Seed Saponins of *Akebia quinata* Decne. II. Hederagenin 3,28-O-Bisglycosides

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The more polar four triterpenoid saponins, D—G, of the seven, A—G, so far isolated in pure state from the seeds of *Akebia quinata* Decne. were characterized as follows: saponin D (mp > 225° (decomp.), [α]D +15°, 3-O-α-L-arabinopyranosyl hederagenin 28-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (IV); E (mp 210—214° (decomp.), [α]D + 6°), 3-O-β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (XI); F (mp 211—214° (decomp.), [α]D -4°, 3-O-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranosyl hederagenin 28-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (XIV); G (mp > 218° (decomp.), [α]D -19°, 3-O-β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (XVI). They are new hederagenin 3,28-O-bisglycosides and related to each other and to saponins A, B, and C.

As described in the preceding paper[1] seven saponins, A—G, were isolated from the seeds of *Akebia quinata* and three, A, B and C, of them were identified as hederagenin 3-O-glycosides, I, II and III, respectively.

This paper deals with a study on the more polar four saponins, D—G, which has led to characterization of them as hederagenin 3,28-O-bisglycosides[2] related to each other and to A, B and C.

Saponin D (IV), colorless needles, mp > 225° (decomp.), [α]D +15° (MeOH), was hydrolyzed with 2N sulfuric acid in 30% ethanol to yield hederagenin, arabino and glucose, and with 1% potassium hydroxide in 30% ethanol to give a compound (V). V gave, on acid hydrolysis, hederagenin and arabino, and shows on thin-layer chromatogram (TLC) the same Rf value and color as those of saponin A (I). The methylester acetate of V, mp 235°, [α]D +72° (CHCl3), was identical with the corresponding derivative of I.

When the permethylate (VI) of IV prepared by the Kuhn method[,]1 mp 109—110°, [α]D +23° (CHCl3), was subjected to methanalysis, three kinds of methylated monosaccharide along with an aglycon (VII) were provided. The sugars were identified on TLC and gas-liquid chromatogram (GLC) as methyl pyranosides of 2,3,4-tri-O-methyl-arabinose, 2,3,4,6-tetra-O-methyl-, and 2,3,4-tri-O-methyl-glucoses, and VII was converted with diazomethane to 23-O-methyl hederagenin methylster, the aglycon of I permethylate. The lithium aluminum hydride reduction of VI yielded two products, a syrup (VIII) and a white powder (IX), mp 95—97°,[α]D +59° (CHCl3), which was proved to be the 28-carbinol corresponding to the permethylate of I by direct comparison with the synthetic sample. VIII shows on a mass spectrum (MS) the peaks due to molecular ion (m/z 442) and to a terminal permethylated hexose residue (m/z 319).[3] The nuclear magnetic resonance (NMR) spectra of VIII and its acetate, a syrup, [α]D

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2) Location: 1276 Katakus, Fukuoka.
-12° (CHCl₃), exhibit one anomic proton signal at 4.27 ppm as a doublet (J = 6.5 Hz) in the former and two acetoxyl in the latter. These data indicate that VIII derived from the 1→6 linked linear glycoconjugate moiety at the 28-carboxyl group of VI is 2,3,4,6-tetra-O-methyl-glucopyranosyl-(1→6)-2,3,4,tri-O-methyl-sorbitol, and that IV is, if glucose is assumed to be of the most common β-series, 28-O-β-glucopyranosyl-(1→6)-β-d-glucopyranoside of I.

When IV was incubated with almond emulsion, glucose and a prosapogenin (X), colorless needles, mp 211−214° (decomp.), [α]₀ +34° (MeOH), were provided, and the latter was further cleaved with acid to give hedergenin, glucose and arabinose. This and the NMR data of VIII imply the existence of β-d-glucopyranosyl residue in Cl conformation at terminal. The NMR spectrum of X in C₆D₆N solution shows two doublets at 4.75 ppm (J = 7 Hz) and 6.00 ppm (J = 7 Hz) which could be attributed to the anomic protons of α-L-arabinopyranosyl (Cl conformation) and β-d-glucopyranosyl (Cl conformation) units. The β-configuration of the two d-glucose residues was also suggested by the molecular rotation differences between IV and X (−127°), and X and I (−35°).

