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The chemical structures of saponin-A (I) (=chikusetusaponin V), $C_{46}H_{54}O_{29}$, $[\alpha]_D^2 +14.5^\circ$ (MeOH) and saponin-D (V) (=ginensoside Rb$_2$), $C_{46}H_{54}O_{28}$, $[\alpha]_D^2 +15.78^\circ$ (MeOH), which were isolated from *Panax pseudoginseng* subsp. *himalaicus* var. *angustifolius* (araliaceae), were established on the basis of physical data and chemical investigations.

One of the authors, Tanaka, was a member of botanical expedition to Eastern Himalaya organized by the University of Tokyo in 1967 and collected the rhizoma of *Panax pseudoginseng* subsp. *himalaicus* var. *angustifolius* (araliaceae). The morphological similarity of this plant to *Panax japonicum* C.A. Meyer, b) which grows in Japan and has been investigated chemically by us, has urged us to study the constituents of both plants, comparatively. The present paper deals mainly with the study on the structures of two main saponins of *Panax pseudoginseng*, which leads to the assignments of the structure I and V, respectively.

### Chart 1. Extraction and Separation of *Panax pseudoginseng* Constituents

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-BuOH layer</td>
<td>extd. with n-BuOH satrd. with H$_2$O</td>
</tr>
<tr>
<td>H$_2$O layer</td>
<td>extd. with MeOH evpd., added H$_2$O</td>
</tr>
<tr>
<td></td>
<td>Aq. Soln.</td>
</tr>
<tr>
<td>1.</td>
<td>silica gel chromatography solv.: 10—25% MeOH-AcOEt satrd. with H$_2$O</td>
</tr>
<tr>
<td>2.</td>
<td>silicic acid chromatography solv.: CHCl$_3$-MeOH-H$_2$O (65:35:10)</td>
</tr>
</tbody>
</table>

![Diagram of Chart 1](image)

Fig. 1. Thin-Layer Chromatogram of *Panax pseudoginseng* Glycosides on Kiesel gel H

solvent: the lower phase of CHCl$_3$-MeOH-H$_2$O (65:35:10)
color reagent: 10% H$_2$SO$_4$

The dried material which has been collected at Western Bhutan was crushed and extracted twice with hot ether and the residue was extracted with hot methanol. The yield of methanol extract from the dried material was 37.5%. The methanol extract was suspended in water and extracted with n-butanol saturated

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with water. The yield of \( \eta \)-butanol extract from the dried material was 18.1\%. The thin-layer chromatogram (TLC) of butanol extract on silica gel H developed with chloroform-methanol-water (65: 35: 10, the lower phase) revealed the presence of more than eight saponins (Fig. 1). The isolation of each saponin was carried out by chromatography on silica gel using ethyl acetate–methanol (20: 1—3: 1) and the each fraction was purified repeatedly by column chromatography on silica gel eluted with chloroform–methanol–water (65: 35: 10, the lower phase). Finally, the saponin A (\( R_f \) 0.054) and the saponin D (\( R_f \) 0.17) were isolated in pure state.

The saponin A (I), \( C_{48}H_{78}O_{19} \cdot 2H_2O, [\alpha]_D^O +14.5^\circ \) (in methanol) was obtained as a white powder reprecipitated from methanol–ethyl acetate. The infrared (IR) spectrum of I shows the presence of hydroxyl group (3400 cm\(^{-1}\)), ester group (1740 cm\(^{-1}\)) and carboxyl group (1728 cm\(^{-1}\)).

On methylation with diazomethane in methanol, I gave a monomethyl ester (II), \( C_{49}H_{75}O_{19} [\alpha]_D^{112} +192.3^\circ \) (in methanol), which shows the ester absorption band at 1738 cm\(^{-1}\) in IR spectrum and O-methyl signal at 3.65 ppm (3H(s)) in nuclear magnetic resonance (NMR) spectrum. Hydrolysis of I with diluted hydrogen chloride gave oleanolic acid, glucose and glucuronic acid which were identified by direct comparison with the authentic samples by TLC and gas liquid chromatography (GLC), respectively.

