Steroid Saponins from Paris polyphylla Sm.—Supplement¹

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(Received June 22, 1981)

Previously, four steroid glycosides (Pa—d) were isolated from the rhizomes of Paris polyphylla Sm. and characterized. In a continuation of our studies on this plant, a further five new steroid glycosides (1, 2, 12, 14 and 16) together with three known compounds (13, 18 and 19; the latter two have been obtained synthetically as acetyl derivatives) have been isolated and their structures established as follows. 1 and 2: (22E,25R)-22-methoxyfurostanol 3,26-O-bisglycosides (proto-type saponins) corresponding to Pa [diosgenin 3-O-α-L-rha-pyr-(1→4)-α-L-rha-pyr-(1→2)-β-D-gluc-pyranoside (3)] and Pb [diosgenin 3-O-α-L-rha-pyr-(1→4)-α-L-rha-pyr-(1→4)-α-L-rha-pyr-(1→2)-β-D-gluc-pyranoside (6)], respectively; 12 and 13: penogenin oligosides having the same sugar moieties as 3 and 6, respectively; 14 and 18: penogenin derivatives carrying 3-O-α-L-rha-pyr-(1→4)-β-D-gluc-pyranoside and hexacetyl 3-O-α-L-rha-pyr-(1→2)-β-D-gluc-pyranoside, respectively; 16 and 19: diosgenin derivatives carrying the same sugar moieties as 14 and 18, respectively.

Keywords—Paris polyphylla; Liliaceae; furostanol glycoside; diosgenin glycoside; penogenin glycoside; arabinofuranoside

In the previous paper,¹ we reported four steroid glycosides (Pa through Pd) from the rhizomes of Himarayan Paris polyphylla Sm. (Liliaceae), which is used as a folk medicine in some parts of Nepal. In China, this plant has been used to treat chronic bronchitis. In a continuation of our studies on the ingredients of this plant, we have obtained a further eight steroid glycosides (1, 2, 12, 13, 14, 16, 18 and 19) together with Pa (3) and Pb (6). This paper deals with their structure determinations.

Separation of the MeOH extractive of the crude drug, commercial dried rhizomes of Paris polyphylla purchased in a market in China, was undertaken as described in Experimental, affording 1, 2, 12, 13, 14, 16, 18 and 19 in addition to Pa—d previously isolated.

Both 1, an amorphous powder (mp 209—212°C), [α]D -135.6°, and 2, an amorphous powder (mp 174—177°C), [α]D -87.0°, showed strong absorptions (3600—3200 cm⁻¹) due to hydroxylic groups, but not due to spiroketal functions in their infrared (IR) spectra and were positive to Ehrlich reagent, which is a convenient reagent to detect proto-type saponins such as proto-dioscin,⁴ for example. They also showed methoxy signals in their 1H nuclear magnetic resonance (¹H NMR) spectra. On the assumption that 1 and 2 were proto-type saponins, the compounds were hydrolyzed with β-glucosidase (almond emulsion) to afford furostanol derivatives, 3, colorless needles, mp 274—276°C, [α]D -133.0°, identical (mp, [α]D) with Pa, and 6, colorless needles, mp 203—206°C, [α]D -128.0°, identical (mp, TLC, ¹³C NMR) with Pb, respectively, both accompanied with r-glucose ([α]D, TLC). Furthermore, the identity of 3 and 6, obtained by enzymic hydrolysis of 1 and 2, with Pa and Pb, respectively, was substantiated by their transformation into the acetylated derivatives (4, colorless needles, mp 122—128°C, [α]D -100.0°, and 7, colorless needles, mp 148—153°C, [α]D -74.0°, respectively) and methylated derivatives (5, colorless needles, mp 160—162°C, [α]D -92.0°, and 8, colorless needles, mp 135—139°C, [α]D -110.0°, respectively). Therefore, 1 and 2 could be deduced to be proto-type saponins corresponding to Pa (3) and Pb (6), respec-
tively. To verify the structures of 1 and 2, they were acetylated with Ac₂O-pyridine, refluxed with Ac₂O for pseudomerization into 4\(^{20(23)}\) and oxidized with CrO₃ in AcOH (Marker's degradation\(^9\)). After treatment of the oxidized products with alkali, 1 and 2 were finally decomposed respectively into 3\(\beta\)-hydroxy-pregn-5,16-dien-20-one glycosides, 9, an amorphous powder (mp 214—216°C), \([\alpha]_D = -42.0^\circ\), and 10, colorless needles, mp 234—237°C, \([\alpha]_D = -117.7^\circ\), respectively, both accompanied with a product formed from the steroidal side chain moiety, which on acetylation followed by methylation with CH₃N₃ afforded methyl 4\((R)\)-methyl-5-hydroxy-
pentanoate-p-glucopyranoside tetraacetate (11) as a colorless oil. The structures of 9, 10 and 11 were supported by their IR, mass (MS) and 1H NMR spectra.