Consequently, saponin D is defined as 3-O-α-L-arabinopyranosyl hedergenin 28-O-β-d-glucopyranosyl-(1→6)-β-d-glucopyranoside and represented by the formula IV.

Saponin E (XI), white powder, mp 210−214° (decomp.), [α]₀ +6° (MeOH), was hydrolyzed in the same manner as in IV to give hedergenin, arabinose, xylose and glucose, and with alkali to yield saponin B (II) which was identified by direct comparison of its methylester peracetate, mp 140−143°, [α]₀ +34° (CHCl₃), with the authentic specimen. The permethylate (XII), white powder, mp 112−113°, [α]₀ +7° (CHCl₃), was methanolized to give the same aglycon VII as that from VI and four kinds of methylated sugar. The latter were identified on TLC and GLC as methyle pyranosides of 2,3,4-tri-O-methyl-xylose, 3,4-di-O-methyl-arabinose, 2,3,4-tri-O-methyl- and 2,3,4,6-tetra-O-methyl-glucoses. The lithium aluminum hydride reduction of XII yielded a syrup together with colorless plates, mp 220−221°, which are identical with the 28-carbinol derived from II permethylate. The syrup shows the same Rf value on TLC and MS as those of VIII. Accordingly, assuming glucose as of D-series, the sugar moiety attached to the 28-carboxyl group of XI is regarded as a disaccharide, d-glucopyranosyl-(1→6)-d-glucopyranose. The mode of linkage of the two glucose units is regarded, in both cases, as β on the basis of the NMR spectrum of XII showing an anomic proton signal of esterglycosidic glucose at 5.40 ppm as a doublet (J = 7 Hz) and of the fact that XI was cleaved with emulsion to give glucose and a prosapogenin (XIII), mp 205−210° (decomp.), [α]₀ +25° (MeOH), consisting of hedergenin, arabinose, xylose, and glucose. The configurations are also supported by the molecular rotation differences between II and XIII (−42°), and XIII and XI (−169°).

Saponin E is thus considered to be 3-O-β-d-xylopyranosyl-(1→2)-α-L-arabinopyranosyl hedergenin 28-O-β-d-glucopyranosyl-(1→6)-β-d-glucopyranoside (XI).

Saponin F (XIV), white powder, mp 211−214° (decomp.), [α]₀ −4° (MeOH), is composed of hedergenin, arabinose and glucose, and gave saponin C (III) on alkali hydrolysis. XIV permethylate (XV), mp 110°, [α]₀ +13° (CHCl₃), shows an anumeric proton signal of esterglycosidic glucose at 5.35 ppm as a doublet (J = 7 Hz) on the NMR spectrum, and its methanolysis yielded VII, as from VI and XII, and methyl pyranosides of 3,4-di-O-methyl-arabinose, 2,3,4-tri-O-methyl- and 2,3,4,6-tetra-O-methyl-glucoses. The reduction products of XV with lithium aluminum hydride were identified as VIII and the 28-carbinol corresponding to III permethylate.

On the basis of the above data and by analogy with the cooccurrence of XI and II, saponin F is regarded as 28-O-β-d-glucopyranosyl-(1→6)-β-d-glucopyranoside of coexisting III, that is 3-O-β-d-glucopyranosyl-(1→2)-α-L-arabinopyranosyl hedergenin 28-O-β-d-glucopyranosyl-(1→6)-β-d-glucopyranoside (XIV).

Saponin G (XVI), white powder, mp $>218^\circ$ (decomp.), $[\alpha]_D^{20} -19^\circ$ (MeOH), consists of hederagenin, arabinose, glucose and rhamnose, and its hydrolysis with alkali afforded a compound (XVII), mp 225—227$^\circ$ (decomp.), $[\alpha]_D^{20} +10^\circ$ (MeOH). XVII was acid hydrolyzed in the same manner as in XVI to give the same products and in a milder condition to provide saponin C (III). The permethylate (XVIII) of XVII prepared by the Hakomori method, colorless needles, mp 211—211.5$^\circ$, $[\alpha]_D^{20} +15^\circ$ (CHCl$_3$), shows on a MS the molecular ion ($m/e$ 1052) and the fragment ions originated from terminal permethylated methylpentose ($m/e$ 189) and hexose ($m/e$ 219) residues, and its methanolysis yielded a compound identical with the aglycon of I permethylate and methyl pyranosides of 2,3,4-tri-O-methyl-

Formulæ I

rhamnose, 2,3,4,6-tetra-O-methyl-glucose and 3-O-methyl-arabinose. If the rhamnose residue in XVII is assumed to be of L-series, as is usually the case in natural glycidosides, the molecular rotation difference (−139°) between XVII and III suggests α-configuration of the L-rhamnose unit. Thus the structure, 3-O-β-D-glucopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-α-L-arabinopyranosyl hederagenin, is assigned to XVII.

