

EXPERIMENTAL

PLANT MATERIAL.—The trunk bark of *T. alata* was obtained from the CIMAP Experimental Station, Hebbale, Coorg District, Karnataka State, India. A voucher specimen is deposited at CIMAP Regional Centre, Bangalore.

EXTRACTION AND ISOLATION.—Air-dried and coarsely powdered trunk bark (1 kg) was extracted with *n*-hexane and MeOH. The extracts were processed according to standard procedures (2). The compounds isolated by column chromatography of the extracts are β -sitosterol (15 mg), betulinic acid (130 mg), arjunic acid (50 mg), arjunolic acid (65 mg), arjunetin (55 mg), and ellagic acid (11 mg). We have also obtained betulinic acid (55 mg) from the less polar fractions of the Et₂O extract of the heartwood (2).

All the compounds isolated were identified by physical properties, spectral data (mmp, co-tlc, ir, uv, ¹H nmr), direct comparison with authentic samples, and preparation of derivatives such as acetates and methyl esters.

Full details of isolation and identification are available on request to the senior author.

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6-METHOXY-7,8-METHYLENEDIOXYCOUMARIN FROM *ARTEMISIA*
DRACUNCULOIDES AND *ARTEMISIA VULGARIS*

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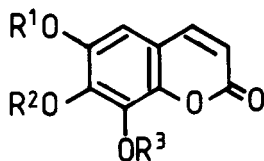
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In 1970, Herz *et al.* (1) reported the isolation of a new C₁₁H₈O₅ coumarin, mp 219–221°, from the above-ground parts of *Artemisia dracunculoides* Pursh. The structure, 6-methoxy-7,8-methylenedioxy coumarin (1), followed from its spectroscopic properties and its conversion to fraxetin (2) by acid-catalyzed acetal exchange with resorcinol. In the literature, this coumarin is sometimes referred to by the trivial name, dracunculin. This name does not, however, appear in the original publication but can be traced to a 1973 review in which the natural coumarins discovered during 1965–1970 were tabulated and those not already possessing a trivial name assigned one (2).

In 1982, Stefanović *et al.* (3) reported the isolation of 7,8-methylenedioxy-9-methoxycoumarin from *Artemisia vulgaris* L. Reference to the original paper revealed that the authors had used a numbering system in which the fully substituted 4a position was numbered 5 and that the structure proposed for the coumarin, mp 226–227°, was in fact 8-methoxy-6,7-methylenedioxy coumarin (3). It was not possible, however, from comparison of the data given in the two publications to conclude whether the two coumarins were isomers as suggested or whether both possessed the same structure with one of the assignments being in error.



- 1** $R^1 = \text{Me}, R^2 R^3 = \text{CH}_2$
2 $R^1 = \text{Me}, R^2 = R^3 = \text{H}$
3 $R^1 R^2 = \text{CH}_2, R^3 = \text{Me}$

Direct comparison of small samples of the two coumarins by mmp, ir, and ^1H -nmr spectra revealed their identity. In an endeavour to determine whether the methoxyl group was at C-6, which seemed probable, or C-8, lanthanide-induced shifts of the ^1H -nmr spectra were obtained (4). However, relative to H-3, the shift of the methoxyl (0.17) induced by $\text{Pr}(\text{fod})_3$ was identical to that experienced by the methylenedioxy signal, compared with 0.30 for H-4 and 0.22 for the aromatic proton, consonant with the latter being at C-5. Confirmation that the methoxyl group was at C-6, as proposed by Herz *et al.* (1), came from the 200 MHz ^1H -nmr spectrum which revealed a small coupling (0.2 Hz) of the methoxyl protons, δ 3.92, with the vicinal aromatic proton, δ 6.57, whereas the methylenedioxy protons resonated as a sharp singlet, δ 6.16. H-5 was also weakly coupled to H-4, δ 7.57, and H-3, δ 6.27 (both dd, J 9.5 and 0.35 Hz).

The structure of the coumarin from *A. vulgaris* thus has to be reassigned as **1** while that from *A. dracunculoides* is confirmed as **1**.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Ir spectra of CHCl_3 solutions were recorded on a Perkin-Elmer 225 spectrophotometer. ^1H -nmr spectra were recorded on a Bruker WP 200 SY spectrometer; chemical shifts are reported in δ (ppm) values with TMS as internal standard.

LANTHANIDE-INDUCED (LIS) EXPERIMENTS.—The normal ^1H -nmr spectrum of each coumarin in CDCl_3 was recorded. A solution of $\text{Pr}(\text{fod})_3$ in CDCl_3 was added, then shaken, and the spectrum rerun. This was repeated four times. In each case the shifts of all the protons were measured relative to TMS and LIS was $\delta\text{H}[\text{Pr}(\text{fod})_3] - \delta\text{H}$ (untreated). The LIS for each proton was divided by LIS of the proton attached to C-3 and average values obtained.

SAMPLE COMPARISON.—The ir and ^1H -nmr spectra and LIS of the two samples were identical. The melting point of the sample from Professor Herz was 210–224°, that from Professor Stefanović 208–217°, and the mixed melting point 208–223°.

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