Scrophulasaponins II—IV, New Saikosaponin Homologs from *Scrophularia kakudensis* FRANCH.

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From the whole plants of *Scrophularia kakudensis*, three new saikosaponin homologs, named scrophulasaponins II—IV, were isolated, together with six known and four artifact saponins; their structures were elucidated by spectroscopic data and chemical evidence.

Keywords *Scrophularia kakudensis*; scrophulasaponin; saikosaponin homolog; Scrophulariaceae; saikosaponin a; buddlejasaponin

In the preceding papers we reported on the isolation and structure elucidation of saikosaponin a and saikosaponin homologs, which belonged to an oleanane-triterpene saponin, from *Buddleja japonica* HEMSL. (Buddlejaceae),[1] *Clinopodium gracile* O. KUNTZE[2] and *C. micranthum* HARA (Labiatae).[3] These saponins were composed of saikosaponin a and additional sugars. Recently, saikosaponin homologs were obtained from *Buddleja officinalis*,[4] *Clinopodium polycephalum*,[5] *Verbascum phlomoides*,[6] *V. songaricum*,[7] *V. nigrum*[8] (Scrophulariaceae) and *Scrophularia ilwensis*.[9] Now we have obtained 13 saponins from *Scrophularia kakudensis* FRANCH. (Scrophulariaceae), and this paper deals with the isolation and structure elucidation of these saponins.

A water extract of the whole plant was passed through a Mitsubishi Diaion HP-20 column, and the adsorbed materials were eluted with 50% aqueous methanol and methanol, successively. The methanol eluate was chromatographed on a preparative octadecyl silica gel (ODS) column, followed by repeated semi-preparative HPLC on a reversed phase column [ODS, phenyl alkyl (PhA)]. We identified six known saponins, saikosaponin a (**1**), buddlejasaponins I—III (**2**—**4**), mimengoside A (**5**) and songarosaponin A (**5b**), four artifact saponins, named buddlejasaponins Ia—IIIa (**2a**—**4a**) and scrophulasaponin Ia (**6a**), and three new saponins, named scrophulasaponins II—IV (**7**—**9**).

Compounds **1**, **2**, **3**, **4**, **5** and **5b** were identified by ^{1}H- and ^{13}C-NMR spectra as saikosaponin a,[10] buddlejasaponin I,[1] buddlejasaponin II,[1] buddlejasaponin III,[1] mimengoside A[4] (=ilwensisaponin A[9]) and songarosaponin A[7] (=ilwensisaponin B[9]).

The ^{1}H-NMR spectra of compounds **2a**, **3a** and **4a** showed one methoxy proton signal and one olefinic proton signal, and the ^{13}C-NMR spectrum of each aglycone moiety was very similar to that of saikosaponin b_3.[10] The ^{13}C-NMR spectrum of each sugar moiety of **2a**, **3a** and **4a** was in agreement with that of **2**, **3** and **4**.[1]

