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Triterpenoidal Saponins from the Leaves of *Kalopanax pictum* var. *chinense*

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Abstract □ One new triterpenoidal bisdesmoside, saponin C (**3**) were isolated from the leaves of *Kalopanax pictum* var. *chinense* along with two known saponins, saponin B (**2**, sapindoside C) and saponin A (**1**, sapindoside B). On the basis of chemical and spectral evidences, the structure of a new triterpenoidal saponin has been elucidated to be 3-*O*-β-D-glucopyranosyl(1→4)-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.

Keywords □ *Kalopanax pictum* var. *chinense*, Araliaceae, leaves, hederagenin monodesmosides, hederagenin heptaglycoside, Korean folk medicine, Kalopanacis cortex

Kalopanax pictum var. *chinense* is a decidous tree of the family of Araliaceae, which is distributed in middle and southern part of Korean peninsula. Stem barks, twigs and leaves of the title plant, including another *Kalopanax spp.* have been used as a Korean folk medicine for the treatment of rheumatic arthritis caused by the wind and dampness, pains in the loin and knee, scabies, anti-diabetes and tonic under the name of Kalopanacis Cortex (Hae Dong Pie)[1,2].

The reports of the isolation and characterization of *Kalopanax spp.* containing saponins and other chemical constituents have been compiled[3-9]. In the previous papers[10-12], we reported the isolation and identification of kitzuta saponin K_3, K_6, K_{12} and (+)-syringaresional-di-β-glucoside from *Kalopanax pictum* var. Maximowiczii and *Kalopanax pictum* Nakai var. *magnificum* and a new saponin, Kalopanaxoside **2** from *Kalopanax pictum* Nakai var. *typicum*.

Continuing the chemical investigations of the *Kalopanax spp.* growing in Korea, this paper deals with the isolation and characterization of two known saponins and one new saponin from the leaves of the title plant. The water suspension of diethylether avoiding the MeOH extract was fractionated on the Amberlite XAD-2 column using the 30%, 70% and 95% MeOH, respectively. The 70% MeOH eluate indicated the presence of 12 different constituents, which were named as saponins A-L. Among them, three different saponin A(**1**), B(**2**) and C(**3**) were separated to the pure state by repeated SiO_2 column chromatography with the solvent systems A, B, C and D.

Saponin A(**1**), a white powder, mp. 220-222℃ (dec), gave a positive reaction in Lieberman-Burchard and Molish test and showed carboxyl (1690 cm^{-1}) and glycosidic (1,100-1,000 cm^{-1}) absorption band in its IR spectrum. Acid hydrolyses of **1** gave **4** as a genin and arabinose, rhamnose and xylose as glycone part. Compound **4** was identified as hederagenin by the comparison with authentic sample.

The ^{1}H-NMR spectrum of **1** showed six tertiary methyl signals at δ 0.90-1.21, secondary methyl signals at δ 1.54 for rhamnosyl methyl together with three anomeric singlet at 5.06, 5.33 and 6.31 ppm. The ^{13}C-NMR analysis (Table I) of **1** showed three anomeric carbon signals at 104.5, 101.3 and 107.5 ppm.

Through partial hydrolysis of **1** afforded **1b** with xylose, **1c** with rhamnose and xylose. Compounds **1b** and **1c** were identified Kizuta-saponin K_6 and K_3 by the comparison of ^{1}H-NMR and ^{13}C-NMR spec-