Per-O-methylsaponin-A (III), \( C_{50}H_{82}O_{21}, [\alpha]_D^{112} +12.6^\circ \) (in chloroform), prepared from I by repeated methylation by the Kuhn's method,\(^9\) gave, on reduction with lithium aluminium hydride, erythrodiol bioside (IV), \( C_{49}H_{82}O_{19}, [\alpha]_D^{37} +37.4^\circ \) (in chloroform), 2,3,4,6-tetra-O-methyl-glucose and 2,3,4,6-tetra-O-methyl-d-sorbitol. Methanalysis of erythrodiol bioside with \( 2N \) hydrogen chloride in methanol gave erythrodiol, colorless needles, mp 234—236\°, methyl 2,3,4,6-tetra-O-methyl-d-glucoside and methyl 3,4-di-O-methyl-d-glucoside. The O-methylated monosaccharides obtained above were identified with the authentic samples by TLC and GLC as described in the experimental part.

All of the properties of the saponin-A mentioned above strongly suggest that this saponin must be identical with chikusetsusaponin-V, the main saponin of \( P. japonicum \) C.A. MEYER,

\[ \text{Chart 2} \]

4) The optical rotation, \( [\alpha]_D^{37} -74.05^\circ \), reported in the previous paper\(^9\) is erroneous and it was revised in this paper.
the structure of which has been established as I. The identity of both compounds finally proved by the direct comparison.

The saponin-D (V), was obtained by repeated precipitation from ethanol as a white powder, C_{54}H_{92}O_{28}·3H_{2}O, [\alpha]_D^o +15.78° in methanol. The IR spectrum of V shows the presence of hydroxyl (3400 cm\(^{-1}\) broad) and olefinic bonds (1620 cm\(^{-1}\)). On acetylation with acetic anhydride and pyridine for 2 days, V gave a pentadecaacetate (VI), C_{54}H_{122}O_{38}, [\alpha]_D^o -9.72° (in chloroform), which shows no hydroxyl absorption band in the IR spectrum, and a tetradecaacetate (VII), C_{54}H_{120}O_{38}, which shows the hydroxyl absorption band at 3466 cm\(^{-1}\) in the IR spectrum. The formation of two kinds of acetylation products from V suggests that one of the hydroxyl groups of this glycoside is sterically hindered.

The acid hydrolysis of V with hydrogen chloride-dioxane-water gave panaxadiol (VIII) and glucose which were identified by TLC, paper partition chromatography (PPC) and GLC. Furthermore, the genuine aglycone of V was established to be 20S-protopanaxadiol (IX) by oxidative degradation of V according to the Smith’s procedure. Consequently, V was deduced to be a glycoside which consists of 20S-protopanaxadiol and four moles of glucose.

On partial hydrolysis with 50\% acetic acid refluxing for 2 hr, V gave a prosapogenin (X), C_{42}H_{72}O_{18}·1/2H_{2}O, colorless needles from methanol, mp 279°. Based on the physical properties, X was suggested to be the prosapogenin, protopanaxadiol (3)-[\beta-D-glucopyranosyl (1→2)-\beta-D-glucopyranoside], which was obtained from ginsenoside Rb, one of the saponins.

from *Panax ginseng* C.A. Meyer, reported by Shibata, *et al.*, and the identity was established by mixed fusion, TLC and the comparison of IR spectra.