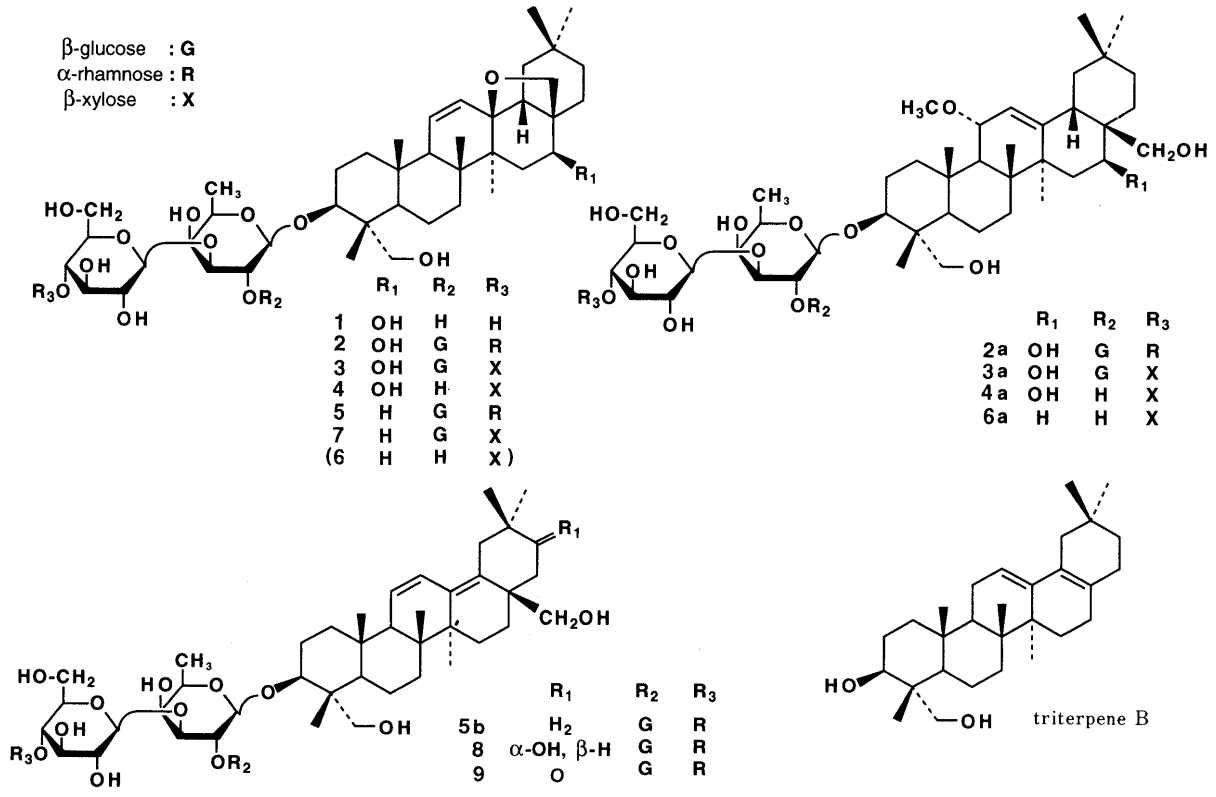

Chart 1

TABLE I. ^{13}C-NMR Chemical Shifts of the Aglycone Moiety in Pyridine-d_5 at 35 °C

	2a	3a	4a	6a	7	8	9
Aglycone moiety							
C- 1	40.1	40.1	40.2	40.2	38.7	38.4	38.4
C- 2	26.4	26.4	26.5	26.3	25.7	26.1	26.1
C- 3	82.8	82.8	81.9	82.0	82.6	82.8	82.6
C- 4	44.0	44.0	43.7	43.9	43.8	42.7	42.7
C- 5	48.2	48.2	47.8	47.8	47.9	47.9	47.8
C- 6	18.4	18.4	18.4	18.3	17.7	18.4	18.3
C- 7	33.3	33.3	33.3	33.2	31.5	32.5	31.3
C- 8	41.0	41.0	41.0	37.5	41.7	40.6	40.7
C- 9	52.1	52.1	52.1	52.8	53.7	54.9	54.9
C-10	38.1	38.1	38.2	38.2	36.3	36.6	36.6
C-11	76.0	76.0	76.0	76.1	132.0	126.8	128.0
C-12	122.6	122.6	122.6	122.6	131.7	126.0	125.5
C-13	148.3	148.3	148.3	149.4	84.9	136.8	137.9
C-14	44.0	44.0	44.0	42.1	44.2	43.8	43.8
C-15	36.9	36.9	36.9	26.5	25.9	29.6	29.2
C-16	66.3	66.3	66.3	22.9	26.0	24.6	25.2
C-17	43.7	43.7	43.9	43.5	42.0	42.6	45.0[a]
C-18	44.1	44.1	44.1	42.3	51.5	134.8	132.5
C-19	47.0	47.0	47.0	47.0	37.4	38.3	39.6
C-20	31.1	31.1	31.1	31.3	31.7	38.3	46.2[a]
C-21	34.3	34.3	34.3	34.7	35.1	72.9	214.9
C-22	26.0	26.0	26.0	31.7	31.1	41.4	48.2
C-23	65.0	65.0	64.4	64.5	64.7	64.8	64.7
C-24	13.3	13.3	13.6	13.7	12.7	12.8	12.8
C-25	17.9	17.9	18.0	17.9	18.8	18.8	18.8
C-26	18.4	18.4	18.4	18.5	19.6	17.0	17.0
C-27	26.3	26.3	26.3	25.3	19.9	20.8	20.8
C-28	68.7	68.7	68.7	68.7	77.2	64.3	67.5
C-29	33.3	33.3	33.3	33.3	33.6	18.1	25.0
C-30	24.1	24.1	24.1	23.8	23.6	29.2	25.2
OMe	54.0	54.0	54.0	54.0			

