# NEW TRITERPENOID SAPOGENOLS FROM ABRUS CANTONIENSIS (I)[1)]

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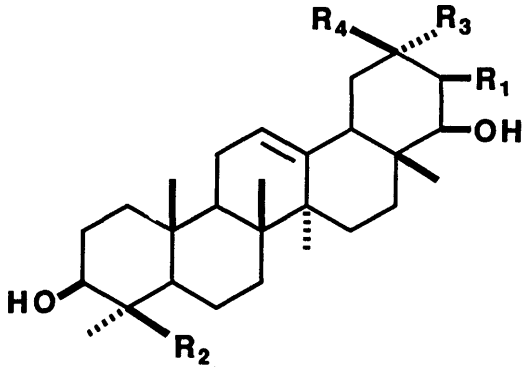
New five triterpenoid sapogenols, designated abrisapogenols B, E, D, F and G (**1**-**5**) were obtained from the hydrolysate of the crude saponin fraction of Abri Herba, the whole plants of Abrus cantoniensis Hance (Leguminosae). Their structures were determined by spectroscopic and X-ray analysis.

**KEYWORDS** Abri Herba; Abrus cantoniensis; Leguminosae; triterpenoid sapogenol; oleanene derivative; cantoniensistriol; sophoradiol; soyasapogenol; kudzusapogenol; abrisapogenol

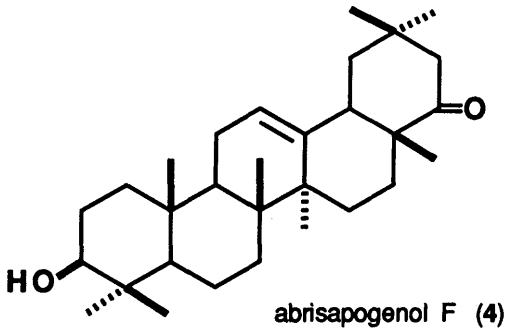
In the course of our systematic studies on the constituents of Pueraria lobata Ohwi (Leguminosae), we found the occurrence of the oleanene glucosides[2)] in Puerariae Radix and P. Flos, and reported that they were effective for hepatic injury induced with $CCl_4$.[3)] In connection with this pharmacological activity and as a part of our programs of the studies on the ingredients of the leguminous plants, we have surveyed the constituents of Abri Herba (Chiku-ts'ao in Chinese), the whole plants of Abrus cantoniensis Hance (Leguminosae), which is a native herb in Kwangtung and Kwangsi provinces of China and has long been used in South China and Southeast Asia as a folk medicine for the treatment of infectious hepatitis.[4)] Its efficacy towards this disease has been substantiated by clinical trials and has become well known in recent years.[5)] Chiang et al. reported that the crude saponin obtained from the title plants is effective against liver disease in pharmacological tests.[6)] And from the hydrolysate of the methanolic extract, they isolated a new sapogenol, cantoniensistriol (**6**), along with the known ones, sophoradiol (**7**),[7)] soyasapogenol A (**8**)[8)] and soyasapogenol B (**9**),[8)] and elucidated the structure of **6**.[5)]

Now, we have also recognized that the crude saponin originating from the methanolic extract of this plant is effective for the hepatic injury induced with $CCl_4$.[9)] The present paper deals with the isolation and structural elucidation of five new sapogenols, named abrisapogenol B, E, D, F and G (**1**-**5**), together with the identification of **6**, **7**, **8**, **9** and kudzusapogenol A (**10**) obtained from the hydrolysate of the biologically active crude saponin.

