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Three New Lupane Type Glycosyl Esters from *Oplopanax japonicus* Leaves

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Three new lupane type glycosyl esters, oplopanaxoside B, C, and D, were isolated from *Oplopanax japonicus* leaves and characterized as 28-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosides of 3β-hydroxylup-20(29)-ene-23,28-dioic acid, 3α,23-dihydroxylup-20(29)-en-28-oic acid and 3β,23-dihydroxylup-20(29)-en-28-oic acid, respectively. Three known glycosides, 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranosides of kaempferol and quercetin, and 3α-hydroxylup-20(29)-ene-23,28-dioic acid 28-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranoside (oplopanaxoside A) were also obtained therefrom.

Keywords——*Oplopanax japonicus*; Araliaceae; oplopanaxoside; flavonol glycoside; lupane; triterpenoid saponin; oplopanaxogenin

The root of *Oplopanax japonicus* NAKAI (=*Echinopanax horridus* DECNE. et PLANCH.) is a Chinese folk medicine used as an anti-pyretic and a cough drug.[1] The constituents reported to have been obtained from this plant are as follows: echinopanacol, echinopanacen,[2] oplopanone,[3] oplodiol,[4] nerolidol, stigmasterol, β-sitosterol, linoleic acid, palmitic acid, oleic acid, stearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid and glucose.[5] In the present study, we examined the constituents of *Oplopanax japonicus* leaves collected in Fujimi (Nagano Prefecture, Japan), and isolated three novel glycosides (**4**-**6**) together with three known ones (**1**-**3**). We describe the isolation and characterization of the six glycosides.

RESULTS AND DISCUSSION

Dried *O. japonicus* leaves were extracted with MeOH, and the MeOH extractive was partitioned between ether and H_2O. The aqueous layer was subjected to reversed phase chromatography on DIAION HP-20 with successive elution solvents of water, 3 : 7 MeOH/H_2O, 7 : 3 MeOH/H_2O, MeOH and $CHCl_3$ to give five fractions (Fr. I-V). Further chromatography of each fraction gave six glycosides: **1** from Fr. II; **2**, **3**, **5** and **6** from Fr. III; **4** from Fr. IV.

Compounds **1** and **2**, turning reddish in the magnesium-hydrochloric acid reaction, were identified as known flavonoid glycosides, 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranosides of kaempferol[6] and quercetin,[7] respectively, mainly on the basis of their chemical and spectral evidences.

Compound **3**, white powder, $C_{48}H_{76}O_{19}$, showed absorption bands due to hydroxyl, esteric, carboxylic and exomethylene groups in the IR spectrum. The ^{1}H-NMR spectrum of **3** exhibited signals due to five tertiary methyl, one secondary methyl, one exomethylene protons. The ^{13}C-NMR spectrum of **3** showed characteristic signals due to one carboxylic, one esteric and two olefinic groups and three anomeric carbons (TABLE I). On acidic hydrolysis, **3** gave glucose, rhamnose and an aglycone (**3a**) which was identified as 3α-hydroxylup-20(29)-ene-23,28-dioic acid[8] by direct comparison with an authentic sample. The glycosylation shift[9] was observed only in the chemical shift of C-28 signal in the ^{13}C-NMR spectrum, which was at δ 175.0 in **3** and at δ 178.8 in **3a**. The FAB-MS spectrum exhibited fragment ion peaks caused by sequential loss of one methylpentosyl and two hexosyl groups, suggested that **3** was a 28-*O*-rhamnosyl-glucosyl-glucoside. This was proved by a selective cleavage reaction of esteric glycoside linkage of **3** giving **3a** as an aglycone and an anomeric mixture of methyl α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-α and β-D-glucopyranosides (**7** (**7a** and **7b**)).[10] Thus, the structure of **3** was characterized as 3α-hydroxylup-20(29)-en-23,28-dioic acid 28-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl ester, previously obtained from leaves

of *Schefflera octophylla* (Araliaceae) by Kitajima and Tanaka.[8] We propose here that **3** and **3a** are to be designated as oplopaxoside A and oplopanaxogenin A, respectively. This is the first isolation of **3** from a plants of this genus.

