Triterpene Saponins from *Abrus cantoniensis* (Leguminosae). I.[1] Isolation and Characterization of Four New Saponins and a New Sapogenol

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From Abri Herba, the whole plant of *Abrus cantoniensis* (Leguminosae), ten new oleanene saponins together with thirteen known ones were isolated. Among them, four saponins called abrisaponins L, A, D_1 and Ca have been elucidated to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl (designated as β-fabatriosyl) abrisapogenol L (1), 3-*O*-β-fabatriosyl abrisapogenol A (2), 3-*O*-β-fabatriosyl abrisapogenol D (3), and 3-*O*-β-fabatriosyl cantoniensistriol (4), respectively.

Key words triterpene; saponin; β-fabatriose; Leguminosae; Fabaceae; *Abrus cantoniensis*

Abri Herba, the whole plant of *Abrus cantoniensis* HANCE (Leguminosae), is used as a folk medicine for hepatitis in China.[2] Its efficacy has been substantiated clinically.[3] Chiang *et al.* confirmed the efficacy of the crude saponin fraction in a pharmacological experimental model.[4] We also reported that the crude saponin fractions of this plant were effective for experimental liver injuries induced by CCl_4.[5] Furthermore, we obtained eight new sapogenols together with seven known ones from the hydrolysate of the crude saponin fraction.[6] We have now isolated twenty three saponins including a new sapogenol. This paper deals with the structural elucidation of four of the new saponins and one new sapogenol together with the identification of thirteen known saponins.

The MeOH extract of the Abri Herba (10 kg) was partitioned between EtOAc and 40% MeOH after the partition with *n*-hexane and 80% MeOH. After evaporation of 40% MeOH fraction, the residue was separated by MCI gel CHP 20P to give fractions 1 (H_2O—40% MeOH), 2 (60% MeOH), 3 (60—70% MeOH), 4 (80% MeOH), 5 (80—90% MeOH), 6 (90% MeOH), 7 (90% MeOH) and 8 (100% MeOH). The crude saponin fraction (frs. 2—7) was followed by various column chromatographies and preparative HPLC to yield saponins **1**—**23**. Saponins **5**—**17** were identified as soyasaponin I (**5**),[7] kaikasaponin III (**6**),[8] dehydrosoyasaponin I (**7**),[9] sophoraflavoside II (**8**),[10] saponin 2 (**9**),[11] soyasaponin A_3 (**10**),[12] kudzusaponin A_3 (**11**),[9b,13] robinioside E (**12**),[14] subproside I (**13**),[13] subproside IV (**14**),[15] wistariasaponin B_2 (**15**),[16] subproside V (**16**),[15] phaseoside IV (**17**)[17] by comparison with the various data including the ^{13}C-NMR spectral data (Tables 1, 2).

Abrisaponin L (**1**), a white powder, $[\alpha]_D^{27}$ −7.2° [pyridine–H_2O (9 : 1)], showed a peak at *m/z* 973 due to $[M-H]^-$ in the negative FAB-MS. The monosaccharide mixture obtained by acid hydrolysis of **1** revealed the presence of glucuronic acid, galactose and rhamnose by TLC. Their absolute configurations were determined to be D-form, except for rhamnose (L-form), according to the procedure developed by Hara *et al.*[18] The exact measurement under high resolution (HR) conditions showed that the composition is $C_{48}H_{78}NaO_{20}$ at *m/z* 997.4977 $[M+Na]^+$ in the HR/positive FAB-MS. The obtained molecular formula was the same as that of **11**. The enzymatic hydrolysis of **1** with glycyrrhizin hydrolase (GH)[19] yielded a new sapogenin, called abrisapogenol L (**1a**), a white powder, $[\alpha]_D^{27}$ +83.8° (pyridine). In the ^{13}C-NMR spectrum of **1a**, similar signals to those of kudzusapogenol A,[20] the sapogenol (**11a**) of **11**, except for E-ring were observed. The differential NOE experiment of **1a** gave some correlations on E-ring as shown in Fig. 1, indicating that the orientations to the hydroxyl groups at C-21, -22 and the hydroxy methyl group at C-20 were all β.

The structure of **1a** was thus determined to be 3β, 21β, 22β, 24, 30-pentahydroxyolean-12-ene, which corresponds to the epimer at C-20 of **11a**. On comparative analysis of the ^{13}C-NMR spectra of **1** and **11**, the signals due to the sugar region and the A—D ring for sapogenol moiety were in agreement. From the above evidence, the structure of **1** was elucidated as 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl abrisapogenol L.

Abrisaponin A (**2**), a white powder, $[\alpha]_D^{27}$ +0.1° [pyridine–H_2O (1 : 1)], furnished abrisapogenol A,[6b] and the same sugar units as **1** by acid hydrolysis. In the negative and HR/positive FAB-MS, **2** showed a peak at *m/z* 941 due to $[M-H]^-$ and at *m/z* 987.4904 $[M-H+2Na]^+$ ($C_{48}H_{77}Na_2O_{18}$), respectively. In the ^{13}C-NMR spectrum of **2**, the signals for aglycone moiety were in good agreement with those of abrisapogenol A except for C-2 and -3 signals due to glycosylation.[21] Since the sugar signals were identical with those of **1**, **2** was concluded to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl abrisapogenol A.

