Chem. Pharm. Bull. **44**(6) 1228—1231 (1996) Vol. 44, No. 6

Triterpene Saponins from *Abrus cantoniensis* (Leguminosae). II.[1] Characterization of Six New Saponins Having a Branched-Chain Sugar

Hideo MIYAO,[a] Yusuke SAKAI,[a] Takashi TAKESHITA,[a] Yasuyuki ITO,[b] Junei KINJO,[a] and Toshihiro NOHARA*,[a]

Faculty of Pharmaceutical Sciences, Kumamoto University,[a] 5–1 Oe-honmachi, Kumamoto 862, Japan and Faculty of General Education, Kyushu Tokai University,[b] Choyo 5435, Aso, Kumamoto 869–14, Japan.

Received January 11, 1996; accepted March 2, 1996

The chemical structures of abrisaponins So_1 (1), So_2 (2), D_2 (3), D_3 (4), F (5) and SB (6), six of twenty-three saponins from Abri Herba, the whole plants of *Abrus cantoniensis* (Leguminosae), were investigated. They were elucidated to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-β-D-glucopyranosyl-(1→3)]-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl (designated as β-abritetraosyl) sophoradiol (1), 3-*O*-β-abritetraosyl sophoradiol 22-*O*-β-D-xylopyranoside (2), 3-*O*-β-abritetraosyl abrisapogenol D (3), 3-*O*-β-abritetraosyl abrisapogenol D 22-*O*-β-D-glucopyranoside (4), 3-*O*-β-abritetraosyl abrisapogenol F (5) and 3-*O*-β-abritetraosyl soyasapogenol B (6), respectively.

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

In the preceding paper,[2] we reported the isolation of twenty-three oleanene saponins from Abri Herba, the whole plant of *Abrus cantoniensis* HANCE (Leguminosae). We also described the structure of four new saponins including a new sapogenol and the identification of thirteen known saponins. This paper presents structural determination of abrisaponins So_1 (**1**), So_2 (**2**), D_2 (**3**), D_3 (**4**), F (**5**) and SB (**6**) which have a branched-chain sugar moiety.

Abrisaponin So_1 (**1**), a white powder, $[\alpha]_D^{27}$ +6.0° [MeOH–H_2O (1 : 1)], showed a peak at *m/z* 1087 due to $[M-H]^-$ in negative FAB-MS. The exact measurement under high resolution (HR) conditions showed that the composition is $C_{54}H_{87}Na_2O_{22}$ at *m/z* 1133.5468 $[M-H+2Na]^+$. In negative FAB-MS, the fragment ion peaks were also observed at *m/z* 941 $[M-\text{deoxyhexose}-H]^-$, 925 $[M-\text{hexose}-H]^-$ and 779 $[M-\text{deoxyhexose}-\text{hexose}-H]^-$. The monosaccharide mixture obtained by acid hydrolysis of **1** revealed the presence of D-glucuronic acid, D-galactose, D-glucose and L-rhamnose. The sapogenol was identified as sophoradiol (**1a**).[3] In the sugar region of the ^{13}C-NMR spectrum for **1**, signals based upon the terminal rhamnopyranosyl and the terminal glucopyranosyl residues were observed.

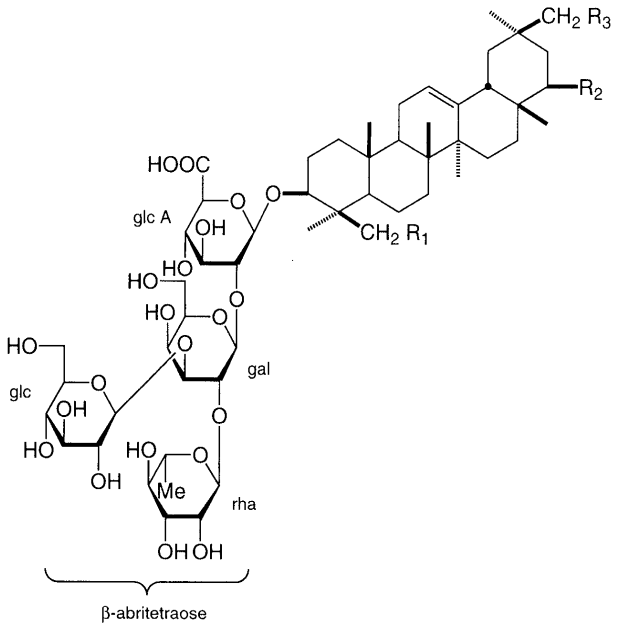
Since the carbon signals due to the E-ring of sapogenol moiety were superimposable on those of **1a**, these sugars were concluded to be composed of a branched-chain sugar which attached at C-3.