Oplopanaxoside B (**4**), white powder, $C_{48}H_{76}O_{19}$, showed similar IR absorption bands to those observed in **3**. Its ^{13}C-NMR spectrum resembled that of **3** excepting for the chemical shifts of the signals due to the carbons around C-3 of the aglycone moiety, suggesting that **4** was an epimer at C-3 of **3** (TABLE I). **4** was hydrolyzed as in the case of **3** to give glucose, rhamnose and an aglycone (**4a**), i.e. oplopanaxogenin B. By selective cleavage of its esteric glycoside linkage, **4** yielded **4a** as an aglycone and an anomeric mixture of methyl oligosaccarides which was identified as **7** (a mixture of **7a** and **7b**) obtained from **3**. When **4a** was methylated with diazomethane followed by oxidation under Jones condition, it gave a ketone (**8**), which was the same as the ketone derived from **3a**. Thus, **4a** was clarified to be an epimer at C-3 of **3a**. The location of the oligosaccaride was deduced to be at the C-28 position of **4a** since the glycosylation shift was observed only at the C-28 carbon signal. Accordingly, **4a** and **4** were determined as 3β-hydroxylup-20(29)-ene-23,28-dioic acid and its 28-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl ester, respectively.

Oplopanaxoside C (**5**), white powder, $C_{48}H_{78}O_{18}$, showed absorption bands of hydroxyl, esteric and exomethylene groups in the IR spectrum, but not of carboxylic acid. Its ^{13}C-NMR spectrum resembled that of **3**, but **5** had a primary carbinyl signal at δ 71.3 instead of the C-23 carboxyl carbon signal at δ 180.4 in **3**, suggesting that **5** was a 23-hydroxylated derivative of **3** (TABLE I). On acidic hydrolysis, **5** gave glucose, rhamnose and an aglycone (**5a**), namely oplopanaxogenin C. On a selective cleavage reaction of esteric glycoside linkage, **5** gave **5a** as an aglycone and the same methyl oligosaccharides (**7**) as **3**. **3** was methylated with diazomethane followed by reduction with lithium borohydride.[11] The product was identified as **5** by direct comparison with an authentic specimen. Therefore, **5a** and **5** were characterized as 3α,23-dihydroxylup-20(29)-en-28-oic acid and its 28-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl ester, respectively.

Oplopanaxoside D (**6**), white powder, $C_{48}H_{78}O_{18}$, showed IR spectrum bands similar to those of **5**, but not that of carboxylic acid observed in the IR spectrum of **5**. Its ^{13}C-NMR spectrum resembled also that of **5**, excepting for the chemical shifts of the signals due to the carbons around C-3 of the aglycone moiety, suggesting that **6** was an epimer at C-3 of **5**, i.e. a 23-hydroxylated derivative of **4**. On acid hydrolysis, **6** gave glucose, rhamnose and an aglycone, namely oplopanaxogenin D (**6a**). **4** was methylated with diazomethane followed by reduction with lithium borohydride to give **6**. Therefore, **6a** and **6** were characterized as 3β,23-dihydroxylup-20(29)-en-28-oic acid and its 28-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl ester, respectively.

As mentioned above, we isolated from *O. japonicus* leaves two flavonoid glycosides and four lupane type triterpenoid glycosides, three of which were novel compounds.

EXPERIMENTAL

All melting points were determined on a Yanaco micro-melting point apparatus (hot stage type) and were uncorrected. Optical rotations were measured with a JASCO DIP-140 polarimeter at rt (20–25℃). IR spectra were recorded with a JASCO IR-810, and NMR spectra with a JEOL GX400 spectrometer (400 MHz for ^{1}H-NMR, 100 MHz for ^{13}C-NMR). Chemical shifts were given in δ (ppm) scale with tetramethylsilane (TMS) as an internal standard. The FAB- and EI-MS were determined on a JEOL JMS-SX102A spectrometer, and a glycerol matrix containing NaI or *m*-nitrobenzylalcohol (NBA) was used for FAB-MS. Gas liquid

