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Triterpenoids from *Codonopsis lanceolata**

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Abstract—Compound C from *Codonopsis* saponin has been identified as albigenic acid. It was not a genuine sapogenin but an acid-induced isomerisation product of echinocystic acid.

In the previous paper[1], we reported the isolation and identification of sterol and triterpenoid components from *Codonopsis lanceolata*, leaving compound C unidentified due to shortage of the material. Present paper describes the chemical and spectral analysis leading to the identification of compound C.

Compound C (**I**), $C_{30}H_{48}O_4$, mp 249-251°, $[\alpha]_D^{20}$+33.0° (c=0.3, MeOH), UVλ_{max} 204nm, showed positive Liebermann-Burchard reaction but negative osmic acid oxidation. Its IR-spectrum showed hydroxyl band at 3540 cm^{-1}, carboxyl absorption at 1698 cm^{-1}, and olefinic absorption at 1630 cm^{-1}. Methylation of **I** with diazomethane afforded monomethyl ester (**II**), mp 223-224°, $[\alpha]_D^{20}$+24.7° (c=0.14, MeOH), which was hydrolysed by 10% KOH to **I** in 30% yield. Acetylation of **II** with acetic anhydride-pyridine gave monomethyl ester diacetate (**III**), mp 191-193°, NMR spectrum of which exhibited seven tertiary methyl signals at δ 0.73, 0.78, 0.80, 0.84, 0.86, 0.87, and 1.17, two acetyl signals at 1.99 and 2.01, one carboxymethyl signal at 3.62, and two acetoxy-methine signals at 4.46 (triplet like) and 5.32 (quartet, J=4. and 7 Hz). Absence of absorption maximum in the region 11.8-12.4 μ in IR spectra of **I** and its derivatives and lacking of the olefinic proton peak in NMR spectrum of **III** demonstrate that the nature of double bond in **I** is regarded as tetra-substituted double bond.

The position of the double bond at 13 : 18 position in **I** was established from the mass spectral fragmentation pattern of **III**. In the high mass range, it exhibited no parent ion peak but a peak at m/e 510 due to the loss of CH_3COOH from molecular ion, and its further decomposition products at m/e 451 (510-$COOCH_3$), 450 (510-CH_3COOH), and 391 (510-CH_3COOH-$COOCH_3$). It showed mass peaks at m/e 260 and 247, which were formed by the rupture of the 11-12 and 8-14 bonds and of 9-11 and 8-14 bonds, respectively, and

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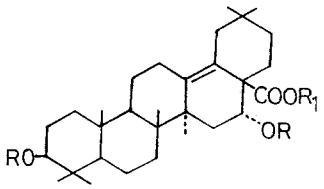
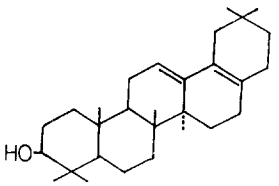
at m/e 187 due to the loss of $COOCH_3$+H from the latter fragment ion.

In addition to these peaks it showed a small but prominent peak at m/e 249 comprising rings A and B which was formed by the cleavage of ring C and an abundant peak at m/e 189 corresponding to the loss of water from it. Mass spectra analysis together with the saponification rate of carbomethoxyl group suggested that the compound should be albigenic acid. This suggestion was conformed by direct comparision with the authentic sample obtained from echinocystic acid by acid treatment.

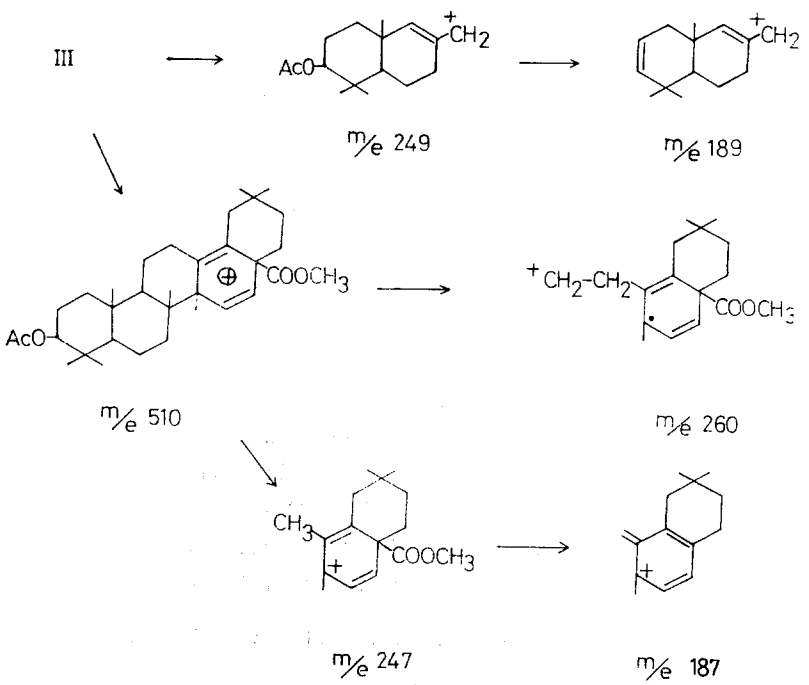
Sapogenin fraction obtained by treatment with HIO_4–alkali[4] failed to show the spot of