Consequently the two moles of glucose out of four in *V* were confirmed to link to the C₃ hydroxyl group of protopanaxadiol moiety, while the location of the other two moles of glucose was decided as follows. According to the Hakomori's method, *V* was methylated repeatedly, but the resulted O-methyl ether (XI), C₆₇H₁₂₉O₂₅, a white powder from aqueous methanol, [α]₂⁰xml +38.6° (in chloroform), still showed the hydroxyl absorption band at 3451 cm⁻¹. Taking account of the presence of one free hydroxyl group in XI, further experiments were carried out. After hydrogenation of XI the formed dihydro-O-methyl ether (XII) was methanolyzed with 2₇ hydrogen chloride in methanol to afford methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside, methyl 2,3,4-tri-O-methyl-D-glucopyranoside and methyl 3,4,6-tri-O-methyl-D-glucopyranoside. The formation of methyl 2,3,4-tri-O-methyl-D-glucopyranoside from XII suggests that two moles of glucose in *V* form a gentiobiose type linkage. Furthermore, acid hydrolysis of XII with concentrated hydrogen chloride gave dihydro-protopanaxadiol (XIII). Based on these experimental data the structure of saponin-D was suggested to be 20S-protopanaxadiol-(3')-[(β-D-glucopyranosyl(1→2)gln→2gln)β-D-glucopyranoside]-

[(20)-β-D-glucopyranosyl(1→6gln)β-D-glucopyranoside]. To confirm the location of the gentiobiose type sugar moiety, compound XII was oxidized with chromium trioxide in pyridine to give a ketone, (XIV), C₆₇H₁₂₉O₂₅. Compound XIV was treated with 6₆ hydrogen chloride in ethanol to afford an aglycone (XV) which shows the absorption maximum at 265 μν(log ε 3.39) in ultraviolet (UV) spectrum. This result suggested that the hydroxyl group which resisted to the methylation by the Hakomori's method was oxidized to a ketone, and the hydrolysis of this ketone with hydrogen chloride was followed by dehydration and hydride shift to afford the α,β-unsaturated ketone. (see Chart) It seems to be very reasonable that the possible location of the free hydroxyl group in XI may be assigned to C-12.

![Chart 4](image)

The configurations of four glucose are assumed to be all β-form from the coupling constants (6—7 Hz) and chemical shifts (δ: 4.27—4.67) in NMR spectrum of XI. Consequently, the structure of *V* was established to be 20S-protopanaxadiol-(3')-[(β-D-glucopyranosyl(1→2gln)β-D-glucopyranoside]-(20)-[(β-D-glucopyranosyl(1→6gln)β-D-glucopyranoside].

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The identity of saponin-D with ginsenoside-Rb₁, one of the saponins from *Panax ginseng* C.A. Meyer, will be reported in the next paper, so that it is noted that the structure of ginsenoside-Rb₁ has been established by this study. The study on the other saponins are now being in progress.

**Experimental**

All melting points were taken on a Yanagimoto micro melting points apparatus and uncorrected. IR absorption spectra were obtained with a Hitachi Model 215. NMR spectra were measured with a Hitachi Model R-20 High Resolution NMR spectrometer and a Hitachi Model R-22 High Resolution NMR spectrometer with tetramethylsilane as an internal standard. The chemical shifts are reported in δ and the solvents used are indicated. Gas chromatography was used with a Hitachi Model K-53 with hydrogen flame ionization detector. The Rf values were determined by thin-layer chromatography on silica gel H using solvent A: chloroform-methanol-water (65: 35: 10 the lower phase); solvent B: phenol saturated with water; solvent C: AcOEt; solvent D: benzene-acetone (2: 1); solvent E: benzene-acetone (3: 1); solvent F: benzene-acetone (4: 1); solvent G: hexane-acetone (4: 3); solvent H: hexane-acetone (2: 1), and spots were detected by spraying 10% H₂SO₄ followed by heating.

**Material**—The material, dried rhizoma of *Panax pseudoginseng* subsp. *himalicus* var. *angustifolia* (Araliaceae), was collected at Khosa (1800 m), Western Bhutan May 10, 1967 by Tanaka, a member of Botanical Expedition of Eastern Himalaya organized by the University of Tokyo (Chief Prof. H. Harata).

**Extraction**—Two hundreds g of crushed material was extracted twice with ether. The residual material was extracted repeatedly with 1 liter of hot methanol. After evaporation of the solvent under a reduced pressure, 75 g of the syrup brown residue was obtained (yield from the dried material 37.5%) and dissolved in water. The aqueous solution was extracted with n-BuOH saturated with water. The n-BuOH layer was concentrated in vacuo to afford 36.3 g of powder (yield from the dried material 18.1%). The n-BuOH soluble fraction was detected by TLC (solvent A) and revealed to contain more than eight saponins (Fig. 1).

