COUMARINS FROM *CHRYSANTHEMUM SEGETUM*

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It has been reported that *Chrysanthemum* species contain sesquiterpene lactones (1–6), flavonoids (7–9) and coumarins (10, 11). As a part of a research program dealing with sesquiterpene lactones of compositae, we examined *Chrysanthemum segetum* L. of which only the flavonoids gossypitrin and quercimetrin have been isolated (12). We wish to report the isolation of three known coumarins, namely, herniarin,umbelliferone and scopoletin.

EXPERIMENTAL[1, 2]

Plant material.—The plant material was collected from Yesilköy (Istanbul, Turkey) and identified in the Department of Botany. The voucher specimen No. 46270 is deposited in the herbarium of the Faculty of Pharmacy (University of Istanbul).

Extraction and fractionation.—Air-dried and powdered aerial parts of the plant (500 g) were extracted with ethanol. This extract was concentrated *in vacuo*. The syrup (120 g) was taken up with warm ethanol and diluted with an equal volume of water which contained lead acetate (4%). After the mixture was allowed to stand overnight a precipitate formed which was removed by filtration. The filtrate was concentrated *in vacuo* and then extracted with chloroform; 1.8 g of chloroform extract was obtained. The extract was chromatographed on a silica gel column (50x4 cm). The solvent was benzene the polarity of which was gradually increased by addition of chloroform.

Benzene-chloroform (7:3) fractions yielded herniarin (major compound); benzene-chloroform (1:1) gave a mixture of two compounds, umbelliferone and scopoletin (minor compounds). These compounds were separated on preparative tlc plates with chloroform-acetone (9:1) as the solvent system (Rf values 0.43 and 0.38 respectively).

Identification of coumarins.—*Herniarin*: The compound was purified by methanol crystallization (240 mg) and showed the following data: mp 115°; uv λ max. (MeOH): 243, 252, 322 nm; ir ν max. (KBr): 1720, 1620, 1508, 1470 cm^{-1}; pmr ($CDCl_3$, TMS) δ: 3.92 (3H, s, OCH_3), 6.30 (1H, d, J=9, H-3), H-6 and H-8 protons at 6.92 (dd, J=2 and 9 Hz), 6.86 (d, J=2 Hz), 7.43 (1H, d, J=9 Hz, H-5), 7.68 (1H, d, J=9 Hz, H-4). From the spectral data, the compound was identified as herniarin.

Umbelliferone: mp 205°; uv λ max. (MeOH): 220, 243, 255, 324 nm. By comparison (mp, uv and tlc) with a reference sample, it was identified as umbelliferone.

Scopoletin: mp 198°; uv λ max. (MeOH): 230, 253, 283, 297, 340 nm; mp, uv and tlc comparison with a reference sample showed the compound was scopoletin.

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[1]Melting points were determined on a Kofler hot plate and uncorrected. Uv spectra were recorded on a Beckman model Instrument GMBH, ir on a Beckman spectrophotometer, pmr on a Varian model A-60A, silica gel 40 (70–230 Mesh) from E. Merck.

[2]Full details of the isolation and identification are available on request to the authors.