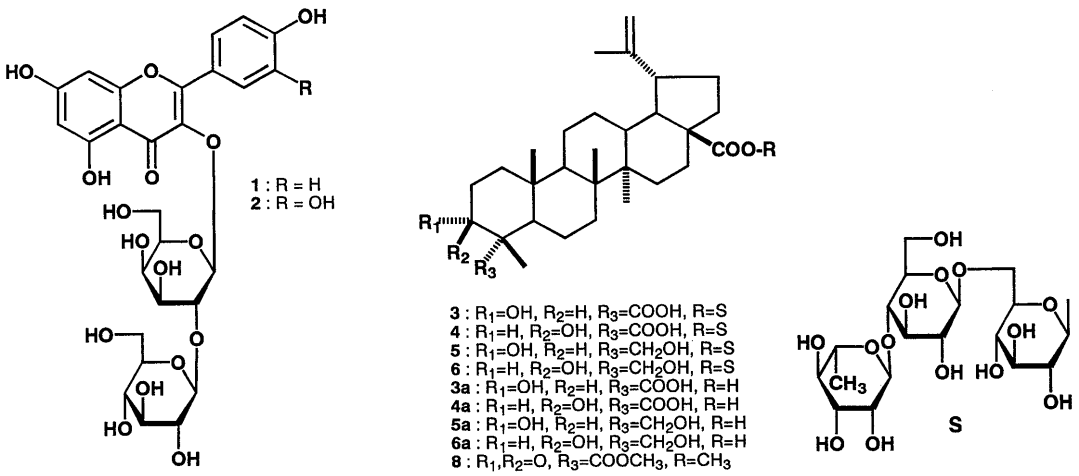

Chart 1.

chromatography (GLC) was run on a Shimadzu GC-6A unit equipped with a flame ionization detector (FID). Experimental conditions for sugar TMS ethers: column, 5% SE-52 on Chromosorb W, 3 mm×2 m; (a) column temp. 175℃, injection temp. 220℃; carrier gas (N_2), 1.5 kg/cm²; (b) column temp. 160℃, injection temp. 180℃; carrier gas (N_2), 1.0 kg/cm². Thin layer chromatography (TLC) was performed on a precoated silica gel plate (Merck), and detection was achieved by spraying 10% H_2SO_4 followed by heating, or by UV irradiation.

Extraction and isolation Dried leaves (1.4 kg) of *O. japonicus* collected in Fujimi (Nagano Prefecture, Japan) in August 1990 were extracted with MeOH (3 *l* ×3) at rt and the MeOH extract was evaporated *in vacuo*. The residue (351 g) was suspended in H_2O (1 *l*) and extracted with Et_2O (500 ml×3) giving an Et_2O ext. (177 g) and the aq. ext. (167 g) after removal of the solvents *in vacuo*. The aq. ext. was subjected to column chromatography on DIAION HP-20 with successive elution systems of H_2O (3 *l*), 3 : 7 MeOH/H_2O (3 *l*), 7 : 3 MeOH/H_2O (4 *l*), MeOH (4 *l*) and $CHCl_3$ (3 *l*) to give five fractions: Fr. I (34.9 g), Fr. II (3.1 g), Fr. III (8.1 g), Fr. IV (12.8 g) and Fr. V (11.5 g). Fr. II (2.0 g) was chromatographed on silica gel with $CHCl_3$-MeOH-AcOEt-H_2O (1 : 2 : 4 : 1, v/v) and then on ODS with 9 : 11 MeOH/H_2O to give **1** (20.5 mg). Fr. III (4.0 g) was subjected to Sephadex LH-20 column chromatography with MeOH followed by silica gel column chromatography with $CHCl_3$-MeOH-H_2O (30 : 10 : 1, v/v) to give **2** (35.4 mg), **3** (1.0 g), **5** (9.6 mg) and **6** (21.3 mg). Fr. IV (1.4 g) was chromatographed on silica gel with $CHCl_3$-MeOH-AcOEt-H_2O (1 : 2 : 4 : 1, v/v) and ODS with 63% MeOH to give **4** (16.3 mg).

Kaempferol 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranoside (1) Yellow powder, $[\alpha]_D$ −30.7° (*c* =0.4, MeOH). IR (KBr), cm^{-1}: 3400, 1660, 1610. FAB-MS, *m/z*: 609 ($[M-H]^-$). ^{1}H-NMR (DMSO-d_6), δ: 8.09 (2H, d, *J*=9.2 Hz), 6.89 (2H, d, *J*=9.2 Hz), 6.40 (1H, d, *J*=2.0 Hz), 6.20 (1H, d, *J*=2.0 Hz). On acid hydrolysis, **1** gave glucose, galactose and kaempferol. **1** was identified as kaempferol 3-*O*-β-D-glucopyranosyl (1→2)-β-D-galactopyranoside[6] by the comparison of the ^{13}C-NMR signals with those reported.[6]