Consequently 1 and 2 can be defined as (22S, 25R)-22-methoxyfurost-5-ene-3,26-diol 26-O-β-D-glucopyranosides of 3-O-α-L-arabinofuranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranosyl and 3-O-α-L-rhamnopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl, respectively.

Next, 12, colorless needles, mp 274—278°C, [α]D = -108.9°, showed absorptions due to hydroxyl (3600—3200 cm⁻¹) and spiroketal side chain (980, 920, 900 and 890) moieties. The mass spectrum of 12 exhibited characteristic peaks, m/z 412 (C₂₇H₄₀O₃³⁺), 155 (C₉H₁₅O₂³⁺), 153 (C₉H₁₅O₄³+) and 126 (C₆H₁₄O⁺), derived from penrogenin. Moreover, the 13C NMR spectrum of 12 revealed signals attributable to the sugar moiety superimposed on those of Pa (3), as described in Experimental. Accordingly, 12 was deduced to be penrogenin 3-O-α-L-arabinofuranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside, whose sugar moiety is identical with that of Pa (3).

13, colorless needles, mp 224—228°C (dec.), was identical (mp, TLC, IR) with Tg, penrogenin tetracyloside, having the same sugar residue as Pb (6) previously isolated from the fresh underground parts of Trillium kamtschaticum Pall.

14, an amorphous powder, [α]D = -98.0°, and 16, colorless needles, mp 239—242°C, were derived into the corresponding acetates, 15, colorless needles, mp 172.5—176°C, [α]D = -44.6°, and 17, colorless needles, mp 174—176°C, [α]D = -37.4°, respectively. Both acetates, 15 and 17, showed peaks derived from the terminal peracetylated-pentosyl hexosyl cation (m/z 547) and -pentosyl cation (m/z 259) in the mass spectra. Furthermore, a comparison of the signals ascribable to the sugar moieties in the 13C NMR spectra of 15 and 17 indicated that the moieties were almost identical. The hexamethyl ether derived from 14, on acid hydrolysis with 2 n HCl-MeOH, gave two methylglycosides of 2,3,5-tri-0-methyl arabinofuranose and 2,3,6-tri-O-methyl glucopyranose besides acylgone derivatives (bethogenin and kryptogenin). Since the mass spectra of 14 and 16 showed peaks at m/z [412, 155, 126] and [306 (C₃H₆O⁻)]²⁺, characteristic of penrogenin and diosgenin, respectively, and the chemical shifts of the signals due to the aglycones in the 13C NMR spectra of 15 and 17 were in good agreement with those of penogenin and diosgenin, respectively, 14 and 16 are penogenin- and diosgenin-glycosides, respectively, having the same sugar moiety, 3-O-α-L-arabinofuranosyl-(1→4)-β-D-glucopyranoside, and correspond to prosapogenins of 12 and 3, respectively.

18, colorless needles, mp 193—195°C, [α]D = -52.0°, and 19, colorless needles, mp 203—207°C, [α]D = -60.0°, isolated after acetylation, were identical (mp, [α]D, TLC, MS) with Tb hexaacetate and Ta hexaaacetate, respectively, previously obtained from the fresh underground parts of T. kamtschaticum Pall.

