Oleanane Saponins from *Sanicula elata* var. *chinensis*

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Eleven new oleanane-type triterpenoid saponins, saniculasaponins I−XI (**1**−**11**), and a known saponin, sandrosaponin IX (**12**), were isolated from the methanol extract of the whole plants of *Sanicula elata* Ham. var. *chinensis* Makino. The structures of the new compounds were elucidated on the basis of chemical and spectroscopic evidence.

Saponins are very rare in the Apiaceae and are only known in *Sanicula*, *Bupleurum*, *Centella*, and *Hydrocotyle*. Oleanane-type saponins, saniculosides A−D,[1,2] N,[3] and R-1,[4] had been isolated from *Sanicula europaea* L. *Sanicula elata* Ham. var. *chinensis* Makino (Apiaceae) has not been used as a medicinal plant in Japan, and the study of its components was not done in detail. As a part of our research on saponins, we have isolated 11 new oleanane-type triterpenoid saponins from *S. elata* var. *chinensis*, named saniculasaponins I−XI (**1**−**11**), and a known saponin, sandrosaponin IX (**12**).[5]

Results and Discussion

A methanol extract of the whole plants of *S. elata* var. *chinensis* was dissolved in water and extracted with diethyl ether. The water layer was passed through a porous polymer gel Diaion HP-20 column. The methanol eluate was separated by preparative HPLC to afford saponins **1**−**11** and sandrosaponin IX (**12**).

The FABMS of saniculasaponin I (**1**) gave a quasi molecular ion peak at *m*/*z* 1154, while the ^{13}C NMR spectrum revealed 55 carbon signals. The molecular ion peak at *m*/*z* 1154 was due to a sodiated molecule $[M + Na]^+$, consistent with a molecular formula $C_{55}H_{86}O_{24}$. The ^{1}H NMR spectrum of **1** (see Table 1) showed signals of an olean-12-ene-type aglycon [seven singlet methyl signals at δ 0.85, 1.02, 1.09, 1.11, 1.25, 1.31, 1.86 and a trisubstituted olefinic proton signal at δ 5.52 (dd, J = 3, 3 Hz)], three anomeric proton signals (δ 4.95, 5.29, 5.66), a methyl signal at δ 2.10 (s) of the acetyl moiety, an olefinic proton signal at δ 5.83 (dq, J = 7, 1.5 Hz), and methyl signals at δ 1.79 (br s) and 2.01 (dq, J = 7, 1.5 Hz), which indicated the presence of an angeloyl moiety in the molecule. In the HMBC spectrum, cross-peaks between H-21 (δ 6.58) and the carbonyl carbon of the acetyl moiety (δ 170.8), C-29 (δ 29.5), and C-30 (δ 20.0) and between H-22 (δ 6.24) and the carbonyl carbon of the angeloyl moiety (δ 168.2), C-16 (δ 73.6), and C-28 (δ 63.2) were observed. Thus, the acetyl moiety and the angeloyl moiety must be linked to C-21 and C-22, respectively. The structure of the aglycon was determined by ^{1}H, ^{13}C, HMQC, and HMBC NMR experiments as 3,21,22-trisubstituted olean-12-ene-3,15,16,21,22,28-hexaol. The ^{13}C NMR of C-15 (δ 67.6) and C-16 (δ 73.6) indicated 15α,16α-orientation of the hydroxyl groups.[6,7] The coupling constants (10 Hz) between H-21 and H-22 indicated the diaxial orientation. The ^{1}H NMR data showed three anomeric protons, and the sugar moieties of **1** were characterized as a β-D-glucuronopyranose, a β-D-glucopyranose, and a β-D-galactopyranose from the 1D HOHAHA spectrum and acid hydrolysis.[8] All of the sugar residues had a β-configuration according to their anomeric proton coupling constants. The positions of the sugar moieties were defined by the HMBC spectrum. Cross-peaks between H-1 of the glucopyranosyl residue (δ 5.66) and C-2 of the glucuronopyranosyl residue (δ 79.0) and between H-1 of the galactopyranosyl residue (δ 5.29) and C-3 of the glucuronopyranosyl residue (δ 88.0) indicated that the glucopyranosyl residue and the galactopyranosyl residue were linked with C-2 and C-3 of the glucuronopyranosyl residue, respectively. Cross-peaks between H-1 of the glucuronopyranosyl residue (δ 4.95) and C-3 of the aglycon (δ 89.5) and reverse cross-peaks between C-1 of the glucuronopyranosyl residue (δ 105.3) and H-3 of the aglycon (δ 3.32) showed that the trisaccharide chain was attached to C-3 of the aglycon. On the basis of these results, the structure of saniculasaponin I (**1**) was deduced to be 3-*O*-[β-D-glucopyranosyl-(1→2)]-β-D-galactopyranosyl-(1→3)-β-D-glucuronopyranosyl-21-*O*-acetyl-22-*O*-angeloyl-3β,15α,16α,21β,22α,28-hexahydroxyolean-12-ene.

The FABMS of saniculasaponin II (**2**) gave a quasi molecular ion peak at *m*/*z* 1124 $[M + Na]^+$, 30 mass units less than that of **1** and in accordance with the molecular formula $C_{54}H_{84}O_{23}$. The ^{1}H and ^{13}C NMR spectra were similar to those of **1** (see Tables 1 and 2). The ^{1}H NMR spectrum showed signals for an acetyl and an angeloyl moiety and three anomeric protons. On acid hydrolysis, D-glucuronic acid, D-glucose, and L-arabinose were detected.[8] The HMBC spectrum indicated that the glucopyranosyl residue and the arabinopyranosyl residue were linked to C-2 and C-3 of the glucuronopyranosyl residue and that the trisaccharide chain was attached to C-3 of the aglycon. Thus, saniculasaponin II (**2**) was identified as 3-*O*-[β-D-glucopyranosyl-(1→2)]-α-L-arabinopyranosyl-(1→3)-β-D-glucuronopyranosyl-21-*O*-acetyl-22-*O*-angeloyl-3β,15α,16α,21β,22α,28-hexahydroxyolean-12-ene.