Abrisaponin D_1 (**3**), a white powder, $[\alpha]_D^{28}$ −0.3° (pyridine), showed the same molecular ion peak and composition as those of **2**. By acid hydrolysis, **3** gave abrisapogenol D,[6a] and the same sugars as **2**. In the ^{13}C-NMR spectrum of **3**, the signals for B—E-ring of sapogenol moiety were in accord with those of abrisapogenol D, whereas the signals due to A-ring and the sugar signals linked at C-3 were identical with those of **2**. Therefore, the structure of **3** was established as 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl abrisapogenol D.

Abrisaponin Ca (**4**), a white powder, $[\alpha]_D^{27}$ −6.1° (pyridine), showed a peak at *m/z* 941.5108 due to

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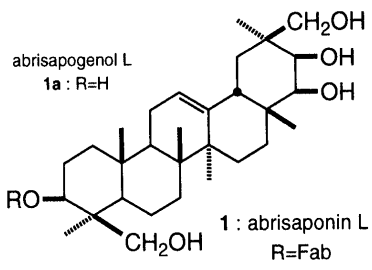
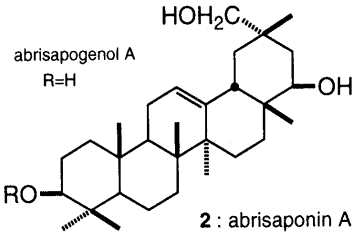


1 : abrisaponin L
R=Fab



2 : abrisaponin A
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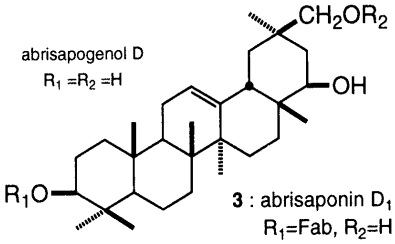
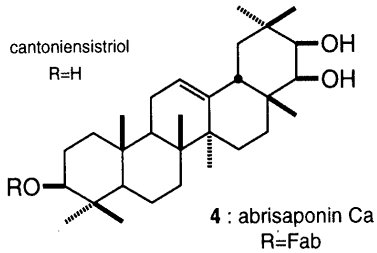
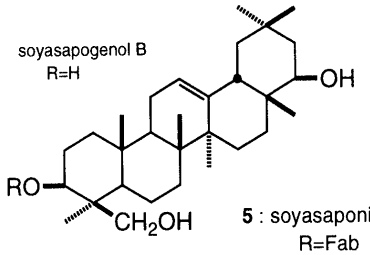


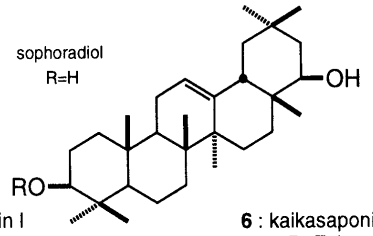
3 : abrisaponin D_1
R_1=Fab, R_2=H
14 : subproside IV
R_1=Fab, R_2=glc