Table I. ^{13}C-chemical shifts (δ) of compounds 1, 2 and 3 in C_5D_5N

Carbon No.	Hedera genin	1	2	3	C-3 sugar	1	2	3	C-28 sugar	1	2	3
3	73.7	81.1	81.1	81.0	Ara-1	104.5	104.4	104.8	Glc-1			95.6
12	122.7	122.0	122.5	122.9	-2	75.6	75.3	75.3	-2			73.9
13	145.0	144.1	144.8	144.0	-3	75.0	74.2	75.0	-3			78.3
23	68.2	64.0	64.0	64.0	-4	69.5	69.4	69.2	-4			70.8
28	180.4	180.4	180.4	176.4	-5	66.0	65.9	64.8	-5			77.1
					Rha-1	101.3	101.4	101.3	-6			69.6
					-2	71.9	71.7	71.8	Glc-1			104.5
					-3	83.0	83.1	83.1	-2			74.2
					-4	73.0	71.8	72.5	-3			76.5
					-5	69.5	69.5	69.5	-4			78.7
					-6	18.4	18.3	18.4	-5			78.0
					Xyl-1	107.5	107.5	107.1	-6			61.3
					-2	75.2	74.8	75.1	Rha-1			102.7
					-3	78.3	76.2	76.3	-2			72.7
					-4	71.0	77.9	77.9	-3			73.7
					-5	67.3	64.7	66.0	-4			73.9
					Glu-1		103.5	103.6	-5			70.3
					-2		75.2	75.2	-6			18.5
					-3		78.1	78.7				
					-4		72.9	72.9				
					-5		78.7	78.1				
					-6		62.6	62.6				

tra with those of authentic samples, respectively[13]. In the negative FAB-MS of **1**, ion at *m/z* 881[M-H] 749[M-(xylose)], 603[M-(xylose+rhamnose] and 471[M-(arabinose+rhamnose+xylose] (=aglycone) indicated that sugar moiety of **1** was consisted of a linear xylose-rhamnose-arabinose unit[14].

Based on these findings, structure of **1** was proposed to be 3-*O*-β-D-xylopyranosyl(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl-23-hydroxyolean-12-en-28-oic acid, which has already been isolated from *Akebia quinata*, *Sapindus mukurossi* and alkaline hydrolysate of saponin F (obtained from *Kalopanax pictum* var. *typicum*). The identification was established by the comparison of physical constants and the ^{13}C-NMR spectrum with those of an authentic sample isolated from *Kalopanax pictum* var. *typicum*.

Saponin B(**2**), a amorphous white, mp. 208-210℃ (dec), gave a positive reaction in Lieberman-Burchard and Molish test and showed carboxyl (1710 cm^{-1}) and glycosidic (1,100-1,000 cm^{-1}) absorption band in its IR spectrum. Acid hydrolysis of **2** afforded hederagenin, arabinose, rhamnose, xylose and glucose.

The ^{1}H-NMR spectrum of **2** showed six tertiary methyl signals at δ 0.90-0.21, secondary methyl signal at δ 1.54 (3H, d, 6.1 Hz) for rhamnosyl methyl together with four anomeric proton singlets at 4.98, 5.06, 5.26 and 6.26 ppm. On partial hydrolysis, **2** gave **2b** with glucose and **2c** are identified by direct comparison of ^{1}H-NMR, ^{13}C-NMR and physicochemical evidences with those of the authentic saponin A(**1**) and kizutasaponin K_6, respectively. In the negative FAB-MS of **2**, ion at *m/z* 1043 [M-H], 881[M-(glucose)], 705[M-(glucose+xylose)], 603[M-(glucose+xylose+rhamnose)] and 471[M-(glucose+xylose+rhamnose+arabinose)] (=aglycone) indicated that the sugar moiety of **2** consisted of a linear glycosyl unit with terminal glucose, which was regarded as β-configuration. From the above results, the structure of **2** was established as 3-*O*-β-glucopyranosyl-(1→4)-β-D-xylopyranosyl-(1→3)-α-L-rhamnosyl-(1→2)-α-L-arabinosyl-23-hydroxyolean-12-en-28-oic acid, which was isolated from *Sapindus mukurossi* (sapindoside C) previously. The identification was established by the comparison of the physical constants and ^{13}C-NMR spectrum with those of an authentic sample isolated from *Sapindus*

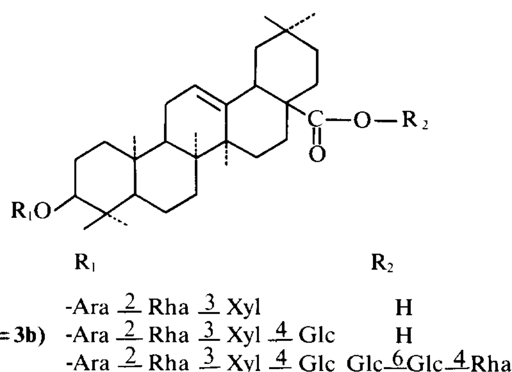

Chart 1

mukurossi.