Recorded on a JEOL GSX-270 (67.80 MHz). *a*) Assignments may be interchanged within a column.

TABLE II. ^{13}C-NMR Chemical Shifts of the Sugar Moiety in Pyridine-d_5 at 35 °C

	2a	8	9	3a	7	4a	6a
Fucose moiety							
C-1	104.0	104.2	104.2	104.1	104.1	106.0	106.0
C-2	77.2	77.2	77.3	77.2	77.0	71.8	71.8
C-3	84.8	84.8	84.8	85.0	85.0	85.7	85.7
C-4	72.0	72.1	72.1	72.1	72.1	72.2	72.2
C-5	70.5	70.5	70.5	70.5	70.5	71.1	71.1
C-6	17.2	17.2	17.2	17.2	17.2	17.2	17.2
Glucose moiety (at C-2 of fuc)							
C-1	104.0	104.1	104.0	104.1	104.1		
C-2	76.3	76.3	76.3	76.3	76.3		
C-3	78.8	78.9	78.9	78.8	78.8		
C-4	72.2	72.3	72.3	72.2	72.2		
C-5	77.5	77.6	77.5	77.5	77.5		
C-6	63.2	63.2	63.2	63.2	63.2		
Glucose moiety (at C-3 of fuc)							
C-1	105.0	105.1	105.0	105.0	105.0	106.5	106.5
C-2	75.6	75.6	75.6	75.1	75.1	75.5	75.5
C-3	76.5	76.5	76.5	76.3	76.3	76.3	76.3
C-4	78.5	78.5	78.5	80.8	80.8	80.9	80.9
C-5	77.3	77.3	77.3	76.6	76.6	76.8	76.8
C-6	61.4	61.4	61.4	61.7	61.7	61.8	61.8
Xylose moiety							
C-1				105.6	105.5	105.7	105.7
C-2				75.0	74.9	75.0	75.0
C-3				78.4	78.4	78.4	78.3
C-4				70.8	70.8	70.8	70.8
C-5				67.4	67.4	67.4	67.4
Rhamnose moiety							
C-1	102.8	102.8	102.8				
C-2	72.6	72.6	72.6				
C-3	72.8	72.8	72.8				
C-4	74.0	74.0	74.0				
C-5	70.4	70.4	70.4				
C-6	18.5	18.6	18.6				

Recorded on a JEOL GSX-270 (67.80 MHz).