The combination of ^1H–^1H shift correlation spectroscopy (COSY) and ^1H detected the heteronuclear multiple bonds correlation (HMBC) spectrum of **1** along with heteronuclear multiple quantum coherence (HMQC) gave the correlations shown in Fig. 1.

The comparative analysis with kaikasaponin III,[2,4] which was the representive saponin having **1a**, supported that the branched-chain sugar was as shown in Fig. 1.

Consequently, the structure of **1** was determined to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-β-D-glucopyranosyl-(1→3)]-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl sophoradiol. Since the sugar moiety is characteristic of this plant, we called it β-abritetraose.

Abrisaponin So_2 (**2**), a white powder, $[\alpha]_D^{27}$ −4.8° [MeOH–H_2O (1 : 1)], furnished sophoradiol, D-glucuronic acid, D-galactose, D-glucose, D-xylose and L-rhamnose by acid hydrolysis. In negative and HR/positive FAB-MS, **2** showed a peak at *m/z* 1219 due to $[M-H]^-$ and at *m/z* 1243.6074 $[M+Na]^+$ ($C_{59}H_{96}NaO_{26}$), respectively. Fragment ion peaks similar to **1** were observed together with an additional peak at *m/z* 1087 $[M-\text{pentose}-H]^-$. In the ^{13}C-NMR spectrum of **2**, the signals due to sugar moiety linked at C-3 and A—D ring for sapogenol moiety



	R_1	R_2	R_3	
1 :	H	OH	H	**abrisaponin So_1**
2 :	H	O-xyl	H	**abrisaponin So_2**
3 :	H	OH	OH	**abrisaponin D_2**
4 :	H	OH	O-glc	**abrisaponin D_3**
5 :	H	=O	H	**abrisaponin F**
6 :	OH	OH	H	**abrisaponin SB**

* To whom correspondence should be addressed.

were superimposable on those of **1**. Additional terminal β-D-xylopyranosyl signals and E-ring signals which were shifted at C-21 (−5.2 ppm) and -22 (+6.7 ppm) due to glycosylation[5] were also observed. Therefore, the structure of **2** was concluded to be 3-*O*-β-abritetraosyl sophoradiol 22-*O*-β-D-xylopyranoside.

Abrisaponin D_2 (**3**), a white powder, $[\alpha]_D^{27}$ +0.9° [pyridine–H_2O (1 : 1)], showed a peak at *m/z* 1103 due to $[M-H]^-$ in the negative FAB-MS, and at *m/z* 1149.5431 $[M-H+2Na]^+$ ($C_{54}H_{87}Na_2O_{23}$) in the HR/positive FAB-MS. By acid hydrolysis, **3** gave abrisapogenol D,[6] together with the same sugar units as **1**. In the ^{13}C-NMR spectrum of **3**, the signals due to the sapogenol moiety were in accord with those of abrisaponin D_1,[2] whereas

Table 1. ^{13}C-NMR Data for Compounds **1**—**6** (Aglycone Moieties)

