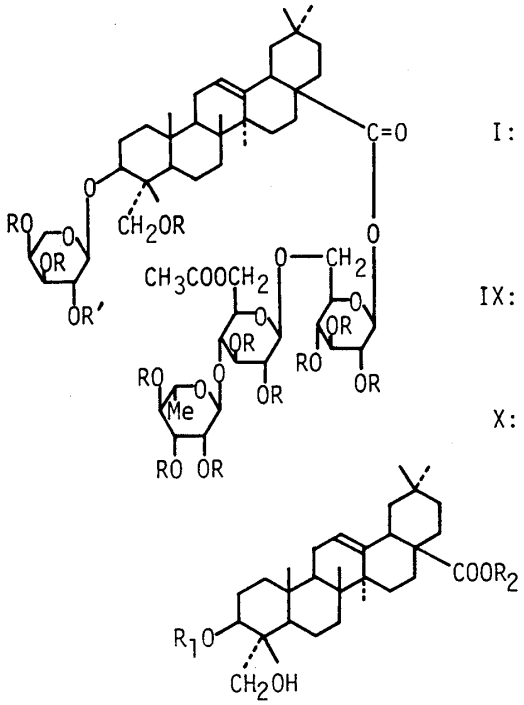
Keywords——*Hedera rhombea*; Araliaceae; hederagenin bisdesmoside; *O*-acetylated saponin; hederagenin glycoside ^{13}C-NMR; Kizuta saponin K_8; Kizuta saponin K_{11}

In the previous papers,[1,3,4] we reported the isolation of fifteen glycosidic constituents from the stem and bark of *Hedera rhombea* BEAN (Araliaceae) and the structural elucidation of twelve of them. This paper describes the structural elucidation of two of the remaining glycosides, named Kizuta saponins K_8 (X) and K_{11} (I), and the identification of the third "glycoside" (XIII) as a glucoside mixture.

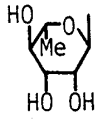
Saponin K_{11} (I), a white powder (MeOH–acetone), mp 187—191 °C (dec.), $[\alpha]_D$ −22.1°, showed absorption bands of ester and hydroxyl groups in the infrared (IR) spectrum. On methanolyisis, I yielded hederagenin, methyl arabinoside, methyl glucoside and methyl rhamnoside. On alkaline hydrolysis with 0.5 N KOH aq., I afforded a prosapogenin (II), which was identified as Kizuta saponin K_6[3] (hederagenin 3-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside). The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of I showed five anomeric carbon signals, suggesting that I was a bisdesmoside which had a trisaccharide moiety at the C-28 position of II. The signal observed at 1.93 ppm (3H, s) in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of I and the signals at 170.8 and 20.6 ppm in the ^{13}C-NMR spectrum of I indicated the presence of an *O*-acetyl group in the molecule. Compound I was treated with 0.1 N KOH aq. at room temperature to give a desacetyl product (III), which was identified as Kizuta saponin K_{12}[3] (3-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl-hederagenin 28-*O*-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester) by direct comparison of the ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample. Compound I is, therefor, a mono-*O*-acetate of III. The determination of the linking position of the acetyl group was attempted by comparing the ^{13}C-NMR data for I and III. The carbon signals of III were assigned as shown in Table I by comparing the data with those of related compounds, including several prosapogenins (IV-VIII) which were obtained by partial acid hydrolysis of III. In the ^{13}C-NMR spectrum, on going from III to I, the signals due to C-6 and C-5 of the outer glucose

moiety were displaced downfield by 2.4 ppm and upfield by 3.2 ppm, respectively, while other signals were observed at similar positions. These data indicated that the *O*-acetyl group of I is located at C-6 of the outer glucose moiety.[5] Finaly, the linking position of the acetyl group was confirmed by methylation analyses. Compound I was methylated according to Kuhn[6] to afford a per-*O*-methyl derivative (IX). On methanolysis, IX yielded methyl 2,3-di-*O*-methyl-glucopyranoside as well as methyl 2,3,4,-tri-*O*-methyl-rhamnopyranoside, methyl 3,4-di-*O*-methyl-arabinopyranoside, methyl 2,3,4-tri-*O*-methyl-glucopyranoside and 23-*O*-methyl-hederagenin. Based on these results, the structure of I was concluded to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl-hederagenin 28-*O*-α-L-rhamnopyranosyl-(1→4)-6-*O*-acetyl-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester.

