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6-METHOXY-7,8-METHYLENEDIOXYCOUMARIN FROM *ARTEMISIA CARRUTHII**

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EXAMINATION of *Artemisia carruthii* Wood resulted in the isolation of 6-methoxy-7,8-methylenedioxy coumarin, recently found in *Artemisia dracunculoides* Pursh.¹ Although sesquiterpene lactones were present in the extractives from the plant, no crystalline material of this class has been obtained.†

The coumarin, C₁₁H₈O₅, had m.p. 224–225°, and gave u.v. and i.r. spectra that identified it as a coumarin. Its NMR spectrum was in full accord with this conclusion and, in addition, showed the presence of the methoxy and methylenedioxy groupings. Besides a three-proton singlet at δ 3.28 and a two-proton singlet at δ 6.25, the only other signals were a one-proton singlet (H-5) at δ 7.06 and the characteristic signals for the H-3 and H-4 protons of the coumarin ring. These were seen as doublets at δ 6.30 and 7.95, ($J = 10$ Hz).

The composition and melting point of the coumarin suggested its identity with the newly described 6-methoxy-7,8-methylenedioxy coumarin,¹ and this was confirmed by a direct comparison of the compounds, which proved to be identical (mix m.p., i.r., TLC).‡

EXPERIMENTAL

Dried and ground *Artemisia carruthii* Wood,§ was extracted with CHCl₃ and the extract evaporated. The residue was partitioned between hexane (5 l.) and methanol-water (3:1, 800 ml), and the hexane layer discarded. Extraction of the alcoholic solution with CHCl₃ gave 73 g of a dark brown syrup. This was chromatographed on silica gel (900 g), eluting with CHCl₃, CHCl₃-EtOAc, EtOAc-acetone and finally acetone (1 l. fractions).

From the CHCl₃ extracts was isolated a colorless, crystalline compound which was recrystallized from pyridine, m.p. 224–225°. (Anal. Calc. for C₁₁H₈O₅: C, 60.00; H, 3.67; found, C, 60.25; H, 3.98.) The mass spectrum showed the molecular ion at m/e 220 (base peak), with prominent peaks at 205 (M-15), 192 (M-28)

* Contribution No. 2730 from the Department of Chemistry, U.C.L.A.

† As shown by the appearance of the characteristic i.r. band at about 1770 cm⁻¹.

‡ We are grateful to Professor Herz for a specimen of the coumarin, isolated from *A. dracunculoides*.

§ We are indebted to Mr. R. J. Barr, El Paso, Texas, U.S.A., for collection and authentication of the plant material used in this study.

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and 177 (M-15-28). The NMR spectrum is described above. A specimen of authentic 6-methoxy-6,7-methylenedioxcoumarin had m.p. 219–221°, and a mixture melted at 221–223°. The i.r. spectra were identical.

The more polar fractions from the chromatographic column gave oily residues from which no crystalline materials have been obtained. Rechromatography of selected fractions was fruitless.

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TRITERPENOID AND STEROID CONSTITUENTS OF *ASTER BACCHAROIDES*

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Plant. *Aster baccharoides* Steetz.

Occurrence. On barren hills in Hong Kong Island, and on the adjacent Chinese mainland.

Uses. Not known.

Previous work. On sister species, reported the occurrence of flavonoids,^{1–3} coumarins,⁴ polyacetylene compounds,^{5–9} saponin^{10–12} and triterpenoids.^{1,13}

Leaves. (Extracted light petroleum, chromatographed—alumina.) *β*-amyrenyl acetate C₃₂H₅₂O₂ (0.042% of leaves, m.p., mixed m.p., [α]_D, and i.r. of acetate and alcohol): from light petroleum fractions. *Friedelin* C₃₀H₅₀O (0.015%; m.p., mixed m.p., [α]_D, and i.r.): from light petroleum–benzene (9:1) fractions. *Triterpene alcohol mixture* from light petroleum–benzene (7:3) fractions, separated by chromatography on argentized kieselgel into *β*-amyrin C₃₀H₅₀O (0.018%; m.p., mixed m.p., [α]_D, i.r., and TLC—argentized kieselgel) and *lupeol* C₃₀H₅₀O (0.003%; m.p., mixed m.p., [α]_D, i.r. and TLC—argentized kieselgel). *α*-Spinasterol C₂₉H₄₈O (0.006%; m.p., mixed m.p., [α]_D, NMR, and mass spectra of alcohol and acetate): from light petroleum–benzene (2:3) fractions.

Stems. (Extracted light petroleum): concentrated extract deposited colourless crystals. (Crystals in light petroleum–benzene, chromatographed—alumina): *Friedelin* (0.054% of stems): from light petroleum–benzene (1:1) fractions. *Friedelan-3β-ol* C₃₀H₅₂O (0.027%;

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