TWO NEW TRITERPENOID SAPOGENOLS AND A NEW SAPONIN
FROM *ABRUS CANTONIENSIS* (II)¹⁾

Yusuke SAKAI, Takashi TAKESHITA, Junei KINJO, Yasuyuki ITO and Toshihiro NOHARA*
Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi, Kumamoto 862,
Japan

Two new oleanene sapogenols, abrisapogenols A (1) and C (2), have been obtained from the methanolysate of the crude saponin fraction. They have been effective for treating a hepatic injury induced by CCl₄ in Abri Herba, the whole plant of *Abrus cantoniensis* HANCE (Leguminosae). Also a novel saponin, abrisaponin I (3) has been obtained from the same saponin fraction.

KEYWORDS Abri Herba; *Abrus cantoniensis*; Leguminosae; oleanene sapogenol; abrisapogenol A; abrisapogenol C; abrisapogenol I; abrisaponin I; hepatic injury

Abri Herba (Chiku-ts'ao in Chinese), the whole plants of *Abrus cantoniensis* HANCE (Leguminosae), is a native herb in Kwangtung and Kwangsi provinces of China. This plant has long been used in South China and Southeast Asia as a folk medicine to treat an infectious hepatitis. The crude saponin fraction of this plant was shown to be effective for a hepatic injury induced by CCl₄.²⁾ In a preceding paper,³⁾ we reported the characterization of five novel triterpenoid sapogenols from the methanolysate of this fraction. We have designated them abrisapogenols B (5), D, E (6), F and G. We also isolated the known sapogenols, sophoradiol (7),⁴⁾ soyasapogenols A, B,⁵⁾ kudzusapogenol A (8)⁶⁾ and cantoniensistriol.²⁾

Now, we have isolated two novel sapogenols named abrisapogenols A (1) and C (2) along with glycyrrhetic acid and glabrolide (9) from the methanolysate of the crude saponin fraction, and obtained a new triterpenoid saponin named abrisaponin I (3) from the same saponin fraction. This paper deals with the structural elucidation of the new compounds.

Abrisapogenol A (1), C₃₀H₅₀O₃, colorless needles, mp 256-259°C, [α]_D +70.8° (CHCl₃:MeOH=1:1), showed characteristic peaks at *m/z* 458 (M⁺), 250 (showing the presence of two hydroxy groups in the D/E ring) and 208 (one hydroxy group in A/B ring) for Δ¹²-oleanene derivative in the EI-MS.⁷⁾ The triacetate (1a) of 1, colorless needles, mp 206-209°C, [α]_D +43.8° (CHCl₃), showed signals due to four protons on the carbon attached to the acetoxy group in the ¹H-NMR spectrum (Table I). They were assigned to the acetoxymethyl of H₂-29 [δ 3.68 and 3.74 (2H, ABq, *J*=10.7 Hz)], and the methine protons of H-22α [δ 4.71 (1H, t, *J*=3.5 Hz)] and of H-3α [δ 4.50 (1H, m)] by comparing with those of abrisapogenol B tetraacetate (5a) and sophoradiol diacetate (7a). The structure of 1 was therefore represented as 3β, 22β, 29-trihydroxyolean-12-ene.

Abrisapogenol C (2), C₃₀H₅₀O₄, colorless needles, mp 273-275°C, [α]_D +84.6° (CHCl₃:MeOH=1:1), showed peaks at *m/z* 474 (M⁺), 266 (showing the presence of three hydroxy group in the D/E ring) and 208 (one hydroxy group in A/B ring) in the EI-MS. This suggested that 2 had one more hydroxy group in D/E ring than 1. The ¹H-NMR spectrum (Table I) of the tetraacetate (2a) of 2, colorless needles, mp 112-116°C, [α]_D +65.3° (CHCl₃), disclosed the presence of signals due to the protons of H-21α at δ 4.98 (1H, d, *J*=2.9 Hz), H-22α at δ 5.17 (1H, d, *J*=3.3 Hz) and H₂-29 at δ 3.87 and 3.54 (2H, ABq *J*=11.0 Hz) geminal to the acetoxy moiety in the D/E ring, which could be assigned by comparing with those