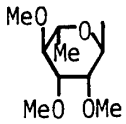
Saponin K_8 (X), a white powder (MeOH–AcOEt), mp 192—195 °C (dec.), $[\alpha]_D$ −2.0°, was methanolyzed to yield hederagenin, methyl arabinoside, methyl glucoside and methyl rhamnoside. On alkaline hydrolysis with 0.5 N KOH aq., X gave a prosapogenin (XI), which was identified as Kizuta saponin K_3[3] (hederagenin 3-*O*-α-L-arabinopyranoside). The ^{13}C-NMR spectrum of X showed four anomeric carbon signals and signals assignable to an *O*-acetyl group (170.8, 20.6 ppm). The ^1H-NMR spectrum of X also indicated the presence of an *O*-acetyl group (1.92 ppm, 3H, s). Compound X was treated with 0.1 N KOH aq. at room temperature to give a desacetyl product (XII), which was identified as Kizuta saponin K_{10}[3]



I: R = H R′ =



IX: R = Me R′ =



X: R = R′ = H

	R_1	R_2
XI:	ara	H
II:	rham$^{1\text{-}2}$ara	H
VIII:	ara	glc
IV:	H	glc$^{1\text{-}6}$glc
V:	ara	glc$^{1\text{-}6}$glc
VII:	rham$^{1\text{-}2}$ara	glc$^{1\text{-}6}$glc
VI:	H	rham$^{1\text{-}2}$glc$^{1\text{-}6}$glc
XII:	ara	rham$^{1\text{-}4}$glc$^{1\text{-}6}$glc
III:	rham$^{1\text{-}2}$ara	rham$^{1\text{-}4}$glc$^{1\text{-}6}$glc

ara, α-L-arabinopyranosyl; rham, α-L-rhamnopyranosyl; glc, β-D-glucopyranosyl

Chart 1

(3-*O*-α-L-arabinopyranosyl-hederagenin 28-*O*-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester) by direct comparison of the ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample. In the ^{13}C-NMR spectrum, on going from XII to X, the carbon signals due to C-6 and C-5 of the outer glucose moiety were displaced downfield by 2.4 ppm and upfield by 3.3 ppm, respectively, while other signals were observed at similar positions. Furthermore, the carbon signals due to the 28-*O*-sugar moiety of X appeared at almost the same positions as those of I. On the basis of these results, the structure of X was established as 3-*O*-α-L-arabinopyranosyl-hederagenin 28-*O*-α-L-rhamnopyranosyl-(1→4)-6-*O*-acetyl-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester.

A glucoside mixture (XIII) shows a single spot on thin-layer chromatography (TLC). However, the aglycone portion obtained on methanolysis of XIII was shown to contain three compounds on gas liquid chromatography (GLC). The retention times (t_R) of these