	1[a]	**2**	**3**	**4**	**5**	**6**
C-1	38.9	39.1	39.1	39.2	38.8	38.5
2	26.5	26.1	26.6	26.6	26.5	26.4
3	90.1	90.9	90.9	91.0	90.3	91.4
4	39.7	39.8	39.9	40.0	39.7	43.8
5	55.9	56.0	56.1	56.2	55.9	56.1
6	18.5	18.5	18.7	18.7	18.5	18.6
7	33.2	33.2	33.4	33.4	32.9	33.2
8	40.8	39.9	40.1	40.2	39.9	39.9
9	47.9	47.9	48.1	48.1	47.9	47.7
10	36.9	36.8	37.0	37.0	36.8	36.4
11	23.8	23.8	23.9	24.0	23.8	24.0
12	122.5	122.9	123.0	123.3	123.1	122.3
13	144.8	144.3	144.2	144.5	141.8	144.8
14	42.4	40.3	42.6	42.5	42.0	42.2
15	26.5	26.3	26.6	26.6	26.5	26.6
16	28.7	28.7	29.0	28.6	27.4	28.6
17	38.0	37.4	38.2	38.1	47.8	38.0
18	45.3	45.8	45.5	45.0	47.8	45.2
19	46.8	46.6	42.0	42.2	46.6	46.7
20	30.9	30.6	35.9	35.2	34.2	30.8
21	42.3	36.9	38.3	37.4	50.9	42.3
22	75.6	82.4	75.4	75.6	216.4	75.5
23	28.5	28.7	28.5	28.9	28.4	23.0
24	16.8	16.8	16.9	17.0	16.8	63.6
25	15.7	15.7	15.8	15.8	15.6	15.8
26	17.2	17.2	17.3	17.4	16.9	16.9
27	25.7	25.5	25.8	26.1	25.5	25.6
28	21.1	21.1	21.1	21.3	20.9	21.1
29	33.3	32.6	28.2	28.6	31.8	33.2
30	28.7	28.4	70.2	77.9	25.3	28.6

Chemical shifts (δ: ppm) were measured in pyridine-d_5. *a*) Assigned in combination with ^{1}H–^{1}H COSY, HMQC and HMBC spectra.

Table 2. ^{13}C-NMR Data for Compounds **1**—**6** (Sugar Moieties)

		1[a]	**2**	**3**	**4**	**5**	**6**
Glc A	C-1	105.4	105.2[c]	105.4[c]	105.3[c]	105.4[c]	105.4[c]
	2	78.7	78.4	78.3	78.7	78.4	78.4
	3	76.0	76.2	76.2	76.3	76.0	76.5
	4	73.5	73.8	73.6	74.0	73.5	73.8
	5	78.7	77.9	78.2[d]	78.4[d]	78.2[d]	78.3[d]
	6	172.6	175.6[b]	172.4	176.1[b]	173.5	172.3
Gal	C-1	102.2	101.8	101.9	102.1	102.0	101.5
	2	77.5	76.2	76.2	76.4	77.0	77.2
	3	84.5	85.1	85.3	85.3	84.9	83.6
	4	70.0	69.2	69.8	70.1	69.2	71.1
	5	75.9	75.4	75.4	75.6[e]	75.6	75.5
	6	62.2	62.1	62.2	62.4	62.1	61.7
Rha	C-1	102.4	102.6	102.4	102.5	102.3	102.9
	2	72.4	72.1	72.1	72.4	72.2	72.4
	3	72.7	72.1	72.3	72.4	72.4	72.8
	4	74.4	74.0[d]	74.1	74.3	74.2	74.3
	5	69.4	69.9	69.3	69.4	69.8	69.3
	6	18.9	18.7	18.9	19.0	18.9	19.0
Glc	C-1	105.5	105.3[c]	105.6[c]	105.5[c]	105.5[c]	105.9[c]
	2	74.9	74.6	74.7	74.8	74.7	75.0
	3	78.5	77.9	78.2[d]	78.4[d]	78.2[d]	78.2[d]
	4	71.5	71.2	71.3	71.6[f]	71.4	71.6
	5	78.1	77.9	77.9[d]	78.1[d]	78.1[d]	77.7[d]
	6	62.5	62.6	62.4	62.7	62.3	62.6
Xyl	C-1		102.2				
	2		74.6[d]				
	3		77.9				
	4		71.0				
	5		66.8				
Glc	C-1				105.6[c]		
	2				75.3[e]		
	3				78.1[d]		
	4				71.5[f]		
	5				78.4[d]		
	6				62.7		

a) Assigned in combination with ^{1}H–^{1}H COSY, HMQC and HMBC spectra. *b*) Carboxylate form. *c*—*f*) Each vertical column can be interchanged.