I R = R_1 = H
II R = H; R_1 = Me
III R = Ac; R_1 = Me



IV



albigenic acid on TLC. Therefore, albigenic acid obtained from *Codonopsis* saponin was shown to be an artefact which was produced from echinocystic acid by isomerisation with acid during hydrolysis of saponin.

EXPERIMENTAL*

Isolation of compound C(I)—Sapogenin fraction of the title plant was chromatographed over silica-gel column, and compound C (albigenic acid) **(I)** was obtained at the end of exhaustive elution with C_6H_6. EtOAc (6:4). It was recrystallized from MeOH to give fine needles, mp 249-252°, $[\alpha]_D^{20}$+33.3° (c=0.3 in MeOH) (lit.[3], mp 246-248°, $[\alpha]_D^{31}$−13°) MS *m/e* 472 (M^+), UV λ_{max}; nm (log ε); 204(4.0, in MeOH), Liebermann-Burchard reaction positive (pink→violet→blue), IR cm^{-1}; 3540(OH), 1698(COOH), 1630(double bond), negative in osmic acid oxidation.

Anal. Calcd for $C_{30}H_{48}O_4$: C, 73.45; H, 10.20. Found: C, 73.98; H, 10.28.

Methylation of albigenic acid—Albigenic acid **(I)** (20 mg) was treated with diazomethane in Et_2O. After evaporation of Et_2O the residue was recrystallized from MeOH to give fine needles of methyl albigenate **(II)**, mp 223-224°, $[\alpha]_D^{20}$+24.7° (c=0.14 in MeOH) (lit.[3], mp 225-226°, $[\alpha]_D^{27}$−10°), IR cm^{-1}; 3540 (OH), 1705 (ester).

Acetylation of methyl albigenate—Methyl albigenate **(II)** (20 mg) in pyridine (1 ml) was treated with Ac_2O (1 ml) for 3hr by gentle boiling. After working up in usual way, the resulting product was recrystallized from MeOH to give fine needles of methyl diacetate **(III)**, mp 191-193° (lit.[3], mp 189-190°), IR cm^{-1}; 1740, and 1243 (acetate).

Periodate oxidation of *Codonopsis* saponin followed by alkaline treatment—A portion (500 mg) of *Codonopsis* saponin fraction was oxidized with $NaIO_4$ (1.5g) in water at 4° for 4 days. The reaction mixture was extracted with BuOH and the BuOH layer was washed with water and then concentrated to dryness by vacuum distillation.

The residue was dissolved in 5% NaOH and the solution was refluxed under N_2-stream for 2hr. The reaction mixture was acidified with d-HCl and extracted with Et_2O extract showed the spots of oleanolic acid and echinocystic acid but not showed that of albigenic acid.

Acid treatment of echinocystic acid—A solution of echinocystic acid (50mg) in 6% HCl-EtOH (50 ml) was heated for 5 hr in boiling water bath. Pouring into water gave solids which were chromatographed and elution with 1% MeOH-$CHCl_3$ yielded norechinocystadienol **(IV)**. mp 221-224°, UV λ_{max}; 237, 244, and 252 nm (log ε 4.25, 4.30 and 4.15) (lit.[4], mp 192-195°, 241 nm, log ε 4.25, no fine structure appeared in the absorption curve reported), unchanged echinocystic acid, mp 303-308°, and albigenic acid, mp 248-250°.

* The melting points were uncorrected. UV spectra were taken in MeOH, IR spectra in KBr. NMR spectrum was taken in $CDCl_3$ using TMS as internal standard at 100 MHz. The authors are gratefull to Dr. D.R. Hahn, College of Pharmacy, Jung-Ang University, for the measurement of mass spectrum.

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