Quercetin 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranoside (2) Yellow powder, $[\alpha]_D$ −20.5° (*c*= 0.4, MeOH). IR (KBr), cm^{-1}: 3400, 1660, 1610. FAB-MS, *m/z*: 625 ($[M-H]^-$). ^{1}H-NMR (DMSO-d_6), δ: 6.84 (1H, d, *J*=8.4 Hz), 7.53 (1H, d, *J*=2.2 Hz), 7.69 (1H, dd, *J*=2.2, 8.4 Hz), 6.39 (1H, d, *J*=2.2 Hz), 6.20 (1H, d, *J*=2.2 Hz). On acid hydrolysis, **1** gave glucose, galactose and quercetin. **2** was identified as quercetin 3-*O*-β-D-glucopyranosyl(1→2)-β-D-galactopyranoside by the comparison of the ^{1}H and ^{13}C-NMR signals with those reported.[7]

Oplopanaxoside A (3) White powder, $[\alpha]_D$ −30.3° (*c* =1.0, pyridine). IR (nujol), cm^{-1}: 3400 (OH), 1720 (ester), 1700 (COOH), 1640, 880 (>C=CH_2). FAB-MS, *m/z*: 979.4832 ($[M+Na]^+$, $C_{48}H_{76}O_{19}\cdot Na$ requires 979.4878). FAB-MS, *m/z*: 955 ($[M-H]^-$), 809 ([M−methylpentose−H]$^-$), 647 ([M−methylpentose−hexose−H]$^-$), 485 ([M−methylpentose−2×hexose−H]$^-$). ^{1}H-NMR (C_5D_5N-D_2O (2 : 1, v/v)), δ: 0.69 (3H, s, H_3-27), 0.79 (3H, s, H_3-25), 0.97 (3H, s, H_3-26), 1.27 (3H, s, H_3-24), 1.66 (3H, s, H_3-30), 1.58 (3H, d, *J*=6 Hz, Rha H_3-6), 4.46, 4.77 (1H each, m, >C=CH_2), 4.81 (1H, d, *J*=8 Hz, outer Glc H-1), 5.43 (1H, s, Rha H-1), 6.06 (1H, d, *J*=7 Hz, inner Glc H-1). ^{13}C-NMR (C_5D_5N-D_2O (2 : 1, v/v)): TABLE I. **3** (40 mg) was acetylated with Ac_2O and pyridine at rt for 12 h to give **3b** (39 mg), colorless needles (MeOH), mp. 168-171℃ (Ref. 8) 168-170℃), which was methylated with diazomethane etherate to give **3c** (30 mg), colorless needles (MeOH), mp 176-178℃ (Ref. 8) 175-178℃). **3c** was identified as decaacetate of 3α-hydroxy-20(29)-ene-23,28-dioic acid 28-*O*-α-L-rhamnopyranosyl(1→4)-*O*-β-D-glucopyranosyl (1→6)-β-D-glucopyranoside methyl ester by mixed fusion with an authentic sample kindly provided by Dr. Kitajima.

Oplopanaxoside B (4) White powder, mp. 280-283℃ (decomp.), $[\alpha]_D$ −27.7° (*c*=1.0, MeOH). IR (nujol), cm^{-1}: 3400 (OH), 1720 (ester), 1700 (COOH), 1640, 880 (>C=CH_2). FAB-MS, *m/z*: 955.4949 ($[M-H]^-$, $C_{48}H_{75}O_{19}$ requires 955.4902), 809 ([M−methylpentose−H]$^-$), 647 ([M−methylpentose−hexose−H]$^-$), 485 ([M−methylpentose−2×hexose−H]$^-$). ^{1}H-NMR (C_5-D_5N-D_2O (2 : 1, v/v)), δ: 0.70 (3H, s, H_3-27), 0.79 (3H, s, H_3-25), 0.97 (3H, s, H_3-26), 1.27 (3H, s, H_3-24), 1.66 (3H, s, H_3-30), 1.59 (3H, d, *J*=6 Hz, Rha H_3-6), 4.46, 4.77 (1H each, m, >C=CH_2), 4.80 (1H, d, *J*=8 Hz, outer Glc H-1), 5.48 (1H, br s, Rha H-1), 6.06 (1H, d, *J*=8 Hz, inner Glc H-1). ^{13}C-NMR (C_5D_5N): TABLE I.

