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Triterpenoid Saponins from the Roots of *Caragana sinica*

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Abstract □ From the roots of *Caragana sinica* (Buc'hoz) Rehder (Leguminosae), a new saponin named caraganoside A was isolated and elucidated as 3-*O*-β-D-xylopyranosyl (1→2)-[β-D-glucopyranosyl (1→3)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester by means of chemical and spectral studies. Kalopanax-saponin F, hemsloside Ma3 and araloside A were also isolated and characterized. The former two compounds were separated as their methylesters.

Keywords □ *Caragana sinica*, Leguminosae, saponin, oleanolic acid glycoside, caraganoside A.

The roots of *Caragana sinica* (Buc'hoz) Rehder (=*C. chamlagu* Lamk.) (Leguminosae) has been used to cure beri-beri, osteromyelitis, and similar malignancies, as well as nettle rash, and dropsy[1]. In Korean folk medicine, it has been used for the treatment of neuralgia, rheumatism and arthritis[2]. The ether extract from the roots of *C. sinica* showed significant antiinflammatory activity[3,4]. By bioassay-directed fractionation, an active principle, (+)-α-viniferin has been characterized[4]. Continuing the search for new components of the polar fraction, which showed significant inhibitory activity in edema induced by carrageenin in mice[4], has led to the isolation of four triterpenoid saponins. In this paper, we report the isolation and structure elucidation of these compounds.

EXPERIMENTAL METHODS

General experimental procedures

Melting points were determined on a Mitamura-Riken apparatus and are uncorrected. Optical rotations were measured on a Rudolph Autopol III automatic polarimeter. IR spectra were recorded on a Perkin-Elmer 283B spectrophotometer. ^{1}H-NMR spectra were obtained either a Varian FT-80A (80 MHz) or a Bruker AM-300 (300 MHz) spectrometer using TMS as an internal standard. ^{13}C-NMR spectra were recorded with a Bruker AM-300 (75.5 MHz) instrument. FAB mass spectra were obtained with Finnigan MAT 90 or Jeol JMS-HX 100 instruments. For TLC, Kieselgel 60 F_{254} sheets (Merck) were used.

Plant material

The dried roots of *Caragana sinica* were purchased from Gyeongdong market in 1989 and were authenticated by Prof. H.-J. Chi of our institute.

Extraction and isolation

The dried and chopped roots (2.2 kg) were refluxed with MeOH (5 times, 4h for each time) on a water bath. The extracts were combined and concentrated *in vacuo* to give a residue, which was suspended in H_2O and successively partitioned with hexane (19.8g), $CHCl_3$ (8.1g) and then BuOH (37.7g). The BuOH soluble fraction (34g) was subjected to SiO_2 column chromatography with $CHCl_3$-MeOH-H_2O (26:14:5, lower phase) to give 24 fractions (E01-E24). The subfraction E22 was recrystallized from MeOH to afford compound **1** as white amorphous powder, mp>300℃; IR ν_{max} (KBr) cm^{-1} 3400 (OH), 1730 (ester), 1610 (COO^-), 1070, 1040 (glycosidic C-O). The subfraction E16 (5.1g) was rechromatographed over SiO_2 with EtOAc-MeOH-H_2O (100:16.5:13.5) to afford 19 subfractions (E101-E119). Subfrac-

tion No. E116 (0.25g) was rechromatographed by Sephadex LH-20 with distilled water to yield pure compound **2** as white amorphous powder, mp>300 ℃; IR ν_{max} (KBr) cm^{-1} 3400 (OH), 1730 (ester), 1610 (COO^-), 1075, 1030 (glycosidic C-O). Subfraction E09 and E10 were combined (0.9g) and purified on a SiO_2 column by elution with EtOAc saturated with H_2O-MeOH (9:1). Subfraction E214 was recrystallized from MeOH to give pure compound **3** as white amorphous powder, mp. 260-262℃; $[\alpha]_D^{23}$ + 12.3℃ (c, 0.3, pyridine); IR ν_{max} (KBr) cm^{-1} 3400 (OH), 1736 (ester), 1640 (C=C), 1072, 1025 (glycosidic C-O); ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 0.88 (3H, s, CH_3), 0.89 (3H, s, CH_3), 0.92 (3H, s, CH_3), 1.09 (6H, s, 2×CH_3), 1.26 (3H, s, CH_3), 1.27 (3H, s, CH_3), 4.75 (1H, d, J=7.0 Hz, anomeric H), 5.28 (1H, d, J=7.6 Hz, anomeric H), 5.38 (1H, d, J=7.5 Hz, anomeric H), 5.43 (1H, br. s, H-12), 6.31 (1H, d, J=7.9 Hz, anomeric H); ^{13}C-NMR: see Table I.