Saniculasaponin III (**3**) had a molecular formula of $C_{54}H_{84}O_{23}$, identical to that of **2**, as determined from FABMS data (see Experimental Section). The ^{1}H and ^{13}C NMR spectra were very similar to those of **2**. The HMBC spectrum showed that the positions of the acetyl and the angeloyl moieties were different from **1** or **2**. The HMBC correlations (see Tables 1 and 2) indicated that the angeloyl and the acetyl groups were attached to C-21 and C-22, respectively. Therefore, saniculasaponin III (**3**) was assigned as 3-*O*-[β-D-glucopyranosyl-(1→2)]-α-L-arabino-

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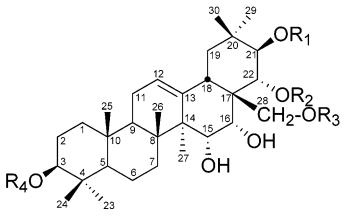
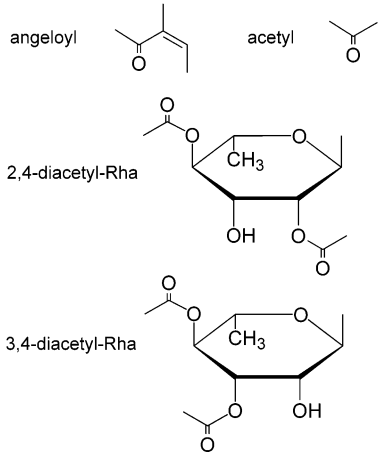
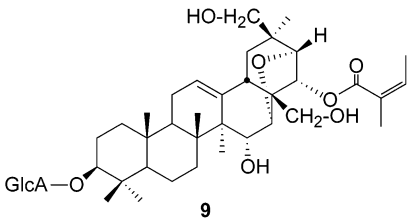
Chart 1



	R_1	R_2	R_3	R_4
1	acetyl	angeloyl	H	-GlcA(3)—Gal, Glc(2)
2	acetyl	angeloyl	H	-GlcA(3)—Ara, Glc(2)
3	angeloyl	acetyl	H	-GlcA(3)—Ara, Glc(2)
4	angeloyl	H	acetyl	-GlcA(3)—Ara, Glc(2)
5	2,4-diacetyl-Rha	angeloyl	H	-GlcA(3)—Gal, Glc(2)
6	2,4-diacetyl-Rha	angeloyl	H	-GlcA(3)—Ara, Glc(2)
7	3,4-diacetyl-Rha	angeloyl	H	-GlcA(3)—Gal, Glc(2)
8	3,4-diacetyl-Rha	angeloyl	H	-GlcA(3)—Ara, Glc(2)





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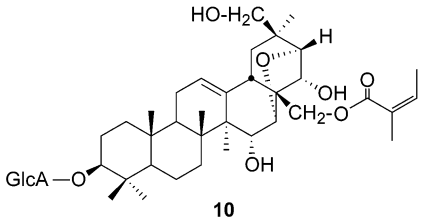
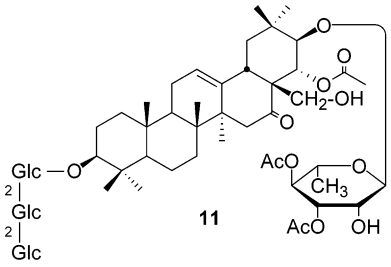
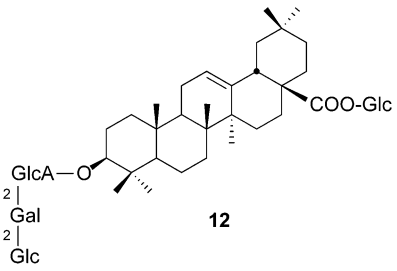


10



11



12

pyranosyl-(1→3)-*β*-D-glucuronopyranosyl-22-*O*-acetyl-21-*O*-angeloyl-3*β*,15α,16α,21*β*,22α,28-hexahydroxyolean-12-ene.

The FABMS of saniculasaponin IV (**4**) exhibited a quasi molecular ion peak at *m/z* 1124 $[M + Na]^+$, consistent with molecular formula $C_{54}H_{84}O_{23}$. On comparison, the NMR data of the sugar moieties were the same as those of **3**. The ^1H and ^{13}C NMR data showed the low-field shifts of H-28 and C-28 (see Tables 1 and 2) due to the acylation. Thus, saniculasaponin IV (**4**) was identified as 3-*O*-[*β*-D-glucopyranosyl-(1→2)]-α-L-arabinopyranosyl-(1→3)-*β*-D-glucuronopyranosyl-28-*O*-acetyl-21-*O*-angeloyl-3*β*,15α,16α,21*β*,22α,28-hexahydroxyolean-12-ene.

The FABMS data of saniculasaponin V (**5**) afforded a quasi molecular ion peak at *m/z* 1342 $[M + Na]^+$, which indicated the molecular formula $C_{63}H_{98}O_{29}$. The ^1H NMR spectrum of **5** revealed signals typical for a saponin, with seven singlet methyl protons and an olefinic proton at *δ* 5.51, two methyl signals at *δ* 1.90 (s) and 2.03 (s) due to acetyl groups, a methine proton at *δ* 6.06 (dq, *J* = 7, 1.5 Hz), and methyl signals at *δ* 1.96 (br s) and 2.19 (dq, *J* = 7, 1.5 Hz) of an angeloyl moiety. The sugar analysis by GC revealed D-glucuronic acid, D-glucose, D-galactose, and L-rhamnose.[8] The ^1H NMR data displayed four sugar anomeric proton signals. The low-field shifts of C-2 and C-4 of the rhamnopyranosyl residue (*δ* 74.3 and 75.4) and the HMBC correlation between H-2 and H-4 of the rhamnopyranosyl residue (*δ* 5.78 and 5.62) and the two acetyl carbonyl carbons (*δ* 170.6 and 170.8) indicated that the two acetyl moieties were linked to C-2 and C-4 of the rham-

