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Studies on the Constituents of Palmae Plants. II.[1] The Constituents of *Rhapis exelsa* HENRY[2] and *R. humilis* BL.[3]

YASUAKI HIRAI, SHUICHI SANADA, YOSHITERU IDA and JUNZO SHOJI*

School of Pharmaceutical Sciences, Showa University, Hatanodai, Shinagawa-ku, Tokyo 142, Japan

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Further studies have been done on the constituents of the stems, underground parts and leaves of two Palmae plants, *Rhapis exelsa* HENRY and *R. humilis* BL. We isolated and identified dioscin, Pb, deltonin, methyl proto-dioscin, methyl proto-Pb and methyl proto-deltonin from the stems, dioscin, methyl proto-dioscin and methyl proto-Pb from the underground parts, and saponaretin (=isovitexin), methyl proto-dioscin, methyl proto-Pb and methyl proto-rhapissaponin from the leaves of *R. exelsa*. On the other hand, we isolated and identified prosapogenin A of dioscin, dioscin, deltonin, methyl proto-prosapogenin A of dioscin, methyl proto-dioscin and methyl proto-deltonin from the stems, dioscin, methyl proto-prosapogenin A of dioscin, methyl proto-dioscin and methyl proto-Pb from the underground parts, and saponaretin, vitexin, isoorientin, methyl proto-prosapogenin A of dioscin, methyl proto-dioscin and methyl proto-Pb from the leaves of *R. humilis*. Methyl proto-rhapissaponin is a new furostanol saponin and its structure has been established to be 26-*O*-*β*-D-glucopyranosyl 22-*O*-methyl-25(*R*)-furost-5-en-3*β*,22,26-triol 3-*O*-[*β*-D-glucopyranosyl(1→4)-*α*-L-rhamnopyranosyl(1→4)-*α*-L-rhamnopyranosyl(1→4)]-[*α*-L-rhamnopyranosyl(1→2)]-*β*-D-glucopyranoside. This is the second report of the isolation of steroidal saponins from Palmae plants, and the results are interesting from the standpoint of chemotaxonomy.

Keywords——*Rhapis exelsa*; *Rhapis humilis*; Palmae; steroidal saponin; furostanol oligoside; diosgenin; flavone glycoside; flavone *C*-glycoside; methyl proto-rhapissaponin

In the preceding paper[1] we reported the isolation and structure elucidation of four steroidal glycosides and two flavonoids from the leaves, stems and underground parts of *Trachycarpus fortunei* (HOOK.) H. WENDL. That was the first report of the isolation of the steroidal saponins from Palmae plants and led us to undertake a series of chemotaxonomical studies on plants of the Palmae family. The present paper is mainly concerned with the isolation and structure elucidation of seven steroidal glycosides and one flavonoidal glycoside from *Rhapis exelsa* HENRY and seven steroidal glycosides and three flavonoidal glycosides from *R. humilis* BL.

The fresh stems, underground parts and leaves of *R. exelsa* and *R. humilis* were separately chopped and extracted with methanol at room temperature. The methanol extracts were treated by the method described in the experimental section, and six compounds, tentatively named Est_1, Est_2, $Est_{3\text{-}a}$, $Est_{3\text{-}b}$, $Est_{4\text{-}a}$ and $Est_{4\text{-}b}$, were isolated from the stems, three compounds named Eu_1, Eu_2 and Eu_3 from the underground parts, and four compounds named El_1, El_2, El_3 and El_4 from the leaves of *R. exelsa*. On the other hand, six compounds named Hst_1, Hst_2, Hst_3, Hst_4, Hst_5 and Hst_6 were isolated from the stems, four compounds named Hu_1, Hu_2, Hu_3 and Hu_4 from the underground parts, and six compounds named Hl_1, Hl_2, Hl_3, Hl_4, Hl_5 and Hl_6 from the leaves of *R. humilis*.

Among the constituents of the stems of *R. exelsa*, Est_1 was positive in the Liebermann–

Burchard reaction and it showed a strong absorption due to hydroxyl groups and characteristic absorption bands of a 25(*R*)-spiroketal moiety in the infrared (IR) spectrum.[4] On hydrolysis with 2 N hydrochloric acid in 50% dioxane, Est_1 gave diosgenin, glucose and rhamnose. The chemical and physical properties of Est_1 appeared to be identical with those of dioscin,[1] based on comparisons of the thin-layer chromatographic (TLC) behavior, mp and the IR and ^{13}C-nuclear magnetic resonance (NMR) spectra.

Est_2 was positive in the Liebermann–Burchard reaction and in the Ehrlich reaction.[5] The IR spectrum of Est_2 showed strong absorption due to hydroxyl groups, while the ^{13}C-NMR spectrum of Est_2 revealed the presence of an *O*-methyl group (δ 47.4) and characteristic signals of a furostanol moiety.[6] On enzymatic hydrolysis with almond emulsin, Est_2 afforded Est_1 (dioscin) and glucose. Accordingly, Est_2 was suggested to be methyl proto-dioscin,[1] and this was confirmed by comparisons of the IR and ^{13}C-NMR spectra with those of an authentic sample.

Fraction Est_3 showed one spot on TLC. The IR spectrum of Fr. Est_3 showed strong absorption bands due to hydroxyl and 25(*R*)-spiroketal groups, while the ^{13}C-NMR spectrum indicated that Fr. Est_3 might be a mixture of two spirostanol glycosides. In order to separate the two glycosides, Fr. Est_3 was methylated by Hakomori's method[7] to afford a mixture of per-*O*-methyl ethers, which were isolated by column chromatography on Sephadex LH-20 and on silica gel to afford per-*O*-methyl ethers of $Est_{3\text{-a}}$ and $Est_{3\text{-b}}$. Each of the per-*O*-methyl ether of $Est_{3\text{-a}}$ and $Est_{3\text{-b}}$ was methanolized to afford diosgenin, per-*O*-methylrhamnopyranose, per-*O*-methylglucopyranose and methyl 3,6-di-*O*-methylglucopyranoside from the former, and diosgenin, per-*O*-methylrhamnopyranose, methyl 2,3-di-*O*-methylrhamnopyranoside and methyl 3,6-di-*O*-methylglucopyranoside from the latter. Based on the chemical data and comparative analysis of the ^{13}C-NMR spectra, the per-*O*-methyl ethers of $Est_{3\text{-a}}$ and $Est_{3\text{-b}}$ were suggested to be per-*O*-methyl ethers of deltonin[8] and Pb,[1] and this was confirmed by mixed fusion tests and by comparing the ^1H-NMR spectra with those of authentic samples. Accordingly, Fr. Est_3 was concluded to consist of deltonin and Pb. Further confirmation was obtained by comparing the ^{13}C-NMR spectra with those of individual authentic samples.