Therefore, buddlejasaponins Ia (**2a**), IIa (**3a**) and IIIa (**4a**) can be formulated as shown in Chart 1. These saponins, **2a**, **3a** and **4a**, might be formed respectively from **2**, **3** and **4** during extraction and chromatographic procedures.[4]

The ^{1}H-NMR spectrum of scrophulasaponin Ia (**6a**) also showed one methoxyl proton signal [δ 3.24 (3H, s)] and one olefinic proton signal [δ 5.49 (1H, d, J=3 Hz)], suggesting that **6a** had the same aglycone moiety as **2a**, **3a** and **4a**. The ^{13}C-NMR spectrum of **6a** was very similar to that of mimengoside B[4] except for a lack of one sugar, and that of the sugar moiety was in agreement with buddlejasaponin III (**4**).[1] Thus scrophulasaponin Ia (**6a**) was concluded to be as shown in Chart 1. As a matter of fact, **6a** is given as an artifact of scrophulasaponin I (**6**), of which the aglycone has an 11-ene and five membered ether ring, but we can't isolate scrophulasaponin I at the present time.

Scrophulasaponin II (**7**) revealed an $[M+Na]^+$ ion peak at m/z 1082 in the FAB-MS. On mild methanolysis, **7** afforded triterpene B as the aglycone moiety,[4] and subsequent acid hydrolysis yielded β-fucose–β-glucose–β-xylose (β-fuc, β-glc, β-xyl) in the ratio of 1:2:1 as the sugar moiety. The NMR spectra of **7** were very similar to those of mimengoside A (**5**),[4] indicating that the terminal α-rhamnose in **5** might be replaced by β-xyl in **7**. For the purpose of investigating the binding site of β-xyl, we empolyed a difference in nuclear Overhauser effect (NOE) experiment. When the signal at δ 5.10 (1H, d, J=8 Hz, H-1 of β-xyl) was irradiated, an NOE was observed at the signal [δ 4.28 (1H, t, J=9 Hz)] due to the H-4 of β-glc attached to the C-3 of β-fuc. Based on the above data, the structure of scrophulasaponin II (**7**) was characterized as shown in Chart 1.

The spectral data of scrophulasaponin III (**8**) was similar to songarosaponin A (**5b**),[7] but the ^{13}C-NMR data of the E-ring carbon of the aglycones were different. **8** showed a quasi-molecular ion peak $[M+Na]^+$ at m/z 1112 in the FAB-MS, and elemental analysis datum was consistent with the molecular formula $C_{54}H_{88}O_{22}\cdot 4H_2O$. Based on the above data, the presence of a hydroxy group which attached to the E-ring of the aglycone was suggested. The connection of the E-ring's protons was determined by the NOE experiment, and by a detailed proton spin decoupling experiment. When the signal due to the H-12 was irradiated, an NOE was observed at the signal due to the H_{eq}-19, and when the H_{ax}-19 was irradiated, an NOE was observed at the signal due to the H_{ax}-21. Since a downfield-shift was observed at the H_{ax}-21 [δ 4.14 (1H, dd, J=15, 3 Hz)], a hydroxy group was attached to the C-21.

The ^{13}C-NMR spectrum of scrophulasaponin IV (**9**) showed a signal at δ 214.9, yet no cross peak in the ^{13}C–^{1}H COSY was observed between δ 214.9 and the proton signals, suggesting the presence of a ketone group. The reduction of **9** with $NaBH_4$ gave scrophulasaponin III (**8**). Therefore, the ketone group was attached to the C-21 of the aglycone, and the structure of **9** was concluded to be

TABLE III. ^{1}H-NMR Chemical Shifts of Compounds **2a**—**9** in Pyridine-d_5 at 35 °C