Saponin C(3), a amorphous powder, mp. 217-219 ℃ (dec), gave a positive reaction in Lieberman-Burchard and Molish test and showed carboxyl (1680 cm^{-1}), ester (1740 cm^{-1}) and glycosidic (1,100-1,000 cm^{-1}) absorption bands in its IR spectrum. The ^{1}H-NMR spectrum of showed six tertiary methyl signals at 0.83-1.15 ppm, seven anomeric proton singlets at 4.97 (glucose), 4.99 (C_3-terminal glucose), 5.05 (arabinose), 5.25 (xylose), 5.81 (rhamnose, C_{28} terminal), 6.23 (C_{28} ester glucose), 6.29 (C_3-inner rhamnose) and 1.53, 1.68 (each 3H, Me of rhamnose×2). The ^{13}C-NMR spectrum (Table I) of **3** showed seven anomeric carbon signals at δ 104.8 (C_3 inner arabinose), 101.3 (C_3 inter rhamnose), 107.1 (C_3 xylose), 103.6 (C_3 terminal glucose), 95.6 (C_{28} inner glucose), 104.5 (C_{28} inter glucose) and 102.7 (C_{28} terminal rhamnose).

In the negative FAB-MS of **3**, pseudo molecular ion was appeared at *m/z* 1513 [M-H]. On acid hydrolysis of **3** afforded **3a** and arabinose, rhamnose, xylose and glucose (1:2:1:3). **3a** was identified as hederagenin. On alkaline hydrolysis of **3** gave **3b** and **3c**. Compound **3b**, a amorphous white powder, mp. 207-209℃, showed carboxyl (1690 cm^{-1}) and glycosidic (1,100-1,000 cm^{-1}) absorption bands in its IR spectrum. The ^{1}H-NMR spectrum showed six tertiary singlets at δ 0.90-1.21, secondary methyl doulet at δ 1.54 (3H, d, 6.1 Hz) for rhamnosyl methyl together with four anomeric proton signals at 4.98, 5.06, 5.26 and 6.26 ppm, exhibited ion at *m/z* 1043 in negative FAB-MS and afforded hederagenin, arabinose, rhamnose, xylose and glucose on acid hydrolysis. The glycosilation shift around 3-C as well as four anomeric carbon singlets at 104.4, 101.4, 107.0 and 103.5 in the ^{13}C-NMR spectrum of **3b** disclosed that **3b**, is a 3-*O*-glycoside of hederagenin which has four monosaccharide units. The negative FAB-MS analysis of **3b** indicated that the sugar moiety of **3b** consisted of linear glucose-xylose-rhamnose-arabinose units.

From these evidences, the structure of **3b** can be formulated as 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-xylopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl-23-hydroxyolean-12-en-28-oic acid. The identification was established by the comparison of physical constants and the ^{13}C-NMR spectrum with those of an authentic saponin **2** obtained from the title plant and sapindoside C.

Compound **3c** were analyzed by TLC and GC, showing the presence of rhamnose and glucose (1: 2). The sequence analysis[15] of **3c** permethylate revealed the formation of three kinds of *O*-methyl alditol acetates (t_R. 4.00 from rhamnose, t_R. 18.30 from inner glucose, t_R. 19.00 from outer glucose), which consisted of terminal rhamnose, 4-linked glucopyranose and 6-linked glucopyranose.