Table I. ^{13}C-NMR Chemical Shifts in Pyridine-d_5

	XI	II	VIII	IV	V	VII	VI	XII	X	III	I
C-3	82.0	81.2	82.1	73.6	82.0	81.2	73.7	82.1	82.1	81.2	81.2
C-23	64.6	64.1	64.6	68.1	64.6	64.2	68.1	64.6	64.6	64.1	64.2
C-28	180.4	180.4	176.7	176.8	176.7	176.8	176.8	176.8	176.7	176.8	176.7
3-*O*-Sugar moiety											
ara-1	106.7	104.4	106.7		106.7	104.3		106.7	106.7	104.2	104.4
ara-2	73.1	75.9	73.1		73.1	76.0		73.1	73.1	75.9	75.9
ara-3	74.8	74.7	74.8		74.7	74.5		74.8	74.8	74.4	74.7
ara-4	69.6	69.4	69.7		69.6	69.2		69.7	69.7	69.1	69.3
ara-5	67.0	65.6	66.7		67.0	65.5		66.9	67.0	65.4	65.6
rham-1		101.8			101.8					101.7	101.8
rham-2		72.4[a]			72.4[a]					72.3[a]	72.4[a]
rham-3		72.6[a]			72.6[a]					72.5[a]	72.6[a]
rham-4		74.2			74.2					74.1	74.2
rham-5		69.8			69.8					69.7	69.8
rham-6		18.5			18.5					18.5	18.5
28-*O*-Sugar moiety											
Inner											
glc-1			95.8	95.8	95.8	95.8	95.8	95.7	95.7	95.7	95.7
glc-2			74.2	73.9	73.9	74.0	74.0	74.0	73.8	73.9	73.9
glc-3			79.3[b]	78.8[b]	78.8[b]	78.8[b]	78.8[b]	78.7[b]	78.8[b]	78.7[b]	78.8[b]
glc-4			71.2	71.0	71.0	71.0	71.0	70.8	71.0	70.8	71.0
glc-5			79.0[b]	78.0[b]	78.0[b]	78.0[b]	78.1[b]	78.0[b]	78.1[b]	78.0[b]	78.2[b]
glc-6			62.3	69.5	69.5	69.5	69.3	69.2	69.4	69.1	69.5
Outer											
glc-1				105.4	105.4	105.3	104.9	104.9	104.8	104.8	104.8
glc-2				75.2	75.2	75.2	75.4	75.3	75.1	75.3	75.1
glc-3				78.4[b]	78.4[b]	78.4[b]	76.6	76.6	76.4	76.5	76.5
glc-4				71.6	71.6	71.6	78.3[b]	78.4[b]	79.3	78.5[b]	79.3
glc-5				78.4[b]	78.4[b]	78.4[b]	77.2	77.1	73.8	77.1	73.9
glc-6				62.7	62.7	62.7	61.4	61.3	63.7	61.3	63.7
rham-1							102.8	102.8	103.0	102.8	103.0
rham-2							72.6[a]	72.6[a]	72.4[a]	72.5[a]	72.4[a]
rham-3							72.8[a]	72.8[a]	72.7[a]	72.7[a]	72.7[a]
rham-4							74.0	74.0	73.8	73.9	73.9
rham-5							70.4	70.4	70.7	70.3	70.7
rham-6							18.4	18.5	18.5	18.5	18.5
$CH_3\underline{C}OO$									170.8		170.8
$\underline{C}H_3COO$									20.6		20.6

a, b) Assignments may be reversed in each column.

compounds coincided with those of campesterol, stigmasterol and β-sitosterol, respectively. The sugar portion of the methanolysate contained only methyl glucoside. The ^{13}C-NMR spectrum of XIII showed signals assignable to one mole of β-D-glucose moiety[7] as well as those due to the mixed aglycone moieties. Based on these findings, XIII is considered to be a mixture of the β-D-glucopyranosides of campesterol, stigmasterol and β-sitosterol.