Oplopanaxoside C (5) White powder, mp. 256-258℃ (decomp.), $[\alpha]_D$ −40.0° (*c*=0.06, MeOH). IR (KBr), cm^{-1}: 3400 (OH), 1725 (COOR), 1640, 880 (>C=CH_2). FAB-MS, *m/z*: 941.5129 ($[M-H]^-$, $C_{48}H_{77}O_{18}$ requires 941.5110), 795 ([M−methylpentose−H]$^-$), 633 ([M−methylpentose−hexose−H]$^-$), 471 ([M−methylpentose−2×hexose−H]$^-$). ^{1}H-NMR (C_5D_5N), δ: 0.90, 0.98, 1.03, 1.17, 1.73 (3H each, s), 1.70 (3H, d, *J*=6.2 Hz), 4.46, 4.77 (1H each, m, >C=CH_2), 4.81 (1H, d, *J*=8 Hz, outer Glc H-1), 5.48 (1H, br s, Rha H-1), 6.06 (1H, d, *J* =8 Hz, inner Glc H-1). ^{13}C-NMR (C_5D_5N): TABLE I.

Oplopanaxoside E (6) White powder, mp. 250-253℃ (decomp.), $[\alpha]_D$ −32.0° (*c*=0.5, MeOH). IR (KBr), cm^{-1}: 3400 (OH), 1725 (COOR), 1640, 880 (>C=CH_2). FAB-MS, *m/z*: 941.5150 ($[M-H]^-$, $C_{48}H_{77}O_{18}$ requires 941.5110), 795 ([M−methylpentose−H]$^-$), 633 ([M−methylpentose−hexose−H]$^-$), 471 ([M−methylpentose−2×hexose−H]$^-$). ^{1}H-NMR (C_5D_5N), δ: 0.90, 0.98, 1.03, 1.17, 1.73 (3H each, s), 1.70 (3H, d, *J*=6.2 Hz), 4.46, 4.70 (1H each, m, >C=CH_2), 4.81 (1H, d, *J*= 8 Hz, inner Glc H-1), 5.48 (1H, br s, Rha H-1), 6.06 (1H, d, *J*=8 Hz, outer Glc H-1). ^{13}C-NMR (C_5D_5N): TABLE I.

Acid hydrolysis of compounds 1-2 Solutions of **1** and **2** (20 mg) in 2 N H_2SO_4 (2 ml) were each heated in a boiling water bath for 2 h, cooled and the precipitates formed were collected by filtration, which were identified as kaempferol and quercetin, respectively, by direct comparison on TLC with respective authentic specimen: *Rf* 0.83 (kaempferol), 0.75 (quercetin). The filtrate was neutralized, derivatized to TMS ether and examined on GLC (condition a): t_R (min), 6.0, 9.0 (glucose), 5.2, 6.3 (galactose).

Acid hydrolysis of compounds 3-6 Solution of **3-6** (20 mg) in 2 N H_2SO_4 (2 ml) were each heated in a boiling water bath for 2 h, cooled and the mixtures were extracted with $CHCl_3$ (1 ml×3). The aq. layers were neutralized, derivatized to TMS ether and examined on GLC (condition b): t_R (min), 11.7, 14.3, 15.9 (glucose), 3.4, 4.6, 6.1 (rhamnose). The $CHCl_3$ solutions were dried over Na_2SO_4 followed by removal of the solvent to give **3a** (5.1 mg), **4a** (9.2 mg), **5a** (5.0 mg) and **6a** (8.2 mg) from **3**, **4**, **5** and **6**, respectively.

Compound **3a**: Colorless needles (hexane-EtOAc), mp. 274-277℃. EI-MS, *m/z*: 486 (M^+), 468, 440, 422, 259, 250, 248, 234, 219, 203, 189 (base peak). ^{1}H-NMR ($CDCl_3$-CD_3OD (3 : 1, v/v)), δ: 0.88, 0.96, 1.02, 1.15, 1.70 (3H each, s, *tert*-CH_3), 3.74 (1H, br s, H-3β), 4.59, 4.72 (1H, each, m, >C=CH_2). ^{13}C-NMR (C_5D_5N): Table I. **3a** was identified as 3α-hydroxylup-20(29)-ene-23,28-dioic acid by the direct comparison of the spectral data with those kindly provided by Dr. Kitajima.[8]

Compound **4a**: Colorless needles (hexane-EtOAc), mp. 281-284℃ (dec.). EI-MS, *m/z*: 486 (M^+), 468, 440, 422, 259, 250, 248, 234, 219, 203, 189 (base peak). ^{1}H-NMR ($CDCl_3$-CD_3OD (3 : 1, v/v)), δ: 0.88, 0.96, 1.02, 1.15, 1.70 (3H each, s, *tert*-CH_3), 3.87 (1H, dd, J = 4, 11 Hz, H-3α), 4.60, 4.72 (1H each, m, >C=CH_2). ^{13}C-NMR (C_5D_5N): Table I.