	2a	3a	4a	6a
Aglycone				
Me	0.90 (3H, s)	0.90 (3H, s)	0.90 (3H, s)	0.90 (3H, s)
	1.00 (3H, s)	1.00 (3H, s)	0.97 (3H, s)	0.98 (3H, s)
	1.07 (3H, s)	1.07 (3H, s)	1.01 (3H, s)	0.98 (3H, s)
	1.10 (3H, s)	1.10 (3H, s)	1.09 (3H, s)	1.00 (3H, s)
	1.10 (3H, s)	1.10 (3H, s)	1.14 (3H, s)	1.13 (3H, s)
	1.38 (3H, s)	1.38 (3H, s)	1.40 (3H, s)	1.33 (3H, s)
H- 3	4.11 (1H, dd, J=12, 5 Hz)		4.23 (1H, dd, J=12, 5 Hz)	
H- 9	1.93 (1H, d, J=8 Hz)	1.94 (1H, d, J=8.5 Hz)	1.97 (1H, d, J=8.5 Hz)	2.00 (1H, d, J=9 Hz)
H-11	3.81 (1H, dd, J=8, 3 Hz)	3.81 (1H, dd, J=8.5, 3 Hz)	3.84 (1H, dd, J=8.5, 3 Hz)	3.84 (1H, dd, J=9, 3 Hz)
H-12	5.52 (1H, d, J=3 Hz)	5.52 (1H, d, J=3 Hz)	5.54 (1H, d, J=3 Hz)	5.49 (1H, d, J=3 Hz)
H-16	4.61 (1H, m)	4.61 (1H, m)	4.62 (1H, m)	
H-23	3.71[a]	3.72 (1H, d, J=11 Hz)	3.72 (1H, d, J=11 Hz)	3.72 (1H, d, J=11 Hz)
			4.38 (1H, d, J=11 Hz)	4.35 (1H, d, J=11 Hz)
H-28				3.59 (1H, d, J=11 Hz)
				3.79 (1H, d, J=11 Hz)
OMe	3.21 (3H, s)	3.21 (3H, s)	3.23 (3H, s)	3.24 (3H, s)
Fucose				
H- 1	4.89 (1H, d, J=8 Hz)	4.90 (1H, d, J=8 Hz)	4.95 (1H, d, J=8 Hz)	4.95 (1H, d, J=8 Hz)
H- 2	4.63 (1H, dd, J=9.5, 8 Hz)	4.65 (1H, dd, J=9.5, 8 Hz)	4.50 (1H, br t, J=9 Hz)	4.50 (1H, dd, J=9.5, 8 Hz)
H- 3	4.05 (1H, dd, J=9, 3 Hz)	4.03 (1H, dd, J=9.5, 3 Hz)	3.97 (1H, dd, J=9.5, 3 Hz)	3.97 (1H, dd, J=9.5, 3 Hz)
H- 4		4.19[a]	4.10 (1H, d, J=3 Hz)	4.10 (1H, d, J=3 Hz)
H- 5	3.61 (1H, m)	3.62 (1H, m)	3.71 (1H, m)	3.70 (1H, m)
H- 6	1.37 (3H, d, J=6.5 Hz)	1.37 (3H, d, J=6.5 Hz)	1.42 (3H, d, J=6.5 Hz)	1.42 (3H, d, J=6.5 Hz)
Glucose (at C-2 of fuc)				
H- 1	5.58 (1H, d, J=8 Hz)	5.57 (1H, d, J=8 Hz)		
Glucose (at C-3 of fuc)				
H- 1	5.24 (1H, d, J=8 Hz)	5.24 (1H, d, J=8 Hz)	5.25 (1H, d, J=8 Hz)	5.24 (1H, d, J=8 Hz)
H- 2	3.93 (1H, t, J=8.5 Hz)	3.99 (1H, t, J=8 Hz)	4.02 (1H, t, J=8.5 Hz)	4.02 (1H, t, J=8.5 Hz)
H- 3	4.22 (1H, t, J=8.5 Hz)	4.25[a]	4.25[a]	4.25[a]
H- 4	4.32 (1H, t, J=9 Hz)	4.28 (1H, t, J=8.5 Hz)	4.29 (1H, t, J=9 Hz)	4.29 (1H, t, J=9 Hz)
H- 5	3.73 (1H, m)	3.89 (1H, m)	3.92 (1H, m)	3.92 (1H, m)
H- 6		4.49 (1H, dd, J=12.5, 3 Hz)	4.46[a]	4.46 (1H, dd, J=12, 2 Hz)
			4.56[a]	4.55 (1H, dd, J=12, 4 Hz)
Xylose				
H- 1		5.10 (1H, d, J=8 Hz)	5.10 (1H, d, J=8 Hz)	5.10 (1H, d, J=8 Hz)
Rhamnose				
H- 1	5.82 (1H, br s)			
H- 6	1.72 (3H, d, J=6.5 Hz)			

as shown in Chart 1.