Methylation of compounds 1 and 2

Compounds **1** (0.2g) and **2** (0.1g) were separately dissolved in MeOH and treated with ethereal CH_2N_2 at room temperature overnight. Workup in the usual manner gave methylated products. The methylester obtained from compound **1** showed two spots in TLC and chromatographed over a SiO_2 column. Elution with EtOAc-MeOH-H_2O (100:16.5:13.5) mixture gave compound **1b** as a minor component and then **1a** as a major one in the order of elution.

Compound **1a** was recrystallized from MeOH to afford pure **1a** as white amorphous powder, mp. 265-268℃; $[\alpha]_D^{16}$+3.0℃ (c, 0.2, pyridine); IR ν_{max} (KBr) cm^{-1} 3420 (OH), 1740 (ester), 1640 (C=C), 1070, 1040 (glycosidic C-O); ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 0.83 (3H, s, CH_3), 0.89 (3H, s, CH_3), 0.92 (3H, s, CH_3), 1.05 (3H, s, CH_3), 1.08 (3H, s, CH_3), 1.24 (3H, s, CH_3), 1.27 (3H, s, CH_3), 3.69 (3H, s, $COOCH_3$), 4.88 (1H, d, J=6.9 Hz, anomeric H), 5.23 (1H, d, J=7.8 Hz, anomeric H), 5.41 (1H, br. s, H-12), 5.49 (1H, d, J=7.7 Hz, anomeric H), 6.31 (1H, d, J=7.8 Hz, anomeric H); ^{13}C-NMR: see Table I; FAB-MS (negative mode, *m/z*) 1101 $[M-H]^-$, 939 $[(M-H)-162]^-$, 807 $[(M-H)-(162+132)]^-$, 777 $[(M-H)-(162+162)]^-$, 645 $[(M-H)-(162+162+132)]^-$, 455 $[(M-H)-(162+132+162+190)]^-$.

Compound **1b** was recrystallized from MeOH to yield pure **1b** as amorphous powder, mp. 264-267℃; $[\alpha]_D^{16}$+5.7℃ (c, 0.1, pyridine); IR ν_{max} (KBr) cm^{-1} 3400 (OH), 1740 (ester), 1640 (C=C), 1080, 1040 (glycosidic C-O); ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 0.83 (3H, s, CH_3), 0.89 (3H, s, CH_3), 0.92 (3H, s, CH_3), 1.06 (3H, s, CH_3), 1.09 (3H, s, CH_3), 1.25 (3H, s, CH_3), 1.27 (3H, s, CH_3), 3.70 (3H, s, $COOCH_3$), 4.92 (1H, d, J=7.5 Hz, anomeric H), 5.38 (1H, d, J=7.7 Hz, anomeric H), 5.42 (1H, br. s, H-12), 5.58 (1H, d, J=7.7 Hz, anomeric H), 6.34 (1H, d, J=7.8 Hz, anomeric H); ^{13}C-NMR: see Table I; FAB-MS (negative mode, *m/z*) 1101 $[M-H]^-$, 939 $[(M-H)-162]^-$, 807 $[(M-H)-(162+132)]^-$, 777 $[(M-H)-(162+162)]^-$, 645 $[(M-H)-(162+162+132)]^-$, 455 $[(M-H)-(162+132+162+190)]^-$.