**Isolation of Glycosides**—The crude glycoside fraction was submitted to column chromatography on silica gel with ethyl acetate saturated with water and eluted with the same solvent containing 5–25% MeOH. The crude saponin-A (Rf 0.054), -B (Rf 0.1), -C (Rf 0.13) and -D (Rf 0.17) were obtained. The crude saponin-A and -D were purified by chromatography on silica gel using CHCl₃-MeOH-H₂O (65: 35: 10 the lower phase) and chromatographically pure saponin-A (14.5 g) and saponin-D (2.1 g) were obtained.

**Saponin-A (I)**—The pure saponin-A (I) was obtained as a white powder by repeated precipitation from MeOH-AcOEt, (mp 241°), [α]D²⁰ +14.5° (c=0.76, MeOH). Anal. Calcd. for C₂₅H₃₅O₁₂: 2H₂O: C, 57.06; H, 8.02. Found: C, 57.32; H, 7.97. 1R νmax cm⁻¹: 5400 (OH broad), 1740 (COOR), 1728 (COOH).

**Hydrolysis of Saponin-A (I)**—I (50 mg) was hydrolyzed with 5 ml of 2N HCl in dioxane-H₂O (1: 1, v/v) with refluxing on a water bath for 4 hr. The reaction mixture was treated as described in the previous paper and oleancolic acid, glucose and glucuronic acid were identified.

**Methylation of I with CH₃_Na (Formation of Chikusetsusaponin V Monomethyl Ester (II))**—I (130 mg) was dissolved in MeOH and excess CH₃_Na in ether was added and allowed to stand for 4 hr. The reaction mixture was treated as described in the previous paper to afford a monomethyl ester, a white powder from EtOH-AcOEt, [α]D²⁰ +192.3° (c=0.56, MeOH). The product was identified with chikusetsusaponin V monomethyl ester by TLC and by comparison of IR spectra.

**Per-O-methylation of I (Formation of Per-O-methylchikusetsusaponin V (III))**—According to the previous paper, I (523 mg) was methylated. The product was obtained by chromatography on silica gel using benzene-acetone (4: 1) as a solvent followed by reprecipitation from dilute MeOH, affording per-O-methylsaponin-A as a white powder (278 mg), C₃₂H₆₅O₁₆: [α]D²⁰ +12.6° (c=0.63, CHCl₃). Anal. Calcd. for C₃₂H₆₅O₁₆: C, 63.74; H, 8.88. Found: C, 63.52; H, 8.77. 1R νmax cm⁻¹: 3550 (OH; nil), 1757 (COOR), NMR (in CDCl₃): δ: 0.78–1.12 (3H (s) x 7, CH₃), 3.34–3.78 (3H (s) x 11, OCH₃), 4.40 (1H (d), J=7 Hz, anomer H), 4.55 (1H (d), J=7 Hz, anomer H), 5.3–5.45 (2H (broad), γC=C=C-H, anomer H). III was identified with per-O-methylchikusetsusaponin V by comparing TLC (solvent H: Rf 0.57; solvent G: Rf 0.77) and IR spectra.

**Reductive Cleavage of Per-O-methylchikusetsusaponin-A (III) with LiAlH₄**—Per-O-methylsaponin-A (200 mg) in absolute ether was reduced with LiAlH₄ (70 mg) under refluxing for 2 hr and the reaction mixture was treated by the same method as described in per-O-methylchikusetsusaponin V. The ether soluble fraction was purified by reprecipitation from dilute MeOH, affording the hexa-O-methylerythroidial biside (IV) as a white powder, [α]D²⁰ +37.4° (c=0.80, CHCl₃). Anal. Calcd. for C₉₇H₁₆O₁₄: C, 67.76; H, 9.76. Found: C, 67.58; H, 9.70. NMR (in CDCl₃): δ: 0.82–1.10 (3H (s) x 7, CH₃), 3.32–3.60 (3H (s) x 6, OCH₃), 4.35 (1H (d), J=7 Hz, anomer H), 4.70 (1H (d), J=7 Hz, anomer H), 5.22 (1H (m), γC=C=C-H. IV was identified with hexa-O-methylerythroidial biside derived from per-O-methylchikusetsusaponin V by comparing IR and NMR spectra.

