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Triterpenoidal Saponins from the Bark of *Kalopanax pictum* var. *typicum*

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Abstract □ One new triterpenoidal saponin, saponin F(**2**) has been isolated from the bark of *Kalopanax pictum* Nakai var. *typicum* (Araliaceae), together with one known saponin, kizuta saponin K_{12} (**1**). On the basis of chemico-spectral evidences, the structure of **2** has been elucidated to be 3-*O*-β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranosyl-23-hydroxyolean-12-en-28-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl ester.

Key words □ *Kalopanax pictum* Nakai var. *typicum*, Araliaceae, hederagenin pentaglycoside, new hederagenin hexaglycoside, Korean folk medicine, Kalopanacis Cortex.

Kalopanax pictum Nakai var. *typicum* is a deciduous tree of the family of Araliaceae, which is distributed throughout Korea. The stem bark of the title plant, including another *Kalopanax* spp. has been used in the traditional Korean folk medicine for neuralgia, anti-rheumatis, arthritis, lumbalgia, antidiabetes and tonic under the name of Kalopanacis Cortex (Hae Dong Pie)[1,2]. The reports of isolation and characterization of *Kalopanax* spp. saponins have been compiled[3-9].

In the previous papers[10,11], we reported the isolation and identification of the kizuta saponins K_3, K_6, K_{12} and (+)-syringaresinol-di-β-D-glucoside from *Kalopanax pictum* var. *maximowiczii* and *Kalopanax pictum* Nakai var. *magnificum*.

Continuing the chemical investigation of the *Kalopanax* spp. grown in Korea, this paper deals with the isolation and structure elucidation of one new saponin together with identification of one known saponin from the stem bark of the title plant.

A suspension of MeOH extract of the sample in water has been washed with EtOAc and extracted with H_2O saturated *n*-BuOH. TLC of the *n*-BuOH fraction indicated the presence of five kinds of saponins tentatively named saponins C-F. Among them two kinds of saponins D (**1**) and F (**2**) have been isolated by using preparative LC according to their t_R (9.50, 10.75), in the yield of 0.65 and 0.58%, respectively.

Saponin D (**1**) was obtained in the form of colorless powder. Its IR spectrum showed the presence of an ester linkage (1732 cm^{-1}). The ^{1}H-NMR spectrum showed six quaternary methyl signals at δ 0.72-1.25 ($CH_3 \times 6$), five anomeric proton signals at δ 4.97 (1H, d, J=7.7 Hz, anomeric H) 5.16(1H,d,J=7.0 Hz, anomeric H), 5.81 (1H, br.s, anomeric H), 6.20 (1H, d, J=7.8 Hz, anomeric H) and 6.27 (1H, s, anomeric H), and secondary methyl doublet at δ 1.61, 1.67 (each 3H, d, J=6.2 Hz, Me of rhamnose).

On acid hydrolysis, **1** afforded hederagnin (**3**) and arabinose, rhamnose and glucose (1:2:2) as glycone component. Furthermore, alkaline hydrolysis was done with **1** and the resulting mixture was extracted with *n*-BuOH. The treatment of *n*-BuOH extract with diazomethane afforded a monomethyl ester, which is identical with authentic specimen, kizuta saponin K_6 monomethyl ester. The aqueous layer was hydrolyzed with HCl and analyzed by GLC and TLC, showed the presence of rhamnose and glucose (molar ratio, 1:2).

These results of above mentioned suggested that **1** is an ester composed of kizuta saponin K_6 as the acidic part, and rhamnose and glucose as the alcohol part. This was supported by the analysis of ^{1}H-NMR and ^{13}C-NMR spectra of **1** as follows. The signal at δ 6.20 ppm (1H, d, J=7.8 Hz) in the

^{1}H-NMR spectrum of **1** can be attributed to the anomeric proton of glucose linked to the C-28 carboxyl group of kizuta saponin K_6 in the ester form.

The ^{13}C-NMR signal in the anomeric carbon of glucose showed at 95.2 ppm, supporting the view that inner glucose is linked C-28 with the ester form. ^{13}C-NMR data are shown in Table I.

The comparison of the ^{13}C-NMR spectrum of **1** with those of known compound showed that the signals due to sugar moieties of **1** are in good agreement with those of authentic kizuta saponin K_6 and K_{12}[12]. On the basis of these observation, saponin **1** can be formulated as 3-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl-23-hydroxyolean-12-en-28-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl ester.