The methylester obtained from compound **2** was purified by SiO_2 column chromatography eluted with EtOAc saturated wth H_2O-EtOAc (gradient, 0 to 5%) and then recrystallized from MeOH to yield pure methylester (**2a**) as colorless needles, mp. 219-222℃; $[\alpha]_D^{19}$−21.5℃, (c, 0.3, MeOH); IR ν_{max} (KBr) cm^{-1} 3400 (OH), 1745 (ester), 1640 (C=C), 1070, 1029 (glycosidic C-O); ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 0.83 (3H, s, CH_3), 0.89 (3H, s, CH_3), 0.92 (3H, s, CH_3), 0.96 (3H, s, CH_3), 1.08 (3H, s, CH_3), 1.26 (3H, s, CH_3), 1.28 (3H, s, CH_3), 3.73 (3H, s, $COOCH_3$), 4.92 (1H, d, J=7.3 Hz, anomeric H), 5.42 (1H, br. s, H-12), 5.76 (1H, s, anomeric H), 6.31 (1H, d, J=7.9 Hz, anomeric H); ^{13}C-NMR: see Table I.

Acid hydrolysis of compounds 1a, 1b, 2 and 3

Compounds **1a**, **1b**, **2** and **3** (ca 10 mg each) were separately hydrolyzed with 5% HCl in 50% dioxane by refluxing for 3h on an water bath, and each reaction mixture was poured onto iced water and filtered. Each filtrate was neutralized with Ag_2CO_3 and filtered, and the solution was evaporated to dryness under reduced pressure. Oleanolic acid, mp. 300-302℃, was identified as the aglycone in each case by direct comparison with an authentic sample. D-Glucose, L-arabinose and D-glucuronic acid from compounds **1a**, **1b** and **2**, and D-glucose, D-xylose and L-arabinose from compound **3** were detected by TLC (precoated cellulose plate, pyridine-EtOAc-HOAc-H_2O=36:36:7:21).

Permethylation of compounds 1a and 1b followed by methanolysis

Compounds **1a** and **1b** were separately permeth-

ylated with NaH (50 mg) and CH_3I (0.5 ml) by Hakomori's method[5]. The reaction product was refluxed with 3% methanolic HCl (2 ml) for 3h. The mixture was poured onto crushed ice, extracted with $CHCl_3$, and then evaporated to dryness *in vacuo*. The residue was subjected to GLC to compare the methylated sugars. Conditions of GLC for identification were previously described[6]. The GLC chromatogram of the methylated sugars from compound **1a** was vertually identical to that of compound **1b**.

Alkaline hydrolysis of compound 3

A solution of **3** (20 mg) in 0.1N-KOH/MeOH (10 ml) was refluxed for 1h. After the solution was neutralized with d-HCl, it was filtered and the filtrate was extracted with BuOH. The BuOH solubles were combined with the precipitate. The mixture was chromatographed over SiO_2 by elution with $CHCl_3$-MeOH-H_2O (7:3:1, lower phase) to give pure prosapogenin A. It was recrystallized from MeOH to afford white amorphous powder, mp. 276-280℃; $[\alpha]_D^{26}$+16.0℃ (c, 0.1, pyridine); IR ν_{max} (KBr) cm^{-1} 3400 (OH), 1705 (COOH), 1640 (C=C), 1080, 1040 (glycosidic C-O); ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 0.84 (3H, s, CH_3), 0.97 (6H, s, 2×CH_3), 1.01 (3H, s, CH_3), 1.08 (3H, s, CH_3), 1.28 (3H, s, CH_3), 1.29 (3H, s, CH_3), 4.74 (1H, d, J=7.0 Hz, anomeric H), 5.28 (1H, d, J=7.7 Hz, anomeric H), 5.37 (1H, d, J=7.5 Hz, anomeric H), 5.47 (1H, br. s, H-12); ^{13}C-NMR: see Table I; FAB-MS (negative mode, *m/z*) 881 $[(M-H)]^-$, 749 $[(M-H)-132]^-$, 719 $[(M-H)-162]^-$, 587 $[(M-H)-(132+162)]^-$, 587 $[(M-H)-(132+162)]^-$, 455 $[(M-H)-(132+162+132)]^-$.

Acid hydrolysis of prosapogenin A

Acid hydrolysis of prosapogenin A (3 mg) was performed in the same manner as described above. Oleanolic acid as the aglycone and D-glucose, D-xylose and L-arabinose as the sugar moieties were identified.