The chloroform soluble fraction was examined by TLC (solvent D) to reveal the presence of two methylated monosaccharides, which were identified with the authentic samples of 2,3,4,6-tetra-O-methylglucose
and 2,3,4,6-tetra-O-methylsorbitol by TLC (solvent D) and GLC (column 3% SE-30 on chromosorb W 3 mm x 1 m, column temp. 150°, N$_2$ flow 0.65 kg/cm$^2$. 2,3,4-Tetra-O-methylglucose: TLC $R_f$ 0.22, $t_k$ (min) 3.4 (TMS derivatives). 2,3,4-Tetra-O-methylerythritol: TLC $R_f$ 0.05, $t_k$ (min) 7.0 (TMS derivatives).

**Methanolation of Hexa-O-methyleneethydiol Biodide (IV)**—Compound IV was refluxed with methanolic 2n HCl for 2 hr, the solution treated as described in the previous paper. Erythritol, methyl 2,3,4,6-tetra-O-methyl-$eta$-D-glucopyranoside and methyl 3,4-di-O-methyl-$eta$-D-glucopyranoside were identified by comparing with the authentic samples. Erythritol: colorless needles from acetone, mp 234—236°. Methyl 2,3,4,6-tetra-O-methyl-$eta$-D-glucopyranoside: $R_f$ 0.34, 0.46 (solvent C), $t_k$ (min) 4.0, 4.8 (column 3% SE-30, column temp. 110°, N$_2$ flow 1.0 kg/cm$^2$. Methyl 3,4-di-O-methyl-$eta$-D-glucopyranoside: $R_f$ 0.10 (solvent C), $t_k$ (min) 12.5.

**Saponin-D (V)**—The pure saponin-D (V) was obtained as a white powder by repeated precipitation from EtOH, (mp 189°), $[a]_D^2$ +15.78° ($c$=1.13, MeOH). Anal. Calcd. for C$_{38}$H$_{52}$O$_{27}$,3H$_2$O: C, 55.75; H, 8.49. Found: C, 55.89; H, 8.21. IR $v_{max}$ cm$^{-1}$: 3400 (OH), 1620 ($\delta$CaC=O).

**Acetylation of V with Acetic Anhydride and Pyridine**—Compound V (145 mg) was acetylated with acetic anhydride (3 ml) and pyridine (3 ml) for 48 hr at room temperature. The reaction mixture was worked up as usual and the products (180 mg) were purified by chromatography on silica gel eluted with benzene-acetone (5:1) to give two kinds of acetates (VI and VII). Pentadecacacetate (VI): A white powder from MeOH–H$_2$O (mp 135°), $[a]_D^2$ -9.72° ($c$=0.72, CHCl$_3$). Anal. Calcd. for C$_{46}$H$_{72}$O$_{28}$: C, 57.66; H, 7.08. Found: C, 58.12; H, 7.16. IR $v_{max}$ cm$^{-1}$: OH (nil), 1750 ($\delta$OCOC$_3$H$_7$), 1230 (C-O-C). Tetradecacacetate (VII): A white powder from MeOH–H$_2$O (mp 132°). Anal. Calcd. for C$_{38}$H$_{56}$O$_{27}$: C, 57.99; H, 7.07. Found: C, 58.09; H, 7.23. IR $v_{max}$ cm$^{-1}$: 3466 (OH), 1753 ($\delta$OCOC$_3$H$_7$), 1230 (C-O-C).

**Hydrolysis of V with 2n HCl in Aqueous Dioxane**—Compound V (30 mg) was hydrolyzed with 2n HCl in dioxane–H$_2$O (1:7) (3 ml) by refluxing on the water bath for 4 hr. After cooling the formed precipitate was filtered and dried. The product was identified to be panaxadiol (VII) by comparing with the authentic sample by TLC. $R_f$ 0.69 (solvent C), 0.29 (solvent E).