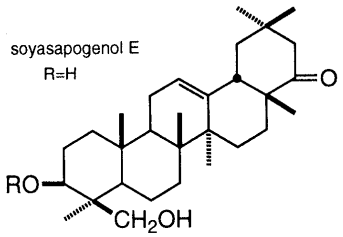
4 : abrisaponin Ca
R=Fab



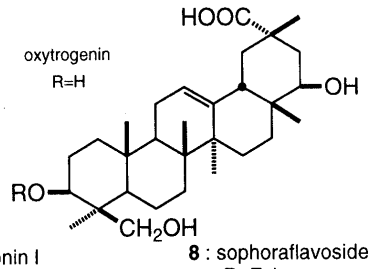
5 : soyasaponin I
R=Fab



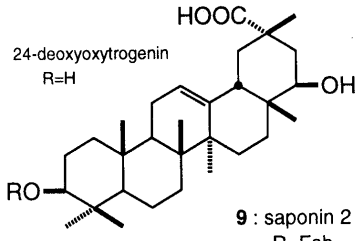
6 : kaikasaponin III
R=Fab



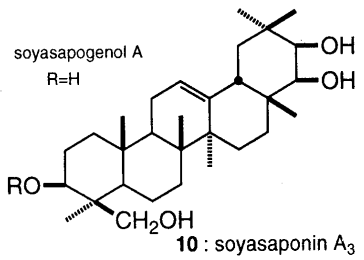
7 : dehydrosoyasaponin I
R=Fab



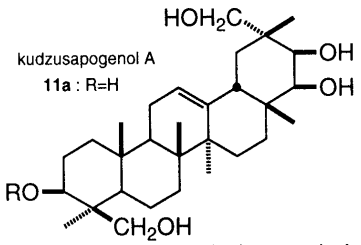
8 : sophoraflavoside II
R=Fab



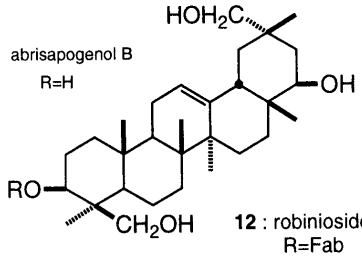
9 : saponin 2
R=Fab



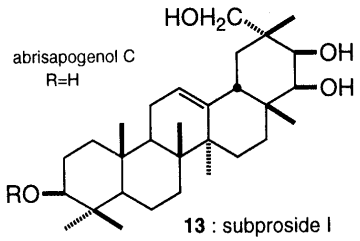
10 : soyasaponin A_3
R=Fab



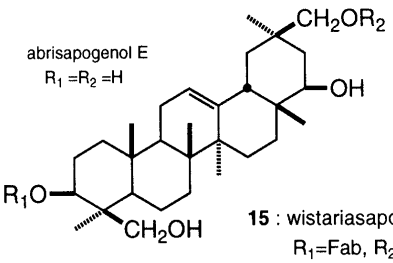
11 : kudzusaponin A_3
R=Fab



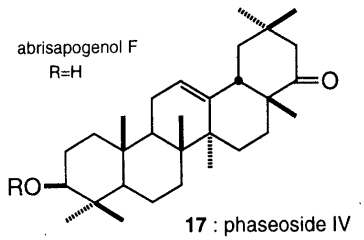
12 : robinioside E
R=Fab



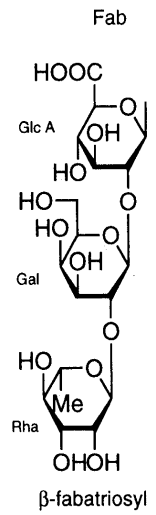
13 : subproside I
R=Fab



15 : wistariasaponin B_2
R_1=Fab, R_2=H
16 : subproside V
R_1=Fab, R_2=glc



17 : phaseoside IV
R=Fab



β-fabatriosyl

Table 1. ^{13}C-NMR Data for Compounds **1**—**17** and **1a** (Aglycone Moieties) (in Pyridine-d_5)

	1	**1a**	**2**	**3**	**4**	**5**[a]	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
C-1	38.8	38.9	39.1	38.9	38.8	38.6	38.8	38.4	38.8	38.7	38.6	38.4	38.9	39.0	38.7	38.8	38.9	38.8
2	26.6	28.4	26.4	26.2	26.5	26.4	26.4	26.6	26.5	26.4	26.6	26.4	26.6	26.6	26.2	26.5	26.5	26.5
3	91.5	80.1	91.4	90.8	89.9	91.2	89.9	91.1	91.2	89.8	91.2	91.0	91.6	91.1	90.3	91.4	91.8	89.9
4	44.0	43.2	39.9	39.7	39.7	43.9	39.7	43.8	43.9	39.6	43.9	43.7	44.1	39.9	39.5	44.0	44.1	39.7
5	56.2	56.3	56.1	55.9	55.8	56.1	55.8	55.9	56.2	55.7	56.1	55.8	56.4	55.9	55.7	56.2	56.4	55.9
6	18.8	19.1	18.5	18.4	18.4	18.5	18.5	18.4	18.6	18.4	18.5	18.4	19.5	18.5	18.3	18.6	18.7	18.5
7	33.0	33.1	33.4	33.1	32.8	33.2	33.3	32.9	33.4	33.1	32.9	32.7	33.6	32.9	32.9	33.4	33.5	33.0
8	40.2	40.2	39.9	39.8	40.2	39.9	40.0	39.7	39.9	39.9	40.2	40.0	39.9	40.3	39.8	39.9	40.0	39.9
9	47.8	48.1	48.1	47.8	47.8	47.8	47.9	47.8	47.8	47.8	47.7	47.6	48.0	47.9	47.6	47.8	48.0	47.9
10	36.5	37.0	36.9	36.7	36.8	36.4	36.8	36.4	36.5	36.8	36.4	36.3	36.6	36.8	36.6	36.5	36.6	36.9
11	24.1	24.1	23.9	23.6	23.8	24.0	23.8	23.9	24.1	23.7	24.1	23.9	24.1	23.9	23.6	24.0	24.1	23.8
12	123.2	122.7	122.9	122.9	122.6	122.3	122.5	122.9	123.2	122.7	122.4	122.3	122.8	122.7	122.8	123.0	123.4	123.1
13	144.2	144.4	144.8	144.3	144.5	144.8	144.8	141.8	144.2	144.2	144.5	144.5	144.8	144.7	144.7	144.5	144.2	141.9
14	42.1	42.0	42.6	42.3	42.0	42.3	42.3	41.9	42.5	42.3	42.1	41.9	42.6	42.1	42.1	42.4	42.5	42.1
15	26.6	26.5	26.3	26.2	26.5	26.6	26.4	26.6	26.3	26.3	26.6	26.4	26.4	26.3	26.2	26.3	26.3	26.5
16	27.5	27.6	29.2	28.7	27.4	28.7	28.6	27.3	28.9	28.8	27.5	27.2	29.2	27.2	28.1	28.9	28.8	27.4
17	39.5	39.5	38.3	37.9	39.1	37.9	38.0	47.6	38.0	37.9	39.1	38.9	38.3	39.1	37.7	38.1	38.1	47.8
18	44.1	44.1	45.2	45.2	43.9	45.3	45.2	47.6	44.8	44.5	43.9	43.1	45.2	43.3	44.4	45.4	45.2	47.8
19	43.3	43.5	41.5	41.9	47.2	46.7	46.7	46.6	41.6	41.4	47.2	40.9	41.6	40.9	41.9	42.0	42.0	46.7
20	40.7	40.7	36.3	35.7	36.5	30.8	30.9	34.0	42.7	42.5	36.5	40.9	36.6	40.9	34.8	35.9	35.1	34.1
21	75.9	76.2	36.6	38.1	74.6	42.2	42.3	50.8	37.4	37.6	74.6	70.2	36.7	70.6	36.9	38.3	37.1	51.0
22	79.1	79.4	75.5	75.1	79.6	75.5	75.5	215.6	75.5	75.3	79.6	79.7	75.7	79.6	75.7	75.3	75.9	215.6
23	23.0	23.6	28.4	28.2	28.4	23.0	28.6	22.9	22.9	28.3	23.0	22.8	23.0	28.3	28.7	23.0	23.0	28.4
24	63.5	64.6	16.8	16.6	16.8	63.6	16.8	63.5	63.5	16.8	63.6	63.5	63.6	16.7	16.6	63.5	63.6	16.8
25	15.8	16.2	15.8	15.5	15.6	15.8	15.6	15.7	15.9	15.6	15.7	15.6	16.0	15.6	15.4	15.9	16.0	15.6
26	16.9	16.9	17.4	17.1	17.0	17.0	17.1	16.6	17.1	17.1	16.8	16.7	17.3	17.3	16.9	17.1	17.3	16.9
27	26.8	26.6	25.4	25.5	26.6	25.7	25.7	25.4	25.4	25.4	26.6	26.4	25.4	26.8	25.8	25.7	25.8	25.5
28	22.4	22.5	20.8	20.8	22.2	21.1	21.1	20.9	20.8	20.9	22.2	22.1	20.8	22.2	21.0	21.0	20.9	21.0
29	26.9	27.0	72.3	27.9	31.5	33.2	33.1	31.8	182.4	181.4	31.5	71.3	72.5	70.8	28.1	28.2	28.3	31.9
30	66.5	67.0	24.5	69.9	21.3	28.6	28.4	25.2	25.0	24.8	21.3	17.4	24.5	17.1	77.5	70.1	77.9	25.3