Table 1. ^{1}H NMR Data (δ) of Compounds **1**−**11** in C_5D_5N

		1	**2**	**3**	**4**	**5**	**6**
aglycon	3	3.32 (dd, 12, 4)[p,†]	3.32 (dd, 12, 4)[p,†]	3.32 (dd, 12, 4)[p,†]	3.32 (dd, 12, 4)[n,†]	3.30 (dd, 12, 4)[†]	3.30 (dd, 12, 4)[r,†]
	5	0.83[α]	0.83[α]	0.84[α]	0.84[α]	0.81[α]	0.80[α]
	12	5.52 (dd, 3, 3)	5.52 (dd, 3, 3)	5.50 (dd, 3, 3)	5.54 (dd, 3, 3)	5.51 (dd, 3, 3)	5.51 (dd, 3, 3)
	15	4.22[α]	4.22[α]	4.19[α]	4.29[α]	4.21[α]	4.22[α]
	16	4.44[α]	4.44[α]	4.40[α]	4.65 (d, 4)	4.44[α]	4.40[α]
	18	3.06[α]	3.09[α]	3.07[α]	2.81 (dd, 14, 4)	2.98[α]	2.98[α]
	21	6.58 (d, 10)[h,i,n]	6.58 (d, 10)[h,i,n]	6.59 (d, 10)[j,h,i]	6.50 (d, 10)[f,g,h]	5.01 (d, 10)[h,i,t]	5.01 (d, 10)[h,i,u]
	22	6.24 (d, 10)[b,g,j]	6.24 (d, 10)[b,g,j]	6.18 (d, 10)[b,g,n]	4.44[α,b,e]	6.15 (d, 10)[b,gj]	6.15 (d, 10)[b,g,j]
	23	1.25 (s)	1.24 (s)		1.23 (s)	1.24 (s)	1.23 (s)
	24	1.11 (s)	1.10 (s)	1.10 (s)	1.09 (s)	1.10 (s)	1.09 (s)
	25	0.85 (s)	0.85 (s)	0.85 (s)	0.87 (s)	0.84 (s)	0.85 (s)
	26	1.02 (s)	1.02 (s)	1.02 (s)	1.16 (s)	1.02 (s)	1.02 (s)
	27	1.86 (s)	1.85 (s)	1.84 (s)	1.85 (s)	1.84 (s)	1.84 (s)
	28	3.51 (d, 11)[e]	3.51 (d, 11)[e]	3.45 (d, 11)[e]	4.35[α,l]	3.41 (d, 11)	3.41 (d, 11)
	28	3.76 (d, 11)[f]	3.76 (d, 11)[f]	3.70 (d, 11)[f]		3.71 (d, 11)[f]	3.71 (d, 11)[f]
	29	1.09 (s)[c]	1.09 (s)[c]	1.10 (s)[c]	1.13 (s)[c]	1.22 (s)[c]	1.23 (s)[c]
	30	1.31 (s)[d]	1.32 (s)[d]	1.30 (s)[d]	1.30 (s)[d]	1.22 (s)[d]	1.23 (s)[d]
ester moiety							
angeloyl	3	5.83 (dq, 7, 1.5)	5.83 (dq, 7, 1.5)	5.98 (dq, 7, 1.5)	5.90 (dq, 7, 1.5)[m]	6.06 (dq, 7, 1.5)	6.06 (dq, 7, 1.5)
	4	2.01 (dq, 7, 1.5)[l]	2.01 (dq, 7, 1.5)[l]	2.11 (dq, 7, 1.5)[l]	2.19 (dq, 7, 1.5)[j]	2.19 (dq, 7, 1.5)[l]	2.19 (dq, 7, 1.5)[l]
	5	1.79 (br s)[k,m]	1.79 (br s)[k,m]	2.02 (br s)[k,m]	1.98 (br s)[i,k]	1.96 (br s)[k,m]	1.96 (br s)[k,m]
acetyl		*aglycon*	*aglycon*	*aglycon*	*aglycon*	*C-2 of Rha*	*C-2 of Rha*
		2.10 (s)[o]	2.10 (s)[o]	1.78 (s)[o]	1.96 (s)[m]	2.03 (s)[n]	2.03 (s)[n]
						C-4 of Rha	*C-4 of Rha*
						1.90 (s)[p]	1.90 (s)[p]
sugar moiety		*GlcA*	*GlcA*	*GlcA*	*GlcA*	*GlcA*	*GlcA*
	1	4.95 (d, 8)[a,†]	4.98 (d, 8)[a,†]	4.98 (d, 8)[a,†]	4.98 (d, 8)[a,†]	4.94 (d, 8)[a,†]	4.97 (d, 8)[a,†]
	2	4.42[α]	4.48[α]	4.48[α]	4.47[α]	4.42[α]	4.48[α]
	3	4.33[α]	4.38[α]	4.37[α]	4.37[α]	4.33[α]	4.37[α]
	4	4.52[α]	4.48[α]	4.48[α]	4.47[α]	4.52[α]	4.48[α]
	5	4.54[α]	4.58[α]	4.58 (d, 10)	4.58 (d, 10)	4.54[α]	4.45 (d, 10)
		Glc	*Glc*	*Glc*	*Glc*	*Glc*	*Glc*
	1	5.66 (d, 8)[q]	5.68 (d, 8)[q]	5.68 (d, 8)[q]	5.68 (d, 8)[o]	5.66 (d, 8)[r]	5.68 (d, 8)[s]
	2	4.06 (dd, 8, 8)	4.08[α]	4.08[α]	4.08[α]	4.06 (dd, 8, 8)	4.08[α]
	3	4.22[α]	4.24[α]	4.24[α]	4.24[α]	4.23[α]	4.24[α]
	4	4.13[α]	4.16 (dd, 9, 9)	4.16[α]	4.16 (dd, 9, 9)	4.14[α]	4.16 (dd, 9, 9)
	5	3.82 (m)	3.84 (m)	3.83 (m)	3.85 (m)	3.83[α]	3.84 (m)
	6	4.33[α]/4.46[α]	4.33[α]/4.45[α]	4.33[α]/4.44[α]	4.33[α]/4.46[α]	4.32[α]/4.45[α]	4.33[α]/4.45[α]
		Gal	*Ara*	*Ara*	*Ara*	*Gal*	*Ara*
	1	5.29 (d, 8)[r]	5.30 (d, 8)[r]	5.30 (d, 8)[r]	5.30 (d, 8)[p]	5.29 (d, 8)[s]	5.30 (d, 8)[t]
	2	4.48[α]	4.45[α]	4.45[α]	4.46[α]	4.45[α]	4.46[α]
	3	4.13[α]	4.09[α]	4.10[α]	4.10[α]	4.12[α]	4.10[α]
	4	4.46[α]	4.23[α]	4.24[α]	4.24[α]	4.45[α]	4.22[α]
	5	4.13[α]	3.79 (br d, 12)/ 4.28[α]	3.79 (br d, 12)/ 4.28[α]	3.79 (br d, 12)/4.28[α]	4.13[α]	3.79 (br d, 11)/ 4.27[α]
	6	4.33[α]/4.48[α]				4.33[α]/N. A.	
						Rha	*Rha*
	1					5.38 (d, 1.5)[e]	5.38 (d, 1.5)[e]
	2					5.78 (dd, 3, 1.5)[o]	5.77 (dd, 3, 1.5)[o]
	3					4.70 (dd, 10, 3)	4.70 (dd, 10, 3)
	4					5.62 (dd, 10, 10)[q]	5.61 (dd, 10, 10)[q]
	5					4.25[α]	4.24[α]
	6					1.36 (d, 6)	1.36 (d, 6)