Compound **5a**: White powder (mp. 270-273℃). EI-MS, *m/z*: 472 (M^+), 454, 436, 395, 248, 223, 203, 189 (base peak). ^{1}H-NMR (C_5D_5N), δ: 0.77, 0.88, 0.97, 1.09, 1.80 (3H each, s, *tert*-CH_3), 3.94 (1H, br s, H-3β), 4.76, 4.94 (1H each, m, >C=CH_2). ^{13}C-NMR (C_5D_5N): Table I.

Compound **6a**: White powder (mp. 265-268℃). EI-MS, *m/z*: 472 (M^+), 454, 436, 395, 248, 223, 203, 189 (base peak). ^{1}H-NMR (C_5D_5N), δ: 0.91, 1.02, 1.04, 1.09, 1.78 (3H each, s, *tert*-CH_3), 2.23 (2H, m), 2.59 (1H, d, J=12 Hz), 2.74 (1H, br t), 3.54, 4.19 (1H each, m, >C=CH_2), 3.71, 4.18 (1H each, d, J=10 Hz), 4.77, 4.94 (1H each, s). ^{13}C-NMR (C_5D_5N): Table I. **6a** was identified as 3β, 23-dyhydroxylup-20(29)-en-28-oic acid by the comparison of the NMR data with those reported.[12]

Selective cleavage of esteric glycoside linkage A solution of a sample (20 mg) and LiI (20 mg) in anhydrous MeOH (2 ml) containing 2,6-lutidine (0.5 ml) was refluxed for 24 h under N_2. After cool, the reaction mixture was diluted with 50% aq. MeOH and deionized with Amberlite MB-3 resin followed by removal of the solvent *in vacuo*. The residue was chromatographed on silica gel ($CHCl_3$-MeOH-H_2O (6 : 4 : 1, v/v)) to give an aglycone and a methyl oligosaccharide (**7**), the latter being identified as an anomeric mixture of methyl α-L-rhamnopyranosyl(1→6)-β-D-glucopyranosyl(1→4)-α- and β-D-glucopyranosides by the direct comparison of the spectral data with those of an authentic sample.[10] The aglycones obtained from **3**, **4**, **5** and **6** were identified as **3a** (6.0 mg), **4a** (7.1 mg), **5a** (4.4 mg) and **6a** (4.2 mg), respectively, by the direct comparison of the spectral data with those of respective authentic sample.

Preparation of 3-oxo-20(29)-ene-23,28-dioic acid dimethyl ester (8) **3a** was treated with diazomethane etherate to give **3a** dimethyl ester (**3d**),[8] colorless needles (MeOH), mp. 251-255℃, $[\alpha]_D$ −10.5° (c=0.5, $CHCl_3$). IR (CCl_4), cm^{-1}: 3630, 3500, 1725, 1640. ^{1}H-NMR ($CDCl_3$), δ: 0.87, 0.92, 1.00, 1.16, 1.69 (3H each, s, *tert*-CH_3), 3.66, 3.70 (3H each, s, OMe), 3.77 (1H, t, J= 5.4 Hz), 4.60, 4.77 (1H each, s). EI-MS, *m/z*: 514 (M^+, $C_{32}H_{50}O_5$), 496, 482, 454, 264, 262, 249, 248, 233, 203, 189 (base peak), 175. A solution of **3d** (10 mg) was oxidized with CrO_3 (3 mg) in AcOH (2 ml) at rt for 8 h[8]. The reaction mixture was diluted with H_2O and extracted with Et_2O. The Et_2O solution was, after the usual treatment, evaporated to dryness, and the residue was purified by silica gel column chromatography (hexane-EtOAc (10 : 1, v/v)) to give **8**, colorless needles (hexane), mp 132-134℃. ^{1}H-NMR ($CDCl_3$), δ: 0.95, 0.98, 0.99, 1.33, 1.69 (3H each, s, *tert*-CH_3), 3.67, 3.71 (3H each, s, $COOCH_3$), 4.60, 4.73 (1H each, m, >C=CH_2). ^{13}C-NMR ($CDCl_3$): Table I. **4a** was treated with diazomethane etherate to give **4a** dimethyl ester (**4b**).[8] Compound **4b**: White powder, mp. 232-233℃, $[\alpha]_D$ −11.0° (c=1.15, $CHCl_3$). IR (CCl_4), cm^{-1}: 3630, 3500, 1725, 1640. ^{1}H-NMR ($CDCl_3$), δ: 1.69, 1.11, 0.97, 0.90, 0.84 (3H each, s, *tert*-Me), 3.71, 3.66 (3H each, s, OMe), 3.99 (1H, dd, J=4, 11 Hz), 4.60 (1H, m), 4.74 (1H, m). EI-MS, *m/z*: 514 (M^+), 496, 482, 454, 432, 395, 273, 264, 262, 251, 249, 233, 203, 189 (base peak), 175, 168, 167, 161, 147, 133, 119, 105. **4b** (10 mg) was oxidized in the same manner as mentioned above for **3d** to give **8**.