Experimental[8]

Isolation——The isolation procedure for saponins K_2 (XIII), K_8 (X) and K_{11} (I) was described in the previous paper.[4]

Saponin K_{11} (I)——A white powder (from MeOH–acetone), mp 187—191 °C (dec.), $[\alpha]_D^{25}$ −22.1° (c=1.41, MeOH). *Anal.* Calcd for $C_{61}H_{98}O_{27}\cdot 5H_2O$: C, 54.13; H, 8.04. Found: C, 53.89; H, 8.09. IR ν_{max}^{KBr} cm^{-1}: 3380, 1725, 1100—1000. ^{1}H-NMR (pyridine-d_5): 0.88, 0.91, 0.99, 1.08, 1.12, 1.17 (each 3H, s, *tert*-Me×6), 1.65, 1.71 (each 3H, d, J=6.3 Hz, C_5-Me of rhamnose unit×2), 1.93 (3H, s, CH_3COO), 5.01 (1H, d, J=7.6 Hz, C_1-H of outer glucose unit), 5.13 (1H, d, J=5.9 Hz, C_1-H of arabinose unit), 5.40 (1H, br s, C_{12}-H), 5.54 (1H, s, C_1-H of rhamnose unit in 28-*O*-sugar moiety), *ca.* 6.23 (C_1-H of inner glucose unit, overlapping), 6.25 (1H, s, C_1-H of rhamnose unit in 3-*O*-sugar moiety). ^{13}C-NMR: Table I.

Methanolysis of I——A solution of I (10 mg) in 10% HCl–MeOH (2 ml) was heated under reflux on a water bath for 2 h. The reaction mixture was neutralized with Ag_2CO_3 and the precipitates were filtered off. The filtrate was concentrated and the residue was crystallized from MeOH to give an aglycone (1.5 mg) as colorless prisms; this product was identified as hederagenin by direct comparison of the TLC behavior [solv., $CHCl_3$–MeOH–HCOOH (100:8:1), toluene–HCOOH–HCOOEt (5:1:4)] and IR spectrum with those of an authentic sample. The mother liquor of crystallization was concentrated and the residue was analyzed by TLC [solv., $CHCl_3$–MeOH–H_2O (25:11:2), *n*-BuOH–AcOH–H_2O (4:1:2)] and GLC-1[9] (as the trimethylsilylether derivative), which revealed the presence of methyl arabinoside (t_R 8 min 46 s, 9 min 10 s), methyl rhamnoside (t_R 10 min 19 s) and methyl glucoside (t_R 29 min 10 s, 30 min 00 s).

Alkaline Hydrolysis of I——i) A solution of I (20 mg) in 0.5 N KOH aq. (1 ml) was heated on a boiling water bath for 0.5 h. The reaction mixture was neutralized with 0.5 N H_2SO_4 and then extracted with *n*-BuOH. The *n*-BuOH layer was washed with water and concentrated. The residue was crystallized from MeOH to give a prosapogenin (II, 6 mg) as colorless needles; this product was identified as Kizuta saponin K_6[3] [hederagenin 3-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside] by direct comparison of the TLC behavior [solv., $CHCl_3$–MeOH–H_2O (25:6:0.7)] and IR and ^{1}H-NMR spectra with those of an authentic sample.

ii) A solution of I (20 mg) in 0.1 N KOH aq. (1 ml) was allowed to stand at room temperature for 20 h. The reaction mixture was neutralized with 0.1 N H_2SO_4 and extracted with *n*-BuOH. The *n*-BuOH layer was washed with water and concentrated. The residue was dissolved in MeOH and then poured into acetone to give a desacetyl product (III, 14 mg) as a white powder. This product was identified as Kizuta saponin K_{12}[3] [3-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl-hederagenin 28-*O*-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester] by direct comparison of the ^{1}H- and ^{13}C-NMR spectra with those of an authentic specimen.

