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RHAMNACEAE

CONSTITUENTS OF THE LEAVES AND ROOT BARK OF *CEANOTHUS VELUTINUS*

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Plant. Ceanothus velutinus. Trival Name: Snowbrush.[1]

Uses. Ornamental.

Source. Lake Kachess Dam Road, Snoqualmie Pass, Washington, U.S.A.

Previous work. Leaves.[2] Root-bark.[3]

Leaves. Ground leaves (1·6 kg) were extracted with light petroleum (30–60°), followed by chromatography on silicic acid. Nonacosane, 1-hexacosanol, velutin (4′,5-dihydroxy-3′,7-dimethoxyflavone),[4] and cinnamic acid were isolated and identified by spectral and physical measurements.

Root Bark. Ground root-bark (2·6 kg) was extracted with light petroleum (30–60°). Concentration of the liquid afforded betulinic acid, ceanothenic acid, and β-sitosterol. Structural assignments were confirmed by spectra and physical comparisons.

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TRITERPENOIDS FROM *DISCARIA LONGISPINA* AND *COLLETIA PARADOXA*

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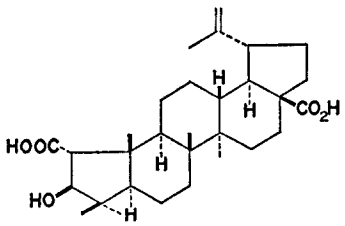
Abstract—Ceanothic and betulinic acids have been isolated from *Discaria longispina*. From *Colletia paradoxa* only ceanothic acid was isolated.

IN CONNECTION with a study of the constituents of Argentine *Rhamnaceae*, we have examined the terpenoids constituents of the roots of the title plants.

As described in the Experimental section *D. longispina* (Hook and Arn.) Miers., yielded two crystalline compounds identified as ceanothic (I)[1,2] and betulinic (II) acids.



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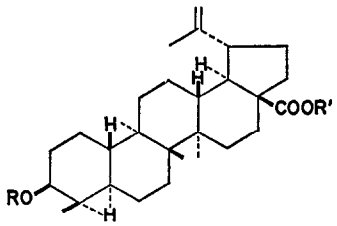

II; R = H; R' = H

IIa; R = $-C(=O)-CH_3$; R' = $-CH_3$

Compound I, m.p. 347–348° was identified as ceanothic acid by direct comparison (i.r., mixed m.p.) with an authentic sample. In addition, methylation of I gave a methyl ester identical with dimethyl ceanothate (i.r., mixed m.p., TLC).

Compound II, m.p. 281–295° was identified as betulinic acid by direct comparison (i.r., mixed m.p., TLC) of its methyl acetyl betulinate (IIa).

From *Colletia paradoxa* (Spreng.) Escal. only ceanothic acid (I) could be isolated, by TLC of the mother liquors of I only several minor components were detected.

It is interesing to note that in contrast to betulinic acid[3,4] the occurrence of ceanothic acid has been reported in relatively few plants belonging to the *Rhamnaceae*.[5,6]

EXPERIMENTAL

Extraction of Discaria longispina

The plant material was collected at Salliqueló (Provincia de Buenos Aires) in January 1969. The powdered roots (2 kg) were extracted with EtOH for 24 hr × 5, after which time the solvent was drained off. Concentration of the combined extracts yielded an oily residue which was dissolved in 2N HCl and throughly extracted with Et_2O; the dried ether extracts (Na_2SO_4) were evaporated to dryness to yield a solid residue (27 g).

Ceanothic Acid

The residue (2 g) in Et_2O was extracted exhaustively with 2% aqueous KOH. A solid (A), which separated at the interface, was removed by filtration. The remaining solution was acidified (10% HCl) and extracted with Et_2O. Evaporation of the solvent gave a residue (1 g) which was crystallized from EtOH, m.p. 347–348°, homogeneous on TLC (silica gel, 2 solvents). I.r. cm^{-1} (KBr) 3470, 3000–2500, 1680, 880; identical with that of an authentic sample of coeanothic acid. Diazomethane gave the dimethyl ester, from MeOH, m.p. 219–223°, $[\alpha]_D^{18}$ +35·2 (*ca.* 0·72, $CHCl_3$). It was identical (i.r., mixed m.p., TLC) to an authentic sample.

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Betulinic Acid

The solid A was suspended in H_2O and by acidification and extraction with Et_2O crude betulinic acid (II) was obtained (215 mg) identified as described below. Methylation with diazomethane gave the ester, from MeOH, m.p. 209–210°, $[\alpha]_D^{18}$ +6·5 (*ca.* 1·00, $CHCl_3$). Acetylation of the ester with Ac_2O–Pyridine gave the acetate, from MeOH, m.p. 206–209°. It was identical (i.r., mixed m.p., TLC) to an authentic sample.

Extraction of Colletia paradoxa

The plant material was collected in Balcarce (Provincia de Buenos Aires) in February 1969. The extraction and isolation procedures were the same as described above. From 1·6 kg of ground roots 18 g of ethereal extracts were obtained.

Ceanothic Acid

From 2 g of the above residue 1·5 g of ceanothic acid were obtained, m.p. 339–341° (decom.) $[\alpha]_D^{18}$ +37·5 (*ca.* 0·85, $CHCl_3$) identical with that of an authentic sample of ceanothic acid (i.r., mixed m.p., TLC). From the mother liquors only several minor components were detected in silica gel plates.

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SOLANACEAE

LUPEOL IN TISSUE CULTURES OF *SOLANUM XANTHOCARPUM*

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Abstract—Triterpenes occurring in tissue cultures of *Solanum xanthocarpum* were investigated. The major component was identified as lupeol from TLC behaviour, i.r. spectra and m.p. of the parent compound and its derivative.

UTILIZATION of plant tissue cultures in the study of biosynthetic pathways of natural compounds is of considerable interest and a few such systems have proved useful for this purpose.[1–3] In the course of investigations on the biosynthesis of steroids present in *Solanum xanthocarpum* tissue cultures,[4,5] the occurrence of triterpenes in the callus was examined. This report concerns the isolation and identification of the major triterpene, lupeol.

EXPERIMENTAL

Four-week-old callus which had been under continuous subculture for the past 4 years and grown on Murashige and Skoog's basal medium with additives[6] was used as source material. 100 gm of oven-dried tissue was powdered and soxhlet extracted with chloroform for 24 hr. The extract was washed first with

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