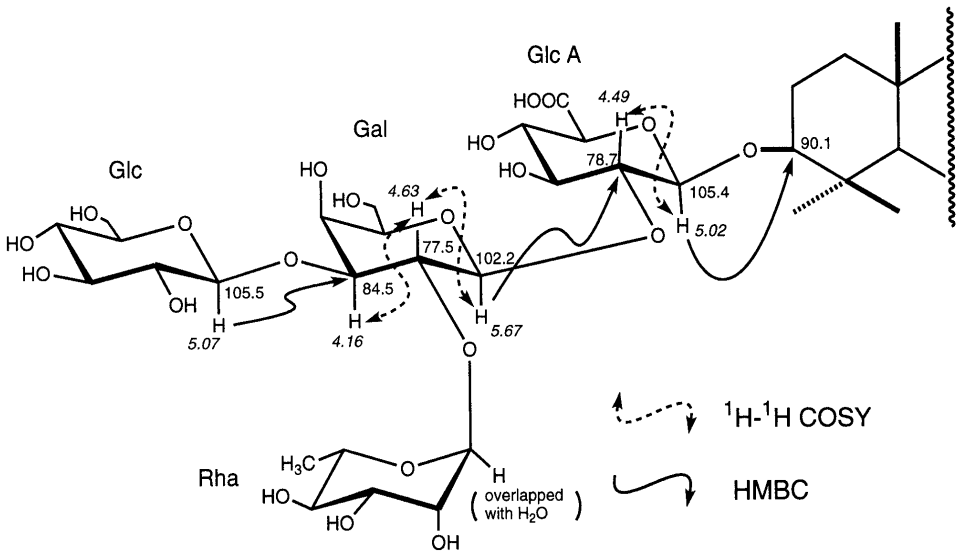


Fig. 1. ^{1}H–^{1}H COSY and HMBC Connectivities for β-Abritetraosyl Moiety of **1**

the signals based on the sugar moiety were in agreement with those of **1**. Consequently, the structure of **3** was established as 3-*O*-*β*-abritetraosyl abrisapogenol D.

Abrisaponin D_3 (**4**), a white powder, $[\alpha]_D^{27}$ −85.2° [pyridine–H_2O (1 : 1)], showed a peak at *m/z* 1265 due to $[M-H]^-$ in negative FAB-MS, and at *m/z* 1289.6169 $[M+Na]^+$ ($C_{60}H_{98}NaO_{28}$) which appeared to have more of a hexosyl unit than **3** in HR/positive FAB-MS. By acid hydrolysis, **4** gave the same components as **3**. In the ^{13}C-NMR spectrum of **4**, the signals due to sugar moiety linked at C-3 and A—D ring for sapogenol moiety were in good agreement with those of **3**. In contrast, additional terminal *β*-D-glucopyranosyl signals and E-ring signals having glycosylation shift at C-30 (+7.2 ppm) were observed. Therefore, the structure of **4** was concluded to be 3-*O*-*β*-abritetraosyl abrisapogenol D 22-*O*-*β*-D-glucopyranoside.

Abrisaponin F (**5**), a white powder, $[\alpha]_D^{27}$ −29.2° [pyridine–H_2O (1 : 1)], showed a peak at *m/z* 1109 due to $[M+Na]^+$ in positive FAB-MS, and at *m/z* 1131.5327 $[M-H+2Na]^+$ ($C_{54}H_{85}Na_2O_{22}$) in HR/positive FAB-MS. By acid hydrolysis, **5** gave abrisapogenol F,[6] together with the same sugar units as those of **1**. In the ^{13}C-NMR spectrum of **3**, the signals for the sapogenol moiety were consistent with those of phaseoside IV,[2,7] whereas the signals based upon the sugar moiety were in agreement with those of **1**. Consequently, the structure of **3** was established as 3-*O*-*β*-abritetraosyl abrisapogenol F.

Abrisaponin SB (**6**), a white powder, $[\alpha]_D^{27}$ −8.9° (pyridine), showed a peak at *m/z* 1103 $[M-H]^-$ and similar fragment ion peaks to those of **1** in the negative FAB-MS. The HR/positive FAB-MS showed that the composition is $C_{54}H_{89}O_{23}$ at *m/z* 1105.5756 $[M+H]^+$. By acid hydrolysis, **6** gave soyasapogenol B[8] together with same sugar units as **1**. In the ^{13}C-NMR spectrum of **6**, the signals for the aglycone moiety were consistent with those of soyasaponin I,[2,8] whereas the signals due to the sugar moiety were superimposable on those of **1**. Therefore, the structure of **6** was established as 3-*O*-*β*-abritetraosyl soyasapogenol B.