Fraction Est_4 showed one spot on TLC and it was positive in the Liebermann–Burchard reaction and in the Ehrlich reaction. The ^{13}C-NMR spectrum indicated that Fr. Est_4 might be a mixture of two furostanol glycosides, which were successively separated by applying triphenylmethylation.[9] The chloroform-soluble triphenylmethyl derivative afforded $Est_{4\text{-a}}$ on treatment with 50% acetic acid, while the water-soluble triphenylmethyl derivative afforded $Est_{4\text{-b}}$ on similar treatment. On enzymatic hydrolysis with almond emulsin $Est_{4\text{-a}}$ gave glucose and deltonin, while $Est_{4\text{-b}}$ afforded glucose and Pb. Based on the chemical and physical properties, $Est_{4\text{-a}}$ and $Est_{4\text{-b}}$ were suggested to be methyl proto-deltonin[8] and methyl proto-Pb,[1] and these assignments were confirmed by comparisons of the IR and ^{13}C-NMR spectra with those of authentic samples. Thus, it was concluded that Fr. Est_4 is a mixture of methyl proto-Pb (36%) and methyl proto-deltonin (64%).

As regards the constituents of the underground parts of *R. exelsa*, Eu_1, Eu_2 and Eu_3 were identified as dioscin, methyl proto-dioscin and methyl proto-Pb, respectively. Furthermore, among the constituents of the leaves of *R. exelsa*, El_1 and El_2 were identified as methyl proto-dioscin and methyl proto-Pb, respectively.

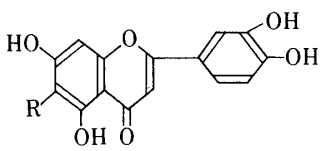
El_3, $C_{64}H_{106}O_{31}$, was positive in the Liebermann–Burchard reaction and in the Ehrlich reaction. The IR spectrum of El_3 showed strong absorption due to hydroxyl groups. The ^{13}C-NMR spectrum of El_3 showed characteristic furostanol carbon signals and an *O*-methyl carbon signal (δ 47.4 ppm). On enzymatic hydrolysis with almond emulsin, El_3 afforded D-glucose and a prosapogenin of El_3 (pro-El_3), $C_{57}H_{92}O_{25}$, which showed characteristic absorption bands due to 25(*R*)-spiroketal in the IR spectrum and five anomeric carbon signals

at δ 100.5, 102.1, 102.3, 102.7 and 106.5 ppm in the ^{13}C-NMR spectrum. Consequently, pro-El_3 was suggested to be a 25(*R*)-spirostanol pentaoside. On acidic hydrolysis, pro-El_3 gave diosgenin, glucose and rhamnose, and the ^{13}C-NMR signals at δ 18.3, 18.6 and 18.9 ppm indicated the presence of three rhamnose moieties in pro-El_3. Methylation of pro-El_3 by Hakomori's method afforded a per-*O*-methyl derivative, which was partially methanolyzed with methanolic 0.5 N hydrochloric acid, and the reaction mixture was further methylated by Hakomori's method. The products were isolated by column chromatography to afford four compounds, tentatively named compounds A, B, C and D. Compound A was identified as 3-*O*-methyldiosgenin and the ^{1}H-NMR spectra of compounds B, C and D showed one anomeric proton signal at δ 4.32 ppm, two anomeric proton signals at δ 4.35 and 5.24 ppm, and four anomeric proton signals at δ 4.35, 4.62, 5.02 and 5.22 ppm, respectively. On methanolysis with methanolic 1 N hydrochloric acid, diosgenin and per-*O*-methylglucopyranose were obtained from compound B, diosgenin, per-*O*-methylrhamnopyranose and methyl 3,4,6-tri-*O*-methylglucopyranoside from compound C, and diosgenin, per-*O*-methylglucopyranose, methyl 2,3-di-*O*-methylrhamnopyranoside and methyl 2,3,6-tri-*O*-methylglucopyranoside from compound D. Accordingly, compounds B, C and D were deduced to be per-*O*-methylates of diosgenin 3-*O*-glucopyranoside, diosgenin 3-*O*-rhamnopyranosyl(1→2)-glucopyranoside and diosgenin 3-*O*-glucopyranosyl(1→4)-rhamnopyranosyl(1→4)-rhamnopyranosyl(1→4)-glucopyranoside, respectively. Consequently, the structure of pro-El_3 was revealed to be diosgenin 3-*O*-[glucopyranosyl(1→4)-rhamnopyranosyl-(1→4)-rhamnopyranosyl(1→4)][rhamnopyranosyl(1→2)]glucopyranoside. The coupling constants of anomeric carbon signals of pro-El_3 in the ^{13}C-NMR spectrum revealed the configurations of the two glucoses to be all β ($J_{C_1-H_1}$ = 153 and 155 Hz) and those of the three rhamnoses to be all α ($J_{C_1-H_1}$ = 169 Hz each). Finally, the structures of pro-El_3 and El_3 were concluded to be diosgenin 3-*O*-[β-D-glucopyranosyl(1→4)-α-L-rhamnopyranosyl(1→4)-α-L-rhamnopyranosyl(1→4)][α-L-rhamnopyranosyl(1→2)]-β-D-glucopyranoside and 26-*O*-β-D-glucopyranosyl 22-*O*-methyl-25(*R*)-furost-5-en-3β,22,26-triol 3-*O*-[β-D-glucopyranosyl-(1→4)-α-L-rhamnopyranosyl(1→4)-α-L-rhamnopyranosyl(1→4)][α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside, respectively. El_3 and pro-El_3 described above are new steroidal oligosides and we propose the names methyl proto-rhapissaponin for the former and rhapissaponin for the latter.