I	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆
1	H	H	—OH	CH ₃	CH ₂ OH	CH ₃
1a	Ac	H	—OAc	CH ₃	CH ₂ OAc	CH ₃
2	H	OH	—OH	CH ₃	CH ₂ OH	CH ₃
2a	Ac	OAc	—OAc	CH ₃	CH ₂ OAc	CH ₃
3	S ₁	H	=O	CH ₂ OH	CH ₃	COOH
3a	S ₂	H	=O	CH ₂ OH	CH ₃	COOMe
4	H	H	=O	CH ₂ OH	CH ₃	COOH
4a	H	H	=O	CH ₂ OH	CH ₃	COOMe
4c	Ac	H	—OAc	CH ₂ OAc	CH ₃	COOMe
5	H	H	—OH	CH ₂ OH	CH ₂ OH	CH ₃
5a	Ac	H	—OAc	CH ₂ OAc	CH ₂ OAc	CH ₃
6	H	H	—OH	CH ₂ OH	CH ₃	CH ₂ OH
7	H	H	—OH	CH ₃	CH ₃	CH ₃
7a	Ac	H	—OAc	CH ₃	CH ₃	CH ₃
8	H	OH	—OH	CH ₂ OH	CH ₂ OH	CH ₃
8a	H	OAc	—OAc	CH ₂ OAc	CH ₂ OAc	CH ₃
10	S ₁	H	—OH	CH ₂ OH	CH ₃	CH ₃
10a	S ₂	H	—OH	CH ₂ OH	CH ₃	CH ₃
II	R ₁	R ₂	R ₃			
4b	Ac	H ₂	CH ₂ OAc			
9	H	O	CH ₃			
9a	Ac	O	CH ₃			

S₁=-glc UA²gal²rha   S₂=-glc UA methyl ester²gal²rha

Table I. ¹H-NMR Data for Derivatives of 1,2,4,5,7,8 and 9 (in CDCl₃)

	H-3	H-21	H-22	H ₂ -24	H ₂ -29	tert Me group	COOMe
1a	4.50 (m)	-	4.71 (t, J=3.5)	-	3.68, 3.74 (ABq, J=10.7)	0.83, 0.87, 0.88, 0.97, 0.98, 1.05, 1.14	-
2a	4.50 (m)	4.98 (d, J=2.9)	5.17 (d, J=3.3)	-	3.54, 3.87 (ABq, J=11.0)	0.81, 0.87, 0.88 0.97x2, 1.10, 1.17	-
4b	4.59 (dd, J=3.4, 10.6)	-	4.17 (d, J=5.8)	4.14, 4.36 (ABq, J=11.9)	-	0.95, 0.97, 0.98, 1.02, 1.16, 1.17	-
4c	4.60 (dd, J=5.5, 10.2)	-	4.66 (dd, J=4.4, 12.4)	4.16, 4.37 (ABq, J=11.7)	-	0.82, 0.95, 0.98, 1.02, 1.16, 1.17	3.74
5a	4.59 (dd, J=5.5, 10.6)	-	4.71 (t, J=3.5)	4.14, 4.37 (ABq, J=11.5)	3.67, 3.73 (ABq, J=10.6)	0.83, 0.90, 0.92, 1.03, 1.05, 1.13	-
7a	4.51 (dd, J=4, 8)	-	4.64 (t, J=4)	-	-	0.82, 0.87, 0.88, 0.90, 0.97, 0.98, 1.00, 1.15	-
8a	4.58 (dd, J=5.5, 10.6)	4.97 (d, J=3.3)	5.16 (d, J=3.3)	4.13, 4.37 (ABq, J=11.0)	3.55, 3.87 (ABq, J=11.0)	0.81, 0.97, 0.98 1.03, 1.10, 1.16	-
9a	4.73 (dd, J=5.1, 11.0)	-	4.22 (d, J=5.8)	-	-	0.93, 0.94, 0.95, 1.04, 1.20, 1.26, 1.35	-

of the tetraacetate (8a) of kudzusapogenol A (8). Since the proton signals due to the A/B ring were consistent with those of 1a, the structure of 2 was determined to be 3 β , 21 β , 22 β , 29-tetrahydroxyolean-12-ene.

On methanolic acid hydrolysis, abrisaponin I methyl ester (3a), a white powder, $[\alpha]_D$ -19.6° (pyridine), gave a new sapogenol, abrisapogenol I methyl ester (4a) C₃₁H₄₈O₅, mp 251-253 °C, colorless plates, $[\alpha]_D$ +31.1° (pyridine). 4a showed peaks at *m/z* 500 (M⁺), 276 (D/E ring) and 224 (A/B ring) in the EI-MS, indicating the presence of two hydroxy

Table II. ^{13}C -NMR Data for **3a** and **10a** (in $\text{C}_5\text{D}_5\text{N}$)