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured with a Union Giken PM-201 automatic digital polarimeter at 20—25°C. IR and UV spectra were obtained with Hitachi IR-215 and Hitachi UV-124 machines, respectively. 13C NMR and 1H NMR spectra were taken with JEOL JNM-FX-90Q (22.5 MHz) and JEOL JNM-PS-100 (100 MHz) spectrometers, respectively. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. Mass spectra were taken with a JEOL JMS D-300 machine. Gas liquid chromatography (GLC) was run on a Shimadzu GC-6A unit with a flame ionization detector using a glass column (3 mm x 2.0 m) packed with neopentylglycol succinate. Paper partition chromatography (PPC) for sugar was conducted on Toyobo Roshi No. 50 paper using the upper layer of n-BuOH-pyridine-water (6: 2: 3) as solvent and aniline phthalate as a staining agent. TLC was performed on precoated silica gel plates 0.25 mm thick (Kieselgel 60, Merck) and detection was achieved by spraying 10% H₂SO₄ followed by heating. Column chromatography was performed on Kieselgel 60 (Merck, 70—230 mesh), Sephadex LH-20 (Pharmacia Fine Chem.) and Amberlite XAD-2 (Organ). Extraction and Isolation of Steroid Saponins—Commercial dried rhizomes (480 g) purchased in a market.
rhizomes of *Paris polyphylla* Sm. (480 g) 
extracted with MeOH (3 l) 
MeOH extractives (74 g) 
defatted with *n*-hexane (0.6 l) 
insoluble portion (65 g) 
partitioned between *n*-BuOH (1.2 l) and water (1.5 l) 
aqueous layer 
BuOH layer (39 g) 

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(i) acetylation with Ac₂O—pyridine 
(ii) column chromatography on silica gel 
using a. benzene—EtOH (30:1) 
b. *n*-hexane—AcOEt (1:1) 
c. benzene—acetone (1:1) 
d. CHCl₃—MeOH—water (7:2:0.2) 
(iii) treated with 3% KOH—MeOH 
(iv) crystallized from MeOH 
(v) passed through Amberlite XAD-2  
Rf values on TLC are for CHCl₃—MeOH—water (7:3:0.5) as a solvent.

Chart 1

in China were extracted with refluxing MeOH (3 l), and the extract was concentrated under reduced pressure to give a residue (74 g), which was treated as shown in Chart 1.

1—An amorphous powder (mp 209—212°C, [x]D +135.6° (c = 0.45, MeOH). IR νmax cm⁻¹: 3600—3300 (OH). Ehrlich reagent: positive. Anal. Calcd for C₄₉H₇₆O₁₉·H₂O: C, 56.91; H, 8.11. Found: C, 56.51; 
H, 7.92. ¹H NMR (d₆-pyridine) δ (ppm): 3.24 (OMe).

Enzymic Hydrolysis of 1—A solution of 1 (60 mg) in dist. water (5 ml) was incubated with almond emulsion (Sigma Chem. Co.) (20 mg) at 37°C for 7 h, then the reaction mixture was evaporated to dryness in vacuo to give a residue, to which MeOH was added. The mixture was filtered. The MeOH solution was evaporated to dryness to give a residue, which was subjected to Sephadex LH-20 column chromatography using MeOH as an eluent to give a glycoside (3), colorless needles (from MeOH), mp 274—276°C, [x]D +133.0° (c = 0.56, MeOH), identical with Pa (30 mg), and a sugar identical with d-glucose (12 mg), Rf 0.46 (on PPC), [x]D +59.5° (c = 0.51, water). 3: Anal. Calcd for C₄₉H₇₆O₁₉·H₂O: C, 60.39; H, 8.52. Found: C, 60.37; H, 8.45. ¹³C NMR (in d₆-pyridine) δ (ppm): aglycone (diosgenin):²⁹ 37.4, 30.0, 77.6, 40.4, 140.8, 121.6, 32.2, 31.6, 50.0, 50.0, 21.0, 39.8, 40.4, 56.6, 32.1, 81.0, 62.7, 16.8, 19.0, 14.0, 109.3, 31.6, 29.1, 30.4, 66.8, 17.1 (C₁₋₄), glucose moiety; 100.0, 78.2, 77.2, 76.2, 77.6, 62.6 (C₄₋₅), rhamnose moiety; 101.6, 72.4, 71.9, 73.6, 69.2, 18.3 (C₁₋₄‴), arabinofuranose moiety; 109.4, 82.5, 77.6, 86.1, 61.2 (C₁₋₄‴).