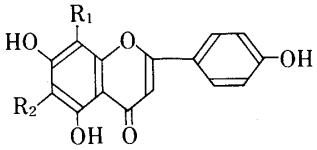
El_4, pale yellow plates, was positive with ferric chloride reagent and with magnesium–hydrochloric acid reagent. Based on the IR, ultraviolet (UV) and ^{13}C-NMR spectra, El_4 was considered to be a flavonoidal glycoside. In the ^{13}C-NMR spectrum of El_4, the chemical shift (δ 79.1 ppm) of the anomeric carbon signal suggested that El_4 is a *C*-glycoside, because the anomeric carbon signal of *C*-glycoside was seen at considerably higher field than that of *O*-glycoside. The ^{1}H-NMR spectrum of El_4 showed signals at δ 6.78 ppm (1H, s, C_3–H), 6.95 and 7.95 ppm (2H each, d, J = 9 Hz, $C_{2',3',5',6'}$–H) and 6.52 ppm (1H, s, C_8–H). Based on the NMR analyses, El_4 was elucidated to be saponaretin (=isovitexin),[10] and this was confirmed by comparisons of the IR spectrum and the TLC behavior with those of an authentic sample.

Among the constituents of the stems of *R. humilis*, Hst_1 was suggested to be a 25(*R*)-spirostanol oligoside on the basis of color reactions, and the IR and ^{1}H-NMR spectra. On acidic hydrolysis, Hst_1 gave diosgenin, glucose and rhamnose. Hst_1 appeared to be identical with prosapogenin A of dioscin,[11] on the basis of comparisons of the IR and ^{13}C-NMR spectra.

Hst_4, $C_{46}H_{76}O_{18}$, gave positive Liebermann–Burchard and Ehrlich reactions, and the ^{13}C-NMR spectrum showed characteristic furostanol carbon signals. On enzymatic hydrolysis with almond emulsin, Hst_4 afforded glucose and a prosapogenin, which was identified as Hst_1 (prosapogenin A of dioscin) by comparisons of the IR and ^{13}C-NMR spectra. The structure of Hst_4 was concluded to be 26-*O*-β-D-glucopyranosyl 22-*O*-methyl-25(*R*)-furost-5-

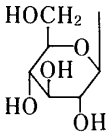


isoorientin (Hl_6) : R=I



saponaretin (El_4, Hl_4) : R_1=H, R_2=I
vitexin (Hl_5) : R_1=I, R_2=H

I :



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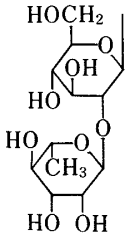

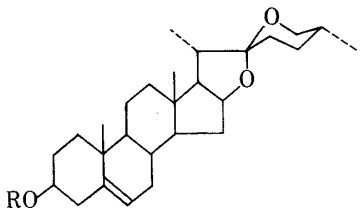

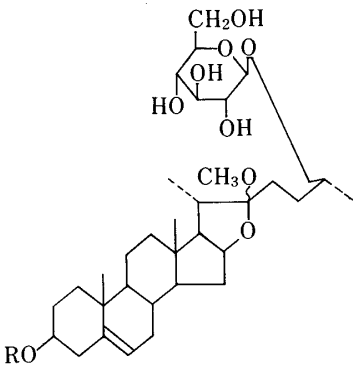

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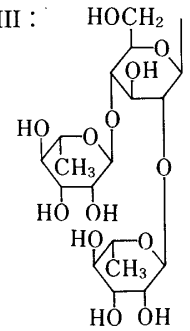
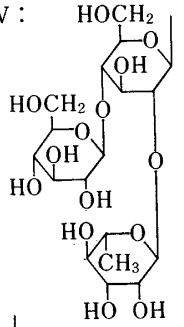
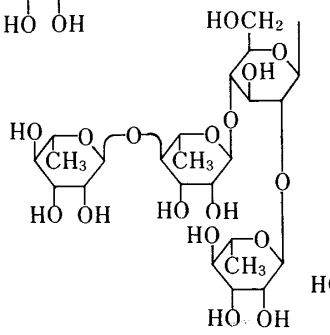


IV :

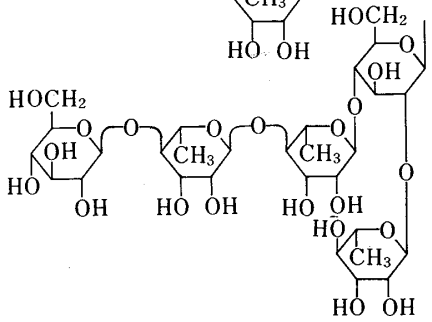


prosapogenin A of dioscin (Hst_1)	: R=II	methyl proto-prosapogenin A of dioscin (Hst_4, Hl_1, Hu_2)	: R=II
dioscin (Est_1, Eu_1, Hst_2, Hu_1)	: R=III	methyl proto-dioscin (Est_2, El_1, Eu_2, Hl_2, Hst_5, Hu_3)	: R=III
deltonin ($Est_{3\text{-}a}$, Hst_3)	: R=IV	methyl proto-deltonin ($Est_{4\text{-}a}$, Hst_6)	: R=IV
Pb ($Est_{3\text{-}b}$)	: R=V	methyl proto-Pb (El_2, $Est_{4\text{-}b}$, Eu_3, Hl_3, Hu_4)	: R=V
rhapissaponin	: R=VI	methyl proto-rhapissaponin (El_3)	: R=VI

V :



VI :



Chart

en-3β,22,26-triol 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranoside by comparisons of the IR and ^{13}C-NMR spectra with those of an authentic sample.[5,8,12] Furthermore, Hst_2, Hst_3, Hst_5 and Hst_6 were similarly identified as dioscin, deltonin, methyl proto-dioscin and methyl proto-deltonin, respectively.

The constituents of the underground parts of *R. humilis*, Hu_1, Hu_2, Hu_3 and Hu_4 were identified by the methods described above as dioscin, methyl proto-prosapogenin A of dioscin, methyl proto-dioscin and methyl proto-Pb, respectively. Furthermore, the constituents of the leaves of *R. humilis*, Hl_1, Hl_2, Hl_3 and Hl_4, were similarly identified as methyl proto-prosapogenin A of dioscin, methyl proto-dioscin, methyl proto-Pb and saponaretin (=isovitexin), respectively.