Saponin F(**2**) was obtained as white powder. The IR spectrum showed the presence of an ester linkage (1735 cm^{-1}). Its ^{1}H-NMR spectrum showed six quaternary signals at δ 0.84-1.16 (3H, s, CH_3×6), six anomeric proton signals at δ 4.97 (1H, d, J=7.8 Hz, anomeric H), 5.16 (1H, d, J=7.0 Hz, anomeric H), 5.20 (1H, d, J=7.6 Hz, anomeric H), 5.81 (1H, br.s, anomeric H), 6.20 (1H, d, J=7.8 Hz, anomeric H), 5.98 (1H, s, anomeric H), and secondary methyl doubles at δ 1.61 and 1.67 (each 3H, d, J=6.2 Hz, Me of rhamnose).

On acid hydrolysis, **2** afforded **3** as the sapogenin, xylose, arabinose, rhamnose, and glucose (molar ratio, 1:1:2:2) as the glycone part.

The alkaline hydrolysis was done with **2** and the resulting mixture was extracted with water saturated *n*-BuOH. By purification through repeated silica gel column chromatography of the *n*-BuOH extract, the prosapogenin **5** was deposited as whitish crystals. The IR spectrum of **5** showed the presence of carboxyl residue (1710 cm^{-1}) and exhibited ion at *m/z* 881 in negative FAB-MS and afforded **3**, arabinose, rhamnose and xylose on acid hydrolysis. The glycosylation shift around 3-C as well as three anomeric carbon signals at δ 107.4, 104.7 and 101.4 in the ^{13}C-NMR spectrum of **5** disclosed that **5** is a 3-*O*-glycoside of **3** which has three monosaccharide units. In the negative FAB-MS of **2**, ion at *m/z* 881 [M$^+$], 749 [M$^+$-(xylose)], 603 [M$^+$-(xylose-rhamnose)] and 471 [M$^+$-(xylose+rhamnose+arabinose)] (=aglycone) indicated that sugar moiety of **2** consists of a linear xylose-rhamnose-arabinose unit.

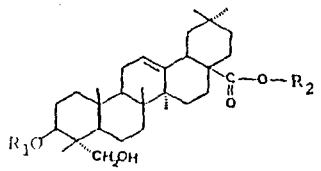
On partial hydrolysis, **5** afforded **6** with xylose. and **7** with xylose, and rhamnose. **6** and **7** identified by comparison of the ^{1}H-NMR and ^{13}C-NMR spectrum with those of authentic sample, are kizuta saponin K_6 and K_3, repsectively.

Methanolysis of permethylate (**8**) of **5** yielded 23-*O*-methyl hederagenin methyl ether and methyl 3,4-di-*O*-methylarabinopyranoside (t_R 25.0), methyl 2,4-di-*O*-methylrhamnopyranoside (t_R 10.1), methyl 2,3,4-tri-*O*-mthyl-xylopyranoside (t_R 6.8). From these results the structure of **5** (prosagogenin of **2**), was established as 3-*O*-β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranoside of **3** and identified with saponin P_g from *Akebia quinata*[13].

The aqueous layer, from the alkaline hydrolysis of **2**, was hydrolyzed with HCl and analyzed by GLC and TLC, showing the presence of rhamnose and glucose (1:2). These experimental facts suggested that **2** was an ester composed of **5** as the acid part, and rhamnose and glucose as the alcohol part. This was supported by analysis of ^{1}H-NMR and ^{13}C-NMR data of **2** as follows. The signal at δ 6.20 ppm (1H, d, J=7.8 Hz) in ^{1}H-NMR spectrum of **2** can be attributed to the anomeric proton of glucose linked to the 28-carboxyl group of **5** in the ester form. The signal of the anomeric carbon of the glucose was observed at 95.2 ppm, supporting the view that the glucose is linked to the C-28 ester form.

Selective cleavage of the ester linkage of 2

According to the reported method[14], **2** afforded permethylate (**8**) of **5**, along with the common methyl trisaccharide, which was identified as methyl-α-L-rhamnopyranosyl(1→4)-β-D-glycopyranosyl-(1→6)-β-D-glucopyranoside by comparison of ^{13}C-NMR spectrum with that authentic sample. The comparion of ^{1}H-NMR and ^{13}C-NMR comparsion of **2**



	R_1	R_2
I	-Ara-(2)-Rha	-Glc-(6)-Glc-(4)-Rha
II	-Ara-(2)-Rha-(3)-Xyl	-Glc-(6)-Glc-(4)-Rha

Chart 1.

with those of known compound showed that the signals due to the sugar moeity of C-28 linked are in good agreement with authentic kizuta saponin K_{12} and chiisanoside[15-17].