Partial hydrolysis of compound 3

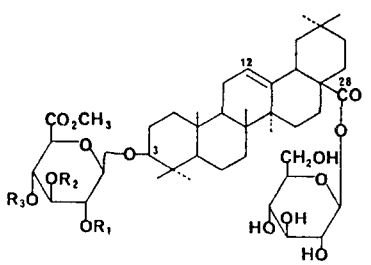
A solution **3** (70 mg) in a mixture of c-HCl (0.5 ml) and MeOH (36 ml) was refluxed for 15 minutes. The reaction mixture was poured onto crushed ice and then filtered. The precipitate was subjected to SiO_2 column chromatography eluting with $CHCl_3$-MeOH-H_2O (7:3:1, lower phase) to yield oleanolic acid (17 mg), prosapogenin B (13 mg) and starting material (28 mg). The prosapogenin B was recrystallized from MeOH to give amorphous powder, mp. 266-269℃; $[\alpha]_D^{25}$+26.5℃ (c, 0.1, pyridine); IR ν_{max} (KBr) cm^{-1} 3420 (OH), 1700 (COOH), 1650 (C=C), 1080, 1035 (glycosidic C-O); ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 0.85 (3H, s, CH_3), 0.97 (3H, s, CH_3), 0.98 (3H, s, CH_3), 1.01 (3H, s, CH_3), 1.02 (3H, s, CH_3), 1.28 (3H, s, CH_3), 1.29 (3H, s, CH_3), 4.76 (1H, d, J=7.4 Hz, anomeric H), 5.39 (1H, d, J=7.7 Hz, anomeric H), 5.49 (1H, br. s, H-12); ^{13}C-NMR: see Table I.

Acid hydrolysis of prosapogenin B

Acid hydrolysis of prosapogenin B was performed in the same manner as described above. Oleanolic acid, D-glucose and L-arabinose were detected.

RESULTS AND DISCUSSION

Repeated column chromatography of the BuOH soluble fraction of the MeOH extract and purification by crystallization led to the isolation of compounds **1**, **2** and **3** in the order of decreasing polarity, among which the former two compounds are major. Compounds **1** and **2** seemed to be the car-



1a R_1=Ara(p) R_2=Glc(p) R_3=H
1b R_1=Glc(p) R_2=Ara(p) R_3=H
2a R_1=R_2=H R_3=Ara(f)

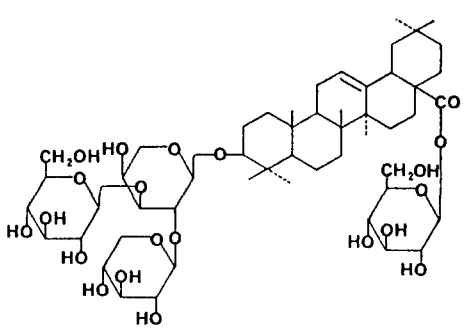


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Table I. ^{13}C-NMR spectral data of compounds **1a**, **1b**, **2a** and **3** and related compounds in pyridine-d_5[1]

Carbon	**1a**	**1b**	**2a**	Carbon	**3**	pro-A*	pro-B*
C-3	89.94	89.93	89.29	C-3	89.19	89.21	88.68
C-12	122.87	122.90	122.83	C-12	122.93	122.51	122.54
C-13	144.14	144.17	144.12	C-13	144.11	144.81	144.82
C-28	176.40	176.48	176.41	C-28	176.44	180.10	180.12
Glc A				Ara			
C-1	105.24	105.28	106.98	C-1	105.13	105.04	107.32
C-2	79.00[a]	78.93	75.08	C-2	77.43	77.37	71.90
C-3	87.78	87.56	75.92	C-3	83.71	83.66	84.13
C-4	72.87	72.90	78.89	C-4	68.99	69.10	69.28
C-5	76.32	76.34	76.81	C-5	66.19	66.12	66.94
C-6	169.89	169.95	170.36				
(OCH_3)	52.16	52.19	52.33				
Ara				Xyl			
C-1	105.24	104.77	108.61	C-1	105.13	105.04	
C-2	71.33	71.38	82.56	C-2	75.30	75.24	
C-3	75.30	75.41	78.45	C-3	78.35	78.28	
C-4	70.08	70.05	87.51	C-4	71.35	71.28	
C-5	67.12	67.14	62.50	C-5	67.10	67.05	
Glc				Glc			
C-1	104.74	104.77		C-1	105.66	105.64	106.28
C-2	76.10	76.16		C-2	76.02	75.95	75.72
C-3	77.34	78.57		C-3	78.49	78.41	78.37
C-4	71.57	71.64		C-4	71.53	71.50	71.61
C-5	78.83[a]	78.93		C-5	79.06	79.00	78.65
C-6	61.92	62.27		C-6	62.52	62.50	62.71
28-*O*-Glc				28-*O*-Glc			
C-1	95.75	95.80	95.73	C-1	95.77		
C-2	74.15	74.19	74.11	C-2	74.15		
C-3	79.28[a]	79.34	79.54[a]	C-3	78.49		
C-4	71.14	71.18	71.09	C-4	71.09		
C-5	78.90[a]	78.93	79.10[a]	C-5	79.06		
C-6	62.24	62.27	62.19	C-6	62.19		