Hl_5 and Hl_6 were pale yellow needles, positive with ferric chloride reagent and with magnesium hydrochloric acid reagent. Based on the IR, UV and ^{13}C-NMR spectra, Hl_5 and Hl_6 were suggested to be flavonoidal glycosides. In the ^{13}C-NMR spectra of Hl_5 and Hl_6, the chemical shifts (δ 78.7 and 79.0 ppm) of the anomeric carbon signals suggested that Hl_5 and Hl_6 are *C*-glycosides as in the case of El_4 (saponaretin) described above. The ^{1}H-NMR spectrum of Hl_5 showed signals at δ 6.78 ppm (1H, s, C_3–H), 6.90, 8.03 ppm (2H each, d, J= 9 Hz, $C_{2',3',5',6'}$–H) and 6.28 ppm (1H, s, C_6–H), while that of Hl_6 showed signals at δ 6.68 ppm (1H, s, C_3–H), 6.89 ppm (1H, d, J=9 Hz, $C_{5'}$–H), 7.39 ppm (1H, d, J=2 Hz, $C_{2'}$–H), 7.42 ppm (1H, dd, J_1=2 Hz, J_2=9 Hz, $C_{6'}$–H) and 6.49 ppm (1H, s, C_8–H). Based on the NMR analysis, Hl_5 and Hl_6 were elucidated to be vitexin[13] and isoorientin,[14] and these identifications were confirmed by comparisons of the IR spectra and the TLC behavior with those of authentic samples.

In this paper the isolation and the structure elucidation are reported of four diosgenin oligosides, namely dioscin, deltonin, Pb and rhapissaponin, four proto-diosgenin bisdesmosides, methyl proto-dioscin, methyl proto-deltonin, methyl proto-Pb and methyl proto-rhapissaponin, and one flavonoidal *C*-glycoside, saponaretin (=isovitexin) from *Rhapis exelsa* HENRY, as well as three diosgenin oligosides, namely prosapogenin A of dioscin, dioscin and deltonin, four proto-diosgenin bisdesmosides, methyl proto-prosapogenin A of dioscin, methyl proto-dioscin, methyl proto-deltonin and methyl proto-Pb, and three flavonoidal *C*-glycosides, saponaretin (=isovitexin), vitexin and isoorientin from *R. humilis* BL. Among the diosgenin and proto-diosgenin oligosides described in this paper rhapissaponin and methyl proto-rhapissaponin are novel steroidal oligosides. Our previous paper was the first report of the isolation of steroidal saponins from a Palmae plant, *Trachycarpus fortunei* (HOOK.) H. WENDL., and this paper is only the second such report. In another preliminary study, a wide distribution of steroidal saponins has been found in Palmae plants and the results will be reported shortly.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus (hot-stage type) and are uncorrected. The optical rotations were measured with a JASCO DIP-140 polarimeter. The IR spectra were recorded with a JASCO IRA-1 instrument, and the UV spectra were measured with a Hitachi 340 spectrometer. The NMR spectra were recorded with a JEOL FX-100 spectrometer (100 MHz for ^{1}H-NMR and 25 MHz for ^{13}C-NMR). Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. Gas-liquid chromatography (GLC) was run on a Shimadzu GC-6A unit equipped with a flame ionization detector. TLC was performed on precoated Kieselgel 60 F_{254} plates (Merck) using $CHCl_3$–MeOH–H_2O (7 : 3 : 0.4, v/v), and detection was achieved by spraying 10% H_2SO_4 or the Ehrlich reagent followed by heating.

Extraction and Isolation of the Compounds from the Stems, Underground Parts and Leaves of *Rhapis exelsa* HENRY and *R. humilis* BL.——I-1) Stems of *R. exelsa*: The fresh stems (2.3 kg) were chopped and extracted with MeOH (5 l×3) at room temperature. The MeOH extract was evaporated to dryness *in vacuo*. The residue (169 g) was suspended in water (1 l) and partitioned with ether (500 ml × 3). The ether layer was concentrated *in vacuo* to afford the ether extract (12 g), and the aqueous layer was partitioned with BuOH saturated with water (500 ml × 3). The BuOH

layer was concentrated under reduced pressure to afford the BuOH extract (15 g). The BuOH extract was subjected to column chromatography on Sephadex LH-20 with MeOH to afford a fraction rich in Est_1, Est_2, $Est_{3\text{-}(a,b)}$ and $Est_{4\text{-}(a,b)}$. This was subjected to column chromatography on silica gel with $CHCl_3$–MeOH–H_2O (75:25:3, v/v) to provide five fractions. Among them, the fraction rich in Est_1 and $Est_{3\text{-}(a,b)}$ was rechromatographed on silica gel with the same solvent as described above to afford Est_1 (0.3 g) and a mixture of $Est_{3\text{-}a}$ and $Est_{3\text{-}b}$ (Fr. Est_3; 0.3 g). The Est_2-rich fraction was refluxed with MeOH for 2 h on a water bath and the solution was evaporated to dryness. The residue was recrystallized from MeOH to afford Est_2 (4.0 g). The fraction rich in Est_2, $Est_{4\text{-}a}$ and $Est_{4\text{-}b}$ was rechromatographed on silica gel with the same solvent as described above to provide fractions rich in Est_2 and in $Est_{4\text{-}a}$ plus $Est_{4\text{-}b}$. Each fraction was refluxed with MeOH and treated as described above to afford Est_2 (0.5 g) from the former, and a mixture of $Est_{4\text{-}a}$ and $Est_{4\text{-}b}$ (Fr. Est_4; 1.6 g) from the latter. I-2) Underground parts of *R. exelsa*: The fresh underground parts (2.6 kg) were treated as described above to afford MeOH extract (130 g), ether extract (7 g) and BuOH extract (26 g). The BuOH extract (26 g) was treated by procedure I-1 to afford Eu_1 (0.3 g), Eu_2 (3.0 g) and Eu_3 (1.3 g). I-3) Leaves of *R. exelsa*: The fresh leaves (1.0 kg) were treated according to procedure I-1 to afford MeOH extract (118 g), ether extract (28 g) and BuOH extract (20 g). The BuOH extract (10.4 g) was subjected to column chromatography on Sephadex LH-20 with MeOH to yield two fractions (Frs. 1 and 2). Fraction 1 was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (7:3:0.4, v/v) to provide four fractions. Each fraction was purified by column chromatography on Sephadex LH-20 with MeOH to afford an El_1-rich eluate, an El_2-rich eluate and an El_3-rich eluate. The El_1-rich eluate was treated with MeOH to afford pure El_1 (1.1 g). The El_2-rich eluate and the El_3-rich eluate were individually refluxed with MeOH (50 ml) for 2 h on a water bath, and each solution was concentrated to 5 ml. These concentrates were diluted with AcOEt (200 ml) to form precipitates of El_2 (3.0 g) and El_3 (0.2 g), which were collected by filtration and dried. Fraction 2 (El_4-rich fraction) was purified by column chromatography on Sephadex LH-20 with MeOH followed by recrystallization from MeOH to afford pure El_4 (0.6 g). II-1) Stems of *R. humilis*: Extraction and isolation of the compounds from the stems (2.4 kg) were carried out according to procedure I-1 to afford MeOH extract (222 g), ether extract (8 g) and BuOH extract (20 g). Hst_1 (0.3 g), Hst_2 (0.1 g), Hst_3 (0.4 g), Hst_4 (0.8 g), Hst_5 (0.7 g) and Hst_6 (1.5 g) were isolated from the BuOH extract. II-2) Underground parts of *R. humilis*: The fresh underground parts (3.0 kg) were treated according to procedure I-2 to afford MeOH extract (130 g), ether extract (8 g) and BuOH extract (21 g). The BuOH extract was treated according to procedure I-2 to give Hu_1 (0.1 g), Hu_2 (0.8 g), Hu_3 (2.1 g) and Hu_4 (3.1 g). II-3) Leaves of *R. humilis*: The fresh leaves (0.9 kg) were treated according to procedure I-3 to afford MeOH extract (125 g), ether extract (25 g) and BuOH extract (12 g). The BuOH extract (12 g) was subjected to column chromatography on Sephadex LH-20 with MeOH to provide two fractions, namely a fraction rich in Hl_1, Hl_2 and Hl_3 (8.5 g) and a fraction rich in Hl_4, Hl_5 and Hl_6 (2.5 g). The former fraction was treated according to procedure I-3 to afford Hl_1 (0.2 g), Hl_2 (0.3 g) and Hl_3 (2.1 g). The latter fraction was chromatographed on an Avicel column, which was successively eluted with $CHCl_3$–MeOH–H_2O (8:1.5:1, v/v, lower phase), (7:2:1, v/v, lower phase), (7:2.5:1, v/v, lower phase) and MeOH. The fraction eluted with the second solvent was evaporated to dryness, and the residue was crystallized from 50% AcOH to afford Hl_5, which was repeatedly recrystallized from MeOH to afford pure Hl_5 (0.1 g). The mother liquor was evaporated under reduced pressure and the residue was repeatedly recrystallized from MeOH to afford Hl_4 (0.04 g). The fraction eluted with the third solvent was evaporated to dryness and the residue was repeatedly recrystallized from MeOH to afford Hl_6 (0.3 g).