The permethylate (XIX) of XVI, white powder, mp 113—115°C, [α]_D −13° (CHCl₃), gave on methanolysis VII and five kinds of methylated sugar. The latter were identified on TLC and GLC as methyl pyranosides of 2,3,4-tri-O-methyl-rhamnose, 3-O-methyl-arabinose, 2,3,4,6-tetra-O-methyl-, 2,3,4-tri-O-methyl- and 2,3,6-tri-O-methyl-glucoses. The lithium aluminum hydride reduction of XIX provided a colorless syrup (XX), [α]_D −34° (CHCl₃), (diacetate, a colorless syrup, [α]_D −45° (CHCl₃)), together with a powder which should be the 28-carbinol corresponding to XVIII. XX exhibits on a MS the molecular ion (m/e 616) and the peak due to a terminal permethylated methylpentose residue (m/e 189). These data

III

mild acid hydrolysis

methanolysis

XVII: R=H
XVIII: R=Me

alkali hydrolysis

mild acid hydrolysis

XIV

VII

LiAlH₄ reduction

methanolysis

XX

Formaldehyde

9) The small J value (1.5 Hz) of the anomeric proton signal of α-L-rhamnose unit at 5.12 ppm on the NMR spectrum of XVIII (cf. Experimental) might be due to the 1C conformation of the unit.
along with the finding that XVI gave saponin F (XIV) on mild acid hydrolysis indicate that
the oligosaccharide moiety conjugated with the 28-carboxy group in XVI is rhamnopyranosyl-
(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranose. On the NMR spectrum of XX the
anomeric proton signals appear at 4.34 ppm (doublet, J = 7 Hz) and 4.99 ppm (singlet) and
they are assigned respectively to those of β-D-glucopyranose (Cl conformation) and of rhamno-
pyranose assumingly of L-series with α-linkage in 1C conformation.

Consequently the structure 3-O-β-D-glucopyranosyl-(1→2)-[x-L-rhamnopyranosyl-(1→4)]-
α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→
6)-β-D-glucopyranoside (XVI) is postulated for saponin G.

There have recently been known several hederagenin 3,28-O-bischlycosides, but the four
saponins, IV, XI, XIV and XVI here reported are somewhat different in their sugar moieties
from those so far recorded. Coexistence of the glycosides closely related to each
other are noted.

**Experimental**

**Saponin D (IV)** — IV was obtained on recrystallization from AcOEt-BuOH as colorless needles, mp
>225° (decomp.), [α]D +15° (c = 1.64, MeOH). IR ν max cm⁻¹: 3350 (OH), 1755, 1740, 1725 (COOR). Anal.
Calcd. for C₄₂H₃₄O₃₉·4H₂O: C, 56.38; H, 8.46. Found: C, 55.66; H, 8.15. IV (50 mg) was hydrolyzed on
refluxing with 2N H₂SO₄ in 30% EtOH (2 ml) for 2 hr. The reaction mixture was diluted with H₂O, the
aglycon precipitated was collected by filtration and the filtrate was neutralized with Amberlite A-400 and
evaporated in vacuo. The aglycon was recrystallized from EtOH to give colorless prisms (23 mg), mp 315—
317° (acetate, mp 162—163°). It was identified as hederagenin by direct comparison (mixed melting point, IR,
TLC) with authentic sample. The sugar portion was examined by paper chromatography (FPC)
and arabinose and glucose were detected. IV (130 mg) was refluxed with 1% KOH in 30% EtOH (8 ml
for 1 hr and the reaction mixture was evaporated in vacuo to a residue (V) (77 mg), which showed on TLC
each spot identical with that of 1 run in parallel and gave on acid hydrolysis hederagenin and arabinose
and TLC and FPC). Acetylation of V with Ac₂O-pyridine followed by methylation with CH₃N and recrystallization
of the product from MeOH gave the methylester acetate as colorless needles, mp 235°, [α]D +72° (c = 1.0, CHCl₃).
Anal. Calcd. for C₄₀H₅₀O₂₃·C₂H₂O₂·C, 67.15; H, 8.45. Found: C, 66.54; H, 8.40. It was identified by direct
comparison with the methylester acetate, mp 238°, [α]D +78° (c = 1.0, CHCl₃), derived from I.