[1]Multiplicities were obtained by DEPT spectra.
*pro-A: prosapogenin A, pro-B: prosapogenin B.
[a]Assignments in each column may be reversed.

boxylate forms from their IR spectra and physical properties [7]. Therefore both compounds were methylated with CH_2N_2 to give methylesters. The TLC chromatogram of compound **1** methylester showed two spots with very close Rf values. Repeated column chromatography allowed isolation of the two saponin methylesters (**1a** and **1b**) in a pure state as indicated by TLC. Acid hydrolysis of **1a** and **1b** afforded the same reaction products; glucuronic acid, glucose and arabinose as the sugar moieties and an aglycone, mp. 300-302℃, which was identified as oleanolic acid by direct comparison with an authentic sample. The molecular mass and sugar sequence of the **1a** were established by FAB mass spectrum in the negative ion mode. The fragmentation pattern for **1a** showed a quasimolecular ion at *m/z* 1101 [M-H] indicating its molecular weight to be 1102. The remarkable intensity of the ion at *m/z* 939 [(M-H)-162] which is the base peak of the spectrum strongly suggested that one mole of

glucose could be linked to oleanolic acid by an ester function[8]. The fragments at *m/z* 807 $[(M-H)-162-132]^-$ and *m/z* 777 $[(M-H)-162-162]^-$ corresponding to the elimination of one mole of arabinose and of one mole of glucose residue from the fragment ion *m/z* 939, respectively, were consistent with the presence of two terminal sugar residues which were attached at inner sugar, glucuronic acid. Therefore the sugar sequence was suggested as arabinose-glucuronic acid-3-*O*-oleanolic acid-28-glucose
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28-*O*-glucose. The FAB mass spectrum of **1b** was vertually identical to that of **1a** suggesting that the difference between **1a** and **1b** could only involve the branched terminal sugar units linked to glucuronic acid. This result was further supported by the fact that the GLC chromatograms of the methylated sugars obtained from **1a**- and **1b**-permethylethers by methanolysis were the same. The very similar ^{1}H- and ^{13}C-NMR spectra of the two methylesters confirmed this point. In the ^{13}C-NMR spectrum of **1a**, glycosidation shifts were observed at the signals of C-1 (−2.1 ppm), C-2 (+3.6 ppm) and C-3 (+9.9 ppm) of the glucuronopyranosyl residue compared with those of 3-*O*-(6-*O*-methyl-β-D-glucuronopyranosyl) oleanolic acid methyl ester[9] indicating that the terminal sugars were attached at C-2 and C-3 hydroxyl groups of the glucuronopyranosyl group[10]. Similarly, the ^{13}C-chemical shift values for glucuronopyranosyl moiety in **1b** were almost superimposable on those of **1a**. The relatively large coupling constant values in the ^{1}H-NMR spectra of **1a** and **1b** indicated the β-configurations for both glucosides and glucuronoside linkages and α-configuration for the arabinoside linkage[11]. The ^{13}C-NMR spectral data of **1a** were very close to those of kalopanax-saponin F which was isolated from araliaceous plant, *Kalopanax septemlobus*[12], except for the chemical shifts of C-5 and C-6 on glucuronic acid residue due to the esterification shifts[13]. Based on the above results, the structure of **1a** was determined to be 3-*O*-α-L-arabinopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→3)]-6-*O*-methyl-β-D-glucuronopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester (=kalopanax-saponin F methylester). Accordingly, the structure of **1b** was proved to be 3-*O*-β-D-glucopyranosyl (1→2)-[α-L-arabinopyranosyl-(1→3)]-6-*O*-methyl-β-D-glucuronopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester (=hemsloside Ma3 methylester). Hemsloside Ma3 was isolated from cucurbitaceous plant, *Hemsleya macrosperma*[14]. It is the second report of the occurrence of both saponins and the first instance of co-occurrence of the two saponins as isomeric pairs in the same plant, which is very rare example. Consequently, the isolation of kalopanax-saponin F and hemsloside Ma3 from Leguminosae is of interest from the chemotaxonomical point of view.