Properties of the Constituents of *Rhapis exelsa* and *R. humilis*——Est_1, Eu_1, Hst_2 and Hu_1: colorless needles from MeOH, mp 243—246 °C (dec.), $[\alpha]_D^{16}$ −110.3° (c=0.55, MeOH). IR (KBr) cm^{-1}: 3600—3200 (OH), 980, 920, 900, 864 (intensity 920 < 900, 25(*R*)-spiroketal), ^{13}C-NMR (pyridine-d_5) δ: 18.4 (C_6 of rha), 18.6 (C_6 of rha), 100.4 (C_1 of glc), 101.9 (C_1 of rha), 103.0 (C_1 of rha). *Anal.* Calcd for $C_{45}H_{72}O_{16}\cdot H_2O$: C, 59.71; H, 8.46. Found: C, 59.75; H, 8.34. These compounds were identified as dioscin by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample. Est_2, El_1, Eu_2, Hl_2, Hst_5 and Hu_3: colorless needles from MeOH, mp 185—189 °C (dec.), $[\alpha]_D^{16}$ −102.9° (c=1.00, pyridine). IR (KBr) cm^{-1}: 3540—3220 (OH), ^{13}C-NMR (pyridine-d_5) δ: 18.5 (C_6 of rha), 18.6 (C_6 of rha), 47.4 (OCH_3), 100.3 (C_1 of glc), 102.0 (C_1 of rha), 102.9 (C_1 of rha), 104.8 (C_1 of glc). *Anal.* Calcd for $C_{52}H_{86}O_{22}$: C, 58.74; H, 8.15. Found: C, 58.85; H, 8.15. These compounds were identified as methyl protodioscin by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample. El_2, Eu_3, Hl_3 and Hu_4: a white powder from MeOH–AcOEt, (mp 189—190 °C (dec.)), $[\alpha]_D^{16}$ −86.4° (c=1.03, pyridine), IR (KBr) cm^{-1}: 3600—3250 (OH), ^{13}C-NMR (pyridine-d_5) δ: 18.3 (C_6 of rha), 18.5 (C_6 of rha), 18.8 (C_6 of rha), 47.4 (OCH_3), 100.4 (C_1 of glc), 102.3 (C_1 of rha), 103.0 (C_1 of rha), 103.0 (C_1 of rha), 104.7 (C_1 of glc). *Anal.* Calcd for $C_{58}H_{96}O_{26}$: C, 57.60; H, 8.00. Found: C, 57.28; H, 8.00. These compounds were identified as methyl proto-Pb by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample. El_3: a white powder from MeOH–AcOEt, (mp 196—199 °C (dec.)), $[\alpha]_D^{20}$ −92.4° (c=1.02, pyridine), IR (KBr) cm^{-1}: 3460—3320 (OH), ^{13}C-NMR (pyridine-d_5) δ: 18.2 (C_6 of rha), 18.5 (C_6 of rha), 18.8 (C_6 of rha), 47.3 (OCH_3), 100.4 (C_1 of glc), 102.0 (C_1 or rha), 102.3 (C_1 of rha), 102.6 (C_1 of rha), 104.8 (C_1 of glc), 106.5 (C_1 of glc). *Anal.* Calcd for $C_{64}H_{106}O_{31}\cdot 2H_2O$: C, 54.61; H, 7.88. Found: C, 54.56; H, 7.63. El_4 and Hl_4: pale yellow plates from MeOH, mp 264—266 °C (dec.), $[\alpha]_D^{20}$ +26.1° (c=0.32, MeOH), UV λ_{max}^{MeOH} nm (log ε): 330 (4.18), 268 (4.18), IR (KBr) cm^{-1}: 3500—3300, 1640, 1610, ^{1}H-NMR (DMSO-d_6) δ: 4.60 (1H, d, J=10 Hz, C_1–H of glc), 6.52 (1H, s, C_8–H), 6.78 (1H,