Octaacetate (4) of 3—3 (85 mg) was acetylated with Ac₂O—pyridine (each 4 ml) at 80°C for 1 h to give a peracetate (4), colorless needles (from MeOH, 68 mg), mp 122—128°C, [x]D −100.0° (c = 0.50, CHCl₃). MS m/z: 777, 396 (C₄₉H₇₆O₂₃), 282 (C₄₉H₇₆O₂), 273 (C₄₉H₇₆O₂), 259 (C₄₉H₇₆O₂), 253, 198 (C₄₉H₇₆O₂), 115 (C₄₉H₇₆O₂).

Octamethylether (5) of 3—3 (50 mg) was methylated by Hakomori's method¹⁰ to give a permethylate (5), colorless needles (from MeOH, 26 mg), mp 160—162°C, [x]D −92.0° (c = 0.50, CHCl₃). MS m/z: 553, 396, 282, 253, 189 (C₄₉H₇₆O₂), 175 (C₄₉H₇₆O₂), 139, 115. ¹H NMR (in CDCl₃) δ (ppm): 0.80 (3H, 18-CH₃),

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0.85 (3H, d, J = 6 Hz, 27-CH₃), 0.98 (3H, d, J = 6 Hz, 21-CH₃), 1.02 (3H, s, 19-CH₃), 3.59-3.70 (OMe), 4.33 (1H, d, J = 7 Hz, glucosyl anomic proton), 5.17 (1H, s, rhamnosyl anomic proton), 5.22 (1H, broad, s, arabinofuranosyl anomic proton).

**Oxidation Products (9 and 11) of 1** — The peracetae (72 mg of 1 in Ac₂O (10 ml) was refluxed for 45 min, then the solution was cooled and EtOH was added. The whole was evaporated to dryness in vacuo, yielding a pale brown residue (60 mg) which included the acetyl (A) compound of 1. AcOH (1.6 ml) and AcONa (32 mg) were added to the residue, and the resulting solution was cooled to 12°C. CrO₃ solution (65 mg in 0.5 ml of 40% AcOH) was added with stirring, and the mixture was allowed to stand for 1 h at room temperature. The reaction mixture was diluted with water (50 ml) and shaken with CHCl₃ to extract oxidation products. Evaporation yielded a syrup (78 mg), which was mixed with an aqueous solution (1.2 ml) containing KOH (165 mg). After further addition of t-BuOH (4 ml), the mixture was incubated at 30°C for 3.5 h. The t-BuOH was distilled off, and the reaction mixture was extracted with n-BuOH. The extract was evaporated to dryness in vacuo to give a residue, which was chromatographed on silica gel using CHCl₃—MeOH—H₂O (7: 3: 0.2) to give a pregnenolone glycoside (9, sugar moiety = S₅), a white powder (mp 214—216°C, 25 mg, [α]D₂⁰ -42.0° (c = 0.50, MeOH). IR νcm⁻¹: 3600—3200 (OH), 1650, 1580 (ν,µ-unsaturated ketone). UV λnm: 279 (ε = 9800). ³¹P NMR (in d₅-pyridine) δ (ppm): 0.95 (3H, d, J = 9 Hz, chelate ring), 1.05 (3H, d, J = 12 Hz, CH₃), 1.75 (3H, d, J = 7 Hz, rhamnosyl 5-CH₃), 2.25 (3H, s, 19-CH₃), 5.80 (1H, d, J = 7 Hz, glucosyl anomic proton), 6.18 (1H, s, arabinofuranosyl anomic proton), 6.63 (1H, br s, rhamnosyl anomic proton). The aqueous layer, after being adjusted to pH 3.0 with 3N HCl, was shaken in turn with n-BuOH and CHCl₃, neutralized with 2N NaOH, and concentrated to afford a salt mixture. The salt were acetylated in a usual way and its acetate was taken up in MeOH. This solution was treated with diazomethane in ether. After removal of the residue, the acetate was chromatographed on a silica gel column with n-hexane-acetone (1:1) to give methyl (4R)-methyl-5-hydroxypentanoate β-D-glycopyranoside tetraacetate (II), a colorless oil (11 mg), [α]D₂⁰ + 18.8° (c = 0.42, CHCl₃). MS m/z: 331 (C₁₄H₁₈O₂³⁺), 243, 242, 200, 169, 157, 145, 140, 129 (C₁₂H₁₄O₂³⁺), 115, 109, 103, 98, 97 (C₁₀H₇O₃³⁺). ¹H NMR (in CDCl₃) δ (ppm): 0.90 (3H, d, J = 7 Hz, sec. CH₃), 2.00-2.08 (12H, 4 × OAc), 3.62 (3H, 1 × OMe), 4.45 (1H, d, J = 7 Hz, glucosyl anomic proton).