Meanwhile the crude saponin fractions of this plant were effective on experimental liver injuries *in vivo*.[9] To date we have obtained twenty three saponins. Since the available amounts of these saponins were limited, we plan to confirm the activities of individual saponins using primary cultured rat hepatocytes.

Experimental[10]

Compound 1 (Abrisaponin So_1) A white amorphous powder, $[\alpha]_D^{27}$ +6.0° [*c*=0.32, MeOH–H_2O (1 : 1)]. HR FAB-MS *m/z*: 1133.5468 (Calcd for $C_{54}H_{87}Na_2O_{22}$: 1133.5484). Negative FAB-MS *m/z*: 1087 $[M-H]^-$, 941 $[M-H-$deoxyhexose$]^-$, 925 $[M-H-$hexose$]^-$, 779 $[M-H-$hexose−deoxyhexose$]^-$. ^{1}H-NMR (in pyridine-d_5) *δ*: 0.87 (3H, s, H-25), 0.99 (3H, s, H-29), 1.00 (3H, s, H-26), 1.18 (3H, s, H-24), 1.21 (3H, s, H-28), 1.27 (3H, s, H-27), 1.27 (3H, s, H-30), 1.40 (3H, s, H-23), 1.73 (3H, d, *J*=6.1 Hz, rha H-6), 3.30 (1H, dd, *J*=4.3, 11.6 Hz, H-3), 3.72 (1H, br s, H-22), 4.16 (1H, dd, *J*=3.1, 9.8 Hz, gal H-3), 4.49 (1H, t, *J*=7.3 Hz, glc A H-2), 4.63 (1H, gal H-2), 5.02 (1H, d, *J*=7.3 Hz, glc A H-1), 5.07 (1H, d, *J*=7.9 Hz, glc H-1), 5.31 (1H, s, H-12), 5.67 (1H, d, *J*=7.9 Hz, gal H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 1 A sample of **1** was hydrolyzed in 3 N HCl/H_2O at 80 °C for 3 h. After filtration of the mixture, the precipitate was identified as sophoradiol by TLC. *Rf*: 0.37 [$CHCl_3$–MeOH (19 : 1)], 0.52 [*n*-hexane–acetone (2 : 1)]. The filtrate was neutralized with 3 N NaOH/H_2O. 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), 0.47 (glucose), 0.38 (galactose), 0.08 (glucuronic acid), reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4].

D, L Determination of Sugars[11] The absolute configuration of glucuronic acid was determined after $NaBH_4$ reduction according to Tanaka *et al.*[12] A sample of **1** (3 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 then 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).

Compound 2 (Abrisaponin So_2) A white amorphous powder, $[\alpha]_D^{27}$ −4.8° [*c*=0.34, MeOH–H_2O (1 : 1)]. HR FAB-MS *m/z*: 1243.6074 (Calcd. for $C_{59}H_{96}NaO_{26}$: 1243.6087). Negative FAB-MS *m/z*: 1219 $[M-H]^-$, 1087 $[M-H-$pentose$]^-$, 1057 $[M-H-$hexose$]^-$, 911 $[M-H-$hexose−deoxyhexose$]^-$, 749 $[M-H-$hexose−deoxyhexose−hexose$]^-$. ^{1}H-NMR (in pyridine-d_5) *δ*: 0.87, 0.95, 1.01, 1.19, 1.24, 1.24, 1.25, 1.38 (each 3H, s, *tert*-Me×8), 1.75 (3H, d, *J*=6.2 Hz, rha H-6), 5.27 (1H, s, H-12), 5.54 (1H, d, *J*=7.3 Hz, gal H-1), 6.13 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 2 A sample of **2** was hydrolyzed in the above manner. The precipitate was identified as sophoradiol by TLC. *Rf*, 0.37 [$CHCl_3$–MeOH (19 : 1)], 0.52 [*n*-hexane–acetone (2 : 1)]. After neutralization, 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), 0.60 (xylose), 0.47 (glucose), 0.38 (galactose), 0.08 (glucuronic acid), reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4].