s, C_3–H), 6.95, 7.95 (2H, each, ABq, J=9 Hz, $C_{2',3',5',6'}$–H), ^{13}C-NMR (DMSO-d_6) δ: 79.1 (C_1 of glc). El_4 and Hl_4 were identified as saponaretin (=isovitexin) by comparing the TLC behavior and the IR spectrum with those of an authentic sample. The ^{1}H- and ^{13}C-NMR data of both compounds agreed very closely with the reported values. Hst_1: colorless needles from aqueous MeOH, mp 264—268 °C (dec.), $[\alpha]_D^{20}$ −92.4° (c=1.03, pyridine), IR (KBr) cm^{-1}: 3540—3330 (OH), 980, 920, 900, 864 (intensity 920<900, 25(R)-spiroketal), ^{13}C-NMR (pyridine-d_5) δ: 18.6 (C_6 of rha), 100.6 (C_1 of glc), 102.0 (C_1 of rha). *Anal.* Calcd for $C_{39}H_{62}O_{12}\cdot 2H_2O$: C, 61.71; H, 8.77. Found: C, 61.33; H, 8.67. Hst_1 was identified as prosapogenin A of dioscin by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample. Hst_3: colorless needles from n-BuOH, mp 297—300 °C (dec.), $[\alpha]_D^{20}$ −88.3° (c=1.00, pyridine), IR (KBr) cm^{-1}: 3600—3200 (OH), 980, 915, 900, 860 (intensity 915<900, 25(R)-spiroketal), ^{13}C-NMR (pyridine-d_5) δ: 18.6 (C_6 of rha), 100.2 (C_1 of glc), 101.7 (C_1 of rha), 105.0 (C_1 of glc). *Anal.* Calcd for $C_{45}H_{72}O_{17}\cdot H_2O$: C, 59.85; H, 8.26. Found: C, 59.62; H, 8.35. Hst_3 was identified as deltonin by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample. Hst_4, Hl_1 and Hu_2: a white powder from MeOH–AcOEt, (mp 178—180 °C (dec.)), $[\alpha]_D^{20}$ −81.2° (c=0.97, pyridine), IR (KBr) cm^{-1}: 3460—3300 (OH), ^{13}C-NMR (pyridine-d_5) δ: 18.5 (C_6 of rha), 47.4 (OCH_3), 100.4 (C_1 of glc), 101.8 (C_1 of rha), 104.7 (C_1 of glc). *Anal.* Calcd for $C_{46}H_{76}O_{18}\cdot 3/2H_2O$: C, 58.52; H, 8.43. Found: C, 58.45; H, 8.13. These compounds were identified as methyl proto-prosapogenin A of dioscin by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample. Hl_5: pale yellow needles from MeOH, mp 264—266 °C (dec.), $[\alpha]_D^{20}$ −21.8° (c=0.25, 50% pyridine), UV λ_{max}^{MeOH} nm (log ε): 330 (4.39), 266 (4.39), IR (KBr) cm^{-1}: 3460—3200, 1650, 1610. ^{1}H-NMR (DMSO-d_6) δ: 4.69 (1H, d, J=10 Hz, C_1–H of glc), 6.28 (1H, s, C_6–H), 6.78 (1H, s, C_3–H), 6.90, 8.03 (2H each, ABq, J=9 Hz, $C_{2',3',5',6'}$–H), ^{13}C-NMR (DMSO-d_6) δ: 78.7 (C_1 of glc). The ^{1}H- and ^{13}C-NMR data of Hl_5 agreed very closely with the reported values for vitexin, and Hl_5 was confirmed to be vitexin by comparing the TLC behavior and the IR spectrum with those of an authentic sample. Hl_6: pale yellow needles from MeOH, mp 237—239 °C (dec.), $[\alpha]_D^{20}$ +31.5° (c=0.51, MeOH), UV λ_{max}^{MeOH} nm (log ε): 348 (4.47), 269 (4.42), 254 (4.37). IR (KBr) cm^{-1}: 3550—3300, 1640, 1610, ^{1}H-NMR (DMSO-d_6) δ: 4.59 (1H, d, J=10 Hz, C_1–H of glc), 6.49 (1H, s, C_8–H), 6.68 (1H, s, C_3–H), 6.89 (1H, d, J=9 Hz, $C_{5'}$–H), 7.39 (1H, d, J=2 Hz, $C_{2'}$–H), 7.42 (1H, dd, J=2, 9 Hz, $C_{6'}$–H), ^{13}C-NMR (DMSO-d_6) δ: 79.6 (C_1 of glc). The ^{1}H- and ^{13}C-NMR data of Hl_6 agreed very closely with the reported values for isoorientin, and Hl_6 was confirmed to be isoorientin by comparing the TLC behavior and the IR spectrum with those of an authentic sample. Hst_6: a white powder from MeOH–AcOEt, (mp 196—199°C (dec.)), $[\alpha]_D^{20}$ −59.8° (c=1.00, pyridine), IR (KBr) cm^{-1}: 3480—3260 (OH), ^{13}C-NMR (pyidine-d_5) δ: 18.6 (C_6 of rha), 100.2 (C_1 of glc), 101.7 (C_1 of rha), 104.8 (C_1 of glc), 105.0 (C_1 of glc). *Anal.* Calcd for $C_{52}H_{86}O_{23}$: C, 57.87; H, 8.03. Found: C, 57.47; H, 7.95. Hst_6 was identified as methyl proto-deltonin by comparisons of the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample.

Isolation of $Est_{4\text{-}a}$ and $Est_{4\text{-}b}$ from Fr. Est_4——Triphenyl chloromethane (200 mg) was added to a solution of Fr. Est_4 (100 mg) in pyridine (2 ml) and the solution was left at room temperature for 2 d. The reaction mixture was diluted with water (50 ml) and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water, dried over Na_2SO_4 and then evaporated to dryness *in vacuo*. The residue was dissolved in 50% AcOH (10 ml) and the solution was heated for 30 min on a boiling water bath. After cooling, the reaction mixture was neutralized with $NaHCO_3$ and evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$–MeOH–H_2O (7:3:0.4, v/v) to afford $Est_{4\text{-}a}$ (64 mg). On the other hand, the aqueous layer was treated by a procedure similar to that described for the $CHCl_3$ solution to afford $Est_{4\text{-}b}$ (36 mg). $Est_{4\text{-}a}$: a white powder from MeOH–AcOEt, (mp 196—199 °C (dec.)). This compound was identical with Hst_6 (methyl proto-deltonin) on the basis of comparisons of the IR and ^{13}C-NMR spectra. $Est_{4\text{-}b}$: a white powder from MeOH–AcOEt, (mp 189—190 °C (dec.)). This compound was identical with El_2, Eu_3, Hl_3 and Hu_4 (methyl proto-Pb) on the basis of comparisons of the TLC behavior, and the IR and ^{13}C-NMR spectra.