a) Reassigned in combination with ^{1}H–^{1}H COSY, HMQC and HMBC spectra.

Table 2. ^{13}C-NMR Data for Compounds **1**—**17** (Sugar Moieties) (in Pyridine-d_5)

		1	**2**	**3**	**4**	**5**[a]	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Glc A	C-1	105.0	104.8	104.9	105.3	105.4	105.3	105.4	105.0	105.2	105.4	105.3	104.9	105.0	104.8	105.0	104.7	105.3
	2	78.1	78.3	78.2	79.2	78.3	79.1	78.4	78.1	79.1	78.4	78.3	78.0	78.3	78.4	78.0	78.0	79.3
	3	76.8[b]	76.7[b]	76.5[c]	76.6[b]	76.6[b]	76.6[b]	77.7[b]	76.4[b]	76.6[b]	76.8[b]	76.5[b]	76.5[c]	76.7[c]	76.3[b]	76.7[b]	77.3[b]	76.7[b]
	4	73.9	73.6	73.5	73.5	73.7	73.5	73.8	73.8	73.4	73.8	73.7	73.8	73.7	73.5	73.8	73.6	73.5
	5	76.9[c]	77.1[c]	78.1	77.4[c]	77.6[c]	77.5[c]	77.8[c]	76.8[c]	77.4[c]	77.6[c]	77.6[c]	77.1	78.1	78.0[c]	76.8[c]	77.6[c]	77.5[c]
	6	176.2[d]	176.7[d]	176.6[d]	172.6	172.3	172.7	172.3	175.7[d]	172.6	171.1	172.3	176.4[d]	176.4[d]	176.3[d]	176.1[d]	176.2[d]	172.6
Gal	C-1	101.8	101.7	101.6	102.1	101.7	102.1	101.7	101.7	102.0	101.8	101.6	101.9	101.8	101.6	101.8	101.9	102.1
	2	77.3[c]	78.1[c]	78.1	78.8[c]	77.7[c]	78.8[c]	78.1[c]	77.4[c]	78.7[c]	77.7[c]	77.7[c]	77.1	78.1	78.1[c]	77.2[c]	77.6[c]	78.8[c]
	3	76.0[b]	75.9[b]	75.6[c]	76.2[b]	76.4[b]	76.2[b]	76.4[b]	76.0[b]	76.1[b]	76.4[b]	76.1[b]	75.7[c]	75.6[c]	75.2[b]	75.9[b]	76.6[b]	76.2[b]
	4	71.0	70.5	70.4	70.5	71.1	70.5	71.1	71.0	70.4	71.2	71.0	71.0	70.1	70.3	71.0	71.0	70.5
	5	76.4[b]	76.6[b]	76.4[c]	76.2[b]	76.5[b]	76.2[b]	76.6[b]	76.2[b]	76.2[b]	76.5[b]	76.3[b]	76.0[c]	76.6[c]	76.1[b]	76.3[b]	77.2[b]	76.3[b]
	6	61.8	62.8	62.4	61.9	61.5	61.9	61.5	61.8	61.8	61.7	61.4	62.0	62.7	62.1	61.8	62.1	62.0
Rha	C-1	102.1	102.4	102.3	102.7	102.3	102.7	102.4	102.1	102.6	102.3	102.3	102.0	102.4	102.3	102.0	101.9	102.8
	2	72.1	71.9	71.9	72.4	72.3	72.4	72.4	72.1	72.3	72.3	72.3	71.9	72.0	72.0	72.0	71.7	72.4
	3	72.1	71.9	71.9	72.7	72.7	72.7	72.7	72.1	72.6	72.7	72.7	71.9	72.0	72.0	72.1	71.8	72.7
	4	74.0	73.7	73.8	74.4	74.3	74.4	74.3	74.0	74.3	74.4	74.3	73.8	73.8	73.9	74.0	74.8	74.4
	5	69.4	69.4	69.1	69.4	69.3	69.5	69.3	69.3	69.4	69.4	69.3	69.5	69.3	69.1	69.3	69.6	69.5
	6	18.8	18.5	18.5	18.9	18.9	18.9	18.9	18.7	18.9	18.9	18.8	18.7	18.6	18.9	18.7	18.5	18.9
Glc	C-1														105.2		104.7	
	2														75.0		75.5	
	3														78.0[c]		77.6[c]	
	4														71.3		71.2	
	5														78.1[c]		77.6[c]	
	6														62.4		62.3	

a) Reassigned in combination with ^{1}H–^{1}H COSY, HMQC and HMBC spectra. *b, c*) Interchangeable in each vertical column. *d*) Carboxylate form.

