[Chem. Pharm. Bull. 22(10)2294—2300(1974)]

UDC 547.597'458.2.02 : 581.192

The Study on the Constituents of *Clematis* and *Akebia* sp. III.[1] The Study on the Structures of Akebosides isolated from the Stem of *Akebia quinata* Decne.

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(Received March 15, 1974)

The structures of three akebosides St_h, St_j, St_k were elucidated and the structures of five akebosides St_b, St_c, St_d, St_e, St_f were also suggested. Four (St_e, St_f, St_j, St_k) of them are newly isolated saponins.

The chemical structures of akebosides St_k (I), St_j (VIII), St_h (XIII) were established to be 3-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside, 3-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl oleanolic acid 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside, and 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-glucopyranoside, respectively.

Furthermore, saponins of seed, leaf, stem, and root of *A. quinata* were compared.

In our previous paper,[1] it has been reported that eight kinds of saponins named as akebosides were isolated from *Akebia quinata*, and aglycons and sugars of these saponins were determined. This paper deals with a study on the structures of akebosides and the relation of each other. The structures of three akebosides St_h, St_j, St_k were elucidated and the structures of five akebosides St_b, St_c, St_d, St_e, St_f were also suggested. Four (St_e, St_f, St_j, St_k) of them are newly isolated saponins.

Akeboside St_k (I), $C_{65}H_{106}O_{31}$, mp 220—222°, $[\alpha]_D^{25}$—16°, (H_2O), is hederagenin bonded with arabinose, glucose, and rhamnose.

Per-O-methylakeboside St_k (II), $C_{83}H_{142}O_{31}$, mp 116—118°, $[\alpha]_D^{25}$—34.8° ($CHCl_3$), was prepared through methylation by the Kuhn method.[3] The nuclear magnetic resonance (NMR) spectrum of II shows anomeric proton signals at 5.35 ppm (1H, doublet, J=7 Hz), 5.17 ppm (1H, singlet), 4.96 ppm (1H, singlet), 4.40 ppm (2H, doublet, J=6 Hz), and 4.19 ppm (1H, doublet, J=5 Hz). The methanolysis of II provided an aglycon (III), mp 200—202°, and four kinds of methylated monosaccharides. III was methylated with diazomethane to give colorless needles (IV), mp 185—187°. (IV) was identified by mixed melting point and thin-layer chromatography (TLC) as 23-O-methylhederagenin methylester. Furthermore, four methylated sugars were identified by TLC and gas-liquid chromatography (GLC) as methyl 2,3,4-tri-O-methyl-L-rhamnoside, methyl 2,3,4-tri-O-methyl-D-glucoside, methyl 2,3,6-tri-O-methyl-D-glucoside, and methyl 3,4-di-O-methyl-L-arabinoside. II gave, on reduction with $LiAlH_4$ in tetrahydrofuran, white powder (V), $C_{56}H_{94}O_{16}$, mp 96—98°, $[\alpha]_D^{25}$+8.6° ($CHCl_3$), and colorless syrup (VI), $[\alpha]_D^{25}$—22.4° ($CHCl_3$). The NMR spectrum of V shows anomeric proton signals at 5.17 ppm (1H, singlet), 4.43 ppm (1H, doublet, J=7 Hz), and 4.36 ppm (1H, doublet, J=5 Hz). The mass spectrum (MS) of V exhibits peaks originated from the aglycon moiety and a terminal permethylated hexose residue at m/e 454 and 189, respectively. The NMR spectrum of VI shows anomeric proton signals at 4.96 ppm (1H, singlet), 4.40 ppm (1H, doublet, J=7 Hz), and methyl signal of rhamnose at 1.34 ppm, (3H, doublet,

1) Part II: M. Fujita, H. Itokawa, and Y. Kumekawa, *Yakugaku Zasshi*, 94, 194 (1974).
2) Location: *Kitashinjuku, 3-20-1, Shinjuku-ku, Tokyo.*
3) R. Kuhn, *Angew. Chem.*, 67, 32 (1955).