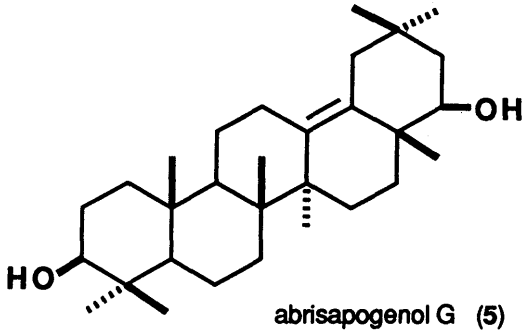
Abrisapogenol B (**1**), $C_{30}H_{50}O_4$, colorless needles, mp 278-280°C, $[\alpha]_D$ +26.1°(pyridine), showed the presence of a total of thirty carbons, in which four oxygenated carbons [ δ 64.4 (t), 73.0 (t), 75.6 (d) and 80.1 (d) ] and two $sp^2$ carbons [ δ 122.4 (d) and 144.9 (s) ] were included in the $^{13}$C-NMR spectrum.[10)] **1** is a typical oleanene-type sapogenol. The $^1$H-NMR spectrum of the corresponding tetraacetate (**11**), $C_{38}H_{58}O_8$, colorless needles, mp 156-157°C, $[\alpha]_D$ +61.3°($CHCl_3$), displayed signals due to one acetoxymethyl ( δ 4.14, 4.37, ABq, J=11.5 Hz) and two methine protons ( δ 4.59, dd, J=5.5, 10.6 Hz and 4.71, t, J=3.5 Hz) assignable to the $H_2$-24, H-3α and H-22α, respectively, by comparing them with those of the acetate of **9**. The signal of the remaining acetoxymethyl group ( δ 3.67, 3.73, ABq, J=10.6 Hz) could be reasonably assigned to the $H_2$-29 by comparison with that ( δ 3.68, 3.77, ABq, J=10 Hz, $H_2$-29) of 3β,24,29-triacetoxyolean-12-ene[11)] derived from azukisapogenol. Therefore, the strucure of **1** was represented as 3β,22β,24,29-tetrahydroxyolean-12-ene.




| | | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|---|
| abrisapogenol B | (1) | H | $CH_2OH$ | $CH_2OH$ | $CH_3$ |
| abrisapogenol E | (2) | H | $CH_2OH$ | $CH_3$ | $CH_2OH$ |
| abrisapogenol D | (3) | H | $CH_3$ | $CH_3$ | $CH_2OH$ |
| cantoniensistriol | (6) | OH | $CH_3$ | $CH_3$ | $CH_3$ |
| sophoradiol | (7) | H | $CH_3$ | $CH_3$ | $CH_3$ |
| soyasapogenol A | (8) | OH | $CH_2OH$ | $CH_3$ | $CH_3$ |
| soyasapogenol B | (9) | H | $CH_2OH$ | $CH_3$ | $CH_3$ |
| kudzusapogenol A | (10) | OH | $CH_2OH$ | $CH_2OH$ | $CH_3$ |




abrisapogenol F (4)




abrisapogenol G (5)

Abrisapogenol E (**2**), $C_{30}H_{50}O_4$, colorless needles, mp 249-252°C, $[\alpha]_D$ +67.7°(methanol), exhibited peaks due to the characteristic fragmentations[12] at m/z 175 ($C_{13}H_{19}$) originating from the A/B ring, and at m/z 250 ($C_{16}H_{26}O_2$), 232 ($C_{16}H_{24}O$), 219 ($C_{15}H_{23}O$) and 201 ($C_{15}H_{21}$) originating from the D/E ring by retro Diels-Alder fission in the EI-MS. These peaks also appeared in **1**. **2** was then converted to the acetate (**12**), colorless needles mp 283-285°C, $[\alpha]_D$ +72.2°($CHCl_3$). Signals of one acetoxymethyl group ( δ 4.11 and 4.37, ABq, J=10.8 Hz) and two methine protons ( δ 4.59, dd, J=5.1, 10.8 Hz and δ 4.66, t, J=3.3 Hz) in the $^1$H-NMR spectrum of **12** could be easily assigned to the $H_2$-24, H-3α and H-22α, respectively. The other one ( δ 3.99 and 4.14, ABq, J=10.4 Hz) was ascribable to the $H_2$-30 because the $^{13}$C-NMR spectra of both **12**[13] and **11**[14] provided analogous chemical shifts except for those of C-8 (+1.0), -15 (+2.5), -18 (-1.8), -21 (+1.0), -22 (+3.3), -29 (-35.2) and -30 (+53.3). Consequently, the structure of **2** was expressed as 3β,22β,24,30-tetrahydroxyolean-12-ene. This compound was identical with the sapogenol of wisteria saponin B obtained almost at the same time from the knots of Wisteria brachybotrys Sieb. et Zucc. by Konoshima et al.[15]