		7	**8**	**9**	**10**	**11**
aglycone	3	3.29 (dd, 12, 4)[r,†]	3.29 (dd, 12, 4)[r,†]	3.32 (dd, 12, 4.5)[r]	3.41 (dd, 12, 4)	3.32 (dd, 12, 4)[q,†]
	5	0.84[α]	0.82[α]	0.92[α]	N.A.[v]	0.72 (br. d, 11)
	12	5.50 (dd, 3, 3)	5.50 (dd, 3, 3)	5.44 (dd, 3, 3)	5.46 (dd, 3, 3)	5.44 (dd, 3, 3)
	15	4.22[α]	4.22[α]	4.20 (d, 5)	4.28 (d, 4)	3.11 (d, 13)/1.93[α,b]
	16	4.53[α]	4.38[α]	4.75 (d, 5)	5.05[α,e]	
	18	3.00[α]	3.02[α]	3.31 (dd, 11, 6)[*]	3.00 (dd, 12, 5.5)	3.05 (dd, 15, 3.5)
	21	4.98 (d, 10)[h,i,u]	4.96 (d, 10)[h,i,u]	4.38 (s)[b,e,j,†,‡,#]	4.45 (s)[b,f,i,l]	4.61 (d, 10)[i,j,t]
	22	6.17 (d, 10)[b,g,j]	6.17 (d, 10)[b,g,j]	6.15 (s)[c,d,n,*,§,ll,¶]	5.12 (s)[c]	5.80 (d, 10)[c,h,k]
	23	1.24 (s)	1.23 (s)	1.30 (s)	1.29 (s)	1.30 (s)
	24	1.10 (s)	1.09 (s)	1.03 (s)	1.01(s)	1.10 (s)
	25	0.85 (s)	0.85 (s)	0.89 (s)	0.88 (s)	0.83 (s)
	26	1.02 (s)	1.03 (s)	1.00 (s)	1.08 (s)	0.99 (s)
	27	1.85 (s)	1.85 (s)	1.99 (s)	2.01 (s)	1.33 (s)
	28	3.41 (d, 11)	3.41 (d, 11)	3.81 (d, 11)[i]	4.46 (d, 11)	4.24[α,g]
	28	3.71 (d, 11)[f]	3.71 (d, 11)[f]	4.00 (d, 11)	4.85 (d, 11)[d]	
	29	1.23 (s)[c]	1.24 (s)[c]	1.39 (s)[f,m]	1.41 (s)[g,m]	1.17 (s)[d]
	30	1.35 (s)[d]	1.35 (s)[d]	3.78 (d, 11)[g,k,†,¶,#]	3.72 (d, 11)[j,h]	1.19 (s)[e]
	30			4.00 (d, 11)[h,l,‡,§,ll]	3.90 (d, 11)[k]	

Table 1. (Continued)

	7	8	9	10	11
ester moiety	*angeloyl*	*angeloyl*	*angeloyl*	*angeloyl*	*acetyl at aglycon*
3	6.06 (dq, 7, 1.5)	6.06 (dq, 7, 1.5)	5.96 (dq, 7, 1.5)	5.93 (dq, 7, 1.5)	2.28 (s)[l]
4	2.19 (dq, 7, 1.5)[l]	2.19 (dq, 7, 1.5)[l]	1.98 (dq, 7, 1.5)[p]	2.04 (dq, 7, 1.5)[o]	
5	1.99 (br s)[k,m]	2.00 (br s)[k,m]	1.85 (br s)[o,q]	1.90 (br s)[n,p]	
	acetyl at C-3 of Rha	*acetyl at C-3 of Rha*			*acetyl at C-3 of Rha*
	1.93 (s)[n]	1.93 (s)[n]			1.94 (s)[n]
	acetyl at C-4 of Rha	*acetyl at C-4 of Rha*			*acetyl at C-4 of Rha*
	2.07 (s)[p]	2.07 (s)[p]			2.07 (s)[p]
sugar moiety	*GlcA*	*GlcA*	*GlcA*	*GlcA*	*inner Glc*
1	4.93 (d, 8)[a,†]	4.96 (d, 8)[a,†]	5.03 (d, 8)[a]	5.00 (d, 8)[a]	4.95 (d, 8)[a,†]
2	4.43[α]	4.46[α]	4.14 (dd, 8, 9)	4.12[α]	4.08[α]
3	4.33[α]	4.38[α]	4.32 (dd, 9, 9)	4.31[α]	4.51[α]
4	4.50[α]	4.48[α]	4.60 (dd, 10, 9)	4.60[α]	4.11[α]
5	4.52[α]	4.58 (d, 9)	4.70 (d, 10)	4.70[α]	3.95[α]
6					4.32[α]/4.45[α]
	Glc	*Glc*			*intermediate Glc*
1	5.66 (d, 8)[s]	5.68 (d, 8)[s]			5.50 (d, 8)[r]
2	4.06[α]	4.08[α]			4.18[α]
3	4.23[α]	4.25[α]			4.29[α]
4	4.13[α]	4.16 (dd, 9, 9)			4.18[α]
5	3.82[α]	3.84 (m)			3.86 (m)
6	4.32[α]/4.45[α]	4.33[α]/4.44[α]			4.35[α]/4.46[α]
	Gal	*Ara*			*terminal Glc*
1	5.29 (d, 8)[t]	5.30 (d, 8)[t]			5.36 (d, 8)[s]
2	4.50[α]	4.46[α]			4.08[α]
3	4.12[α]	4.10[α]			4.18[α]
4	4.45[α]	4.23[α]			4.10[α]
5	4.14[α]	3.79 (br d, 12)/4.28[α]			3.97[α]
6	4.30[α]/4.48[α]				4.30[α]/4.57[α]
	Rha	*Rha*			*Rha*
1	5.41 (d, 1.5)[e]	5.44 (d, 1.5)[e]			5.58 (d, 1.5)[f]
2	4.81 (dd, 3, 1.5)	4.81 (dd, 3, 1.5)			4.71 (dd, 3, 1.5)
3	5.76 (dd, 10, 3)[o]	5.75 (dd, 10, 3)[o]			5.74 (dd, 10, 3)[m]
4	5.87 (dd, 10, 10)[q]	5.86 (dd, 10, 10)[q]			5.88 (dd, 10, 10)[o]
5	4.35[α]	4.35[α]			4.44[α]
6	1.33 (d, 6)	1.33 (d, 6)			1.40 (d, 6)

[a−u] The HMBC correlations were observed between carbons that have the same superscripts in the same compound in Table 2. [v] N.A: not assigned. *,†,‡,||,¶,§,# ROE correlation were observed between the protons that have the same superscripts. [α] Overlapped with other signals.

nopyranosyl residue. The positions of the four sugar residues were determined by HMBC and ROE spectra (see Tables 1 and 2). In the HMBC spectrum, cross-peaks between H-1 of the rhamnopyranosyl residue (δ 5.38) and C-21 (δ 88.0) and reverse cross-peaks between H-21 (δ 5.01) and C-1 of the rhamnopyranosyl residue (δ 100.6) showed that the rhamnopyranosyl residue was connected to C-21. The same conclusion with regard to the rhamnopyranosyl residue was also deduced from ROE experiments. On the basis of these results the structure of saniculasaponin V (**5**) was assigned as 3-*O*-[β-D-glucopyranosyl-(1→2)]-β-D-galactopyranosyl-(1→3)-β-D-glucuronopyranosyl-21-*O*-(2,4-diacetyl)-α-L-rhamnopyranosyl-22-*O*-angeloyl-3β,15α,16α,21β,22α,28-hexahydroxyolean-12-ene.