D, L Determination of Sugars A sample of **2** (1 mg) was treated in the above manner. The derivatives were analyzed by GC. The t_R of the peaks was at 11.1 min (L-rhamnose), 12.5 min (D-xylose), 22.5 min (D-glucose) and 23.4 min (D-galactose).

Compound 3 (Abrisaponin D_2) A white amorphous powder, $[\alpha]_D^{27}$ +0.9° [*c*=0.33, pyridine–H_2O (1 : 1)]. HR FAB-MS *m/z*: 1149.5431 (Calcd for $C_{54}H_{87}Na_2O_{23}$: 1149.5433). Negative FAB-MS *m/z*: 1103 $[M-H]^-$, 941 $[M-H-$hexose$]^-$, 633 $[M-H-$hexose−deoxyhexose−hexose$]^-$. ^{1}H-NMR (in pyridine-d_5) *δ*: 0.86, 0.96, 1.16, 1.20, 1.20, 1.27, 1.38 (each 3H, s, *tert*-Me×7), 1.75 (3H, d, *J*=6.1 Hz, rha H-6), 4.95 (1H, d, *J*=7.3 Hz, glc A H-1), 4.99 (1H, d, *J*=6.7 Hz, glc H-1), 5.34 (1H, s, H-12), 6.12 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 3 A 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)]. After neutralization, 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), 0.47 (glucose), 0.38 (galactose), 0.08 (glucuronic acid), reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4].

Compound 4 (Abrisaponin D_3) A white amorphous powder, $[\alpha]_D^{27}$ −85.2° [*c*=0.32, pyridine–H_2O (1 : 1)]. HR FAB-MS *m/z* 1289.6169 (Calcd for $C_{60}H_{98}O_{28}Na$: 1289.6142). Negative FAB-MS: *m/z* 1265 $[M-H]^-$, 1119 $[M-H-$deoxyhexose$]^-$, 1103 $[M-H-$hexose$]^-$, 795 [aglycone+hexose−H]$^-$. ^{1}H-NMR (in pyridine-d_5) *δ*: 0.85, 0.96, 1.21, 1.25, 1.25, 1.38, 1.53 (each 3H, s, *tert*-Me×7), 1.77 (3H, d, *J*=6.1 Hz, rha H-6), 5.37 (1H, s, H-12), 5.55 (1H, d, *J*=7.9 Hz, gal H-1), 6.15 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 4 A sample of **4** 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)]. After neutralization, 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), 0.47 (glucose), 0.38 (galactose), 0.08 (glucuronic acid), reagent: *o*-aminobenzenesulfonic

acid/2 M H_3PO_4].

D, L **Determination of Sugars** A sample of **4** (1 mg) was treated in the above manner. The derivatives were analyzed by GC. The t_R of the peaks was at 11.1 min (L-rhamnose), 22.5 min (D-glucose) and 23.4 min (D-galactose).

Compound 5 (Abrisaponin F) A white amorphous powder, $[\alpha]_D^{27}$ $-29.2°$ [$c=0.37$, pyridine–H_2O (1:1)]. HR FAB-MS m/z 1131.5327 (Calcd for $C_{54}H_{85}Na_2O_{22}$: 1131.5328). Positive FAB-MS: m/z 1109 $[M+Na]^+$, 963 $[M+Na-deoxyhexose]^+$, 947 $[M+Na-hexose]^+$. ^{1}H-NMR (in pyridine-d_5) δ: 0.86, 0.87, 0.92, 0.98, 1.17, 1.20, 1.30, 1.38 (each 3H, s, *tert*-Me × 8), 1.74 (3H, d, $J=6.1$ Hz, rha H-6), 5.28 (1H, s, H-12), 5.61 (1H, d, $J=7.9$ Hz, gal H-1), 6.20 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 5 A sample of **5** was hydrolyzed in the above manner. The precipitate was identified as abrisapogenol F by TLC. *Rf*, 0.43 [$CHCl_3$–MeOH (19:1)], 0.52 [*n*-hexane–acetone (2:1)]. After neutralization, 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), 0.47 (glucose), 0.38 (galactose), 0.08 (glucuronic acid), reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4].