Partial Acid Hydrolysis of III——A solution of III (9.8 g) in 0.05 N H_2SO_4–EtOH (300 ml) was heated under reflux for 2 h. The reaction mixture was neutralized with 0.2 N NaOH and then concentrated. The residue was partitioned between water and *n*-BuOH. The *n*-BuOH layer was concentrated and the residue was chromatographed on silica gel (460 g) with a gradient of $CHCl_3$–MeOH (MeOH 0—8%) and then with $CHCl_3$–MeOH–H_2O (25:3:0.3 → 25:4:0.4 → 25:5:0.5 → 25:6:0.7 → 25:7:0.9 → 25:11:2) to give Frs. 1—10. Recrystallizations of Frs. 1, 2 and 3 from MeOH afforded hederagenin, compound XI (=Kizuta saponin K_3)[3] and compound II (=Kizuta saponin K_6)[3], respectively. Fr. 4 (200 mg) was rechromatographed on silica gel (40 g) with $CHCl_3$–MeOH–H_2O (25:3:0.3) to give compound IV (135 mg). Fr. 5 (260 mg) was rechromatographed on silica gel (50 g) with $CHCl_3$–BuOH–H_2O (6:4:1) to give compound V (=saponin D isolated from *Akebia quinata*)[10] (180 mg). Frs. 6 and 9 gave compounds VI (155 mg) and VII (270 mg), respectively. Frs. 7 and 10 gave compound XII (=Kizuta saponin K_{10})[3] and unchanged III, respectively. Compound V (80 mg) was hydrolyzed with cellulase (Sigma Chemical Co., Lot 68C-9510, 100 mg) in AcOH–AcONa buffer solution (pH 5.0, 50 ml) at 37 °C for 15 h. The reaction mixture was extracted with *n*-BuOH. The *n*-BuOH layer was washed with water and concentrated. The residue was chromatographed on silica gel (20 g) with $CHCl_3$–MeOH–H_2O (25:3:0.3) to give compound VIII (=prosapogenin of saponin D isolated from Akebia quinata)[10] (15 mg) and compound XI (=Kizuta saponin K_3)[3] (35 mg).

Compound IV, colorless needles (from MeOH), mp 185—188 °C (dec.), $[\alpha]_D^9$ +17.1° (c=3.00, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3350, 1725, 1100—1000. ^{1}H-NMR (pyridine-d_5): 0.87 (6H), 1.02 (3H), 1.05 (3H), 1.15 (3H), 1.19 (3H) (each s, *tert*-Me×6), 5.03 (1H, d, J=7.1 Hz, C_1-H of terminal glucose unit), 5.45 (1H, br s, C_{12}-H), 6.25 (1H, d, J=7.1 Hz, C_1-H of inner glucose unit). ^{13}C-NMR: Table I.

Compound V, a white powder (from MeOH–AcOEt), mp 207—210 °C (dec.), $[\alpha]_D^{18}$ +15.3° (c=2.00, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3350, 1725, 1100—1000. ^{1}H-NMR (pyridine-d_5): 0.87 (6H), 0.91 (3H), 0.98 (3H), 1.11 (3H), 1.18 (3H) (each s, *tert*-Me×6), 4.96 (1H, d, J=6.8 Hz, C_1-H of arabinose unit), 5.01 (1H, d, J=7.1 Hz, C_1-H of terminal glucose unit), 5.42 (1H, br s, C_{12}-H), 6.23 (1H, d, J=7.1 Hz, C_1-H of inner glucose unit). ^{13}C-NMR: Table I.

Compound VI, a white powder (from MeOH–AcOEt), mp 198—202 °C (dec.), $[\alpha]_D^9$ −3.3° (c=3.00, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1100—1000. ^{1}H-NMR (pyridine-d_5): 0.88 (6H), 1.01 (3H), 1.06 (3H), 1.13 (3H), 1.18 (3H) (each s, *tert*-Me×6), 1.68 (3H, d, J=6.1 Hz, C_5-Me of rhamnose unit), 4.99 (1H, d, J=7.8 Hz, C_1-H of outer glucose unit), 5.43 (1H, br s, C_{12}-H), 5.84 (1H, s, C_1-H of rhamnose unit), 6.23 (1H, d, J=7.1 Hz, C_1-H of inner glucose unit). ^{13}C-NMR: Table I.