J=7 Hz). MS of VI exhibits the peak of molecular ion at *m/e* 616 and a peak originated from the hexose residue at *m/e* 189. These data suggest that VI is consisted of rhamnose, glucose, and sorbitol. The methanolysis of V provided an aglycon (VII), mp 202—203°, and three kinds of methylated monosaccharides. VII was identified as 23-methoxyolean-12-ene-3,28-diol. Three methylated sugars were identified as methyl 2,3,4-tri-O-methyl-L-rhamnoside, methyl 2,3,4-tri-O-methyl-D-glucoside, and methyl 3,4-di-O-methyl-L-arabinoside. VI was also methanolized to give two kinds of methylated monosaccharides and polyalcohol. They are identified as methyl 2,3,4-tri-O-methyl-L-rhamnoside, methyl 2,3,6-tri-O-methyl-D-glucoside, and 2,3,4-tri-O-methyl-D-sorbitol. When I was heated with 0.05N H_2SO_4 in 50% ethanol, the hydrolysate was shown by TLC to contain hederagenin, akebosides St_b, St_d, St_f, St_g, St_l, and unchanged I.

In NMR spectrum of II, the coupling constant of anomeric protons at 4.40 ppm and 4.19 ppm indicate that the protons at C-1 and C-2 in both sugar units are oriented nearly trans-diaxial,[4] and hence that D-glucopyranose is β-linked in Cl conformation and L-arabinopyranose is α-linked in Cl.[5] Furthermore, for the determination of the configuration, Klyne's rule[6] was applied to hederagenin, akebosides St_b, St_d, and St_f which were suggested as partial hydrolyzate compounds of akeboside St_k. The result is shown in Table I. These data suggest the structure of C-3 glycoside in I to be represented as hederagenin α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranoside. In NMR spectra of II and VI the coupling constant of anomeric proton signals at 5.35 ppm and 4.40 ppm indicate that D-glucopyranose is β-linked in Cl. Furthermore, since generally rhamnopyranose is oriented as 1C conformation, the coupling constant and chemical shift of anomeric proton signal at 4.96 ppm in NMR spectrum of VI suggested that L-rhamnopyranose is α-linked in 1C.

Consequently, the structure of I is defined as 3-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside.

Akeboside St_j (VIII), $C_{65}H_{106}O_{30}$, mp 224—226°, $[\alpha]_D^{25}$—11.1° (H_2O), is oleanolic acid bonded with arabinose, glucose, and rhamnose.

Per-O-methylakeboside St_j (IX), $C_{82}H_{140}O_{30}$, mp 126—128°, $[\alpha]_D^{25}$—35.3° ($CHCl_3$), prepared through methylation by Kuhn method. The NMR spectrum of IX shows anomeric proton signals at 5.35 ppm (1H, doublet, J=7 Hz), 5.17 ppm (1H, singlet), 4.96 ppm (1H, singlet), 4.40 ppm (2H, doublet, J=7 Hz), and 4.18 ppm (1H, doublet, J=6 Hz). IX exhibits on a MS the peaks at *m/e* 597, 437, and 189 and these fragments are explained as originated from methylated trisaccharide moiety, aglycon moiety, and a terminal hexose residue, respectively. Methanolysis of IX is afforded to give oleanolic acid (X), mp 296—297°, methyl 2,3,4-tri-O-methyl-L-rhamnoside, methyl 2,3,4-tri-O-methyl-D-glucoside, methyl 2,3,6-tri-O-methyl-D-glucoside, and methyl 3,4-di-O-methyl-L-arabinoside. IX gave, on reduction with $LiAlH_4$ in tetrahydrofuran, white powder (XI), $C_{55}H_{92}O_{15}$, mp 103—104°, $[\alpha]_D^{25}$+9.1° ($CHCl_3$), and colorless syrup (VI). The NMR spectrum of XI shows anomeric proton signals at 5.17 ppm (singlet), 4.40 ppm (doublet, J=7 Hz), and 4.18 ppm (doublet, J=6 Hz), and the MS of XI exhibits these originated from aglycon moiety and a terminal hexose residue at *m/e* 424 and 189 respectively. Methanolysis of XI provided aglycone (XII) mp 231—232° and three kinds of methylated sugars. XII was identified as erythrodiol by comparison with authentic sample. Methylated sugars were identified as methyl 2,3,4-tri-O-methyl-L-rhamnoside, methyl 2,3,4-tri-O-methyl-D-glucoside, and methyl 3,4-di-O-methyl-L-arabinoside.

4) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
5) K. Miyahara and T. Kawasaki, *Chem. Pharm. Bull.* (Tokyo), **17**, 1369 (1969); J. Sakakibara, Y. Hotta, and M. Yasue, *Yakugaku Zasshi*, **91**, 1318 (1971); R. Higuchi, K. Miyahara, and T. Kawasaki, *Chem. Pharm. Bull.* (Tokyo), **20**, 1935 (1972).
6) W. Klyne, *Biochem. J.*, **47**, XLI (1950).

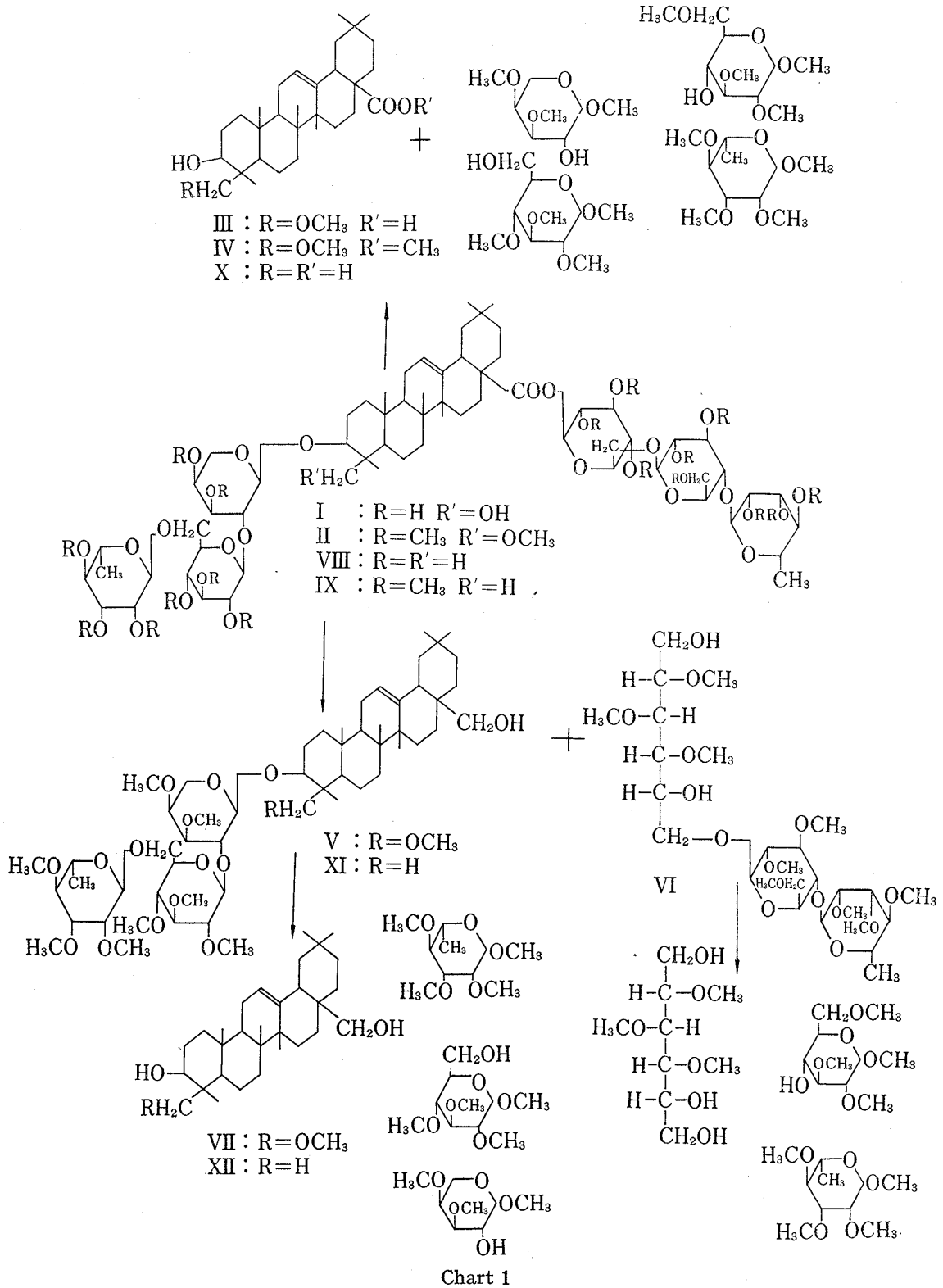

Chart 1

The total structure of VIII was suggested as 3-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl oleanolic acid 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside in relation to akeboside St_k (I).