Enzymatic Hydrolyses of Est_2, $Est_{4\text{-}a}$, $Est_{4\text{-}b}$, El_3 and Hst_4——An aqueous solution of each of Est_2 (100 mg), $Est_{4\text{-}a}$ (50 mg), $Est_{4\text{-}b}$ (100 mg), El_3 (50 mg) and Hst_4 (50 mg) was incubated with almond emulsin (50 mg) at 37 °C for 4 h. The precipitate was collected by filtration, dried and subjected to column chromatography on silica gel with $CHCl_3$–MeOH–H_2O (8:2:0.2, v/v). The aqueous filtrate was evaporated to dryness *in vacuo* and the residue was examined by GLC (column, 5% SE-52 on Chromosorb W 3 mm × 2 m; column temp., 200 °C; injection temp., 220 °C; carrier gas, N_2 1.0 kg/cm^2; t_R (min) 8.8, 12.0 (TMS-glucose)). The hydrolysate of each compound was characterized as follows. Hydrolysate of Est_2: the prosapogenin was obtained as colorless needles from MeOH, mp 243—246 °C (dec.), and was found to be identical with Est_1, Eu_1, Hst_2 and Hu_1 (dioscin) by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra. Hydrolysate of $Est_{4\text{-}a}$: the prosapogenin was obtained as colorless needles from n-BuOH, mp 297—300 °C (dec.), and was identical with Hst_3 (deltonin) on the basis of comparisons of the TLC behavior, and the IR and ^{13}C-NMR spectra. Hydrolysate of $Est_{4\text{-}b}$: the prosapogenin was obtained as colorless needles from MeOH, mp 243—245 °C (dec.), $[\alpha]_D^{16}$ −104.7° (c=0.55, MeOH), IR (KBr) cm^{-1}: 3600—3240 (OH), 984, 920, 902, 865 (intensity 920<902, 25(R)-spiroketal), ^{13}C-NMR (pyridine-d_5) δ: 18.4 (C_6 of rha), 18.6 (C_6 of rha), 18.8 (C_6 of rha), 100.4 (C_1 of glc), 102.0 (C_1 of rha), 102.3 (C_1 of rha), 103.0 (C_1 of rha). *Anal.* Calcd for $C_{51}H_{82}O_{20}\cdot 3/2H_2O$: C, 58.77; H, 8.22. Found: C, 58.64; H, 8.25. This compound was identified as Pb by comparisons of the TLC behavior, and the IR and ^{13}C-NMR spectra with those of an authentic sample. Hydrolysate of El_3: the prosapogenin (pro-El_3)

was obtained as colorless needles from aqueous MeOH, mp 224—227 °C (dec.), $[\alpha]_D^{20}$ −110.0° (c=1.04, pyridine), IR (KBr) cm^{-1}: 3600—3200 (OH), 980, 920, 900, 867 (intensity 920<900, 25(*R*)-spiroketal), ^{13}C-NMR (pyridine-d_5) δ: 18.2 (C_6 of rha), 18.5 (C_6 of rha), 18.7 (C_6 of rha), 100.5 (d, $J_{C_1-H_1}$=153 Hz, C_1 of glc), 102.1 (d, $J_{C_1-H_1}$=169 Hz, C_1 of rha), 102.3 (d, $J_{C_1-H_1}$=169 Hz, C_1 of rha), 102.7 (d, $J_{C_1-H_1}$=169 Hz, C_1 of rha), 106.5 (d, $J_{C_1-H_1}$=155 Hz, C_1 of glc). *Anal.* Calcd for $C_{57}H_{92}O_{25}\cdot H_2O$: C, 57.27; H, 7.92. Found: C, 57.43; H, 8.18. Hydrolysate of Hst_4: the prosapogenin was obtained as colorless needles from aqueous MeOH, mp 264—268 °C (dec.), and was found to be identical with Hst_1 (prosapogenin A of dioscin) by comparing the TLC behavior, and the IR and ^{13}C-NMR spectra.

Acidic Hydrolyses of Est_1, Rhapissaponin (Pro-El_3), and Hst_1——Est_1 (20 mg), rhapissaponin (5 mg) and Hst_1 (10 mg) were separately hydrolyzed with 2 N HCl–50% dioxane (5 ml) by refluxing for 2 h on a water bath, then each reaction mixture was diluted with water and extracted with $CHCl_3$. The $CHCl_3$ extracts were individually washed with water, dried over Na_2SO_4 and evaporated *in vacuo*. Each residue was repeatedly recrystallized from acetone to afford a common aglycone (8 mg from Est_1, 2 mg from rhapissaponin and 4 mg from Hst_1) as colorless needles, mp 205—209 °C, IR (KBr) cm^{-1}: 3400 (OH), 980, 920, 900, 860 (intensity 920<900, 25(*R*)-spiroketal). *Anal.* Calcd for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found: C, 78.31; H, 10.51. The common aglycone was identified as diosgenin by mixed fusion and by comparing the IR spectrum with that of an authentic sample. Each aqueous layer was neutralized with $NaHCO_3$ and the neutral solution was evaporated to dryness under reduced pressure. Each residue was derivatized to the trimethylsilyl (TMS) ether and examined by GLC under the same conditions as described above. Sugars from Est_1, rhapissaponin and Hst_1: t_R (min) 3.4, 4.4 (rhamnose), 8.8, 12.0 (glucose).

Methylation of Fr. Est_3 by Hakomori's Method——According to Hakomori's method, NaH (250 mg) was washed with anhydrous benzene followed by petroleum ether, then warmed with dimethylsulfoxide (DMSO, 10 ml) at 65 °C in an oil bath for 1 h with stirring under an N_2 flow. A solution of Fr. Est_3 (100 mg) in a small amount of DMSO was then added and the mixture was stirred for 1 h under an N_2 flow. CH_3I (2 ml) was then added and the reaction mixture was allowed to stand at room temperature for 1 h with stirring. After dilution with water, the reaction mixture was extracted with $CHCl_3$ and the organic layer was washed with water, dried and evaporated to dryness. The residue was chromatographed on Sephadex LH-20 with MeOH, and then on silica gel with hexane–acetone (3 : 1, v/v) to afford two per-*O*-methylates, per-*O*-methylate of $Est_{3\text{-}a}$ (58 mg) and per-*O*-methylate of $Est_{3\text{-}b}$ (36 mg). Per-*O*-methylate of $Est_{3\text{-}a}$: colorless needles from aqueous MeOH, mp 101—103 °C, IR (Nujol) cm^{-1}: OH (nil), ^{1}H-NMR ($CDCl_3$) δ: 0.79 (3H, s, CH_3), 1.02 (3H, s, CH_3), 3.33—3.57 (OCH_3), 4.28 (1H, d, J=7 Hz, C_1–H of glc), 4.38 (1H, d, J=7 Hz, C_1–H of glc), 5.27 (1H, br s, C_1–H of rha), 5.31 (1H, m, olefinic H). Per-*O*-methylate of $Est_{3\text{-}a}$ was identified as deltonin per-*O*-methylate by mixed fusion and by comparing the IR spectrum with that of an authentic sample. Per-*O*-methylate of $Est_{3\text{-}b}$: colorless needles from aqueous MeOH, mp 126—127 °C, IR (Nujol) cm^{-1}: OH (nil), ^{1}H-NMR ($CDCl_3$) δ: 0.79 (3H, s, CH_3), 1.03 (3H, s, CH_3), 3.33—3.50 (OCH_3), 4.40 (1H, d, J=7 Hz, C_1–H of glc), 5.02 (1H, br s, C_1–H of rha), 5.21 (2H, br s, 2×C_1–H of rha), 5.34 (1H, m, olefinic H). Per-*O*-methylate of $Est_{3\text{-}b}$ was identified as Pb per-*O*-methylate by mixed fusion and by comparing the IR spectrum with that of an authentic sample.