$C_{48}H_{77}O_{18}$ $[M-H]^-$ in the HR/negative FAB-MS. The monosaccharide mixture obtained by acid hydrolysis of **4** revealed the presence of the same sugar units as those of **1**—**3**. The sapogenol, however, was identified as cantoniensistriol.[3,20] In the ^{13}C-NMR spectrum, the signals due to sugar moiety were superimposable on those of **6**. Since the signals at C-2 and -3 of the aglycone moiety were shifted to a lower field by glycosylation, the structure

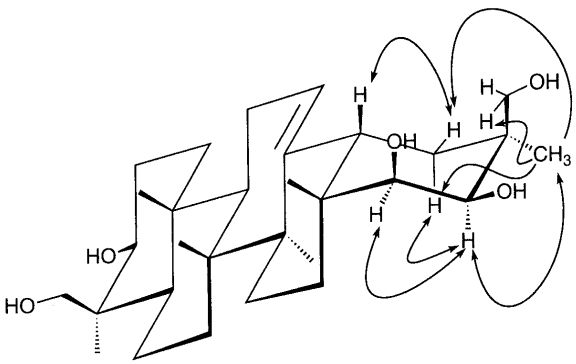


Fig. 1. The Differential NOE Experiment of **1a**

of **4** was characterized as 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl cantoniensistriol.

Since the sugar moiety in saponins such as **1**—**4** is widely distributed and characteristic comprising glc A in leguminous plants,[7-17] we called it β-fabatriose.

Experimental

The optical rotations were measured with a JASCO DIP-360 automatic digital polarimeter. IR spectra were recorded with a JEOL FT-IR spectrometer, JIR-6500W. ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL JNM-GX 270, 400 NMR spectrometers, and chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. The FAB-MS were measured with a JEOL DX-300 spectrometer. HR FAB-MS were measured with a JEOL DX-303 HF spectrometer and taken in a glycerol matrix containing NaI. TLC was performed on precoated Kieselgel 60 F_{254} plates (Merck). HPLC was carried out using the system of a pump: CCPM (Tosoh), UV detector: UV-970 (JASCO) and a column heater: U-620 (Sugai). HPLC conditions for the analytical experiment were the same as those described previously.[9b] The HPLC conditions for the preparative experiment were as follows: column, Nova-Pak HR C_{18} (6 μm, 25×100 mm) with Radial-Pak 40×10 module (Waters/Millipore), solvent, CH_3CN–H_2O–TFA (30—50 : 70—50 : 0.05) (v/v). Column chromatography was carried out on Kieselgel 60 (70—230 mesh, and 230—400 mesh, Merck), Sephadex LH-20 (Pharmacia), Bondapak C_{18} (Waters), Chromatorex ODS-DU 3050MT (Fuji Silysia) and MCI gel CHP 20P (Mitsubishi Chemical Ind.).

Extraction and Isolation Abri Herba (10 kg) was purchased from Uchida Wakanyaku Co., Ltd., Tokyo. The crude drugs were extracted with MeOH. The extract (133 g) was first partitioned between *n*-hexane and 80% MeOH, then the 80% MeOH fraction (fr.) was adjusted to 40% MeOH by adding water; the 40% MeOH fr. was partitioned with EtOAc. After evaporation of the 40% MeOH fr., the residue (72 g) was subjected to MCI gel CHP 20P column chromatography using 0%→100% MeOH to give frs. 1 to 7. A part (0.65 g) of fr. 2 (60% fr., 6.5 g) was further separated by Sephadex LH-20 (MeOH), preparative HPLC [CH_3CN–H_2O–TFA (30 : 70 : 0.05)] and silica gel [$CHCl_3$–MeOH–H_2O (6 : 4 : 1)] to provide compound **16** (0.0031%, from crude drugs) and abrisaponin D_3 (0.00057%). A part (3.0 g) of fr. 3 (60—70% fr., 7.9 g) was separated as described above to provide compounds **1** (0.00032%), **11** (0.0008%), **12** (0.0011%), **13** (0.00026%), **15** (0.00051%), **8** (0.0005%), **3** (0.00021%), **2** (0.00052%), **9** (0.00019%), **14** (0.00030%), abrisaponin D_2 (0.00015%) and abrisaponin So_2 (0.00016%). A part (0.17 g) of fr. 4 (80% fr., 6.1 g) was separated by preparative HPLC [CH_3CN–H_2O–TFA (45 : 55 : 0.05)] to provide compounds **10** (0.0039%), **4** (0.0014%), abrisaponin SB (0.0029%), abrisaponin So_1 (0.016%) and **5** (0.0054%). A part (27 mg) of fr. 5 (80—90% fr., 2.7 g) was separated as described above to provide compounds **5** (0.01%) and **6** (0.005%). In a similar manner, a part (0.25 g) of fr. 6 (90% fr., 0.48 g) gave abrisaponin F (0.016%) and **6** (0.00015%). A part (70 mg) of fr. 7 (90% fr., 0.28 g) was separated by preparative HPLC [CH_3CN–H_2O–TFA (50 : 50 : 0.05)] to provide compounds **7** (0.0005%) and **17** (0.00022%).