The FABMS data for saniculasaponin VI (**6**) showed a quasi molecular ion peak at *m*/*z* 1312 $[M + Na]^+$, 30 mass units less than that of **5**, and indicated the molecular formula $C_{62}H_{96}O_{28}$. On acid hydrolysis, the sugar components D-glucuronic acid, D-glucose, L-arabinose, and L-rhamnose were detected.[8] In comparison with **5**, the ^{1}H NMR spectrum was very similar, except that the signals due to the β-D-galactopyranosyl residue in **5** were replaced by an α-L-arabinopyranosyl residue in **6**. Hence, the structure of saniculasaponin VI (**6**) was concluded to be 3-*O*-[β-D-glucopyranosyl-(1→2)]-α-L-arabinopyranosyl-(1→3)-β-D-glucuronopyranosyl-21-*O*-(2,4-diacetyl)-α-L-rhamnopyranosyl-22-*O*-angeloyl-3β,15α,16α,21β,22α,28-hexahydroxyolean-12-ene.

Saniculasaponin VII (**7**) had a molecular formula $C_{63}H_{98}O_{29}$, identical to that of **5**, as determined from a quasi molecular ion peak at *m*/*z* 1342 $[M + Na]^+$ in the FABMS data. The ^{1}H and ^{13}C NMR spectra were very similar to those of **5**; however, the HMBC spectrum indicated that the positions of the two acetyl groups were different from **5**. Cross-peaks between the carbonyl carbon of the acetyl group (δ 170.4) and H-3 of the rhamnopyranosyl residue (δ 5.76) and another acetyl carbonyl carbon (δ 170.3) and H-4 of the rhamnopyranosyl residue (δ 5.87) were observed. Accordingly, the two acetyl moieties were linked to C-3 and C-4 of the rhamnopyranosyl residue. Thus, the complete structure of saniculasaponin VII (**7**) was defined as 3-*O*-[β-D-glucopyranosyl-(1→2)]-β-D-galactopyranosyl-(1→3)-β-D-glucuronopyranosyl-21-*O*-(3,4-diacetyl)-α-L-rhamnopyranosyl-22-*O*-angeloyl-3β,15α,16α,21β,22α,28-hexahydroxyolean-12-ene.

Saniculasaponin VIII (**8**) gave a quasi molecular ion by FABMS at *m*/*z* 1312 $[M + Na]^+$, 30 mass units less than **7**, and indicated the molecular formula $C_{62}H_{96}O_{28}$. Comparison between the signals observed for **7** and **8** revealed similarity, except that the signals due to the β-D-galactopyranosyl residue in **7** were replaced by an α-L-arabinopyranosyl residue in **8**. The sugar components were identified by acid hydrolysis as D-glucuronic acid, D-glucose, L-arabinose, and L-rhamnose.[8] Thus, the structure of saniculasaponin VIII (**8**) was assigned as 3-*O*-[β-D-glucopyranosyl-(1→2)]-α-L-arabinopyranosyl-(1→3)-β-D-glucurono-

Table 2. ^{13}C NMR Data (δ) of Compounds **1**−**10** in C_5D_5N

		1	**2**	**3**	**4**	**5**	**6**
aglycone	1	39.0	39.0	39.0	39.1	39.0	39.0
	2	26.7	26.7	26.7	26.7	26.7	26.7
	3	89.5[a]	89.5[a]	89.5[a]	89.5[a]	89.5[a]	89.5[a]
	4	39.6	39.6	39.6	39.6	39.6	39.6
	5	55.6	55.6	55.6	55.6	55.5	55.5
	6	18.9	18.8	18.9	18.8	18.8	18.8
	7	36.8	36.8	36.7	36.7	36.8	36.8
	8	41.5	41.5	41.4	41.5	41.5	41.5
	9	47.2	47.2	47.2	47.2	47.2	47.2
	10	37.0	37.0	37.0	37.0	37.0	37.0
	11	24.0	24.0	24.0	24.1	24.0	24.0
	12	125.5	125.5	125.4	125.6	125.4	125.4
	13	143.7	143.7	143.7	143.6	143.7	143.7
	14	47.8	47.8	47.9	48.0	47.6	47.6
	15	67.6	67.6	67.5	67.5	67.7	67.6
	16	73.6[b]	73.6[b]	72.7[b]	72.2[b]	74.1[b]	74.1[b]
	17	48.4	48.4	48.4	47.5	48.7	48.7
	18	41.1	41.0	41.0	41.4	41.1	41.1
	19	47.0	47.0	46.9	47.0	47.2	47.2
	20	36.3	36.3	36.2	36.1	37.4	37.4
	21	79.3[c,d]	79.3[c,d]	78.9[c,d]	81.2[c,d]	88.0[c,d,e]	88.1[c,d,e]
	22	73.5[e,f]	73.5[e,f]	74.2[e,f]	71.1	74.6[f]	74.6[f]
	23	27.9	27.9	27.9	27.9	27.9	27.9
	24	16.8	16.8	16.8	16.8	16.8	16.8
	25	15.8	15.7	15.9	15.9	15.8	15.8
	26	17.6	17.6	17.6	17.7	17.6	17.6
	27	21.3	21.2	21.1	21.1	21.2	21.2
	28	63.2[g]	63.2[g]	63.4[g]	65.9[e]	63.5[g]	63.5[g]
	29	29.5[h]	29.5[h]	29.5[h]	29.8[f]	30.5[h]	30.5[h]
	30	20.0[i]	20.0[i]	20.2[i]	20.1[g]	20.0[i]	20.0[i]
ester moiety							
angeloyl	1	168.2[j,k]	168.2[j,k]	167.9[j,k]	168.6[h,i]	168.1[j,k]	168.1[j,k]
	2	129.2[l]	129.2[l]	129.0[l]	129.6[j]	129.2[l]	129.2[l]
	3	136.6[m]	136.6[m]	137.1[m]	136.7[k]	138.9[m]	138.9[m]
	4	15.8	15.8	15.8	15.9	16.1	16.1
	5	20.7	20.7	20.9	21.0	21.0	21.0