Methanolyses of Per-*O*-methylates of $Est_{3\text{-}a}$ and $Est_{3\text{-}b}$ with Methanolic 1 N HCl——Per-*O*-methylates of $Est_{3\text{-}a}$ (5 mg) and $Est_{3\text{-}b}$ (5 mg) were individually refluxed with methanolic 1 N HCl (5 ml) for 2 h. After cooling, each reaction mixture was neutralized with Ag_2CO_3 and the resulting precipitate was filtered off. The filtrate was concentrated to dryness and the residue was examined by TLC (solvent: hexane–acetone (3 : 1, v/v)) and GLC (column, 5% NPGS on Shimalite W 3 mm×2 m; column temp. 150 °C; injection temp. 170 °C; carrier gas N_2, 1.0 kg/cm^2). TLC *Rf*: per-*O*-methylates of $Est_{3\text{-}a}$ and $Est_{3\text{-}b}$ 0.39 (diosgenin). GLC t_R (min) as TMS derivative: Per-*O*-methylate of $Est_{3\text{-}a}$ 2.4 (methyl 2,3,4-tri-*O*-methylrhamnopyranoside), 5.1, 7.0 (methyl 2,3,4,6-tetra-*O*-methylglucopyranoside), 6.4 (methyl 3,6-di-*O*-methylglucopyranoside); per-*O*-methylate of $Est_{3\text{-}b}$ 2.4 (methyl 2,3,4-tri-*O*-methylrhamnopyranoside), 6.4 (methyl 3,6-di-*O*-methylglucopyranoside), 6.6 (methyl 2,3-di-*O*-methylrhamnopyranoside).

Methylation of Rhapissaponin by Hakomori's Method——Rhapissaponin (12 mg) was methylated according to Hakomori's method, and the reaction mixture was treated by the same procedure as described above. Rhapissaponin per-*O*-methylate was crystallized from aqueous MeOH to afford colorless needles, mp 104—106 °C, IR (Nujol) cm^{-1}: OH (nil), ^{1}H-NMR ($CDCl_3$) δ: 0.79 (3H, s, CH_3), 1.03 (3H, s, CH_3), 3.30—3.58 (OCH_3), 4.40 (1H, d, J=7 Hz, C_1–H of glc), 4.60 (1H, d, J=7 Hz, C_1–H of glc), 5.05 (1H, br s, C_1–H of rha), 5.22 (2H, br s, 2×C_1–H of rha), 5.35 (1H, m, olefinic H).

Partial Methanolysis of Rhapissaponin Per-*O*-methylate with Methanolic 0.5 N HCl——A solution of rhapissaponin per-*O*-methylate (15 mg) in 2 ml of methanolic 0.5 N HCl was refluxed for 15 h. After cooling, the reaction mixture was neutralized with $NaHCO_3$ and evaporated to dryness *in vacuo*. The residue was methylated by Hakomori's method. The reaction mixture was treated in the usual way. The product was chromatographed on silica gel with hexane–acetone (4 : 1, v/v) to afford four compounds, tentatively named compounds A (7 mg), B (2 mg), C (3 mg) and D (2 mg). Compound A: a colorless syrup (not crystallized), IR (Nujol) cm^{-1}: OH (nil). This compound was identified as 3-*O*-methyl diosgenin by comparing the TLC behavior with that of an authentic sample. Compound B: a colorless syrup (not crystallized), IR (Nujol) cm^{-1}: OH (nil), ^{1}H-NMR ($CDCl_3$) δ: 4.32 (1H, d, J=7 Hz, C_1–H of glc). Compound C: a colorless syrup (not crystallized), IR (Nujol) cm^{-1}: OH (nil), ^{1}H-NMR ($CDCl_3$) δ: 4.35 (1H, d, J=7 Hz, C_1–H of glc), 5.24 (1H, br s, C_1–H of rha). Compound D: a colorless syrup (not crystallized), IR

(Nujol) cm^{-1}: OH (nil), ^{1}H-NMR ($CDCl_3$) δ: 4.35 (1H, d, $J=7$ Hz, C_1–H of glc), 4.62 (1H, d, $J=7$ Hz, C_1–H of glc), 5.02 (1H, br s, C_1–H of rha), 5.22 (1H, br s, C_1–H of rha).

Methanolysis of Compounds B, C and D with Methanolic 1 N HCl——Compounds B (2 mg), C (3 mg) and D (2 mg) were individually refluxed with methanolic 1 N HCl (2 ml) for 2 h. After cooling, each reaction mixture was neutralized with Ag_2CO_3 and the resulting precipitate was filtered off. The filtrate was concentrated to dryness and the residue was examined by GLC (under the same conditions as described above). t_R (min): compound B 5.1, 7.0 (methyl 2,3,4,6-tetra-*O*-methylglucopyranoside); compound C 2.4 (methyl 2,3,4-tri-*O*-methylrhamnopyranoside), 13.8 (methyl 3,4,6-tri-*O*-methylglucopyranoside); compound D 5.1, 7.0 (methyl 2,3,4,6-tetra-*O*-methylglucopyranoside), 6.6 (methyl 2,3-di-*O*-methylrhamnopyranoside), 15.0, 19.6 (methyl 2,3,6-tri-*O*-methylglucopyranoside).

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References and Notes

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