Compound **2a** afforded oleanolic acid, glucose, arabinose and glucuronic acid on acid hydrolysis. Based on analysis of the ^{1}H- and ^{13}C-NMR spectra as well as comparison of the physical properties with published values[15,16], **2a** was proved to be identical with 3-*O*-α-L-arabinofuranosyl (1→4)-6-*O*-methyl-β-D-glucuronopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester (=araloside A methylester), which has so far been isolated from many araliaceous plants such as Aralia[17-19], Panax[15,16,20-24], Kalopanax[12], Tetrapanax[25] plants. It should be noted that this is the first isolation of this saponin from Leguminosae plants.

Compound **3** gave oleanolic acid, glucose, xylose and arabinose on acid hydrolysis. The NMR spectra of **3** showed that **3** is a bisdesmoside carrying four monosaccharide units. Alkaline hydrolysis of **3** afforded a prosapogenin A, mp. 276-280℃. This evidence coupled with an anomeric carbon signal due to an ester glucosyl linkage at δ 95.77 and the coupling constant (J=7.9 Hz) of the anomeric proton signal at δ 6.31 suggested that **3** is a β-glucopyranosyl ester of prosapogenin A. The FAB mass spectrum of prosapogenin A showed deprotonated molecular ion at *m/z* 881 $[(M-H)]^-$, followed by three fragments at *m/z* 749 $[(M-H)-132]^-$, *m/z* 719 $[(M-H)-162]^+$ and *m/z* 455 $[(M-H)-132-162-132]^-$. These fragments, indicative of the loss of two terminal sugar residues showed, as for compounds **1a** and **1b**, the presence of the branched sugar chain and the sugar sequence was suggested as pentose-pentose-3-*O*-oleanolic acid. Mild acid hydrolysis
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glucose
of **3** supported this result. The prosapogenin B, mp. 266-269℃, obtained after partial hydrolysis of **3** yielded glucose and arabinose together with oleanolic acid on acid hydrolysis. This result coupled with the above observations demonstrated that the sugar

sequence of prosapogenin B must be glucose-arabinose-3-*O*-oleanolic acid. The comparison of the ^{13}C-NMR spectrum of prosapogenin B with that of oleanolic acid 3-*O*-α-L-arabinopyranoside[26] established the position of the terminal glucose to be at C-3 of the arabinose moiety. Therefore the structure of prosapogenin B determined as oleanolic acid 3-*O*-β-D-glucopyranosyl (1→3)-α-L-arabinopyranoside. On the other hand, the substantial (−5.47 ppm) downfield and the relatively weak (−2.28 ppm) upfield shifts observed on the C-2 and on the C-1, respectively, of prosapogenin A compared to prosapogenin B clearly indicated that C-2 hydroxyl group of arabinose moiety bears the terminal sugar, xylose. These results indicated that the structure of prosapogenin A was established to be oleanolic acid 3-*O*-β-D-xylopyranosyl (1→2)-[β-D-glucopyranosyl (1→3)]-α-L-arabinopyranoside. Based on the above results, the structure of **3** was determined as 3-*O*-β-D-xylopyranosyl (1→2)-[β-D-glucopyranosyl (1→3)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester. This saponin has not been reported previously and has been named caraganoside A.

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