Compound 1 (Abrisaponin L) A white amorphous powder, $[\alpha]_D^{27}$ −7.2° [*c*=0.32, pyridine–H_2O (9 : 1)]. HR FAB-MS *m/z* 997.4977 (Calcd for $C_{48}H_{78}NaO_{20}$: 997.4983). Negative FAB-MS: *m/z* 973 $[M-H]^-$, 827 $[M-H-rha]^-$, 665 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.65, 0.89, 1.26, 1.29, 1.42, 1.42 (each 3H, s, *tert*-Me×6), 1.80 (3H, d, *J*=6.2 Hz, rha H-6), 4.95 (1H, d, *J*=6.2 Hz, glc A H-1), 5.38 (1H, s, H-12), 5.57(1H, d, *J*=7.3 Hz, gal H-1), 6.09 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sugars for 1—4 A small sample of **1** was hydrolyzed in 3 N HCl/H_2O at 80 °C for 3 h. After filtration of the mixture, the filtrate was neutralized with 3 N NaOH/H_2O. After desalting, the sugar mixture was subjected to TLC analysis [TLC, Kieselgel 60 (Merck Art 5553), *n*-PrOH–acetone–H_2O (5 : 3 : 1), *Rf*: 0.74 (rhamnose), 0.38 (galactose), 0.08 (glucuronic acid), reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4]. In the above manner, the sugars for **2**—**4** were also confirmed to be composed of the same units.

D, L Determination of Sugars The absolute configuration of glucuronic acid was determined after $NaBH_4$ reduction according to Tanaka *et al.*[22] A sample of **1** (1 mg) was methylated in ethereal CH_2N_2. To a methanolic solution of the methylated sample for **1** was added $NaBH_4$ (*ca.* 5 mg), and the mixture was kept at r.t. for 30 min. The reaction mixture was worked up with MCI gel CHP 20P. The MeOH eluate was evaporated and heated in 2 N HCl/H_2O at 90 °C for 3 h. The precipitate was removed by filtration and the supernatant was neutralized with 2 N KOH/H_2O. After desalting with Amberlite MB-3, the sugar fraction was dissolved in pyridine (0.1 ml), then the mixture was added to a pyridine solution (0.2 ml) of L-cysteine methyl ester hydrochloride (0.1 mol/l) and warmed at 60 °C for 2 h. The mixture was evaporated under N_2 stream and dried *in vacuo*. The obtained syrup was trimethylsilylated with trimethylsilylimidazole (0.1 ml) at 60 °C for 1 h. After the addition of *n*-hexane (0.1 ml) and H_2O (0.1 ml), the *n*-hexane layer was taken off and checked by GC. The retention time (t_R) of the peaks was at 11.1 min (L-rhamnose), 22.5 min (D-glucose), and 23.4 min (D-galactose).

Enzymatic Hydrolysis of 1 To a solution of **1** (9.8 mg) in acetate buffer (pH 4.2, 2 ml) was added GH (50 μl) and the mixture was incubated at 37 °C for 2 d. When the hydrolysis had been completed, the hydrolysate was partitioned with *n*-BuOH and H_2O. The *n*-BuOH ext. was evaporated and purified over silica gel column chromatography with $CHCl_3$–MeOH–H_2O (6 : 4 : 1→10 : 10 : 3) to yield **1a** (2.2 mg), a white amorphous powder, $[\alpha]_D^{27}$ +83.8° (*c*=0.19, pyridine). HR FAB-MS *m/z* 489.3583 (Calcd for $C_{30}H_{49}O_5$: 489.3580). Negative FAB-MS: *m/z* 489 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.94 (3H, s, H-25), 1.01 (3H, s, H-26), 1.30 (3H, s, H-27), 1.34 (3H, s, H-28), 1.46 (3H, s, H-29), 1.58 (3H, s, H-23), 2.89 (1H, dd, *J*=5.1, 13.9 Hz, H-18), 3.65 (1H, dd, *J*=4.8, 11.4 Hz, H-3), 3.73, 4.53 (2H, ABq, *J*=11.0 Hz, H-24), 3.84 (1H, d, *J*=2.9 Hz, H-22), 4.15 (1H, d, *J*=3.3 Hz, H-21), 4.33, 4.42 (2H, ABq, *J*=10.6 Hz, H-30), 5.35 (1H, s, H-12). ^{13}C-NMR: Table 1.

Compound 2 (Abrisaponin A) A white amorphous powder, $[\alpha]_D^{27}$ +0.1° [*c*=0.53, pyridine–H_2O (1 : 1)]. HR FAB-MS *m/z*: 987.4904 (Calcd for $C_{48}H_{77}Na_2O_{18}$: 987.4905). Negative FAB-MS *m/z*: 941 $[M-H]^-$, 633 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.88, 0.94, 1.20, 1.20, 1.22, 1.32, 1.36 (each 3H, s, *tert*-Me×7), 1.77 (3H, d, *J*=6.1 Hz, rha H-6), 4.86 (1H, d, *J*=6.7 Hz, glc A H-1), 5.29 (1H, s, H-12), 5.41 (1H, d, *J*=7.3 Hz, gal H-1), 6.07 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol for 2 A small sample of **2** was hydrolyzed in the same manner. After filtration of the mixture, the precipitate was identified as abrisapogenol A by TLC. *Rf*: 0.16 [$CHCl_3$–MeOH (19 : 1)], 0.27 [*n*-hexane–acetone (2 : 1)].