Akeboside St_h (XIII), $C_{59}H_{96}O_{26}$, mp 221—222°, $[\alpha]_D^{25}$ −7.3° (MeOH), is hederagenin bonded with arabinose, glucose, and rhamnose. Its permethylate (XIV), $C_{73}H_{126}O_{26}$, mp 119—120°, $[\alpha]_D^{25}$ −3.3° ($CHCl_3$), was also prepared by the Kuhn method. The NMR spectrum of XIV shows anomeric proton signals at 5.33 ppm (doublet, J=6 Hz), 5.18 ppm (singlet), 4.97 ppm

Table I. Optical Rotations of Saponins

Saponin	$[\alpha]_D$	$[M]_D$	ΔM
Akeboside St_f	+ 8.2°	+ 74.8°	−240.8°
Akeboside St_d	+41.2°	+315.6°	+ 33.5°
Akeboside St_b	+46.7°	+282.1°	−100.2°
Hederagenin	+81°	+382.3°	

(singlet), 4.71 ppm (doublet, J=6 Hz), and 4.17 ppm (doublet, J=7 Hz). The MS of XIV exhibits fragments originated from the aglycone moiety, trisaccharide moiety, and a terminal hexose residue at *m/e* 597, 467, and 189 respectively. Methanolysis of XIV provided an aglycon, mp 203—205°, identical with III and four kinds monomethylated saccharides identical with methanolysis of II. XIV gave, on reduction with $LiAlH_4$ in tetrahydrofuran, white powder (XV), $C_{47}H_{78}O_{11}$, mp 108—109°, $[\alpha]_D^{25}$+27.3° ($CHCl_3$), and colorless syrup identical with VI. The NMR spectrum of XV shows anomeric proton signals at 5.18 ppm (1H, singlet) and 4.17 ppm (1H, doublet J=7 Hz). The MS of XV exhibits peaks originated from an aglycon moiety and a terminal hexose residue at *m/e* 456 and 189, respectively. Methanolysis of XV provided an aglycon identical with VII and methyl 2,3,4-tri-O-methyl-L-rhamnoside