**Decacetate (7) of 6.** 6 (30 mg) was acetylated with Ac₂O-pyridine (each 2 ml) at 80°C for 1 h to give 7 (30 mg) as colorless needles (from MeOH, 21 mg, mp 148—153°C, [α]D₂⁰ + 74.0° (c = 1.00, CHCl₃). MS m/z: 503 (C₂₃H₃₇O₅²⁺), 414, 396, 282, 273, 253.

**Decamethyl Ether (8) of 6.** 6 (50 mg) was methylated by Hakomori's method to give 8 (10 mg) as colorless needles (from MeOH, 12 mg, mp 135—139°C, [α]D₂⁰ + 110.0° (c = 0.50, CHCl₃). MS m/z: 1154 (M⁺), 414, 396, 363 (C₁₄H₁₈O₂³⁺), 282, 253, 189 (C₁₂H₁₄O₂²⁺). ¹H NMR (in CDCl₃) δ (ppm): 0.79 (3H, s, 18-CH₃), 0.85 (3H, d, J = 7 Hz, 27-CH₃), 0.97 (3H, d, J = 6 Hz, 21-CH₃), 1.03 (3H, s, 19-CH₃), 1.20, 1.22, 1.24 (each 3H, d, J = 6 Hz, rhamnosyl 5-CH₃), 3.35—3.75 (OMe), 4.38 (1H, d, J = 7 Hz, glucosyl anomic proton), 5.02 (1H, s, rhamnosyl anomic proton), 5.20 (2H, s, 2 × rhamnosyl anomic proton).

**Oxidation Products (10 and 11) of 2** — The peracetate (150 mg of 2) was oxidized in the manner described for 1 to give a pregnenolone glycoside (10, sugar moiety = S₅), colorless needles (from MeOH, 62 mg) mp 234—237°C, [α]D₂⁰ + 117.7° (c = 0.51, MeOH) and methyl (4R)-methyl-5-hydroxypentanoate β-D-glycopyranoside tetraacetate (11), a colorless oil (30 mg), [α]D₂⁰ + 18.2° (c = 0.92, CHCl₃). ¹H NMR (in d₅-pyridine) δ (ppm): 0.95 (3H, d, J = 13 Hz, 19-CH₃), 1.06 (3H, s, 18-CH₃), 1.60 (6H, d, J = 6 Hz, 2 × rhamnosyl 5-CH₃), 1.77 (3H, d, J = 6 Hz, rhamnosyl 5-CH₃), 2.24 (3H, s, 21-CH₃), 5.75 (1H, d, J = 7 Hz, glucosyl anomic proton), 6.22, 6.35, 6.56 (each 1H, s, rhamnosyl anomic proton).