Based on the above observation, the structure of **2** can be formulated as 3-*O*-β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranosyl-23-hydroxy-olean-12-en-28-*O*-α-L-rhamnopyranosyl-(1→4)-β-D-glycopyranosyl-(1→6)-β-D-glycopyranosyl ester.

EXPERIMENTAL

All melting points were measured with Electrothermal Digital melting point apparatus and uncorrected. IR spectra were taken by Bio-Rad FT-infrared spectrometer Model FTS-40. GLC was perfomed on a Shimadzu GC-9A gas chromatograph. ^{1}H-NMR spectra were measured on a Bruker AM-200, AM-100 spectrometer and ^{13}C-NMR spectra were measured on a JEOL FX-100 spectrometer, using tetramethylsilan as an internal standard. Chemical shifts are given in δ (ppm). Mass spectra were recorded on a JEOL MS spectrometer. Elemental analysis was performed by Perkin-Elmer 240EA. Optical rotation was measured with Rudolph Autopol-TM-III automatic polarimeter. Preparative liquid chromatography was carried out on a column of μ-Bondapak C_{18}, JAIGEL ODP-90 with Japan Analytical Industry LC-20. For column chromatography, Silicagel 60 F_{254} (thickness 0.2 mm, Merck) was used. GC-MS were taken on Shimazu GC-MS 7000s, glass column 2.6×1.5 m packed with 5% ECNSS-M on Chromosorb W, injection temp. 200℃, column temp. 170℃, carrier gas He at 35 ml/min, spearator temp 250℃, ionization voltage 70 eV, accelerating voltage 1.5 kV. Solvent A, homogenous of $CHCl_3$:MeOH:H_2O (70:30:4 v/v); solvent B, the upper phase of *n*-BuOH:HOAc:H_2O (4:1:5 v/v).

Extraction and isolation of saponins 1 and 2

Air dried barks *Kalopanax pictum* var. *typicum* (3 kg), collected in Kang Won province, Korea, were extracted with hexane and hot MeOH. A suspension of MeOH extract in H_2O was washed with EtOAc and then extracted with water saturated *n*-BuOH. The *n*-BuOH layer was concentrated to dryness to give a crude saponins (45 g), which was dissolved in small quantitative MeOH and poured in acetone. The resulting precipitate (36 g) showed the presence of five kinds of saponins by TLC, which were named saponin C-F according to their R_f. Among them D (R_f 0.28) and F (R_f 0.21) were separated by using preparative LC according to their t_R (9.50, 10.75) with 30% acetonitrile in water.

Saponin D (1)

A white powder, mp. 225-227 (dec.). $[\alpha]_D$ -8.0° (*c* 0.05, MeOH) Anal. Calcd. for $C_{59}H_{96}O_{26}$ $3H_2O$; C 55.5: H 8.25, Found: C 55.25: H 8.25. IR ν_{max}^{KBr} cm^{-1} 3380 (OH) 1751 (Ester), 1100-1000 (C-O), 1057 (CH_2OH), ^{1}H-NMR: 0.72 (3H, s), 0.98 (6H, s), 1.24 (9H, s, CH_3×3), 1.65, 1.71 (each 3H, d, J=6.2 Hz, Me of rhamnose ×2) 4.97 (1H, d, anomeric H, C-28, outer glucose), 5.16 (1H, d, anomeric H, arabinose), 5.81 (1H, br.s, anomeric H, rhamnose in C-28 sugar moiety, terminal), 6.20 (1H, d, anomeric H, inner glucose in C-28-sugar moiety), 6.27 (1H, s, anomeric H, rhamnose, in 3-*O*-sugar moiety). ^{13}C-NMR data are listed in Table I.