Compound VII, a white powder (from MeOH–AcOEt), mp 205—209 °C (dec.), $[\alpha]_D^{18}$ −6.9° (c=3.58, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3350, 1720, 1100—1000. ^{1}H-NMR (pyridine-d_5): 0.87 (6H), 0.98 (3H), 1.06 (3H), 1.12 (3H), 1.17 (3H) (each s, *tert*-Me×6), 1.62 (3H, d, J=5.9 Hz, C_5-Me of rhamnose unit), 5.41 (1H, br s, C_{12}-H), 6.21 (1H, s, C_1-H of rhamnose unit), 6.24 (1H, d, J=6.6 Hz, C_1-H of inner glucose unit). ^{13}C-NMR: Table I.

Compound VIII, colorless needles (from dil. MeOH), mp 202—205 °C (dec.), $[\alpha]_D^9$ +36.0° (c=0.50, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3380, 1725, 1100—1000. ^{1}H-NMR (pyridine-d_5): 0.89 (9H), 0.97 (3H), 1.14 (3H), 1.19 (3H) (each s, *tert*-Me×6), 4.98 (1H, d, J=7.0 Hz, C_1-H of arabinose unit), 5.44 (1H, br s, C_{12}-H), 6.30 (1H, d, J=7.1 Hz, C_1-H of glucose unit). ^{13}C-NMR: Table I.

Per-*O*-methylation of I——According to Kuhn's methylation procedure, a solution of I (50 mg) in dimethylformamide (0.5 ml) with Ag_2O (250 mg) and MeI (0.3 ml) was shaken at room temperature for 70 h. Then $CHCl_3$ was added and the mixture was filtered. The filtrate was concentrated and the residue was chromatographed on silica gel (10 g) with a gradient of benzene–acetone (acetone 0—15%) to give a per-*O*-methylate (IX, 20 mg). IX, a white powder (from hexane), mp 119—122 °C. *Anal.* Calcd for $C_{75}H_{126}O_{27}$: C, 61.71; H, 8.70. Found. C, 61.95; H, 8.80. IR ν_{max}^{KBr} cm^{-1}: 1740, 1150—1050. ^{1}H-NMR ($CDCl_3$): 0.70 (3H), 0.75 (3H), 0.90 (9H), 1.13 (3H) (each s, *tert*-Me×6), 1.26, 1.28 (each 3H, d, J=6.1 Hz, C_5-Me of rhamnose unit ×2), 2.08 (3H, s, CH_3COO), 4.82 (1H, br s, C_1-H of rhamnose unit in 28-*O*-sugar moiety), 5.14 (1H, br s, C_1-H of rhamnose unit in 3-*O*-sugar moiety), 5.29 (1H, br s, C_{12}-H), 5.38 (1H, d, J=7.3 Hz, C_1-H of inner glucose unit).

Methanolysis of IX——A solution of IX (15 mg) in 10% HCl–MeOH (2 ml) was heated under reflux for 2 h. The reaction mixture was neutralized with Ag_2CO_3 and the precipitates were filtered off. The filtrate was concentrated and the residue was crystallized from MeOH to give an aglycone (2.5 mg) as colorless needles. This product was identified as 23-*O*-methyl-hederagenin by direct comparison of the TLC behavior and IR and ^{1}H-NMR spectra with those of an authentic sample. The mother liquor of crystallization was analyzed by TLC [solv., benzene–acetone (4 : 1, 5 : 1)] and GLC-2,[9] which revealed the presence of methyl 2,3,4-tri-*O*-methyl-rhamnopyranoside (t_R 4 min 02 s, 5 min 58 s), methyl 3,4-di-*O*-methyl-arabinopyranoside (t_R 15 min 24 s, 30 min 48 s), methyl 2,3-di-*O*-methyl-glucopyranoside (t_R 63 min 43 s, 92 min 48 s) and methyl 2,3,4-tri-*O*-methyl-glucopyranoside (t_R 19 min 29 s, 26 min 02 s).