		1	**2**	**3**	**4**	**5**	**6**
acetyl		*aglycone*	*aglycone*	*aglycone*	*aglycone*		
	1	170.8[n,o]	170.8[n,o]	170.8[n,o]	170.5[l,m]		
	2	21.1	21.1	20.7	20.6		
						C-2 of Rha	*C-2 of Rha*
	1					170.6[n,o]	170.6[n,o]
	2					20.9	20.9
						C-4 of Rha	*C-4 of Rha*
	1					170.8[p,q]	170.8[p,q]
	2					20.8	20.8
sugar moiety		*GlcA*	*GlcA*	*GlcA*	*GlcA*	*GlcA*	*GlcA*
	1	105.3[p]	105.5[p]	105.4[p]	105.4[n]	105.3	105.4[r]
	2	79.0[q]	79.2[q]	79.3[q]	79.3[o]	79.0[r]	79.3[s]
	3	88.0[r]	86.2[r]	86.2[r]	86.3[p]	87.9[s]	86.2[t]
	4	71.9	71.5	71.5	71.5	71.8	71.5
	5	77.3	77.5	77.3	77.3	77.4	77.3
	6	171.8	171.8	171.8	171.8	171.8	171.8
		Glc	*Glc*	*Glc*	*Glc*	*Glc*	*Glc*
	1	104.0	103.8	103.8	103.8	103.9	103.8
	2	76.4	76.4	76.4	76.4	76.4	76.4
	3	78.6	78.6	78.6	78.6	78.6	78.6
	4	72.7	72.6	72.6	72.6	72.6	72.6
	5	77.7	77.8	77.8	77.7	77.7	77.8
	6	63.5	63.4	63.4	63.4	63.5	63.4
		Gal	*Ara*	*Ara*	*Ara*	*Gal*	*Ara*
	1	105.3	105.2	105.2	105.2	105.3	105.2
	2	73.0	72.9	72.9	72.9	73.0	72.9
	3	75.4	74.7	74.7	74.7	75.4	74.7
	4	70.2	69.7	69.7	69.8	70.2	69.7
	5	77.4	67.8	67.8	67.8	77.3	67.7
	6	62.0				62.0	
						Rha	*Rha*
	1					100.6[t]	100.6[u]
	2					74.3	74.3
	3					67.6	67.6
	4					75.4	75.4
	5					67.7	67.7
						18.0	18.0

		7	**8**	**9**	**10**	**11**
aglycone	1	39.0	39.0	38.9	39.0	38.8
	2	26.7	26.7	26.7	26.7	26.6
	3	89.5[a]	89.5[a]	89.5[a]	89.0[a]	88.9[a]
	4	39.6	39.6	39.5	39.5	39.6
	5	55.5	55.6	55.6	55.6	55.7
	6	18.8	18.8	18.7	18.7	18.3
	7	36.8	36.8	35.9	35.8	32.6
	8	41.5	41.5	41.5	41.6	48.8
	9	47.2	47.2	47.2	47.2	46.7
	10	37.0	37.0	37.0	37.0	36.7
	11	24.0	24.0	24.0	24.1	23.9
	12	125.5	125.5	124.8	124.6	125.4
	13	143.7	143.7	145.5	145.6	140.0
	14	47.6	47.6	47.2	47.5	40.0
	15	67.5	67.6	68.9	69.1	45.2
	16	74.4[b]	74.3[b]	82.1[b,c]	80.8[b,c]	211.3[b,c]
	17	48.7	48.7	51.5	50.5	59.8
	18	41.1	41.1	41.1[d]	42.1[d,e]	47.1
	19	47.2	47.2	36.9[e]	37.1[f]	46.3
	20	37.4	37.4	44.3	43.6	37.2
	21	88.4[c,d,e]	88.4[c,d,e]	85.6[f,g,h]	88.4[g,h]	84.7[d,e,f]
	22	74.8[f]	74.8[f]	78.7[i]	74.1	75.3[g]
	23	27.9	27.9	28.2	28.2	28.2
	24	16.7	16.8	17.0	17.0	16.9
	25	15.8	15.8	15.6	15.6	15.6
	26	17.6	17.6	17.9	18.0	16.9
	27	21.2	21.2	23.1	23.4	27.1
	28	63.5[g]	63.5[g]	59.0	62.5	65.9[h]
	29	30.4[h]	30.5[h]	24.6[j,k,l]	25.0[i,j,k]	30.1[i]
	30	20.1[i]	20.1[i]	70.2[m]	70.3[l,m]	19.4[j]
ester moiety						

		7	**8**	**9**	**10**	**11**
acetyl		*C-3 of Rha*	*C-3 of Rha*			*C-3 of Rha*
	1	170.4[n,o]	170.5[n,o]			170.5[m,n]
	2	20.8	20.8			20.7
		C-4 of Rha	*C-4 of Rha*			*C-4 of Rha*
	1	170.3[p,q]	170.4[p,q]			170.3[o,p]
	2	20.8	20.8			20.8
sugarmoiety		*GlcA*	*GlcA*	*GlcA*	*GlcA*	*innerGlc*
	1	105.3[r]	105.4[r]	107.2[r]	107.2	104.7[q]
	2	79.0[s]	79.3[s]	75.6	75.6	83.6[r]
	3	88.0[t]	86.2[t]	78.2	78.2	78.3
	4	71.8	71.5	73.5	73.4	70.9
	5	77.3	77.4	77.8	78.0	77.7
	6	171.8	171.9	N.D.[v]	N.D.	63.1
		Glc	*Glc*			*intermediate Glc*
	1	104.0	103.8			103.6
	2	76.4	76.4			85.7[s]
	3	78.6	78.6			77.6
	4	72.6	72.6			71.9
	5	77.7	77.8			77.6
	6	63.5	63.4			62.7
		Gal	*Ara*			*terminal Glc*
	1	105.3	105.2			106.4
	2	73.3	72.9			76.8
	3	75.4	74.7			77.7
	4	72.0	69.7			71.3
	5	77.4	67.8			79.3
	6	62.0				62.9

Table 2. (Continued)

		7	8	9	10	11		7	8	9	10	11
angeloyl	1	168.2[j,k]	168.2[j,k]	168.1[n,o]	167.9[n]							
	2	129.2[l]	129.2[l]	128.2[p]	128.5[o]			*Rha*	*Rha*			*Rha*
	3	138.8[m]	138.8[m]	139.2[q]	137.8[p]		1	104.0[u]	104.0[u]			103.5[t]
	4	16.0	16.1	16.0	16.0		2	69.7	69.7			69.6
	5	20.9	20.9	20.6	20.8		3	73.0	73.3			73.1
							4	72.1	72.1			71.9
acetyl						*aglycon*	5	67.8	67.9			68.2
						170.3[k,l]	6	17.9	17.9			17.8
						20.8						

[a−u] The long-range HMBC correlations were observed between protons that have the same superscripts in the same compound in Table 1. [v] N.D.; not detected.

pyranosyl-21-*O*-(3,4-diacetyl)-α-L-rhamnopyranosyl-22-*O*-angeloyl-3*β*,15α,16α,21*β*,22α,28-hexahydroxyolean-12-ene.

