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

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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 $CCl_4$, 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.

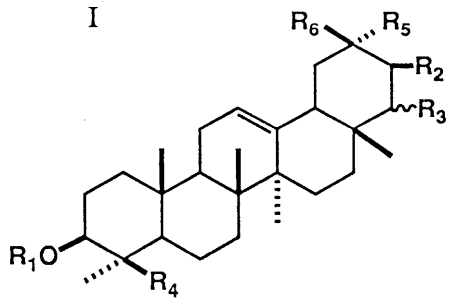
**KEYWORDS** Abri Herba; *Abrus cantoniensis*; Leguminosae; oleanene sapogenol; abrisapogenol A; abrisapogenol C; abrisapogenol I; abrisaponin I; hepatic injury

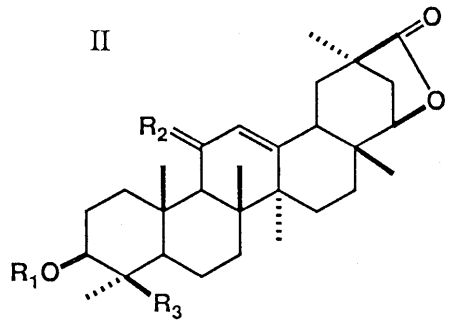
Abri Herba (Chiku-ts'ao in Chinese), the whole plants of *Abrus cantoniensis* HANCE (Leguminosae), is a native herb in Kwangtung and Kwangsi provinces of China. This plant has long been used in South China and Southeast Asia as a folk medicine to treat an infectious hepatitis. The crude saponin fraction of this plant was shown to be effecive for a hepatic injury induced by $CCl_4$.[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 glycyrrhetinic 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**), $C_{30}H_{50}O_3$, colorless needles, mp 256-259°C, $[\alpha]_D$ +70.8° ($CHCl_3$: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 $\Delta^{12}$-oleanene derivative in the EI-MS.[7] The triacetate (**1a**) of **1**, colorless needles, mp 206-209°C, $[\alpha]_D$ +43.8°($CHCl_3$), showed signals due to four protons on the carbon attached to the acetoxy group in the $^1$H-NMR spectrum (Table I). They were assigned to the acetoxymethyl of $H_2$-29 [$\delta$3.68 and 3.74 (2H, ABq, *J*=10.7 Hz)], and the methine protons of H-22$\alpha$ [($\delta$ 4.71(1H, t, *J*=3.5 Hz)] and of H-3$\alpha$ [$\delta$ 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 3$\beta$, 22$\beta$, 29-trihydroxyolean-12-ene.

Abrisapogenol C (**2**), $C_{30}H_{50}O_4$, colorless needles, mp 273-275°C, $[\alpha]_D$ +84.6° ($CHCl_3$: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 $^1$H-NMR spectrum (Table I) of the tetraacetate (**2a**) of **2**, colorless needles, mp 112-116°C, $[\alpha]_D$ +65.3° ($CHCl_3$), disclosed the presence of signals due to the protons of H-21$\alpha$ at $\delta$ 4.98 (1H, d, *J*=2.9 Hz), H-22$\alpha$ at $\delta$ 5.17 (1H, d, *J*=3.3 Hz) and $H_2$-29 at $\delta$ 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 | $CH_3$ | $CH_2OH$ | $CH_3$ |
| **1a** | Ac | H | —OAc | $CH_3$ | $CH_2OAc$ | $CH_3$ |
| **2** | H | OH | —OH | $CH_3$ | $CH_2OH$ | $CH_3$ |
| **2a** | Ac | OAc | —OAc | $CH_3$ | $CH_2OAc$ | $CH_3$ |
| **3** | $S_1$ | H | =O | $CH_2OH$ | $CH_3$ | COOH |
| **3a** | $S_2$ | H | =O | $CH_2OH$ | $CH_3$ | COOMe |
| **4** | H | H | =O | $CH_2OH$ | $CH_3$ | COOH |
| **4a** | H | H | =O | $CH_2OH$ | $CH_3$ | COOMe |
| **4c** | Ac | H | ····OAc | $CH_2OAc$ | $CH_3$ | COOMe |
| **5** | H | H | —OH | $CH_2OH$ | $CH_2OH$ | $CH_3$ |
| **5a** | Ac | H | —OAc | $CH_2OAc$ | $CH_2OAc$ | $CH_3$ |
| **6** | H | H | —OH | $CH_2OH$ | $CH_3$ | $CH_2OH$ |
| **7** | H | H | —OH | $CH_3$ | $CH_3$ | $CH_3$ |
| **7a** | Ac | H | —OAc | $CH_3$ | $CH_3$ | $CH_3$ |
| **8** | H | OH | —OH | $CH_2OH$ | $CH_2OH$ | $CH_3$ |
| **8a** | H | OAc | —OAc | $CH_2OAc$ | $CH_2OAc$ | $CH_3$ |
| **10** | $S_1$ | H | —OH | $CH_2OH$ | $CH_3$ | $CH_3$ |
| **10a** | $S_2$ | H | —OH | $CH_2OH$ | $CH_3$ | $CH_3$ |

| II | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| **4b** | Ac | $H_2$ | $CH_2OAc$ |
| **9** | H | O | $CH_3$ |
| **9a** | Ac | O | $CH_3$ |

$S_1$=-glc UA-(2)-gal-(2)-rha $S_2$=-glc UA methyl ester-(2)-gal-(2)-rha

Table I. $^1$H-NMR Data for Derivatives of **1**,**2**,**4**,**5**,**7**,**8** and **9** (in $CDCl_3$)

| | 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 3β, 21β, 22β, 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**) $C_{31}H_{48}O_5$, 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 $C_5D_5N$)

| | 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 $^1$H-NMR data (Table I) of both compounds showed the same signals due to the three protons assignable to H-3α and $H_2$-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 H-22α, which is the methine proton attached to the γ-lactone, by comparison with that of H-22α (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 adjucent to the acetoxyl moiety, the latter of which was assignable to H-22β (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 3β, 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→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl] abrisapogenol I.

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