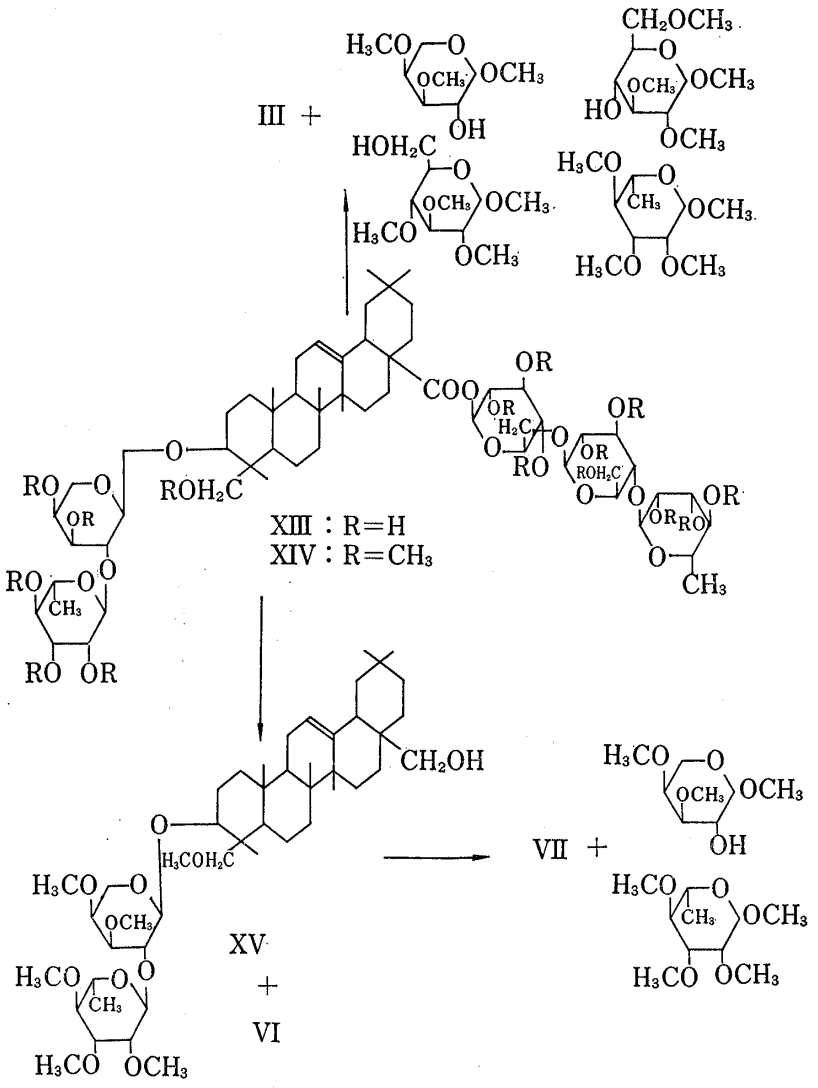

Chart 2

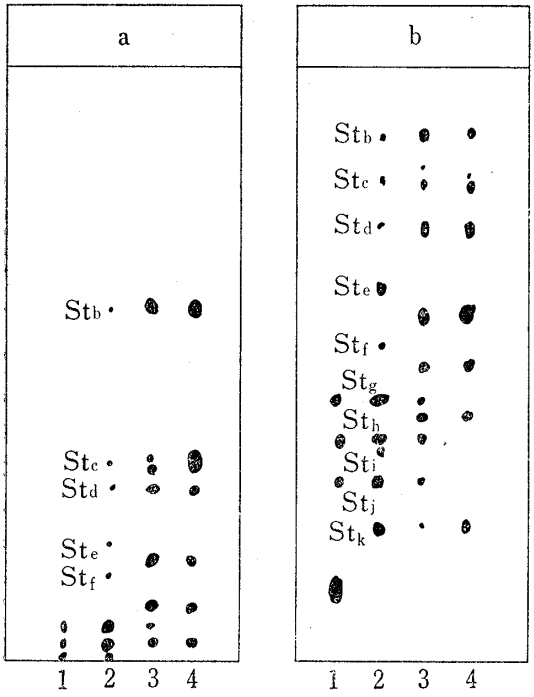

Fig. 1. Thin-Layer Chromatogram of Saponins isolated from Each Part of *A. quinata*

solvent: a. $CHCl_3$–MeOH–H_2O (13:7:3) (bottom layer)
b. $CHCl_3$–MeOH–H_2O (25:17:3)
1. root, 2. stem, 3. leaf, 4. seed

and methyl 3,4-di-O-methyl-L-arabinoside. When XIII was heated with 0.1N H_2SO_4 in 50% ethanol, the hydrolysate was shown by TLC to contain hederagenin, akebosides St_b and St_c.

These data indicate the structure of XIII to be represented as 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-glucopyranoside.

XIII has the same structure with that proposed by Kochetokov and cowokers for kalopanax saponin B of *Kalopanax sepemlobus* Koidz. (Araliaceae).[7] From the above results and previous paper,[1] the structure of akebosides St_b, St_c, St_d, St_e, and St_f were also suggested as below: St_b; hederagenin 3-O-α-L-arabinopyranoside, St_c; hederagenin 3-O-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside, St_d; hederagenin 3-O-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranoside, St_e; oleanolic acid 3-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranoside, St_f; hederagenin 3-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranoside.

We have compared saponins of seed, leaf, stem, and root of *A. quinata*. The result was indicated in Fig. 1. In Fig. 1, it is suggested that the distribution of various saponins of *A. quinata* is different at each part of the plant. 3-O-Glycosides of saponins were not contained in root. Akebosides St_b and St_d were contained in leaf and seed. A small quantity of 3-O-glycosides was contained in stem and the content of them is much increased in seed than in stem. Root contains akebosides St_{g_1, g_2}, St_h, St_j, and saponin bonded with many sugars. Akeboside St_{g_1, g_2}, St_h, St_j, and St_k were obseerved in leaf.

Experimental

All melting points were determined on a micro melting points apparatus and uncorrected. Optical rotation were measured with a JASCO DIP-SL automatic polarimeter. IR spectra were measured with Hitachi IR 215. NMR spectra were obtained with NEVA T-60 spectrometer with tetramethylsilane as internal standard. The chemical shifts are reported in δ and the solvents used are indicated. MS were taken at Hitachi RMU-7L. GLC used was Yanagimoto G-80 flame ionization detector (FID) using glass column (1500×4ϕ) packed with 1.5% SE-30 on chromosorb w (60—80 mesh) and 15% 1,4-butanediol succinate on chromosorb w (60—80 mesh). TLC was performed on Kieselgel 60 F_{254} using solvent system, benzene–acetone (1:1) and ligroin-methyl ethyl ketone (1:1) (for methylated sugars), $CHCl_3$–MeOH (40:1) and benzene–AcOEt (7:3) (for aglycon).