The FABMS of saniculasaponin IX (**9**) gave a quasi molecular ion peak at *m*/*z* 785 $[M + Na]^+$ and indicated the molecular formula $C_{41}H_{62}O_{13}$. The ^1H NMR spectrum displayed two methine singlets at low field (*δ* 4.38 and 6.15), an angeloyl moiety, and an anomeric proton (*δ* 5.03). HMQC data showed that the methine protons could be attributed to H-21 (*δ* 4.38) and H-22 (*δ* 6.15). The HMBC experiments supported this conclusion and showed correlations between the proton at *δ* 4.38 and C-29 (*δ* 24.6) and C-19 (*δ* 36.9) and between the proton at *δ* 6.15 and C-18 (*δ* 41.1). Long-range HMBC correlation between H-22 and the carbonyl carbon of the angeloyl moiety (*δ* 168.1) revealed that the angeloyl moiety was linked to C-22 (*δ* 78.7). On acid hydrolysis, D-glucuronic acid was detected.[8] In the ^{13}C NMR spectrum, the low-field shift of C-30 (*δ* 70.2) indicated that the hydroxyl group was connected to C-30. Furthermore, the ^{13}C NMR data showed that C-16 (*δ* 82.1) and C-21 (*δ* 85.6) were at low field. It is suggested that the low-field shifts are due to dehydration between OH-16 and OH-21, with formation of a five-membered ether ring. Therefore, the dihedral angle between H-21 and H-22 falls near 90°, so that the coupling of these two protons causes the signals to appear like a singlet. The HMBC data showed a correlation between H-21 and C-16, supporting this suggestion. Accordingly, H-21 was *β*-oriented. This assignment was supported by the ROE enhancements observed for H-21 and H-22 on irradiation of H-30 (*δ* 3.78 and 4.00). Thus, the structure of saniculasaponin IX (**9**) was assigned as 3-*O*-*β*-D-glucuronopyranosyl-22-*O*-angeloyl-3*β*,15α,22α,28,30-pentahydroxy-16α,21α-epoxyolean-12-ene.

The FABMS data of saniculasaponin X (**10**) showed a quasi molecular ion peak at *m*/*z* 785 $[M + Na]^+$, which supported a molecular formula of $C_{41}H_{62}O_{13}$. The ^1H NMR spectrum was very similar to that of **9**, which showed two methine singlets of H-21 and H-22 at low field (*δ* 4.45 and 5.12), an angeloyl group, and one anomeric proton at *δ* 5.00. In the ^1H and ^{13}C NMR experiments, H-28 (*δ* 4.46 and 4.85) and C-28 (*δ* 62.5) were located at low field compared with **9**. These data suggested that the angeloyl moiety was attached to C-28. Consequently, the structure was assigned as 3-*O*-*β*-D-glucuronopyranosyl-28-*O*-angeloyl-3*β*,15α,22α,28,30-pentahydroxy-16α,21α-epoxyolean-12-ene.

Saniculasaponin XI (**11**) had a molecular formula $C_{60}H_{94}O_{27}$ as determined from a quasi molecular ion peak at *m*/*z* 1270 $[M + Na]^+$ in its FABMS spectrum. An NMR experiment showed that the aglycon of **11** differed slightly from that of the other compounds. The ^1H NMR spectrum showed signals of an olean-12-ene-type aglycon, four anomeric protons, three methyl singlets (*δ* 1.94, 2.07, and 2.28), and a set of methylene protons at *δ* 1.93 (overlapped) and 3.11 (d, $J = 13$ Hz). The HMQC and HMBC spectra defined that the methylene signals were assigned to C-15 of the aglycon (*δ* 45.2). The ^{13}C NMR displayed a carbonyl carbon at low field (*δ* 211.3). The long-range HMBC coupling between H-22 (*δ* 5.80) and the carbonyl carbon at *δ* 211.3 established that the carbonyl was at C-16 of the aglycon. Further supporting information was obtained from the observed HMBC between H-15 (*δ* 1.93, 3.11) and the ketonic carbonyl carbon. Thus, the aglycon was determined to be 3,21,22-trisubstituted olean-12-ene-16-keto-3,21,22,28-tetraol. The ^1H NMR data showed four anomeric protons at *δ* 4.95 (d, $J = 8$ Hz), 5.36 (overlapped), 5.50 (d, $J = 8$ Hz), and 5.58 (d, $J = 1.5$ Hz) together with a methyl signal at *δ* 1.40 (d, $J = 6$ Hz), suggesting the presence of a rhamnopyranosyl residue. On acid hydrolysis, D-glucose and L-rhamnose were detected.[8] The 1D HOHAHA experiment revealed that these sugars were three D-glucoses and a L-rhamnose. The positions of sugar components were determined by HMBC and ROE studies (see Tables 1 and 2). Therefore, the structure of saniculasaponin XI (**11**) was assigned as 3-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-glucopyranosyl-(1→2)-*β*-D-glucopylanosyl-21-*O*-(3,4-diacetyl)-α-L-rhamnopyranosyl-22-*O*-acetyl-3*β*,21*β*,22α,28-tetrahydroxyolean-16-keto-12-ene.

Experimental Section

General Experimental Procedures. Optical rotations were taken on a JASCO DIP 1000 digital polarimeter. NMR spectra were recorded in C_5D_5N on a JEOL α-400 instrument at 400 MHz for ^1H and 100 MHz for ^{13}C NMR at 35 °C. Mass spectral data were obtained on a JEOL JMS-SX 102 mass spectrometer. Preparative HPLC was performed on a JASCO system 800 instrument. GC was performed on a Hitachi G-3000 instrument.

Plant Material. *Sanicula elata* var. *chinensis* was collected in Shizuoka, Japan, in July 2001 and identified by Prof. Akira Ueno, School of Pharmaceutical Sciences, University of Shizuoka. A voucher specimen is deposited at the herbarium of University of Shizuoka, No. 20010728.

Extraction and Isolation. Dried whole plants of *S. elata* var. *chinensis* (720 g) were extracted with MeOH. The MeOH extract was concentrated under reduced pressure to give 109 g of residue, which was dissolved in H_2O and then extracted with diethyl ether. The H_2O layer was applied to a Mitsubishi Diaion HP-20 column (9 × 45 cm), and the adsorbed material was eluted with 40% MeOH (10 L), then with MeOH (8 L) to give 40% MeOH eluate (3.2 g) and MeOH eluate (6.6 g). Three grams of MeOH eluate was subjected to HPLC (column ODS, 5 × 100 cm, solvent CH_3CN-H_2O (15:85) → (31:69) linear gradient, flow rate 45 mL/min, detection UV 205 nm) to afford 37 fractions. Fractions 27−36 were subjected further to preparative HPLC to give compounds **1**−**12**.