Conversion of 3 to 5 by reduction with $LiBH_4$ Treatment of **3** (120 mg) in MeOH (4 ml) with CH_2N_2 etherate gave a methyl ester of **3**: amorphous powder. ^{1}H-NMR (C_5D_5N), δ: 0.83, 0.89, 1.17, 1.30, 1.69 (3H each, s, CH_3), 1.70 (3H, d, J=6 Hz, Rha H_3-6), 3.66 (3H, s, OCH_3), 4.92 (1H, d, J=8 Hz, outer Glc H-1), 5.83 (1H, s, Rha H-1), 6.33 (1H, d, J=7 Hz, inner Glc H-1). The methyl ester of **3** was heated at 60℃ with $LiBH_4$ (100 mg) in EtOH (10 ml) for 96 h. After decomposition of the excess reagent with acetone (1 ml) followed by removal of the solvent *in vacuo*, and silica gel chromatography with $CHCl_3$-MeOH-H_2O (30 : 10 : 1, v/v) **5** (20 mg) and the starting material (7 mg) were obtained.

Conversion of 4 to 6 by reduction with $LiBH_4$ **4** (20 mg) was methylated as in the case of **3** to give a methyl ester of **4** as amorphous powder. ^{1}H-NMR (C_5D_5N), δ: 0.85, 0.96, 1.12, 1.50, 1.71 (3H each, s, CH_3),

TABLE I. ^{13}C-NMR Signals of Oplopanaxosides and Their Aglycones

Carbons	A(3)	B(4)	C(5)	D(6)	3a	4a	5a	6a	8	7	
										7a	7b
1	33.1	38.6	33.7	39.1	32.8	38.5	33.7	38.6	38.7		
2	26.0	27.9	26.8	27.8	26.1	27.4	26.7	27.9	34.6		
3	72.8	74.0	75.8	73.2	72.9	73.3	75.7	73.4	211.2		
4	51.8	54.6	43.7	42.9	51.9	54.4	43.7	48.7	61.4		
5	45.2	52.0	40.8	48.6	45.0	51.4	40.8	42.9	51.2		
6	21.6	21.4	18.5	18.5	21.0	20.8	18.4	18.6	21.3		
7	34.5	34.7	34.3	34.3	34.7	34.5	34.4	34.5	33.3		
8	41.7	39.6	41.3	41.1	41.8	41.3	41.2	41.1	40.8		
9	51.0	51.3	49.7	49.7	51.0	50.6	49.7	49.7	49.9		
10	36.8	37.0	37.5	37.3	37.4	37.3	37.6	37.6	36.2		
11	20.9	21.9	21.0	21.1	21.7	21.5	21.1	21.2	21.2		
12	26.0	26.2	26.0	26.0	26.1	25.9	26.1	26.1	25.4		
13	38.4	38.6	38.3	38.3	38.6	38.5	38.6	39.1	38.2		
14	42.8	43.0	42.8	42.7	42.9	42.7	42.9	42.9	42.5		
15	30.0	30.3	30.1	29.9	30.2	30.1	30.2	30.3	29.6		
16	32.2	32.4	30.8	30.8	33.0	32.5	32.8	32.8	32.0		
17	56.9	57.1	57.0	56.9	66.6	56.6	56.6	56.6	56.5		
18	47.3	47.5	47.4	47.4	47.8	47.7	47.7	47.7	49.3		
19	49.7	50.1	50.8	50.9	49.7	49.6	50.8	49.7	46.9		
20	150.8	151.0	150.9	150.8	151.3	150.8	161.3	151.3	150.5		
21	30.8	31.1	32.2	32.2	31.2	31.0	31.2	31.2	30.5		
22	37.4	37.2	36.9	36.8	37.5	37.4	37.3	37.3	36.9		
23	180.4*	181.9	71.3	67.6	179.5	179.4	71.3	67.8	173.9		
24	18.0	14.2	18.0	12.9	17.9	12.0	18.0	12.9	16.6		
25	16.7	16.9	16.7	16.8	16.7	16.6	16.6	16.8	15.6		
26	16.6	16.5	16.4	16.4	16.7	16.6	16.4	16.4	15.8		
27	14.8	15.1	14.9	14.8	14.8	14.7	14.9	14.9	14.7		
28	175.0*	175.1	175.0	174.9	178.8	178.9	178.9	178.9	176.6		
29	109.9	110.0	110.0	110.0	109.9	109.7	109.9	109.9	109.7		
30	19.4	19.6	19.3	19.3	19.4	19.3	19.4	19.4	19.3		
23-OMe	—	—	—	—	—	—	—	—	52.5		
28-OMe	—	—	—	—	—	—	—	—	51.3		
Glc (inner)											
1	95.2	95.4	95.3	95.2						101.0	105.5
2	73.9	74.0	74.0	74.0						73.6	74.9
3	78.5	78.9	78.7	78.6						75.0	78.2
4	70.8	71.3	70.8	70.7						72.2	71.4
5	77.8	78.0	78.2	78.1						72.5	76.8
6	69.4	69.8	69.4	69.3						70.1	69.9
Glc (outer)											
1	104.8	105.1	105.2	105.0						104.8	104.6
2	75.1	75.3	75.3	75.2						75.0	75.0
3	76.4	76.6	76.4	76.4						76.2	76.2
4	78.4	78.8	78.0	77.9						78.1	78.1
5	76.9	77.2	77.2	77.0						76.8	76.8
6	61.3	61.7	61.3	61.2						61.1	61.1
Rha (terminal)											
1	102.6	102.8	102.7	102.6						102.4	102.4
2	72.5	72.8	72.8	72.7						72.4	72.4
3	72.3	72.5	72.6	72.5						72.5	72.5
4	73.8	74.1	74.0	73.9						73.6	73.6
5	70.2	70.4	70.3	70.3						70.1	70.1
6	18.3	18.4	18.5	18.5						18.2	18.2
OMe										55.0	56.7