Compound 6 (Abrisaponin SB) A white amorphous powder, $[\alpha]_D^{27}$ $-8.9°$ ($c=0.40$, pyridine). HR FAB-MS m/z 1105.5756 (Calcd for $C_{54}H_{89}O_{23}$: 1105.5794). Negative FAB-MS: m/z 1103 $[M-H]^-$, 941 $[M-H-hexose]^-$, 795 $[M-H-hexose-deoxyhexose]^-$, 633 $[M-H-hexose-deoxyhexose-hexose]^-$. ^{1}H-NMR (in pyridine-d_5) δ: 0.73, 0.98, 1.00, 1.23, 1.29, 1.29, 1.45 (each 3H, s, *tert*-Me × 7), 1.72 (3H, d, $J=6.2$ Hz, rha H-6), 4.98 (1H, d, $J=6.6$ Hz, glc A H-1), 5.16 (1H, d, $J=7.7$ Hz, glc H-1), 5.30 (1H, s, H-12), 5.78 (1H, d, $J=7.3$ Hz, gal H-1), 6.20 (1H, s, rha H-1). ^{13}C-NMR: Tables 1 and 2.

Identification of Sapogenol and Sugars for 6 A sample of **6** was hydrolyzed in the above manner. The precipitate was identified as soyasapogenol B by TLC. *Rf*, 0.24 [$CHCl_3$–MeOH (19:1)], 0.42 [*n*-hexane–acetone (2:1)]. After neutralization, 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), 0.47 (glucose), 0.38 (galactose), 0.08 (glucuronic acid), reagent: *o*-aminobenzenesulfonic acid/2 M H_3PO_4].

Acknowledgments We express our appreciation to Prof. H. Okabe and Mr. H. Hanazono of Fukuoka University for measurements of HR FAB-MS, and to Dr. Y. Kido, Dr. S. Yahara, Mr. K. Takeda, Mr. T. Iriguchi and Ms. T. Fujii of this Faculty for measurement of NMR spectra and MS.

References and Notes

1) Part L in a series of studies on leguminous plants.
2) Miyao H., Sakai Y., Takeshita T., Nohara T., *Chem. Pharm. Bull.*, **44**, 1222—1227 (1996).
3) Chiang T. C., Chang H. M., *Planta Medica*, **46**, 52—55 (1982); Kinjo J., Miyamoto I., Murakami K., Kida K., Tomimatsu T., Yamasaki M., Nohara T., *Chem. Pharm. Bull.*, **33**, 1293—1296 (1985).
4) Kitagawa I., Taniyama T., Hong W. W., Hori K., Yoshikawa M., *Yakugaku Zasshi*, **108**, 538—546 (1988).
5) Kasai R., Suzuo M., Asakawa J., Tanaka O., *Tetrahedron Lett.*, **1977**, 175—178; Tori K., Seo S., Yoshimura Y., Arita H., Tomita Y., *ibid.*, **1977**, 179—182.
6) Takeshita T., Hamada S., Nohara T., *Chem. Pharm. Bull.*, **37**, 846—848 (1989).
7) Yahara S., Irino N., Takaoka T., Nohara T., *Natural Medicines*, **48**, 312—313 (1994).
8) Kitagawa I., Wang H. K., Taniyama T., Yoshikawa M., *Chem. Pharm. Bull.*, **36**, 153—161 (1988).
9) Takeshita T., Ito Y., Sakai Y., Nohara T., Yasuhara M., Saito H., Kitagawa I., Ariga T., Irino N., Takaoka T., *J. Pharmacobio-Dyn*, **13**, s-54 (1990).
10) The instruments used to obtained physical data and the experimental conditions for chromatography were the same as described previously.[2]
11) Hara S., Okabe H., Mihashi K., *Chem. Pharm. Bull.*, **35**, 501—506 (1987).
12) Tanaka R., Nagao T., Okabe H., Yamauchi T., *Chem. Pharm. Bull.*, **38**, 1153—1157 (1990).