Saponin K_8 (X)——A white powder (from MeOH–AcOEt), mp 192—195 °C (dec.), $[\alpha]_D^{25}$ −2.0° (c=2.41, MeOH). *Anal.* Calcd for $C_{55}H_{88}O_{23}\cdot 4H_2O$: C, 55.69; H, 8.76. Found: C, 55.45; H, 8.84. IR ν_{max}^{KBr} cm^{-1}: 3380, 1725, 1100—1000. ^{1}H-NMR (pyridine-d_5): 0.91 (9H), 0.98 (3H), 1.06 (3H), 1.17 (3H) (each s, *tert*-Me ×6), 1.70 (3H, d, J=6.1 Hz, C_5-Me of rhamnose unit), 1.92 (3H, s, CH_3COO), 5.40 (1H, br s, C_{12}-H), 5.53 (1H, s, C_1-H of rhamnose unit), 6.23 (1H, d, J=6.8 Hz, C_1-H of inner glucose unit). ^{13}C-NMR: Table I.

Methanolysis of X——X (10 mg) was methanolyzed in the same way as described for I to give hederagenin (2 mg), methyl arabinoside, methyl glucoside and methyl rhamnoside.

Alkaline Hydrolysis of X——i) A solution of X (15 mg) in 0.5 N KOH aq. (1 ml) was heated on a boiling water bath for 0.5 h. The reaction mixture was neutralized with 0.5 N H_2SO_4 and then extracted with *n*-BuOH. The *n*-BuOH layer was washed with water and concentrated. The residue was crystallized from dil. MeOH to give a prosapogenin (XI, 4 mg) as colorless needles; this product was identified as Kizuta saponin K_3[3] (hederagenin 3-*O*-α-L-arabinopyranoside) by direct comparison of the TLC behavior [solv., $CHCl_3$–MeOH–H_2O (25 : 5 : 0.5)] and IR and ^{1}H-NMR spectra with those of an authentic sample.

ii) A solution of X (25 mg) in 0.1 N KOH aq. (1 ml) was allowed to stand at room temperature for 20 h. The reaction mixture was neutralized with 0.1 N H_2SO_4 and then extracted with *n*-BuOH. The *n*-BuOH layer was washed with water and concentrated. The resulting residue (16 mg) was identified as Kizuta saponin K_{10}[3] [3-*O*-α-L-arabinopyranosyl-hederagenin 28-*O*-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester] by direct comparison of the ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample.

A Glucoside Mixture (XIII)——XIII (20 mg) was methanolyzed and worked up in the same way as described for I to give an aglycone fraction and a sugar fraction. GLC-3[9] of the aglycone fraction showed the presence of campesterol (t_R 13 min 55 s, trace), stigmasterol (t_R 14 min 48 s) and β-sitosterol (t_R 16 min 48 s). Stigmasterol and β-sitosterol were in the ratio of *ca.* 1 : 1. The sugar fraction was examined by TLC [solv., $CHCl_3$–MeOH–H_2O (25 : 11 : 2)] and GLC-1 (as trimethylsilylether derivative), which revealed the presence of methyl glucoside. ^{13}C-NMR (pyridine-d_5): 102.8 (C-1′), 78.7 (C-3′), 78.5 (C-3), 78.3 (C-5′), 75.5 (C-2′), 71.9 (C-4′).

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References and Notes

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8) The instruments used to obtain the physical data were the same as those described in the previous paper.[4)]
9) GLC was run on a Shimadzu GC-6AM unit with a flame ionization detector, using glass columns (2 m × 4 mm i.d.) packed with 5% SE-30 on Chromosorb W (60—80 mesh) (GLC-1 and GLC-3) or with 15% 1,4-butanediol succinate on Chromosorb W (100—120 mesh) (GLC-2); column temperature, programmed from 150 °C (20 min hold) to 240 °C at 5 °C/min (GLC-1), 280 °C (GLC-3) or 198 °C (GLC-2).
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