* In consideration of glycosylation shift, the signals assigned to C_{23} and C_{28} by Kitajima and Tanaka[8] must be exchanged.

1.70 (3H, d, J=6 Hz, Rha H_3-6), 3.63 (3H, s, OCH_3), 4.90 (1H, d, J=8 Hz, outer Glc H-1), 5.87 (1H, s, Rha H-1), 6.36 (1H, d, J=7 Hz, inner Glc H-1). The methyl ester of **4** was treated as described above for **3** methyl ester to give **6** (4 mg) and the starting material **4** (2 mg).

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REFERENCES AND NOTES

1) Jiang su xin yi yuan, "Zhong yao da ci dian" (中薬大辞典), Shanghai ren min Pub. Co., Shanghai, 1977, p. 1266.
2) T. Kariyone, S. Morotomi, *Yakugaku Zasshi*, **47**, 671 (1927).
3) K. Takeda, H. Minato, M. Ishikawa, *Tetrahedron Suppl.*, **7**, 219 (1965).
4) H. Minato, M. Ishikawa, *J. Chem. Soc.*(*C*), 423 (1963).
5) M. Takahashi, T. Sato, C. K. Chan, *Annu. Rep. Tohoku Coll. Pharm.*, **27**, 91 (1980).
6) M. Haraguchi, M. Motidome, O. R. Gottlieb, *Phytochemistry*, **27**, 2291 (1988).
7) D. Strack, B. Meurer, V. Wray, L. Grotjahn, F. A. Austenfeld, R. Wiermann, *Phytochemistry*, **23**, 2970 (1984).
8) J. Kitajima, T. Tanaka, *Chem. Pharm. Bull.*, **37**, 2727 (1989).
9) H. Kimata, T. Nakashima, S. Kokubun, K. Nakayama, Y. Mitoma, T. Kitahara, N. Yata, O. Tanaka, *Chem. Pharm. Bull.*, **31**, 1998 (1983).
10) M. Miyakoshi, Y. Ida, S. Isoda, J. Shoji, *Phytochemistry*, **33**, 891 (1993).
11) Cleavage of the esteric glycoside linkage might have occurred in this reaction, since a few spots appeared in the less polar region on TLC plate.
12) A. Ikuta, H. Itokawa, *Phytochemistry*, **27**, 2813 (1988). cf.: The carbon signals for triterpenoids in our report were mainly referred to those reported by Kitajima and Tanaka.[8)]