**Permethylate (VI) of IV** — IV (900 mg) was methylated in dimethylformamide (9 ml) with Ag₂O
(2 g) and CH₂Cl₂ (10 ml) for 150 hr according to the Kuhn method. The precipitates were filtered off, the
filtrate was diluted with H₂O and extracted with CHCl₃. The CHCl₃ layer was washed with H₂O, dried and
evaporated. The residue was then passed through a silica gel column by using hexane-AcOEt (1:1) to
give VI (157 mg) as white powder, mp 109—110°, [α]D +23° (c = 3.3, CHCl₃). IR ν max cm⁻¹: 1755, 1725
(COOR), none of OH. NMR: 5.40 ppm (IH, d, J = 7 Hz, anomeric proton of ester-glycosidic glucose). **Methanalysis of VI** — VI (65 mg) was refluxed with 10% HCl-MeOH (5 ml) for 3 hr, the reaction
mixture was neutralized with Ag₂CO₃, filtered, evaporated and the residue was recrystallized from MeOH
to give an aglycon (VII) (10 mg) as colorless needles, mp 203—206°, IR ν max cm⁻¹: 3500, 3200 (OH), 1725
(COOR). The mother liquor of recrystallization was examined by TLC and GLC and three methylated
sugars were detected and identified as methyl pyranosides of 2,3,4,6-tetra-O-methyl- and 2,3,4,tri-O-methyl-
glucoses and 2,3,4,6, tri-O-methyl-arabinose by comparison with the synthetic samples including 2,3,6,4,
2,4,6- and 3,4,6-tri-O-methyl-α-D-glucopyranosides. VII was methylated with CH₃I to yield colorless
needles (AcOEt), mp 190—192°, which was identified (mixed mp, TLC) with the aglycon of I permethylate.

**LiAIH₄ Reduction of VI** — VI (40 mg) in anhydrous tetrahydrofuran (4 ml) and LiAlH₄ (18 mg) were
refluxed for 3 hr. Excess reagent was decomposed with H₂O, the reaction mixture was evaporated in vacuo
and extracted with CHCl₃. The extracts were dried, evaporated and the residue was separated by chromatography
on silica gel using hexane-AcOEt (1:1) into two fractions, a colorless syrup (VIII), Mass Spectrum m/e:

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Chirva, P.K. Kintya, and V.A. Sonovskii, ibid., 6, 431 (1970) [C. A., 74, 13384 (1974)]; M.M.

11) For general methods, except for the mass spectra of VIII and XX (accelerating potential of 6.1 KV,
imonizing potential of 30 eV, source temperature of 100°), refer to the preceding paper.

Nishimura, R. Higuchi, K. Miyahara, and T. Kawasaki, Meeting of Kyushu Branch, Pharmaceutical
442 (M+, C_{19}H_{38}O_{14})^{+}, 219) (C_{18}H_{37}O_{5})^{+}; NMR: 4.27 ppm (1H, d, J=6.5 Hz, anomic proton), and a white powder (IX), mp 90–97°C, [α]_{D}^{25} = +59° (c=0.54, CHCl_{3}). VIII was acetylated with Ac_{2}O-pyridine to give an acetate, a syrup, [α]_{D}^{20} = −12° (c=1.4, CHCl_{3}), NMR (benzene): 1.74 ppm (3H, s, -OCOCH_{3}), 1.81 (3H, s, -OCOCH_{3}). IX was identified (mixed mp, IR, TLC) with a product from I permethylate on LiAlH_{4} reduction in the same manner as in VI.