Compound 3 (Abrisaponin D_1) A white amorphous powder, $[\alpha]_D^{28}$ −0.3° (*c*=0.31, pyridine). HR FAB-MS *m/z*: 987.4904 (Calcd for $C_{48}H_{77}Na_2O_{18}$: 987.4905). Positive FAB-MS *m/z*: 965 $[M+Na]^+$, 819 $[M+Na-rha]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.84, 0.95, 1.17, 1.20, 1.20, 1.25, 1.34 (each 3H, s, *tert*-Me×7), 1.72 (3H, d, *J*=5.5 Hz, rha H-6), 5.34 (1H, s, H-12), 5.46 (1H, d, *J*=7.3 Hz, gal H-1), 6.09 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol for 3 A small sample of **3** was hydrolyzed in the above manner. The precipitate was identified as abrisapogenol D by TLC. *Rf*: 0.20 [$CHCl_3$–MeOH (19 : 1)], 0.35 [*n*-hexane–acetone (2 : 1)].

Compound 4 (Abrisaponin Ca) A white amorphous powder, $[\alpha]_D^{27}$ −6.1° (*c*=0.38, pyridine). HR FAB-MS *m/z*: 941.5108 (Calcd for $C_{48}H_{77}O_{18}$: 941.5110). Negative FAB-MS *m/z*: 941 $[M-H]^-$, 795 $[M-H-rha]^-$, 633 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.86, 1.00, 1.20, 1.26, 1.29, 1.30, 1.43, 1.45 (each 3H, s, *tert*-Me×8), 1.78

(3H, d, J=5.9 Hz, rha H-6), 5.08 (1H, d, J=7.0 Hz, glc A H-1), 5.78 (1H, d, J=7.7 Hz, gal H-1), 6.34 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol for 4 A small sample of **4** was hydrolyzed as above. The precipitate was identified as cantoniensistriol by TLC. *Rf*: 0.28 [$CHCl_3$–MeOH (19 : 1)], 0.49 [*n*-hexane–acetone (2 : 1)].