Experimental

General Procedures ^{1}H- and ^{13}C-NMR spectra were obtained with a JEOL GSX-270 and GSX-500 FT-NMR, and chemical shifts were given in ppm with tetramethylsilane as an internal standard. FAB-MS were recorded on a JEOL JMS-SX102 mass spectrometer. Optical rotations were measured with a JASCO DIP-360 digital polarimeter. Gas chromatograhy (GC) was run on a Hitachi G-3000 Gas Chromatograph. Preparative and semi-preparative HPLC were carried out on a column of Develosil Lop-ODS (50 mm × 50 cm) and YMC D-ODS-5AQ, Develosil PhA-7 (20 mm × 25 cm), respectively.

Extraction and Isolation *S. kakudensis* was collected in Shizuoka, Japan in August, 1992. The dried whole plants (1.3 kg) were extracted twice with hot H_2O. The extract was passed through a Mitsubishi Diaion HP-20 column. After the content of the column was washed with H_2O, the adsorbed materials were eluted successively with 50% aqueous MeOH (yield 61 g) and MeOH (yield 18 g). The MeOH eluate (2 g) was chromatographed on preparative HPLC [Develosil Lop-ODS, 50 mm × 50 cm × 2, MeOH–H_2O (53 : 47)—(77 : 23) linear gradient] to give 24 fractions identified as fr. A—X. Fraction N is a pure compound, **8** (69 mg). From fr. O, compounds **2a** (23 mg) and **3a** (23 mg) were obtained, from fr. Q, compounds **4a** (13 mg) and **9** (7 mg) were obtained, from fr. S, compounds **2** (15 mg) and **3** (10 mg) were obtained, from fr. T, compounds **5** (27 mg) and **7** (10 mg) were obtained, from fr. U, compound **4** (20 mg) was obtained, from fr. V, compound **1** (6 mg) was obtained, from fr. W, compound **6a** (21 mg) was obtained, and from fr. X, compound **5b** (10 mg) was obtained. All were isolated by semi-preparative HPLC [YMC D-ODS-5 AQ or Develosil PhA-7, 20 mm × 25 cm, MeCN–H_2O system].

Buddlejasaponin Ia (2a) Amorphous powder. $[\alpha]_D^{25}$ +6.4° (c=0.84, MeOH). *Anal.* Calcd for $C_{55}H_{92}O_{23}\cdot 11/2H_2O$: C, 54.13; H, 8.51. Found: C, 54.04; H, 8.25. FAB-MS m/z 1144 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Buddlejasaponin IIa (3a) Amorphous powder. $[\alpha]_D^{25}$ +14.6° (c=0.79, MeOH). *Anal.* Calcd for $C_{54}H_{90}O_{23}\cdot 11/2H_2O$: C, 53.76; H, 8.44. Found: C, 53.46; H, 8.14. FAB-MS m/z: 1130 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Buddlejasaponin IIIa (4a) Amorphous powder. $[\alpha]_D^{25}$ +3.3° (c=0.91, MeOH). *Anal.* Calcd for $C_{48}H_{80}O_{18}\cdot H_2O$: C, 59.86; H, 8.58. Found: C, 59.61; H, 8.86. FAB-MS m/z: 968 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Scrophulasaponin Ia (6a) Amorphous powder. $[\alpha]_D^{25}$ +8.7° (c=1.31, MeOH). *Anal.* Calcd for $C_{48}H_{80}O_{17}\cdot 3/2H_2O$: C, 60.29; H, 8.75. Found: C, 60.27; H, 8.83. FAB-MS m/z: 952 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Scrophulasaponin II (7) Amorphous powder. $[\alpha]_D^{25}$ +44.9° (c=1.07, MeOH). *Anal.* Calcd for $C_{53}H_{86}O_{21}\cdot 4H_2O$: C, 55.39; H, 8.42. Found: C, 55.31; H, 8.39. FAB-MS m/z: 1082 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Scrophulasaponin III (8) Amorphous powder. $[\alpha]_D^{25}$ −9.7° (c=0.98, MeOH). *Anal.* Calcd for $C_{54}H_{88}O_{22}\cdot 4H_2O$: C, 55.85; H, 8.33. Found: C, 55.65; H, 8.29. FAB-MS m/z: 1112 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Scrophulasaponin IV (9) Amorphous powder. $[\alpha]_D^{25}$ +27.1° (c=1.67, MeOH). *Anal.* Calcd for $C_{54}H_{86}O_{22}\cdot 9/2H_2O$: C, 55.51; H, 8.20. Found: C, 55.36; H, 7.97. FAB-MS m/z: 1110 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I—III.