Hydrolysis of IV with Emulsin—IV (570 mg) in H_{2}O (25 ml) was incubated with almond emulsin^{13} (80 mg) at 37°C for 2 days and the hydrolysate was shaken with n-BuOH saturated with H_{2}O. The aqueous layer shows only one spot of glucose on PPC and the organic layer was concentrated and chromatographed over silica gel (CH_{2}Cl_{2}-MeOH-H_{2}O (7:3:1, bottom layer)) to provide a prosapogenin (X) as colorless needles (dil. MeOH), mp 211–214°C (decomp.), [α]_{D}^{25} = +34° (c=3.64, MeOH), Δ_{f}^{M/D} (IV-X) = −127°, (IX-I) = −35° ([M]_{0} of methyl b-glucopyranoside: β, −62°; α, +278°). IR ν_{max} cm^{-1}: 3350 (OH), 1755, 1725 (COOR). NMR (CD_{3}N): 4.75 ppm (1H, d, J=7 Hz, anomeric proton of arabinose), 6.00 (1H, d, J=7 Hz, anomeric proton of ester glycosidic glucose). The acid hydrolysate of X was shown by PPC and TLC to contain heterosuglin, glucose and arabinose.

Saponin E (XI)—White powder (precipitated from MeOH with ether), mp 210–214°C (decomp.), [α]_{D}^{25} = +6° (c=1.8, MeOH). IR ν_{max} cm^{-1}: 3350 (OH), 1755, 1740, 1725 (COOR). Anal. Calcd. for C_{33}H_{43}O_{14}·4H_{2}O: C, 55.02; H, 8.18. Found: C, 55.43; H, 8.02. Acid hydrolysis and examination of the product were carried out in the same way as in IV, and heterosuglin, arabinose, xylose and glucose were identified. XI (180 mg) was cleaved as IV with alkali, the product was successively acetylated (Ac_{2}O-pyridine), methylated (CH_{3}ONa) and chromatographed over silica gel (hexane-AcOEt (3:1)) to give colorless needles (Me_{2}CO) (80 mg), mp 140–143°C, [α]_{D}^{25} = +34° (c=1.0, CHCl_{3}). Anal. Calcd. for C_{26}H_{33}O_{12}·2C: 63.45; H, 7.84. Found: C, 63.55; H, 7.99. It was identified by direct comparison with the methylester peracetae of II.

Permethylation (XII) of XI—XI (500 mg) was methylated, worked up, and the product was purified in the same way as in IV to give XII (180 mg) as a white powder (precipitated from CHCl_{3} with hexane), mp 112–113°C, [α]_{D}^{25} = +7° (c=3.8, CHCl_{3}). IR ν_{max} cm^{-1}: 3350, 1755, 1740 (COOR), none of OH. NMR: 5.40 ppm (1H, d, J=7 Hz, anomeric proton of ester glycosidic glucose). Anal. Calcd. for C_{49}H_{57}O_{22}·2C: 62.78; H, 8.92. Found: C, 62.23; H, 8.82.

Methanolation of XII—XII (20 mg) was methanolized as VI to give VII (mixed mp, TLC) and methyl pyranosides of 2,3,4-tri-O-methyl-xylene, 3,4-di-O-methyl-arabinosine, 2,3,4,6-tetra-O-methyl-glucoses (identified on TLC and GLC with comparing by the synthetic samples) including three di-O-methyl-β-L-arabinopyranosides and four tri-O-methyl-a-D-glucopyranosides.

LiAlH_{4} Reduction of XII—XII (120 mg) was reduced with LiAlH_{4} (50 mg) and the products were separated in the same way as in IV to give a syrup (30 mg) and colorless plates (MeOH) (10 mg), mp 220–221°C, [α]_{D}^{25} = +34° (c=1.7, CHCl_{3}). IR ν_{max} cm^{-1}: 3500 (OH), none of C=O. Anal. Calcd. for C_{46}H_{51}O_{21}·C: 68.45; H, 9.74. Found: C, 68.13; H, 9.26. The syrup was identical with VIII on TLC and MS, and the crystals were identified (TLC, IR, mixed mp) with one of the LiAlH_{4} reduction products of II permethylate.

Hydrolysis of XI with Emulsin—The procedure is same as for VI. XI (560 mg) gave glucose (PPC) and a white powder (precipitated from MeOH with ether) (XIII) (390 mg), mp 205–210°C (decomp.), [α]_{D}^{25} = +25° (c=4.55, MeOH), Δ_{f}^{M/D} (XIII–II) = −42°, (XI–XIII) = −169° ([M]_{0} of methyl b-glucopyranoside: β, −62°; α, +278°). IR ν_{max} cm^{-1}: 3350 (OH), 1755, 1740, 1725 (COOR). Anal. Calcd. for C_{46}H_{51}O_{21}·3H_{2}O: C, 57.96; H, 8.46. Found: C, 58.19; H, 8.32. XIII was acid hydrolysate as IV to yield heterosuglin (TLC and mixed mp) arabinose, xylose and glucose (PPC).