Compound 5 (Soyasaponin I) A white amorphous powder, $[\alpha]_D^{27}$ −0.8° (c=0.33, MeOH). Negative FAB-MS: m/z 941 $[M-H]^-$, 795 $[M-H-rha]^-$, 633 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.71 (3H, s, H-25), 0.95 (3H, s, H-26), 0.98 (3H, s, H-29), 1.20 (3H, s, H-28), 1.27 (3H, s, H-30), 1.28 (3H, s, H-27), 1.42 (3H, s, H-23), 1.75 (3H, d, J=6.1 Hz, rha H-6), 2.37 (1H, br d, J=13.4 Hz, H-18), 3.24 (1H, d, J=11.6 Hz, H-24 ax), 3.39 (1H, br d, J=7.3 Hz, H-3), 3.73 (1H, br s, H-22), 4.25 (1H, d, J=11.6 Hz, H-24 eq), 4.96 (1H, d, J=6.7 Hz, glc A H-1), 5.29 (1H, s, H-12), 5.72 (1H, d, J=7.3 Hz, gal H-1), 6.21 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 6 (Kaikasaponin III) A white amorphous powder, $[\alpha]_D^{27}$ −6.7° (c=0.32, pyridine). IR (KBr): 3413 (ν_{O-H}), 1724 ($\nu_{C=O}$, COO^- form) cm^{-1}. Negative FAB-MS: m/z 925 $[M-H]^-$, 779 $[M-H-rha]^-$, 617 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.87, 1.01, 1.01, 1.21, 1.24, 1.28, 1.30, 1.43 (each 3H, s, *tert*-Me×8), 1.78 (3H, d, J=6.2 Hz, rha H-6), 5.08 (1H, d, J=7.9 Hz, glc A H-1), 5.32 (1H, s, H-12), 5.75 (1H, d, J=7.7 Hz, gal H-1), 6.34 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 7 (Dehydrosoyasaponin I) A white amorphous powder, $[\alpha]_D^{27}$ −25.2° [c=0.53, pyridine–H_2O (1 : 1)]. Negative FAB-MS: m/z 939 $[M-H]^-$, 793 $[M-H-rha]^-$, 631 $[M-H-rha-gal]^-$, 455 $[M-H-rha-gal-glc\ A]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.71, 0.86, 0.87, 0.96, 1.17, 1.31, 1.45 (each 3H, s, *tert*-Me×7), 1.78 (3H, d, J=6.7 Hz, rha H-6), 4.99 (1H, d, J=7.3 Hz, glc A H-1), 5.25 (1H, s, H-12), 5.78 (1H, d, J=7.9 Hz, gal H-1), 6.28 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 8 (Sophoraflavoside II) A white amorphous powder, $[\alpha]_D^{27}$ −8.6° [c=0.36, pyridine–H_2O (1 : 1)]. Negative FAB-MS: m/z 971 $[M-H]^-$, 825 $[M-H-rha]^-$, 487 $[M-H-rha-gal-glc\ A]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.67, 0.91, 1.18, 1.18, 1.21, 1.36 (each 3H, s, *tert*-Me×6), 1.72 (3H, d, J=5.5 Hz, rha H-6), 5.30 (1H, s, H-12), 5.49 (1H, d, J=7.4 Hz, gal H-1), 6.02 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 9 (Saponin 2) A white amorphous powder, $[\alpha]_D^{28}$ −16.6° (c=0.41, pyridine). Negative FAB-MS: m/z 955 $[M-H]^-$, 809 $[M-H-rha]^-$, 647 $[M-H-rha-gal]^-$, 471 $[M-H-rha-gal-glc\ A]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.87, 0.96, 1.22, 1.22, 1.24, 1.34, 1.34 (each 3H, s, *tert*-Me×7), 1.72 (3H, d, J=5.5 Hz, rha H-6), 5.32 (1H, s, H-12), 5.49 (1H, d, J=7.4 Hz, gal H-1), 6.12 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 10 (Soyasaponin A_3) A white amorphous powder, $[\alpha]_D^{27}$ −14.2° (c=0.55, pyridine). Negative FAB-MS: m/z 957 $[M-H]^-$, 811 $[M-H-rha]^-$, 649 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.70, 0.95, 1.25, 1.28, 1.32, 1.45, 1.45 (each 3H, s, *tert*-Me×7), 1.79 (3H, d, J=6.2 Hz, rha H-6), 5.00 (1H, d, J=6.2 Hz, glc A H-1), 5.31 (1H, s, H-12), 6.30 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 11 (Kudzusaponin A_3) A white amorphous powder, $[\alpha]_D^{27}$ −13.1° [c=0.53, pyridine–H_2O (1 : 1)]. Negative FAB-MS: m/z 973 $[M-H]^-$, 827 $[M-H-rha]^-$, 665 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.69, 0.95, 1.30, 1.34, 1.42, 1.50 (each 3H, s, *tert*-Me×6), 1.76 (3H, d, J=6.1 Hz, rha H-6), 4.96 (1H, d, J=6.7 Hz, glc A H-1), 5.34 (1H, s, H-12), 5.77 (1H, d, J=7.3 Hz, gal H-1), 6.26 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 12 (Robinioside E) A white amorphous powder, $[\alpha]_D^{26}$ −8.3° [c=0.39, pyridine–H_2O (1 : 1)]. Negative FAB-MS: m/z 957 $[M-H]^-$, 811 $[M-H-rha]^-$, 649 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.71, 0.89, 1.19, 1.22, 1.36, 1.41 (each 3H, s, *tert*-Me×6), 1.78 (3H, d, J=6.1 Hz, rha H-6), 4.88 (1H, d, J=7.3 Hz, glc A H-1), 5.27 (1H, s, H-12), 5.48 (1H, d, J=7.9 Hz, gal H-1), 5.99 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 13 (Subproside I) A white amorphous powder, $[\alpha]_D^{27}$ −5.7° [c=0.43, pyridine–H_2O (1 : 1)]. Negative FAB-MS: m/z 957 $[M-H]^-$, 811 $[M-H-rha]^-$, 649 $[M-H-rha-gal]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.85, 0.94, 1.20, 1.27, 1.31, 1.33, 1.41 (each 3H, s, *tert*-Me×7), 1.74 (3H, d, J=6.1 Hz, rha H-6), 4.88 (1H, d, J=6.7 Hz, glc A H-1), 5.30 (1H, s, H-12), 5.43 (1H, d, J=7.9 Hz, gal H-1), 6.04 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 14 (Subproside IV) A white amorphous powder, $[\alpha]_D^{27}$ +0.4° [c=0.52, pyridine–H_2O (1 : 1)]. Negative FAB-MS: m/z 1103 $[M-H]^-$, 957 $[M-H-deoxyhexose]^-$, 795 $[M-H-deoxyhexose-hexose]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.84, 0.97, 1.20, 1.20, 1.23, 1.26, 1.36 (each 3H, s, *tert*-Me×7), 1.74 (3H, d, J=4.9 Hz, rha H-6), 4.90 (1H, d, J=7.3 Hz, glc A H-1), 5.32 (1H, s, H-12), 6.12 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 15 (Wistariasaponin B_2) A white amorphous powder, $[\alpha]_D^{27}$ −2.1° [c=0.54, pyridine–H_2O (1 : 1)]. Negative FAB-MS: m/z 957 $[M-H]^-$, 811 $[M-H-deoxyhexose]^-$, 649 $[M-H-deoxyhexose-hexose]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.66, 0.89, 1.15, 1.17, 1.25, 1.37 (each 3H, s, *tert*-Me×6), 1.73 (3H, d, J=5.1 Hz, rha H-6), 5.31 (1H, s, H-12), 5.49 (1H, d, J=7.4 Hz, gal H-1), 6.03 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 16 (Subproside V) A white amorphous powder, $[\alpha]_D^{27}$ +4.6° [c=0.33, MeOH–H_2O (1 : 1)]. Negative FAB-MS: m/z 1119 $[M-H]^-$, 973 $[M-H-deoxyhexose]^-$, 811 $[M-H-deoxyhexose-hexose]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.70, 0.83, 1.13, 1.16, 1.23, 1.41 (each 3H, s, *tert*-Me×6), 1.78 (3H, d, J=5.9 Hz, rha H-6), 5.32 (1H, s, H-12), 5.41 (1H, d, J=7.8 Hz, gal H-1), 5.85 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Compound 17 (Phaseoside IV) A white amorphous powder, $[\alpha]_D^{27}$ −22.1° [c=0.49, pyridine–H_2O (1 : 1)]. Positive FAB-MS: m/z 947 $[M+Na]^+$, 801 $[M+Na-rha]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.86, 0.86, 0.91, 0.97, 1.17, 1.19, 1.28, 1.42 (each 3H, s, *tert*-Me×8), 1.77 (3H, d, J=6.1 Hz, rha H-6), 5.06 (1H, d, J=7.3 Hz, glc A H-1), 5.72 (1H, d, J=7.3 Hz, gal H-1), 6.31 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

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