Akeboside St_k (I)——As we reported in previous paper, I was obtained as white powder, mp 220—222° (decomp.), $[\alpha]_D^{25}$ −16° (c=0.5, H_2O). *Anal.* Calcd. for $C_{65}H_{106}O_{31}\cdot 7H_2O$: C, 51.72; H, 7.96. Found: C, 51.47; H, 7.10.

Permethylate (II) of I——According to the Kuhn method, I (1 g) in dimethylformamide (6 ml) was methylated with Ag_2O (6 g) and methyl iodide (6 ml) at room temperature for 90 hr under stirring. The reaction mixture was filtered and the filtrate was methylated again in the same method with additional Ag_2O (4 g) and methyl iodide (4 ml). Reaction mixture was filtered and the filtrate was diluted with water

7) A.Ya. Khorlin, A.G. Ven'yaminova, and N.K. Kochetokov, *Izv. Akad. Nauk. SSSR, Ser, Khim.*, **1966**, 1588 [*C.A.*, **66**, 65803w (1967)].

and then precipitate was dissolved with KCN (solid). The reaction mixture was extracted with $CHCl_3$ several times, washed with water, dried with $MgSO_4$ and evaporated. The residue was repeatedly precipitated from hexane, white powder (II), mp 116—118°, $[\alpha]_D^{25}$ −34.8° (c=0.8, $CHCl_3$). *Anal.* Calcd. for $C_{83}H_{142}O_{31}$: C, 60.95; H, 8.69. Found: C, 60.45; H, 8.77. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1745 (ester), OH (nil). NMR ($CDCl_3$) δ: 5.35 (1H, d. J=7 Hz), 5.17 (1H, s.), 4.96 (1H, s.), 4.40 (2H, d. J=7 Hz), 4.19 (1H, d. J=5 Hz).

Methanolysis of II——II (25 mg) was refluxed with 2N HCl in MeOH (20 ml) for 2 hr, the mixture was neutralized with Ag_2CO_3 and filtered. The filtrate was evaporated and the residue was recrystallized from MeOH to provide an aglycon (III) as colorless needles, mp 200—202°. III was methylated with diazomethane to give colorless needles (from AcOEt), mp 185—187° (IV). In the mother liquor of recrystallization was shown the existence of four kinds of methylated monosaccharids which were identical on TLC and GLC with the authentic samples of methyl 2,3,4-tri-O-methyl-L-rhamnoside, methyl 2,3,4-tri-O-methyl-D-glucoside, methyl 2,3,6-tri-O-methyl-D-glucoside, and methyl 3,4-di-O-methyl-L-arabinoside, respectively.

$LiAlH_4$ Reduction of II——II (130 mg) in tetrahydrofuran (6 ml) was reduced with $LiAlH_4$ (50 mg) under refluxing for 3 hr. The reaction mixture was treated with water under cooling to decompose the excess $LiAlH_4$ and acidified with 2% H_2SO_4 and dissolved the precipitation. The solution was extracted with $CHCl_3$, washed with water, dried over $MgSO_4$ and evaporated. The residue was submitted to column chromatography on silica gel and eluted with AcOEt affording white powder (V), mp 96—98°, $[\alpha]_D^{25}$ +8.6° (c=0.4, $CHCl_3$). *Anal.* Calcd. for $C_{56}H_{94}O_{16}$: C, 65.75; H, 9.20. Found: C, 66.88; H, 8.92. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), C=O (nil). Mass Spectrum m/e: 454 ($C_{31}H_{52}O_2^+$), 189 ($C_9H_{17}O_4^+$). NMR ($CDCl_3$) δ: 5.17 (1H, s.), 4.43 (1H, d. J=7 Hz), 4.36 (1H, d. J=5 Hz). Elution with AcOEt gave colorless syrup (VI), $[\alpha]_D^{25}$ −22.4° (c=0.7, $CHCl_3$). Mass Spectrum m/e: 616 ($C_{27}H_{52}O_{15}^+$), 189. NMR ($CDCl_3$) δ 4.96 (1H, s.), 4.40 (1H, s.), 1.34 (3H, d. J=7 Hz).