Abrisapogenol D (**3**), $C_{30}H_{50}O_3$, was obtained as colorless needles, mp 290-291°C, $[\alpha]_D$ +76.7°(pyridine), the acetate of which, colorless needles, mp 222-224°C, $[\alpha]_D$ +76.5°($CHCl_3$), showed signals of 1H, t (J=3.3 Hz) at δ 4.66, and 1H, dd (J=4.0, 7.7 Hz) at δ 4.50 ascribable to the H-22α and H-3α respectively in the $^1$H-NMR spectrum. The remaining signal of the ABq (J=11.0 Hz) at δ 3.99 and 4.12 was assigned to the acetoxymethyl group at C-30 by comparing it with that of **12**. Hence, the structure of **3** could be determined to be 3β,22β,30-trihydroxyolean-12-ene.

Abrisapogenol F (**4**), $C_{30}H_{48}O_2$, colorless needles, mp 66-67°C, $[\alpha]_D$ +15.4°($CHCl_3$), showed the presence of the carbonyl group in the IR (1696 $cm^{-1}$) and $^{13}$C-NMR ( δ 216.5) spectra.[16] The EI-MS provided a peak due to the D/E ring, indicating the location of the carbonyl group on the D/E ring. This compound was thus identified with 3β-hydroxyolean-12-en-22-one derived from **7**. Its $^{13}$C-NMR chemical shifts supported this structure.

Abrisapogenol G (**5**), $C_{30}H_{50}O_2$, colorless needles, mp 231-233°C, $[\alpha]_D$ -5.3°($CH_3OH$),

showed signals due to two oxygenated carbons at δ 78.0 and 79.0, and one tetra-substituted double bond at δ 131.7 and 137.3 in the $^{13}$C-NMR spectrum, thus it appeared that the double bond shifted into an unusual position. Another signal due to a proton (1H, dd, J=7.5, 9.4 Hz) adjacent to the hydroxyl group, except for that of the H-3α (1H, dd, J=5.1, 11.0 Hz), could not be assigned. Therefore, the single crystal of **5** was subjected to X-ray analysis. Crystal data were $C_{30}H_{50}O_2 \cdot H_2O$, M.W.=460.7, monoclinic $P2_1$, a=15.199(2), b=12.115(2), c=7.244(1) Å, β=95.75(1)°, V=1327.1 Å$^3$, Z=2, Dx=1.152 g/cm$^3$, F(000)=512, λ = 0.518 mm$^{-1}$ (Cu·$K_\alpha$=0.5418 Å). Refinements of 1934 observed reflections converged at R=0.058. The structure was established as shown in the formulae.

The structural analysis of the other substances are under investigation.

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13) $^{13}$C-NMR Data of **12**: δ 38.4, 26.7, 80.1, 43.8, 55.9, 19.3, 33.5, 41.0, 47.6, 36.7, 23.6, 123.0, 143.1, 41.6, 28.3, 26.2, 38.4, 41.4, 41.4, 36.2, 39.8, 77.8, 23.5, 65.4, 15.5, 16.6, 25.8, 29.6, 32.9, 70.0 ($C_1$-$C_{30}$).
14) $^{13}$C-NMR Data of **11**: δ 38.8, 26.8, 80.1, 43.3, 55.9, 19.3, 33.0, 40.0, 47.6, 36.8, 23.0, 122.8, 143.4, 41.6, 25.8, 26.8, 38.5, 43.2, 41.0, 36.4, 38.8, 74.5, 23.6, 65.4, 15.5, 16.7, 26.1, 29.9, 68.1, 16.7 ($C_1$-$C_{30}$).
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16) $^{13}$C-NMR Data of **4**: δ 38.6, 27.2, 78.9, 38.8, 55.3, 18.3, 32.7, 39.6, 47.6, 37.0, 23.5, 123.7, 141.6, 41.9, 25.3, 28.1, 47.6, 47.6, 46.7, 32.0, 50.8, 216.5, 27.2, 15.5, 15.5, 16.8, 25.4, 29.7, 34.1, 20.5 ($C_1$-$C_{30}$).

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