The filtrate was neutralized with Ag$_2$CO$_3$ and evaporated in vacuo. The residue was identified to be glucose by comparing with a authentic sample by PFC, TLC and GLC. PFC paper: Toyko-Roshi No. 51, solvent: BuOH–AcOH–H$_2$O (4:1:5 the upper layer). $R_f$ 0.16, $R_f$ 0.27 (solvent B) GLC column: SE-52, 3 mm x 2 m, column temperature: 175°, carrier gas, N$_2$, 18 ml/min, sample: TMS derivatives. $t_k$ (min) 11.6 ($\alpha$-glucose), 16.7 ($\beta$-glucose).

**Oxidative Degradation of V with NaIO$_4$**—To the solution of V (500 mg) in MeOH–EtOH–H$_2$O (20 ml–33.3 ml–100 ml) NaIO$_4$ (1.69 g) was added. The solution was stirred for 120 hr at 2°. The formed precipitate was filtered off and the filtrate was added water (50 ml) and concentrated in vacuo to 150 ml. The solution was extracted with BuOH saturated with MeOH and the residue was dissolved in EtOH (2.5 ml)–MeOH (5 ml). To this solution a solution of KOH (1.25 g) in H$_2$O (17.5 ml) was added and the mixture was heated at 95° for 4 hr under N$_2$ gas flow. The reaction mixture was neutralized with 2n H$_2$SO$_4$ and extracted with ether. The ether solution was washed with water and dried over Na$_2$SO$_4$. The ether solution was evaporated and the residue was purified by chromatography on silica gel eluted with benzene-acetone (3:1) to afford colorless needles (14.2 mg) from benzene, mp 199°, which was identified to be 20-protopanaxadiol (IX) by comparing IR spectra, TLC and GLC. TLC $R_f$ 0.20 (solvent F, 20R-protopanaxadiol $R_f$ 0.23). GLC column: 1.5% SE-30 on chromosorb W DMCS, 3 mm x 2 m, column temperature: 280°, carrier gas: N$_2$ flow 1.5 kg/cm$^2$, sample: TMS derivatives. $t_k$ (min) 5.2 (20S-protopanaxadiol).

**Partial Hydrolysis of Saponin-D (V)**—Compound V (200 mg) was heated with 50% AcOH for 2 hr on the water bath. The formed precipitate was filtered, washed with water and dried. The product was recrystallized from MeOH to give colorless needles, mp 279°. IR $v_{max}$ cm$^{-1}$: 3350 (OH), 1620 (C=O). Anal. Calcd. for C$_{30}$H$_{44}$O$_{11}$,1/2H$_2$O: C, 63.53; H, 9.04. Found: C, 63.54; H, 9.04. This product was identified to be prosapogenin of ginsenoside Rh$_b$ by comparing TLC and IR spectra and by mixed fusion.

**Methylation of V by the Hakomori’s Method**—According to the Hakomori’s method, NaH (500 mg) was warmed with dimethylsulfoxide (DMSO 25 ml) at 70° for 1 hr with stirring under N$_2$ gas flow. To this reagent compound V (510 mg) in DMSO (5 ml) was added and the mixture was kept at 70° for 10 min with stirring under N$_2$ gas flow. CH$_3$I (5 ml) was added and the reaction mixture was allowed to stand at room temperature for 6 hr with stirring. After dilution with water, the reaction mixture was extracted with CHCl$_3$ and the organic layer was washed with water, dried and concentrated to dryness. The residue was chromatographed on silica gel eluted with benzene-acetone (4:1) to give tetradeca-O-methyl ether of V (XI, 239 mg), a white powder, (mp 87°), $[a]_D^2$ +38.60° ($c$=0.57, CHCl$_3$), IR $v_{max}$ cm$^{-1}$: 3451 (OH), IR $v_{max}$ cm$^{-1}$: 3436 (OH). Anal. Calcd. for C$_{46}$H$_{72}$O$_{27}$, C, 56.53; H, 8.26. Found: C, 62.22; H, 9.04. NMR (in CDCl$_3$) $\delta$: 0.8—1.0 (3H (d) x 5, CH$_3$), 1.3 (3H (s), CH$_3$), 1.6, 1.7 (3H (s) x 2, CH$_3$), 3.33—3.67 (3H (s) x 14, OCH$_3$), 4.27 (1H (d), $J$=6 Hz, anomer H), 4.34 (1H (d), $J$=7 Hz, anomer H), 4.46 (1H (d), $J$=7 Hz, anomer H), 4.67 (1H (d), $J$=7 Hz, anomer H), 5.12 (1H (broad)). $\gamma$C=C=CH$_2$.

