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; cantoniensisistriol; 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 glucosides² in Puerariae Radix and P. Flos, and reported that they were effective for hepatic injury induced with CCl₄.³ 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, cantoniensisistriol (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 CCl₄.⁹ 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), C₃₀H₅₀O₄, colorless needles, mp 278-280°C, [a]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 sp² carbons [δ 122.4 (d) and 144.9 (s)] were included in the ¹³C-NMR spectrum.¹⁰ 1 is a typical oleanane-type sapogenol. The ¹H-NMR spectrum of the corresponding tetraacetate (II), C₃₈H₇₈O₈, colorless needles, mp 156-157°C, [a]D +61.3°(CHCl₃), displayed signals due to one acetoxymethyl (δ 4.14, 4.37, ABq, J=11.5 Hz) and two methane protons (δ 4.59, dd, J=5.5, 10.6 Hz and 4.71, t, J=3.5 Hz) assignable to the H₂-24, H-3₂ 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-29 by comparison with that (δ 3.68, 3.77, ABq, J=10 Hz, H₂-29) of 3β,24,29-triacetoxylcodel-12-ene¹¹ derived from azukisapogenol. Therefore, the structure of 1 was represented as 3β,22β,24,29-tetrahydroxyolean-12-ene.¹²

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Abrisapogenol E (2), C$_{30}$H$_{50}$O$_{4}$, colorless needles, mp 249-252°C, [α]$_D$ +67.7° (methanol), exhibited peaks due to the characteristic fragmentations 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 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, [α]$_D$ +72.2° (CHCl$_3$). Signals of one acetoxyethyl group (δ 4.11 and 4.37, ABq, δ=10.8 Hz) and two methine protons (δ 4.59, dd, δ=5.1, 10.8 Hz and δ 4.66, t, δ=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, δ=10.4 Hz) was ascribable to the H$_2$-30 because the $^{13}$C-NMR spectra of both 12 and 11 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 (+33.3). 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 roots of Wisteria brachybotrys Sieb. et Zucc. by Konoshima et al.

Abrisapogenol D (3), C$_{30}$H$_{50}$O$_{4}$, was obtained as colorless needles, mp 290-291°C, [α]$_D$ +76.7° (pyridine), the acetate of which, colorless needles, mp 222-224°, [α]$_D$ +76.5° (CHCl$_3$), showed signals of 1H, t (δ=3.3 Hz) at δ 4.66, and 1H, dd (δ=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 (δ=11.0 Hz) at δ 3.99 and 4.12 was assigned to the acetoxyethyl 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, [α]$_D$ +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. 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, [α]$_D$ -5.3° (CH$_3$OH),
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 13C-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-3a (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 C39H50O22H2O, M.W.=640.7, monoclinic P21, a=15.199(2), b=12.115(2), c=7.244(1) Å, β=95.75(1)°, V=1327.1 Å3, Z=2, Dx=1.152 g/cm3, F(000)=512, λ = 0.518 mm−1, Cu-Kα=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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REFERENCES AND NOTES

1) Part 13 in the series of the studies on the leguminous plants.
10) This 13C-NMR spectrum was measured in pyridine-d5 and other 1H- and 13C-NMR spectra in this article were in CDCl3.
13) 13C-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 (C1-C30).
14) 13C-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 (C1-C30).
16) 13C-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 (C1-C30).

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