Synthesis of 23-Methoxyolean-12-ene-3,28-diol——Hederagenin (300 mg) in acetone (3 ml) was refluxed with Ag_2O (690 mg) and methyl iodide (3 ml) for 3 hr.[8] The reaction mixture was purified by column chromatography on silica gel using $CHCl_3$–MeOH (40: 1), followed by recrystallization from MeOH, affording the 23-O-methyl-hederagenin methylester. 23-O-Methyl-hederagenin methylester in tetrahydrofuran (3 ml) was reduced with $LiAlH_4$ (130 mg) under refluxing for 3 hr. The mixture was treated with usual method and recrystallized from MeOH affording colorless needles, mp 206—208°. Mass Spectrum m/e: 472 (M^+, $C_{31}H_{52}O_3^+$), 454, 216, 203. NMR ($CDCl_3$) δ: 3.4 (3H, s. CH_2OCH_3). IR ν_{max}^{KBr} cm^{-1}: C=O (nil).

Methanolysis of VI——VI (14 mg) was refluxed with 2N HCl in MeOH (10 ml) for 2 hr and worked up as in II. Methylated monosaccharides were identical with methyl 2,3,4-tri-O-methyl-L-rhamnoside and methyl 2,3,6-tri-O-methyl-D-glucoside, respectively. 2,3,4-Tri-O-methyl-D-sorbitol was identified by comparison with the authentic sample.

Synthesis of 2,3,4-Tri-O-methyl-D-sorbitol——D-Glucose (1 g) in pyridine was heated with trityl chloride (1 g), filtrated, evaporated, and dried. The residue was methylated by Hakomori method.[9] The reaction mixture was detritylated with HBr, filtrated and the filtrate was extracted with $CHCl_3$ dried on $MgSO_4$, and evaporated. The residue was reduced with $LiAlH_4$.

Partial Hydrolysis of I——I (100 mg) was refluxed with 0.05N H_2SO_4 in 50% EtOH (20 ml) for 2 hr and neutralized with Ag_2CO_3. The hydrolysate was shown by TLC to contain hederagenin, akebosides St_b, St_d, St_f, St_g, St_i, and unchanged I.

Akeboside St_j (VIII)——VIII was obtained as colorless needles, mp 224—226° (decomp.), $[\alpha]_D^{25}$ −11.1° (c=0.6, H_2O). *Anal.* Calcd. for $C_{65}H_{106}O_{30}\cdot 8H_2O$: C, 51.66; H, 8.08. Found: C, 51.34; H, 7.54.

Permethylate of VIII——VIII was methylated in the same method as I and precipitated from hexane as white powder (IX), mp 126—128°, $[\alpha]_D^{25}$ −35.3° (c=0.7, $CHCl_3$). *Anal.* Calcd. for $C_{82}H_{140}O_{30}$: C, 61.35; H, 9.73. Found: C, 61.34; H, 9.20. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1745 (ester), OH (nil). Mass Spectrum m/e: 597 ($C_{27}H_{49}O_{14}^+$), 437 ($C_{30}H_{45}O_2^+$), 189. NMR ($CDCl_3$) δ: 5.35 (1H, d. J=7 Hz), 5.17 (1H, s.), 4.96 (1H, s.), 4.40 (2H, d. J=7 Hz), 4.18 (1H, d. J=6 Hz).

Methanolysis of IX——IX (40 mg) was hydrolyzed in the same method as II. Methanolysate was recrystallized from MeOH as colorless needles (X), mp 296—297°, and identified with authentic sample of oleanolic acid. Mother solution was shown to contain methyl 2,3,4-tri-O-methyl-L-rhamnoside, methyl 2,3,4-tri-O-methyl-D-glucoside, methyl 2,3,6-tri-O-methyl-D-glucoside, and methyl 3,4-di-O-methyl-L-arabinoside by TLC.

$LiAlH_4$ Reduction of XI——XI (500 mg) was reduced with $LiAlH_4$ in the same method as II. Reaction product was submitted to column chromatography on silica gel and eluted with AcOEt affording white powder (XI), mp 103—104°, $[\alpha]_D^{25}$ +9.1° (c=0.6, $CHCl_3$). *Anal.* Calcd. for $C_{55}H_{92}O_{15}$: C, 66.53; H, 9.27. Found: C, 66.11; H, 9.27. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), CO (nil). Mass Spectrum m/e: 424 ($C_{30}H_{46}O^+$), 189. NMR ($CDCl_3$) δ: 5.17 (1H, s.), 4.40 (1H, d. J=7 Hz), 4.18 (1H, d. J=6 Hz), and colorless syrup (VI).