Mild Methanolysis and Subsequent Acid Hydrolysis of 2a—4a, 6a—9

TABLE III. (continued)

	7	8	9
Aglycone			
Me	0.82 (3H, s)	0.83 (3H, s)	0.80 (3H, s)
	0.92 (3H, s)	0.98 (3H, s)	0.96 (3H, s)
	0.97 (3H, s)	1.05 (3H, s)	1.02 (3H, s)
	0.97 (3H, s)	1.07 (3H, s)	1.06 (3H, s)
	1.07 (3H, s)	1.11 (3H, s)	1.14 (3H, s)
	1.33 (3H, s)	1.29 (3H, s)	1.19 (3H, s)
H- 3	4.12 (1H, dd, J=12, 5 Hz)	4.17 (1H, dd, J=12, 5 Hz)	4.17 (1H, dd, J=12, 5 Hz)
H- 9			
H-11	5.94 (1H, br d, J=10 Hz)	5.72 (1H, br d, J=10 Hz)	5.76 (1H, br d, J=10 Hz)
H-12	5.53 (1H, dd, J=10, 3 Hz)	6.65 (1H, br d, J=10 Hz)	6.59 (1H, dd, J=10, 3 Hz)
H-16			
H-23	3.72 (1H, d, J=11 Hz)	3.72 (1H, d, J=11 Hz)	3.73 (1H, d, J=11 Hz)
	4.36 (1H, d, J=11 Hz)	4.38 (1H, d, J=11 Hz)	4.39 (1H, d, J=11 Hz)
H-28	3.32 (1H, br d, J=7 Hz)		3.79 (1H, br d, J=11 Hz)
	3.71 (1H, d, J=7 Hz)		3.88 (1H, br d, J=11 Hz)
OMe			
Fucose			
H- 1	4.90 (1H, d, J=8 Hz)	4.94 (1H, d, J=8 Hz)	4.92 (1H, d, J=8 Hz)
H- 2	4.66 (1H, dd, J=9.5, 8 Hz)	4.66 (1H, br t, J=8.5 Hz)	4.66 (1H, br t, J=8.5 Hz)
H- 3	4.03 (1H, dd, J=9.5, 3 Hz)	4.08 (1H, dd, J=9, 3 Hz)	4.06 (1H, dd, J=9, 3 Hz)
H- 4		4.16[a]	4.16[a]
H- 5	3.60 (1H, m)	3.63 (1H, m)	3.62 (1H, m)
H- 6	1.39 (3H, d, J=6.5 Hz)	1.42 (3H, d, J=6.5 Hz)	1.42 (3H, d, J=6.5 Hz)
Glucose (at C-2 of fuc)			
H- 1	5.57 (1H, d, J=8 Hz)	5.58 (1H, d, J=8 Hz)	5.58 (1H, d, J=8 Hz)
Glucose (at C-3 of fuc)			
H- 1	5.24 (1H, d, J=8 Hz)	5.25 (1H, d, J=8 Hz)	5.25 (1H, d, J=8 Hz)
H- 2	4.00 (1H, t, J=8.5 Hz)	3.92 (1H, t, J=8.5 Hz)	3.93 (1H, t, J=8.5 Hz)
H- 3	4.21 (1H, t, J=8.5 Hz)	4.16 (1H, t, J=8.5 Hz)	4.16 (1H, t, J=8.5 Hz)
H- 4	4.28 (1H, t, J=9 Hz)	4.37 (1H, t, J=9 Hz)	4.38 (1H, t, J=9 Hz)
H- 5	3.89 (1H, m)	3.75 (1H, m)	3.74 (1H, m)
H- 6	4.49 (1H, dd, J=12, 3 Hz)	4.10[a]	4.10[a]
		4.18[a]	4.18[a]
Xylose			
H- 1	5.10 (1H, d, J=8 Hz)		
Rhamnose			
H- 1		5.82 (1H, br s)	5.82 (1H, br s)
H- 6		1.73 (3H, d, J=6.5 Hz)	1.72 (3H, d, J=6.5 Hz)