**Catalytic Reduction of XI and Hydrolysis of Dihydrosaponin-D Tetradeca-O-methyl Ether (XII)**—Compound XI (300 mg) was catalytically reduced on PtO$_2$ (100 mg) in EtOH (20 ml) and the reaction mixture
was filtered. The filtrate was evaporated in vacuo and the residue was preparatively purified by TLC (solvent H) to give dihydrosaponin-D tetradeca-O-methyl ether (XII). NMR (in CDCl₃) δ: 0.8–1.0 (3H (s) × 7, CH₃), 1.3 (3H (s), CH₃).

Compound XII (26.8 mg) was hydrolyzed with methanolic 2N HCl refluxing for 4 hr. The reaction mixture was neutralized with Ag₂CO₃ and evaporated to dryness. The residue was examined by TLC and GLC. TLC (solvent G): Rf 0.80, 0.88 (α- and β-methyl 2,3,4,6-tetra-O-methyl-d-glucopyranoside); 0.49, 0.61 (α- and β-methyl 2,3,4-tri-O-methyl-d-glucopyranoside); 0.54 (α- and β-methyl 3,4,6-tri-O-methyl-d-glucopyranoside).

GLC (column: 5% NPGS on microsorb W; column temperature: 170°; carrier gas: N₂ 0.7 kg/cm²) tₚ (min) 5.7, 4.4 (α-and β-methyl 2,3,4,6-tetra-O-methyl-d-glucopyranoside); 8.5, 11.2 (α- and β-methyl 2,3,4-tri-O-methyl-d-glucopyranoside); 9.6, 10.8 (trace) (α- and β-methyl 3,4,6-tri-O-methyl-d-glucopyranoside).

Furthermore, compound XII (20 mg) was hydrolyzed with conc. HCl (1 ml) for 8 hr at room temperature. The reaction mixture was diluted with water and extracted with ether. The ether extract was examined by TLC (solvent D) and the product was identified with an authentic sample of dihydroprotoxpanaxadiol (XIII, Rf 0.32).

Chromium Trioxide Oxidation of XII —To a solution of compound XII (278 mg) in pyridine (5 ml) was added the solution of CrO₃ (500 mg) in pyridine (10 ml) dropwise with stirring and the mixture was kept at room temperature overnight. The reaction mixture was poured into water and extracted with CHCl₃. The CHCl₃ solution was washed with water and dried over anhyd. Na₂SO₄. Evaporation of the solvent in vacuo gave white powder which was purified by recrystallization from aqueous ethanol. Compound XIV was obtained as a white powder, (mp 73°), IR νmax cm⁻¹: OH (nil), 1711 (six membered ketone). Anal. Calcd. for C₄₈H₇₀O₂₃: C, 62.53; H, 9.26. Found: C, 62.83; H, 9.13.

Degradation of XIV with Methanolic 7% HCl —Compound XIV (150 mg) was refluxed with methanolic 7% HCl for 4 hr and the reaction mixture was neutralized with Ag₂CO₃ and evaporated to dryness. The residue was purified by chromatography on silica gel eluted with benzene-acetone (8:1–6:1) to give a trace of aglycone (XV). TLC (solvent F) Rf 0.22, UV λmax (log ε): 265 (3.39); λmax (log ε): 257 (3.42).

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