Methanolysis of XI——XI (40 mg) was refluxed in the same method as II. Methanolysate was recrystallized from MeOH as colorless needles (XII) mp 231—232° and identified with authentic sample

8) J.J. Scheidegger and E. Cherbuliez, *Helv. Chim. Acta*, **38**, 547 (1955).
9) S. Hakomori, *J. Biochem.*, **55**, 205 (1964).

of erythrodiol. The mother liquor was shown to contain methyl 2,3,4-tri-O-methyl-L-rhamnoside, methyl 2,3,4-tri-O-methyl-D-glucoside, and methyl 3,4-di-O-methyl-L-arabinoside by TLC.

Akeboside St_h (XIII)——XIII was obtained as white powder, mp 221—222° (decomp.), $[\alpha]_D^{25}$ −7.3° (c=1.0, MeOH). *Anal.* Calcd. for $C_{59}H_{96}O_{26}\cdot 7H_2O$: C, 52.88; H, 7.63. Found: C, 52.60; H, 5.17.

Permethylate of XIII——XIII (700 mg) was methylated in the same method as I and precipitated from hexane as white powder (XIV), mp 119—120°, $[\alpha]_D^{25}$ −3.3° (c=0.6, $CHCl_3$). *Anal.* Calcd. for $C_{73}H_{126}O_{26}$: C, 61.77; H, 8.89. Found: C, 61.35; H, 9.05. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1745 (ester), OH (nil). Mass Spectrum m/e: 597, 467, 189. NMR ($CDCl_3$) δ: 5.33 (1H, d. J=6 Hz), 5.18 (1H, s.), 4.97 (1H, s.), 4.71 (1H, d. J=6 Hz), 4.17 (1H, d. J=7 Hz).

Methanolysis of XIV——XIV (40 mg) was hydrolyzed in the same method as II. The hydrolysate was recrystallized from MeOH as colorless needles mp 203—205° identical with III. The mother solution was shown to contain four kinds of methylated sugars identical with methanolysate of II by TLC.

$LiAlH_4$ Reduction of XIV——XIV (200 mg) was reduced with $LiAlH_4$ in the same method as II. Reaction mixture was chromatographed on silica gel affording white powder (XV), mp 108—109°, $[\alpha]_D^{25}$ +27.3° (c=1.0, $CHCl_3$). *Anal.* Calcd. for $C_{47}H_{78}O_{11}$: C, 68.95; H, 9.54. Found: C, 68.14; H, 10.05. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), CO (nil). Mass Spectrum m/e: 456, 189. NMR ($CDCl_3$) δ: 5.18 (1H, s.), 4.17 (1H, d. J= 7 Hz), and colorless syrup (VI).

Methanolysis of XV——XV (20 mg) was methanolyzed in the same method as II. An aglycon was identical with VII and methylated monosaccharides were identical with methyl 2,3,4-tri-O-methyl-L-rhamnoside and methyl 3,4-di-O-methyl-L-arabinoside.

Partial Hydrolysis of XIII——XIII (20 mg) was refluxed in same method as I. The hydrolysate was shown by TLC to contain hederagenin, akebosides St_b and St_c.

Extract of Saponin from Seed, Leaf, and Root——The commercially available seed (18 g) were defatted with benzene (30 ml) and extracted with MeOH (60 ml) for 8 hr. Extracted solution was partitioned between water and AcOEt–*n*-BuOH (1: 1), and the aqueous layer was extracted with *n*-BuOH saturated with water. The organic layer and *n*-BuOH layer were used independently as samples of TLC. Leaves (100 g) and roots (50 g) were defatted with benzene (100—500 ml) and extracted with MeOH (100—300 ml) respectively.

Acknowledgement The authors were deeply grateful to Prof. T. Kawasaki of Kyushu University and Prof. T. Miyazaki of this school for useful discussion and for authentic sample. We thank K. Tanaka of Science University of Tokyo for authentic sample. Thanks are also due to the members of Central Analytical Laboratory of this school for elemental analysis and for the measurement of NMR and Mass spectra.