CORIAMYRTIN AND OTHER METABOLITES OF *CORIARIA RUSCIFOLIA*

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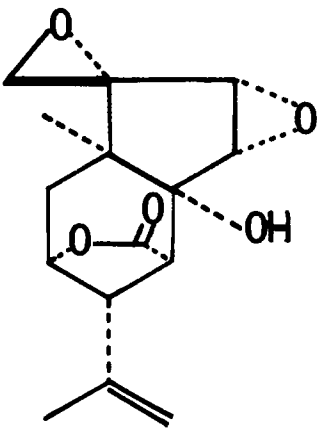
Coriamyrtin is a picrotoxinoid lactone isolated from *Coriaria japónica* (1) and *C. myrtifolia* (2). Okuda and Yoshida proposed a structure and absolute configuration for it by analogy with picrotoxin (3). The chemical study of New Zealand *C. ruscifolia* L. led Easterfield and Aston (2) to isolate tutin, another picrotoxinoid sesquiterpene lactone. However in the case of *C. ruscifolia* L., the only representative in Chile of the family Coriaceae (4), coriamyrtin was isolated instead of tutin.

The structure of coriamyrtin was determined as structure **1** by spectroscopic methods: ir, ^{1}H-nmr, ^{13}C-nmr (5) and ms. In addition, the compounds β-sitosterol and ursolic acid were isolated. The ir spectra of these compounds were superimposable with authentic samples[1] of β-sitosterol and ursolic acid, and the mixture melting points were undepressed. Furthermore, the following phenolic compounds were isolated: quercetin, quercetin-3-*O*-galactoside, avicularin and quercitrin. They were identified on the basis of their physical properties as compared with authentic samples[1] (Rf, mixture melting point) and by direct comparison of their uv spectral data with those found in the literature (6).

EXPERIMENTAL

Voucher specimens are deposited in the Herbarium of the Botany Institute of the Universidad Austral of Chile (Herbarium No. 3810–3800). The aerial part of a dried ground plant (7200 g), collected in Pishuinco, Province of Valdivia in January of 1977, was exhaustively extracted with 95% ethanol after prior treatment with benzene to remove the lipid fraction. The ethanol extract was concentrated *in vacuo* and diluted with distilled water, which was successively extracted with benzene, chloroform, ethyl acetate and amyl alcohol; thereby 30 g of benzene extract, 15 g of chloroform extract, 112 g of ethyl acetate extract, and 127 g of amyl alcohol extract were obtained.



1–Coriamyrtin

β-Sitosterol and ursolic acid.—The benzene extract was chromatographed over silica gel (Merck) and eluted with solvents and solvent mixtures of increasing polarity beginning with petroleum ether (60–80°C). A white crystalline powder was obtained from the fraction eluted with benzene. It was crystallized from ethanol (1.50 g, mp 135°C). The mp and mmp determination with an authentic sample of β-sitosterol indicated the identity of this compound to be β-sitosterol. The ir (Nujol) gave 3600, 3200, 1040, and 700 cm^{-1}. By means of the usual methods of acetylation, the acetate of β-sitosterol (mp 126°C) was obtained; it gave bands (Nujol) at 1740, 1250, and 1080 cm^{-1}. From the fraction eluted with ben-

[1]These authentic samples were kindly donated by Dr. M. Silva of the University of Concepción.

zene-methanol (7:3) was obtained a white solid which crystallized from ethanol (2.5 g, mp 278–280°C); ir (Nujol): 3600–3300, 1700, and 700 cm^{-1}. The identity of this compound was verified as ursolic acid by no depression in mixture mp with an authentic sample. The acetate of this white solid had a mp of 289–290°C; it gave ir bands (Nujol) at 3200, 1740, 1250, 1050 cm^{-1}.

CORIAMYRTIN (1).—The chloroform extract was chromatographed over 100 g of silica gel with solvents and solvent mixtures of increasing polarity. The fraction eluted by chloroform-methanol (1:1) yielded a white solid which, after successive recrystallizations from methanol yielded, 3 g of a crystalline product, mp 228°C; Rf 0.13 (chloroform/silica gel); ir (Nujol) 3600–3200 (OH), 1770, 1760 (lactone), 1650 (C=C), and 1160 cm^{-1} (epoxide).

QUERCETIN AND QUERCETIN-3-O-GALACTOSIDE.—From the ethyl acetate fraction, which was chromatographed over a cellulose column and later over polyamide, was isolated 1.5 g of quercetin and 1.2 g of quercetin-3-O-galactoside.

AVICULARIN AND QUERCITRIN.—The amylic fraction, when chromatographed in a manner similar to that of the anterior fraction, yielded two flavonoids which, upon comparison with authentic samples[1], were identified as avicularin (0.50 g) and quercitrin (0.80 g).

EXTRACTION OF THE FRUITS.—The fruit of *C. ruscifolia* L. (500 g) was exhaustively extracted with refluxing methanol. The methanol extract was chromatographed over silica gel with appropriate eluents; this permitted the isolation of the compounds β-sitosterol, ursolic acid and coriamyrtin.

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