Recorded on a JEOL GSX-500 (500 MHz). *a*) Overlapped with other signals.

Each compound (*ca.* 0.5 mg) was refluxed with AcCl–MeOH (1 : 20) (1 ml) for 3 h. The reaction mixture was concentrated to afford a residue, which was then partitioned between EtOAc and H_2O. The EtOAc layer was concentrated and subjected to HPLC to reveal a peak due to saikogenin A (**2a**, **3a**, **4a**) and triterpene B (**6a**, **7**). The retention time of this material was in accordance with that of authentic saikogenin A and triterpene B. The H_2O layer was concentrated and the residue was heated at 100 °C with 5% H_2SO_4 aq. (2 drops) for 30 min. The reaction mixture was diluted with H_2O and passed through an Amberlite IR-45 column. The eluate was concentrated to give a residue, which was reduced with $NaBH_4$ (*ca.* 1 mg) in H_2O (0.2 ml) for 1 h at room temperature and passed through an Amberlite IR-120 column. The eluate was concentrated to dryness under reduced pressure, and then boric acid was removed by co-distillation with MeOH. The residue was acetylated with Ac_2O–pyridine (1 : 1) (2 drops) at 100 °C for 1 h. The reagents were evaporated off and the residual alditol acetates were analyzed by GC. HPLC conditions: column, YMC Pack R-ODS-7, 4.6 mm × 25 cm; flow rate, 1.3 ml/min; solvent, MeCN–H_2O (55 : 45); UV, 250 nm; t_R, 14.0 min (saikogenin A); column, YMC ODS S-5 C_8, 4.6 mm × 25 cm; flow rate, 1.0 ml/min; solvent, MeCN; UV, 250 nm; t_R, 10.7 min (triterpene B). GC conditions: column, Supelco SP-2380, 0.25 mm × 30 m; column temperature, 250 °C; carrier gas, N_2; t_R, 4.7 min (rhamnitol acetate), 5.0 min (fucitol acetate), 6.9 min (xylitol acetate), 10.4 min (glucitol acetate).

Reduction of 9 A mixture of **9** (7 mg) and $NaBH_4$ (*ca.* 1 mg) in MeOH (1 ml) was stirred for 3 h at room temperature. After the reaction mixture was diluted with H_2O, it was then passed through a Mitsubishi Diaion HP-20 column and washed with H_2O, and subsequently eluted with MeOH. The MeOH eluate was then chromatographed on HPLC to give **8** (2 mg), which was detected by HPLC and ^{1}H-NMR to be comparable to authentic **8**.

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