Saponin F (2)

A white powder, mp. 223-225℃ (uncorr.) $[\alpha]_D$ -48° (*c* 0.05, MeOH). Anal. Calcd., for $C_{64}H_{104}O_{30}$; C 56.8: H 7.7 Found: C 56.0: H 7.6 IR ν_{max}^{KBr} 3400 (OH), 1732 (COO-R), 1640 (C=C), 1100-1000 (glycosidic C-O), ^{1}H-NMR: 0.84, 0.85, 0.95, 1.08, 1.12, 1.16 (3H, s, CH_3×6), 1.61 (3H, d, CH_3 of rhamnose J=6.2 Hz), 1.67 (3H, d, CH_3 of rhamnose J=6.2 Hz), 4.97 (1H, d, anomeric H, C-28 outer), 6.20 (1H, d, glucose anomeric H, C-28 ester), 5.16 (1H, arabinose, anomeric H), 5.20 (xylose, anomeric H), 5.81 (rhamnose, anomeric H, C-28 terminal), 5.98 (rhamnose, anomeric H, C-3 inner).

Hydrolysis of 1 and 2

A solution of saponins (each 100 mg) in 2N HCl-dioxane (1:1) was heated under reflux (90℃, 4 h), and diluted with H_2O, then extracted with $CHCl_3$. The residue from $CHCl_3$ extract was chromatographed on silica gel column chromatography (elution solvent; $CHCl_3$:MeOH, 7:3).

The eluates (from **1** and **2**) were concentrated separately, the resulted residues were recrystalyzed in MeOH to gave same aglycone **3**, colorless prism, mp. >300℃, which were identified as hederagenin by direct comparisons. After being neutralized with Amberite MB-3, the filtrate was concentrated to a

Table I. ^{13}C-Chemical shifts (δ) of **1**, **2** in C_5D_5N

Carbon No.	Hederagenin	1	2	C-3 sugar	1	2	C-28 sugar	1	2
3	73.7	81.1	81.2	Ara-1	104.2	104.7	Glc-1	95.2	95.2
12	122.7	122.5	122.6	Ara-2	75.8	75.6	Glc-2	73.8	73.7
13	145.0	144.1	144.1	Ara-3	74.4	74.8	Glc-3	78.3	78.4
23	68.2	64.0	64.0	Ara-4	69.7	69.6	Glc-4	70.7	70.5
28	180.4	176.5	176.6	Ara-5	66.4	66.2	Glc-5	77.2	76.3
				Rha-1	101.6	101.4	Glc-6	69.1	69.3
				Rha-2	72.2	71.9	Glc-1	104.6	104.7
				Rha-3	72.6	83.1	Glc-2	75.8	75.2
				Rha-4	73.9	73.7	Glc-3	76.5	76.9
				Rha-5	69.7	70.3	Glc-4	78.3	78.4
				Rha-6	18.4	18.5	Glc-5	77.8	77.6
				Xyl-1		107.4	Glc-6	61.3	61.3
				Xyl-2		75.3	Rha-1	102.7	102.5
				Xyl-3		78.3	Rha-2	72.2	72.4*
				Xyl-4		71.0	Rha-3	72.5	72.3*
				Xyl-5		67.4	Rha-4	73.9	73.9
							Rha-5	*70.3*	*70.3*
							Rha-6	18.5	18.3

*May be reversed

small volume and examined by TLC and GLC, to show the presence of glucose, rhamnose, arabinose from **1**, glucose, rhamnose, arabinose and xylose (t_R 17.5, 7.7, 7.4, 10.1) from **2**.

Alkaline hydrolysis

1 and **2** (each 100 mg) were heated on water bath with 0.5 N KOH in MeOH for 1 h. The reaction mixture was diluted with H_2O, neutralized with Amberite MB-3, extracted with EtOAc (1:1). The organic layer washed with H_2O and concentrated to give prosapogenins **4** and **5**.

4: colorless needle (MeOH), mp. 248-249℃ (dec.), $[\alpha]_D$+18.8° (pyridine). Anal. Calcd. for $C_{41}O_{66}O_{12}$. $2H_2O$, C 62.55: H 8.94, Found: C 62.4: H 8.96. IR ν_{max}^{KBr} cm^{-1}, 3400 (OH), 1700 (COOH). ^{1}H-NMR δ: 0.69 (3H, s), 0.70 (3H, s), 0.80 (3H, s), 1.15 (6H, s), 1.25 (3H, s), 5.16 (1H, s, anomeric, arabinose), 6.27 (1H, br.s. anomeric rhamnose), **5**: A white powder, mp. 220-222℃ (dec.), $[\alpha]_D$+17.5° (*c* 0.05, MeOH), Anal. Calcd for $C_{46}H_{74}O_6$; C 57.30: H 8.70. Found: C 57.28: H 8.66, IR ν_{max}^{KBr} cm^{-1} 3380 (OH), 1710 (COOH), 1636 (C=C), 1100-1000 (glycosidic C-O). ^{1}H-NMR (pyridine-d_5), δ 0.90, 0.91, 0.97, 1.0 1.1, 1.22 (3H, s, CH_3×6), 1.61 (3H, d, Me of rhamnose J=6.1 Hz), 5.16 (1H, d, J=7.0 Hz, anomeric H), 5.20 (1H, d, anomeric, J=7.6 Hz), 5.98 (1H, s, anomeric H).