In ^{1}H-NMR and ^{13}C-NMR spectra of **3**, the singlet at δ 6.23 (1H, d, J=8.1 Hz) can be attributed to the anomeric proton of glucose linked to the C-28 carboxyl group of **2**. The singlet of anomeric carbon of the glucose was observed at δ 95.6, supporting the view that glucose is linked to the C-28 ester form. The comparison of ^{1}H-NMR and ^{13}C-NMR spectra of **3** with those of known compounds showed that singlet due to the sugar moiety of C-28 linked is in good agreement with authentic kizuta-saponin K_{12} and chiisanoside[16-18].

Based on the above results, the structure of saponin C(3) was elucidate as 3-*O*-β-D-glucopyranosyl-(1→4)-β-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.

EXPERIMENTAL

General procedure

Acid hydrolysis of saponins **1**, **2** and **3** were accomplished by refluxing with 2 N-HCl: dioxane (1:1, v/v) at 90℃ for 4 h and partial hydrolysis by heating in the sealed tube with 1.5% H_2SO_4 at 70℃ for 7 h. Alkaline hydrolysis of bisdesmoside was carried out using 0.5 N KOH in MeOH for 1 h. Acid and alkali

in the hydrolyzed solution ,were neutralized with Amberite MB 3. Acetylation was performed with AC_2O/pyridine at room temp. and permethylation was carried out according to the Hakomori method.

Melting points were measured with Gallenkamp MFB melting point apparatus and were uncorrected. IR absorption spectra were taken by a Nicolet 5-MX infrared spectrometer. Optical rotations were obtained on a Autopol TM III Automatic polarimeter. MS was taken on a JEOLJMS-SX-102 spectrometer. GC was performed on a shimadzu GC-9A gas chromatograph. ^{1}H-NMR spectra were measured on JEOL GSX 500 (500 MHz), JEOL, GX 400 (400 MHz) and Varian XL-200 (200 MHz) spectrometer and ^{13}C-NMR spectra were measured on JEOL GX 400 (100 MHz) spectrometer using TMS as an internal standard. Chemical shifts are given δ (ppm). Elemental analysis was performed by Perkin-Elmer 240 Elemental analyzer.

Extraction, fractionation and isolation of K. pictum var. chinense

Extraction and fractionation of this plant was carried out as described previously[10-12]. The ether avoided H_2O layer was chromatographed on Amberlite XAD-2 using H_2O, 30%, 70% and 95% MeOH as elution solvents. From the 70% MeOH fraction, thin layer chromatogram indicated the presence of 12 different constituents which were tentatively named saponins A-L. Among them, three different saponins A(**1**), B(**2**) and C(**3**) were separated in a pure state by repeated SiO_2 column chromatograph with the solvent systems I), $CHCl_3$: MeOH : H_2O = 70 : 30 : 4. 2) $CHCl_3$: MeOH : H_2O = 6 : 4 : 1. The saponin A(**1**) and B(**2**) were separated with solvent system I) and C(**3**) from solvent system II).

Saponin A(1)

White powder, mp. 220-222℃, $[\alpha]_D^{20}$ 17.5 (c=0.05 MeOH). Anal. Calcd. for $C_{46}H_{74}O_{16}$: C, 57.30; H, 8.70, Found: C, 57.14; H, 8.46, IR ν_{max}^{KBr} (cm^{-1}) : 3380, 1710, 1638, 1100-1000. ^{1}H-NMR (pyridine-d_5) δ 0.90, 0.91, 0.97, 1.00, 1.10, 1.22, (3H, *s*, CH_3×6), 1.54 (3H, *d*, J=6.1 Hz), 5.06 (1H, *d*, J=6.6 Hz), 5.33 (1H, *d*, J=7.5 Hz), 5.44 (1H, *d*, 12-H, olefinic), 6.31 (1H, *s*.), ^{13}C-NMR see Table I.