Saponin F (XIV)—White powder (precipitated from MeOH with ether), mp 211–214°C (decomp.), [α]_{D}^{25} = −4° (c=2.65, MeOH). IR ν_{max} cm^{-1}: 3350 (OH), 1755, 1740, 1725 (COOR). Anal. Calcd. for C_{45}H_{50}O_{19}·2H_{2}O: C, 53.88; H, 8.19. Found: C, 53.41; H, 8.01. Hydrolyses conducted in the same way as for IV yielded with acid arabinose, and ester glycosidic glucose, and with alkali a compound, colorless needles (MeOH), mp 245–246°C (decomp.), [α]_{D}^{25} = +38° (c=0.72, pyridine), which is identical with III (mixed mp, IR, TLC).

Permethylation (XV) of XIV—XIV (440 mg) was methylated and worked up as IV to give XV (157 mg) as a white powder (precipitated from CHCl_{3} with hexane), mp 110°C, [α]_{D}^{25} = +13° (c=2.77, CHCl_{3}). IR ν_{max} cm^{-1}: 1755, 1740 (COOR), none of OH. NMR: 5.35 ppm (1H, d, J=7 Hz, anomeric proton of ester glycosidic glucose).

Methanolysis of XV—The products obtained and characterized in the same way as in VI and XII were VII and methyl pyranosides of 2,3,4,6-tetra-O-methyl- and 2,3,4-tri-O-methyl-glucoses and 3,4-di-O-methyl-arabinosine.

LiAlH_{4} Reduction of XV—The reduction of XV (55 mg) as VI with LiAlH_{4} (30 mg) afforded a colorless syrup (14 mg) and a white powder (precipitated from MeOH) (27 mg), mp 105–107°C, [α]_{D}^{25} = +31° (c=0.5, CHCl_{3}). IR ν_{max} cm^{-1}: 3500 (OH), none of C=O. The former was identical with VIII on TLC and the latter was identified by direct comparison with the corresponding reduction product of III permethylate.

13) Sigma Chemical Company.
Saponin G (XVI)—A white powder (precipitated from MeOH with ether), mp \( >218^\circ \) (decomp.), \([\alpha]_D^20 +19^\circ \) (c=4.4, MeOH). IR \( \bar{v}_{\text{max}} \text{ cm}^{-1} >3350 \) (OH), 1755, 1740, 1725 (COOR). Anal. Calcd. for \( C_{49}H_{106}O_{37} \), \( \gamma \)H,O: C, 51.40; H, 7.72. Found: C, 51.71; H, 8.01. In a similar manner to IV, XVI was cleaved with acid and alkali respectively to give hederagenin, arabinose, glucose and rhamnose and to yield colorless needles (dil. MeOH) (XVII), mp 225—227° (decomp.), \([\alpha]_D^20 +10^\circ \) (c=3.05, MeOH), \( A[M]_D^2 \) (XVII-III) =139° ([M]_D of methyl L-rhamnose: \( \alpha = -111^\circ \); \( \beta = +170^\circ \)). IR \( \bar{v}_{\text{max}} \text{ cm}^{-1} >3350 \) (OH), 1690 (COOR). Anal. Calcd. for \( C_{36}H_{82}O_{17} \), 3H,O: C, 57.88; H, 8.43. Found: C, 58.37; H, 8.55. On refluxing XVI with 0.1N H_2SO_4 in 50% EtOH for 2 hr, a mixture of unchanged XVI, XIV, XVII, III and hederagenin (TLC) was provided.

Acid Hydrolysis of XVII—Acid hydrolysis of XVII with 2N H_2SO_4 gave hederagenin, arabinose, glucose and rhamnose (TLC and PPC), while partial hydrolysis with 0.1N H_2SO_4 afforded unchanged XVII, III, I and hederagenin (TLC).