Saniculasaponin I (1): 41.6 mg; amorphous powder; $[\alpha]^{23}_D$ −31.5 (*c* 2.40, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1154 $[M + Na]^+$.

Saniculasaponin II (2): 26.6 mg; amorphous powder; $[\alpha]^{23}_D$ −24.5 (*c* 1.22, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1124 $[M + Na]^+$.

Saniculasaponin III (3): 49.2 mg; amorphous powder; $[\alpha]^{23}_D$ −19.1 (*c* 2.38, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1124 $[M + Na]^+$.

Saniculasaponin IV (4): 12.8 mg; amorphous powder; $[\alpha]^{23}_D$ +2.20 (*c* 0.66, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1124 $[M + Na]^+$.

Saniculasaponin V (5): 18.8 mg; amorphous powder; $[\alpha]^{23}_D$ −32.1 (*c* 0.93, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1342 $[M + Na]^+$.

Saniculasaponin VI (6): 18.6 mg; amorphous powder; $[\alpha]^{23}_D$ −33.7; (*c* 0.90, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1312 $[M + Na]^+$.

Saniculasaponin VII (7): 8.2 mg; amorphous powder; $[\alpha]^{23}_D$ −120.5 (*c* 0.39, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1342 $[M + Na]^+$.

Saniculasaponin VIII (8): 27.0 mg; amorphous powder; $[\alpha]^{23}_D$ −10.0 (*c* 0.13, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1312 $[M + Na]^+$.

Saniculasaponin IX (9): 18.8 mg; amorphous powder; $[\alpha]^{23}_D$ +17.9 (*c* 0.62, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 785 $[M + Na]^+$.

Saniculasaponin X (10): 2.8 mg; amorphous powder; $[\alpha]^{23}_D$ −0.00 (*c* 0.15, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 785 $[M + Na]^+$.

Saniculasaponin XI (11): 18.0 mg; amorphous powder; $[\alpha]^{23}_D$ −42.1 (*c* 0.88, C_5H_5N); ^1H and ^{13}C NMR, see Tables 1 and 2; FABMS *m*/*z* 1270 $[M + Na]^+$.

Sandrosaponin IX (12): 19.8 mg; amorphous powder; $[\alpha]^{23}_D$ −7.3 (*c* 0.97, C_5H_5N); ^1H NMR (C_5D_5N, 400 MHz) δ 6.31 (1H, d, J = 8 Hz, anomeric of Glc at C-28), 5.38 (1H, d, J = 8 Hz, anomeric of Gal), 5.23 (1H, d, J = 8 Hz, anomeric of Glc), 5.06 (1H, d, J = 8 Hz, anomeric of GlcA), 3.86 (1H, m, Glc-5), 3.30 (1H, dd, J = 12, 4 Hz, H-3), 3.18 (1H, dd, J = 14, 4.5 Hz, H-18), 1.31 (3H, s, H-23), 1.25 (3H, s, H-27), 1.14 (3H, s, H-24), 1.08 (3H, s, H-26), 0.90 (3H, s, H-29), 0.88 (3H, s, H-30), 0.83 (3H, s, H-25); ^{13}C NMR (C_5D_5N, 100 MHz) aglycon (C-1→30) δ 38.8 (CH_2), 26.6 (CH_2), 89.5 (CH), 39.6 (C), 55.9 (CH), 18.6 (CH_2), 32.6 (CH_2), 40.0 (C), 48.0 (CH), 37.0 (C), 23.5 (CH_2), 123.0 (CH), 144.1 (C), 42.2 (C), 28.3 (CH_2), 23.8 (CH_2), 47.1 (C), 41.8 (CH), 46.3 (CH_2), 30.8 (C), 34.1 (CH_2), 33.2 (CH_2), 28.3 (CH_3), 16.9 (CH_3), 15.6 (CH_3), 17.5 (CH_3), 26.1 (CH_3), 176.4 (C=O), 33.2 (CH_3), 23.7 (CH_3), GlcA (C-1→6) 105.0, 84.1, 77.7, 72.3, 77.7, 172.4, Gal (C-1→6) 104.4, 84.5, 75.0, 69.0, 76.4, 61.5, Glc (C-1→6) 106.5, 76.7, 77.8, 71.2, 79.2, 62.6, Glc at C-28 (C-1→6) 95.8, 74.2, 79.0, 71.3, 79.3, 62.4; FABMS *m*/*z* 1142 $[M + Na]^+$.

Acid and Alkaline Hydrolysis of Saponins. Each saponin (1 mg) was dissolved in 1 M NaOH (200 μL) and stirred for 3 h at room temperature. The solution was then acidified with 2 M HCl (300 μL) and extracted twice with EtOAc. For ester analysis, the EtOAc layer was washed with H_2O, *O*-(4-nitrobenzyl)-*N*,*N*′-diisopropylisourea (1 mg) was added, and then the mixture was heated at 80 °C for 1 h. The reaction mixture was concentrated, and the residue was subjected to HPLC analysis (column Develosil PhA (Nomura Chemical), 4.6 mm × 25 cm, solvent CH_3CN-H_2O (45:55), flow rate 1.0 mL/min, detection UV 273 nm) for detection of esters. Acetic acid (t_R, 9.4 min) was detected for **1**−**8** and **11** and angelic acid (t_R, 20.6 min) for **1**−**10**. The H_2O layer was heated 100 °C for 1 h. The solution was diluted with H_2O and extracted twice with EtOAc. Then $AgCO_3$ (3 mg) was added to the H_2O layer, and the mixture was stirred and centrifuged. The supernatant was concentrated, and the residue was dissolved in pyridine (30 μL) containing D-cysteine methyl ester (3 mg) and stirred for 1.5 h at 60 °C. After derivatization, a mixture of hexamethyldisilazane and trimethylsilyl chloride (9:1, 20 μL) was added to the solution and stirred for 30 min at 60 °C. The reaction solution was centrifuged, then the supernatant was analyzed by GC (column Supelco SPB-1, 0.25 mm × 27 m, column temperature 215 °C, carrier gas N_2). D-Glucuronic acid (t_R, 15.6 min) was identified for **1**−**10**, D-glucose (t_R, 20.7 min) for **1**−**8** and **11**, D-galactose (t_R, 22.8 min) for **1**, **5**, and **7**, L-arabinose (t_R, 11.9 min) for **2**−**4**, **6**, and **8**, and L-rhamnose (t_R, 13.8 min) for **5**−**8** by comparing their retention times with those of authentic samples.[8]

References and Notes

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