Saponin B(2)

Amorphous white powder, mp. 208-210℃, $[\alpha]_D^{20}$ −8.10° (c=1.2, MeOH). Anal. Calcd. for $C_{52}H_{84}O_{21}$: C, 59.7, H, 8.0, Found: C, 58.0, H, 7.80. IR ν_{max}^{KBr} cm^{-1} 3400, 1690, 1100-1000. ^{1}H-NMR (pyriding-d_5) δ 0.90, 0.91, 0.97, 0.98, 1.09, 1.21 (3H, *s*, CH_3×6), 1.54 (3H, *d*, J=6.1 Hz), four anomerics, δ 4.98 (1H, *d*, J=7.9 Hz, glucose, β-configuration), 5.06 (1H, *d*, J=6.6 Hz, arabinose, α-configuration), 5.26 (1H, *d*, J=7.6 Hz, xylose), 6.26 (1H, *s*, rhamnose). ^{13}C-NMR (400 MHz), see Table I. Negative FAB-MS m/z 1043 [M-H], 881, 705, 603, 471 (=aglycone).

Saponin C(3)

Amorphous white powder, mp. 217-219℃, $[\alpha]_D^{25}$ −26.4° (c=0.9, MeOH). Anal. Calcd. for $C_{70}H_{11}O_{35}$: C, 55.48, H, 7.53. Found: C, 55.50, H, 7.58, IR ν_{max}^{KBr} cm^{-1} 3420, 1740, 1680. ^{1}H-NMR (pyriding-d_5), δ 0.83, 0.85, 0.95, 1.08, 1.10, 1.15 (3H, *s*, CH_3×6), 1.53 (3H, *d*, J=6.1 Hz), 1.68 (3H, *d*, J=6.1 Hz). Seven anomerics, δ 4.97 (1H, *d*, J=7.7 Hz, anomeric), 4.99 (1H, *d*, J=7.9 Hz, anomeric), 5.05 (1H, *d*, J=6.6 Hz, anomeric), 5.25 (1H, *d*, J=7.7 Hz, anomeric), 5.81 (1H, *s*, anomeric), 6.23 (1H, *d*, J=8.1 Hz), 6.29 (1H, *s*, anomeric) and exhibited pseudo molecular ion at m/z 1513 in negative FAB-MS. ^{13}C-NMR (400 MHz) see Table I.

Acid hydrolysis of saponins 1, 2 and 3

Acid hydrolysis of saponins **1**, **2** and **3** (each 100 mg) was carried out, respectively. Hederagenin was identified as the genin of these saponins by a direct comparison with the authentic sample. Arabinose, rhamnose and xylose from saponin **1**, arabinose, rhamnose, xylose and glucose (1:1:1:1) from **2**, arabinose, rhamnose, xylose and glucose (1:2:1:3) from **3** were detected by TLC.

Partial hydrolysis of saponins 1 and 2

The partial hydrolysis of saponins **1** and **2** (each 30 mg) was carried out, respectively. The reaction mixture was diluted with H_2O and then extracted with H_2O saturated n-BuOH. The organic layer was concentrated, *in vacuo*. The resulted residue was chromatographed on SiO_2 with solvent system A afforded hederagenin, **1b** and **1c** (kizuta saponins K_6 and K_3) from saponin A(**1**) and hederagenin, **2b** and **2c** identified as saponin B(**2**) and kuzutasaponin K_6, respectively.

Permethylation and methanolysis of saponin A(1) and

B(2)