Permethylate of 5

5 was methylated by the Hakomori method. **5** (50 mg), DMSO 6.0 m*l* and NaH 350 mg streaming with N_2 for 2 h, in the ultrasonicator. After cooling, added 30 m*l* of CH_3I, allowed for another 1 h in the ultrasonicator. The reaction mixture was diluted with H_2O and extrated with $CHCl_3$. The $CHCl_3$ extract evaporated and recrystalized from MeOH to give **8** as colorless needles, mp. 120-122℃ (uncorr.), IR: no OH. Anal. Calcd. for $C_{81}H_{138}O_{30}$: C 61.1: H 8.7, Found: C 61.0: H 8.6, IR ν_{max}^{KBr} no OH, 1724 (COOR) 1096, 1060 (CH_2-O-CH_2), ^{1}H-NMR ($CDCl_3$) δ 0.72 (3H, s, CH_3), 0.92 (6H, s, CH_3×2), 1.22 (3H, s, CH_3), 1.26 (6H, s, CH_3×2).

Methanolysis of 8

8 (20 mg) was boiled with 8% HCl-MeOH (3 m*l*) for 3 h. The hydrolysate was neutralized with Amberite MB-3 and the filtrate was evaporated. The residue was recrystallized from MeOH to give colorless needles, mp. 188℃, which were identified with 23-*O*-methyl hederagenin methyl ether by direct comparison (^{1}H-NMR, IR). The methylated sugar in the mother liquid was identified with methyl 3,4-di-*O*-methyl-L-arabinopyranoside, methyl 2,4-di-*O*-me-

thyl-L-rhamnopyranoside and methyl 2,3,4-tri-*O*-methyl-L-xylopyranoside by GLC.

Partial hydrolysis of 5

A solution of **5** (30 mg) in a sealed tube with aqueous 1.5% H_2SO_4 (12 m*l*) was heated at 70℃ for 7 h. The reaction mixture was diluted with H_2O and then extracted with H_2O saturated *n*-BuOH. The BuOH layer was concentrated. The resulting residue was chromatographed on SiO_2 with solvent A afforded **6** with xylose and **7** with xylose, rhamonose, respectively. Identification of **6** and **7** was achieved by comparison of the ^1H and ^{13}C-NMR spectra with those of authentic samples of kizuta saponin K_6 and K_3. The new saponin, **2** was named kalopanaxoside II.

Selective cleavage of the ester-glycoside linkage

Saponin (200 mg), anhydrous LiI (200 mg), 2,6-lutidine (18 m*l*) and MeOH (4 m*l*, anhydrous) was refluxed for 16 h. The resulted solution was deionized (Amberilite MB-3), concentrated to dryness. Suspended in H_2O, chromatographed (Amberlite XAD-2) and eluted with H_2O gave methlglycoside (**9**) and subsequent elution with MeOH afforded **2**. **9** was permethylated as above mentioned. **9** permetylate was treated with 90% HCOOH (1.8 m*l*) at 100℃ for 1 h. The reaction mixture was evaporated to remove HCOOH under the reduced pressure. The residue was treated with 0.13 M H_2SO_4 at 10℃ for 15 h, neutralized, washed with water. The filtrate and washing were combined, concentrated to about 3.7 m*l* and reduced with $NaBH_4$ (45 mg). Standing at the room temperature for 2 h, acidified (Dowex 50W H^+ form), concentrated to dryness. Boric acid in the residue was removed by treated codistillation with MeOH. The resulting methylated alditols mixture was acetylated with Ac_2O-pyridine (1:1) at 100℃ for 1 hr. The regants were removed by codistillation with toluene. The methylated alditiol acetates mixture was subjected to GC-MS analysis.

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