Permyethylate (XVIII) of XVII—Methylation of XVII (100 mg) as I by the Hakomori method and purification of the product over silica gel (solvent, AcOEt) gave XVIII as colorless needles (MeOH), mp 211—211.5°, \([\alpha]_D^20 +15^\circ \) (c=1.9, CHCl_3). IR \( \bar{v}_{\text{max}} \text{ cm}^{-1} >1720 \) (COOR), none of OH. NMR: 5.13 ppm (1H, d, \( J=1.5 \) Hz, anomic proton of rhamnose). Mass Spectrum \( m/e >1052 \) (M^+, C_{57}H_{108}O_{37}^+), 219 (C_{19}H_{19}O_4^+), 189 (C_{14}H_{15}O_7^+). Anal. Calcd. for C_{49}H_{106}O_{37}: C, 64.66; H, 9.23. Found: C, 64.99; H, 9.19.

Methanolation of XVIII—XVIII was methanolyzed as VI to give colorless needles (AcOEt), mp 219°, (acetate mp 213°), identical with the aglycon of I permyethylate, and methyl pyranosides of 2,3,4,tri-O-methyl-rhamnose, 3- or 4-O-methyl-arabinose, and 2,3,4,6-tetra-O-methyl-glucose (PPC and GLC). The mixture of methylated sugars was acetylated with Ac_2O—pyridine and the product was shown to contain methyl 2,4-di-O-acetyl-3-O-methyl-arabinopyranoside and not 2,3-di-O-acetyl-4-O-methyl derivative by comparison on GLC with synthetic samples.

Permyethylate (XIX) of XVI—Prepared by the Kuhn method. A white powder (precipitated from CHCl_3 with hexane), mp 113—115°, \([\alpha]_D^20 -13^\circ \) (c=1.7, CHCl_3). IR \( \bar{v}_{\text{max}} \text{ cm}^{-1} >1755, 1740 \) (COOR), none of OH. NMR: 4.99 ppm (1H, s, anomic proton of rhamnose), 5.15 (1H, s, anomic proton of rhamnose), 5.41 (1H, d, \( J=7 \) Hz, anomic proton of ester glycosidic glucose). Anal. Calcd. for C_{49}H_{108}O_{37}: C, 60.70; H, 8.78. Found: C, 60.93; H, 8.74.

Methanolation of XIX—Cleavage and identification of the products were carried out in the same way as in VI. The aglycon was VII and the sugar portion consisted of the third from XVIII and methyl 2,3,4-tri-O-methyl- and 2,3,6-tri-O-methyl-glucopyranosides.

LiAlH_4 Reduction of XIX—XIX was reduced and worked up as VI and the crude product was extracted successively with ether and CHCl_3. The ether extractive was a white powder (precipitated from MeOH), mp 118—120°, \([\alpha]_D^20 +16^\circ \) (c=0.5, CHCl_3). IR \( \bar{v}_{\text{max}} \text{ cm}^{-1} >3500 \) (OH), none of C=O. The CHCl_3 extractive was placed on a silica gel column and eluted with AcOEt—MeOH (50:1) to give a colorless syrup (XX), \([\alpha]_D^20 -34^\circ \) (c=1.25, CHCl_3). MS: \( m/e >616 \) (M^+, C_{58}H_{102}O_{37}^+), 189 (C_{19}H_{15}O_7^+). NMR: 1.30 ppm (3H, d, \( J=7 \) Hz, 6-CH_3 of rhamnose), 4.36 (1H, d, \( J=7 \) Hz, anomic proton of glucose), 4.99 (1H, s, anomic proton of rhamnose). XX was acetylated to yield an acetate as a colorless syrup, \([\alpha]_D^20 -45^\circ \) (c=0.85, CHCl_3). NMR (benzene): 1.48 ppm (3H, d, \( J=7 \) Hz, 6-CH_3 of rhamnose), 1.74 (3H, s, -OCH_3), 1.82 (3H, s, -OCH_3), 5.22 (1H, d, \( J=1.5 \) Hz, anomic proton of rhamnose).

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14) 2,3,4-tri-O-methyl-\( \alpha \)-L-rhamnopyranosyl-(1\( \rightarrow \)4)-2,3,6-tri-O-methyl-\( \beta \)-D-glucopyranosyl-(1\( \rightarrow \)6)-2,3,4-tri-O-methyl-D-sorbitol, a colorless syrup, \([\alpha]_D^20 -33^\circ \) (c=4.2, CHCl_3), (A. Ya. Khorlin, A.G. Venyaminova, and N.K. Kochetkov, Bull. Acad. Sci. USSR, 9, 1530 (1966) [C.A., 66, 63803 (1967)].