**Found. C, 58.96; H, 8.27. MS m/z: 430 (C₂₃H₃₇O₅²⁺), 412 (C₂₁H₃₅O₅), 155 (C₈H₁₄O₂)²⁺.**
13. Colorless needles (from MeOH), mp 224–228°C (dec.), [α]D +320° (c = 0.50, MeOH). IR νmax cm⁻¹: 3600–3200 (OH), 890, 920, 900, 890 (intensity 900–920, C=O-spiroketal side chain). Anal. Calcd for C₄₁H₇₂O₁₅·3H₂O: C, 56.44; H, 8.17. Found: C, 56.21; H, 8.08. Identical with Tg in terms of mp, RF value on TLC and IR.


Hexaacetate (15) of 14—Colorless needles (from MeOH), mp 172.5–176°C, [α]D +44.6° (c = 0.92, CHCl₃). MS (m/z): 684, 547, 412, 394, 282, 259, 157, 139, 115, 109. 13C NMR (in CDCl₃) δ ppm: aglycone (prenogenin): 37.2, 30.7, 76.6, 39.0, 140.5, 121.8, 32.1, 131.5, 50.2, 36.9, 21.0, 39.8, 40.3, 56.6, 32.0, 80.8, 62.3, 16.3, 19.4, 41.7, 14.5, 109.2, 31.5, 28.9, 29.7, 70.7, 17.1 (C₁₋₇), sugar moiety; 107.4, 99.5, 81.7, 81.2, 79.8, 76.0, 73.5, 72.8, 72.1, 63.2, 62.3.

Methanalysis of Hexamethylen Ether of 14—14 (10 mg) was methylated by Hakomori's method to give a permethyl ether (6 mg) of 14, a white solid, RF 0.41 (on TLC, solv. n-hexane–acetone (2:1)), MS m/z: 412, 394, 376, 175, 101. The hexamethylen ether (4 mg) of 14 was subjected to methanalysis under reflux with 1 N HCl-MeOH (5 ml) for 2 h to give both benzogen and kryptogen (RF 0.62 and 0.12, respectively, on TLC, solv. n-hexane–AcOEt (1:1)) and methylglycosides, which were examined by GLC comparison with authentic samples. GLC, column temp. 108°C, N₂ 1.25 kg/cm²; tR, 5.5, 7.4 min (methyl 2,3,5-tri-O-methyl α- and β-arabinofuranoside); column temp. 180°C, tR, 1.60, 2.05 min (methyl 2,3,6-tri-O-methyl α- and β-glucopyranoside).


Found: C, 61.56; H, 8.38. MS m/z: 396 (C₉₂H₁₄₂O₄), 282 (C₇₂H₁₃₀), 253, 139 (C₆₀H₁₁₄O₃).}

Hexaacetate (17) of 16—Colorless needles (from MeOH), mp 174–176°C, [α]D −34.7° (c = 0.54, CHCl₃), MS (m/z): 684, 547, 396, 282, 259, 253, 139, 115. 13C NMR (in CDCl₃) δ ppm: aglycone (diosgenin): 37.2, 30.7, 76.6, 39.0, 140.5, 121.8, 32.1, 131.5, 50.2, 36.9, 21.0, 39.8, 40.3, 56.6, 32.0, 80.8, 62.3, 16.3, 19.4, 41.7, 14.5, 109.2, 31.5, 28.9, 29.7, 76.9, 17.1 (C₁₋₇), sugar moiety; 107.4, 99.5, 81.7, 81.2, 79.8, 76.0, 73.5, 72.8, 72.1, 63.2, 62.3.

18. Colorless needles (from MeOH), mp 193–195°C, [α]D −52.0° (c = 0.50, CHCl₃), MS (m/z): 561, 412, 394, 273, 155, 139, 126, 111. IR νmax cm⁻¹: 1750 (OAc), 980, 920, 900, 860 (intensity 900>920, C=O-spiroketal side chain), MS (m/z): 684, 561, 414, 396, 282, 273, 253, 139. Anal. Calcd for C₄₉H₇₂O₁₅·3H₂O: C, 62.81; H, 7.65. Found: C, 62.50; H, 7.60.

Acknowledgement The authors are grateful to Mr. H. Fujimura and Mr. K. Goto for measurement of the 13C NMR spectra and to the members of the Central Analysis Room of Tokushima University for measurement of the 1H NMR and mass spectra and for microanalyses.

References and Notes


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