3a 10a			3a 10a			3a 10a			3a 10a			3a 10a		
C-1	38.5	38.6	C-11	23.9	24.0	C-21	46.7	42.3	glcUA			3	76.5	76.4
2	28.0	25.6	12	124.5	122.3	22	212.9	75.5	C-1	105.5	105.4	4	71.1	71.1
3	91.3	91.3	13	141.5	144.8	23	23.0	23.0	2	78.2	78.1	5	76.5	76.4
4	41.9	43.9	14	43.8	42.3	24	63.5	63.5	3	76.5	76.4	6	61.5	61.6
5	56.0	56.1	15	26.6	26.4	25	15.7	15.8	4	74.3	74.3	rha		
6	19.0	18.9	16	26.2	28.6	26	16.6	17.0	5	77.7	77.6	C-1	102.4	102.3
7	33.0	33.2	17	47.4	37.9	27	25.1	25.7	6	170.4	170.3	2	72.3	72.3
8	39.7	39.9	18	47.6	45.2	28	25.3	28.6	gal			3	72.7	72.7
9	48.4	47.8	19	44.0	46.8	29	21.2	33.2	C-1	101.7	101.7	4	73.5	73.6
10	36.4	36.4	20	45.6	30.9	30	176.7	21.1	2	76.9	76.7	5	69.4	69.3
												6	18.4	18.9

groups in the A/B ring, and a methoxycarbonyl and a carbonyl groups in the D/E ring. **4a** was then reduced by NaBH_4 then acetylated to give two products **4b** and **4c**. The ^1H -NMR data (Table I) of both compounds showed the same signals due to the three protons assignable to $\text{H-3}\alpha$ and $\text{H}_2\text{-24}$ adjacent to the acetoxyl moieties. Furthermore, a signal at δ 4.17 (1H, d, $J=5.8$ Hz) in **4b** could be assigned to the $\text{H-22}\alpha$, which is the methine proton attached to the γ -lactone, by comparison with that of $\text{H-22}\alpha$ (δ 4.22 1H, d, $J=5.8$ Hz) of grabrolide monoacetate (**9a**). On the other hand, **4c** showed not only a methoxycarbonyl at δ 3.74 (3H, s) but also a methine proton adjacent to the acetoxyl moiety, the latter of which was assignable to $\text{H-22}\beta$ (δ 4.66, 1H, dd, $J=4.4, 12.4$ Hz). Therefore, the structure of **4b** and **4c** could be depicted as shown in the formulae. Finally, the reduction of **4a** by LiAlH_4 provided two products, one of which was identical with **6**. Therefore, **4a** was elucidated as **3** β , 24-dihydroxy-22-oxo-30-methoxycarbonyl-olean-12-ene. Meanwhile, the ^{13}C -NMR spectral data (Table II) for the sugar moiety of **3a** were superimposable on those of soyasaponin I methyl ester (**10a**).⁸⁾ Consequently, **3** was concluded to be 3-O-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-galactopyranosyl-(1 $\rightarrow$ 2)- β -D-glucuronopyranosyl] abrisapogenol I.

ACKNOWLEDGEMENTS The authors are grateful to Prof. Isao Kitagawa, Faculty of pharmaceutical sciences, Osaka University and Dr. Takao Konoshima, Kyoto Pharmaceutical University, for their valuable suggestions.

REFERENCES AND NOTES

- 1) Part 17 in the series of the studies on the leguminous plants.
- 2) a) T.C.Chiang and H.M.Chang, *Planta Medica*, **46**, 52 (1982); b) T.Takeshita, J.Kinjo, T.Nohara, H.Itoh, Y.Niiho and T.Yamazaki, Abstract Papers, The 34 th Annual Meeting of the Japanese Society of Pharmacognosy, Osaka, 1985, P.65.
- 3) T.Takeshita, S.Hamada and T.Nohara, *Chem. Pharm. Bull.*, **37**, 846 (1989).
- 4) a) M.Takahashi, S.Ishimasa and Y.Koyama, *Yakugaku Zasshi*, **80**, 698 (1960); b) T.C.Chiang and H.M.Chang, *J. Chem. Soc., Chem. Commun.*, 1982, 785.
- 5) a) H.M.Smith, J.M.Smith and F.S.Spring, *Tetrahedron*, **4**, 111, (1958); b) I.Kitagawa, M.Yoshikawa, H.K.Wang, M.Saito, V.Tosirisuk, T.Fujiwara and K.Tomita, *Chem. Pharm. Bull.*, **30**, 2294 (1982).
- 6) J.Kinjo, I.Miyamoto, K.Murakami, K.Kida, T.Tomimatsu, M.Yamasaki and T.Nohara, *Chem. Pharm. Bull.*, **33**, 1293 (1985).
- 7) H.Budzikiewicz, C.Djerassi and D.H.Williams, "Structure Elucidation of Natural Products by Mass Spectrometry", vol.2, Holden-Day Inc., San Francisco, 1964, p.121.
- 8) M.Yoshikawa, H.K. Wang, H.Kayakiki, T.Taniyama and I.Kitagawa, *Chem. Pharm. Bull.*, **33**, 4267 (1985).

(Received January 16, 1990)