The Saponins **1** and **2** were permethylated, respectively. A mixture of 100 mg of sample, 2.5 m*l* DMSO and 150 mg NaH were reacted under streaming N_2 gas for 2 h in an ultrasonicator. After cooling with ice water, 10 m*l* of CH_3I, was added and reacted for another 1 h in the ultrasonicator. Then, the reaction mixture was diluted with water and extracted with $CHCl_3$. The organic layer was washed with H_2O, then dehydrated with Na_2SO_4, concentrated, and the resulted permethylate **5** from saponin A(**1**) and **6** from saponin B(**2**) were purified on SiO_2 column chromatography with the elution solvent system of benzene:acetone=4:1. Each 500 mg of permethylate **5** and **6** were treated with 15 mg of 8% HCl-methanol for 2 h in the water bath, neutralized, filtered and concentrated *in vacuo*. The concentrate was dissolved in acetone, then was analyzed by GC. Compound **5** afforded methyl-3,4-tri-*O*-methyl-xylopyranoside (t_R 6.8), methyl-3,4-di-*O*-methylarabinopyranoside (t_R 25.0), methyl-2,4-di-*O*-methyl rhamnopyranoside (t_R 10.6) and 23-*O*-methyl hederagenin methylester. Compound **6** afforded colorless needles mp. 188℃, which were identified with 23-*O*-methylhederagenin methylester and sugars in the mother liquid were identified as methyl 2,4-di-*O*-methyl-xylopyranoside (t_R 7.0), methyl-2,3,4,6-tetra-*O*-methylglucopyranoside (t_R 13.7), methyl-3,4-di-*O*-methylarabinopyranoside (t_R 28.0) and methyl-2,4-di-*O*-methylrhamnopyranoside (t_R 10.1) by GC.

Alkaline hydrolysis of saponin 3

Alkaline hydrolysis was carried out as usual method. The resulting mixture was distributed between *n*-BuOH and water. The *n*-BuOH extract was washed with H_2O and concentrated to give **3b**.

Compound 3b

mp. 207-209℃ $[\alpha]_D^{20}-8.1$ (c=1.2 MeOH). Anal Calcd. for $C_{52}H_{84}O_{21}$: C, 59.7; H, 8.0, Found: C, 58.0; H, 7.80 IR ν_{max}^{KBr} cm^{-1} 3400, 1690, 1100-1000. ^{1}H-NMR (pyridine-d_5) δ 0.90-1.21 (3H, *s*, $CH_3\times6$), four anomerics δ 4.98 (1H, *d*, J=7.9 Hz), 5.06 (1H, *d*, J=6.6 Hz), 5.26 (1H, *d*, J=7.6 Hz), 6.26 (1H, *s*, rhamnose), 1.54 (3H, *d*, J=6.1 Hz, Me of rhamnose), which was identified as saponin B(**2**). The mother liquid, **3c**, if anhydrous sugar may be formed partially, it must be the conversion to its original sugar form by the acid treatment[20]. The acid hydrolyzate was deionized with Amberite MB-3, to identify rhamnose and glucose by TLC.

Sequence analysis by GC-MS

The solution of saponin C(**3**) (20 mg) in DMSO (400 μ*l*) was added to the saturated solution of *t*-BuOK in DMSO (400 μ*l*) and the reaction mixture was sonicated for 1 h at the room temperature. To this reaction mixture, CH_3I (600 μ*l*) was added upon cooling and the mixture was further sonicated for another 1 h at the room temperature. The reaction mixture was diluted with water and extracted with $CHCl_3$. The organic layer was washed with water, dried and concentrated to dryness. The residue thus obtained was treated with 90% HCOOH (10 m*l*) at 100℃ for 1 h. The reaction mixture was evaporated to remove HCOOH. The residue was treated with 0.13 M H_2SO_4 at 100℃ for 16 h. The reaction mixture was neutralized and washed with water, then, concentrated to about 10 m*l*. To this $NaBH_4$ (110 mg) was added and kept at the room temp. for 2 h. The mixture was acidified by passing a column of Dowex 50W-XI (H^+ from) and concentrated to dryness. Boric acid in the residue was removed by repeated co-distillation with MeOH. The resulting methylated alditol mixture was acetylated. The methylated alditol acetate mixture thus obtained was subjected to GC-MS. GC-MS was taken on Shimazu GC-MS-7000s, glass column 2.6 mm×1.5 m packed with ECNSS-M on chromosorb W, injection temp. 200℃, column temp. 170℃, carrier gas He at 35 ml/min, separator temp. 250℃. Ionization voltage eV accelerating voltage 1.5 kV.

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