FLAVONOID GLYCOSIDES FROM *SMYRNIUM PERFOLIATUM, S. CRETICUM* AND *S. ROTUNDIFOLIUM*

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As part of our continuing study of the chemical systematics of the genus *Smyrnium* L. (Umbelliferae), we report here the isolation and identification of nine flavonoids from *S. perfoliatum* L., *S. rotundifolium* Mill. and *S. creticum* Mill. Aerial parts of *S. perfoliatum* yielded quercetin 3-β-D glucoside (6 mg), kaempferol (5 mg) and its 3-β-D-glucoside (7 mg) and 3,4'-β-D-diglucoside (16 mg). *S. rotundifolium* provided kaempferol (5 mg) and its 3-β-D-galactoside (10 mg), kaempferol 3-methyl ether 7-β-D-glucoside (15 mg) and a kaempferol 3-diglycoside (15 mg). From the third species, *S. creticum*, three flavonoids were obtained, namely, kaempferol (10 mg), quercetin (10 mg) and its 3-β-D-galactoside (400 mg). We previously reported kaempferol and quercetin glucosides, as well as eremophilane sesquiterpene lactones, from *S. olastrum* (1,2) and *S. connatum* (3,4). In addition, an earlier study with *S. rotundifolium* (5) found hydrocarbons, steroidal glycosides and trace amounts of alkaloids.

EXPERIMENTAL

PLANT MATERIAL.—Above-ground parts of *S. perfoliatum* and *S. creticum* were collected in the European section of Turkey near Kirklareli and Tekirdag, respectively, (vouchers ISTE 21008 and ISTE 43813). *S. rotundifolium* was collected near Izmir in the western part of Turkey (voucher ISTE 19055). Plant material was identified by Professor A. Baytop (Univ. of Istanbul). Voucher specimens are deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Dried and powdered aerial parts of the three species (1 kg each) were each extracted in a Soxhlet sequentially with petroleum ether (bp 30–60°), benzene, chloroform and ethanol. Two-dimensional paper chromatography and tlc showed that only the alcoholic extracts contained flavonoids. Each of the ethanol extracts was concentrated to a small volume *in vacuo* and the resulting syrups were partitioned between water and ethyl acetate. The ethyl acetate extracts were concentrated and separately chromatographed over Polyclar (5×50 cm columns). Elution was initiated with water, with the progressive addition of ethanol up to 100%. The flavonoids of each extract were eluted sequentially. Prior to spectral analysis, all flavonoids were cleaned over Sephadex LH-20.

All flavonoids were identified by spectral and hydrolytic data as well as authentic sample comparison (except kaempferol 3,4'-diglucoside) and color reactions (6). Acid hydrolysis of the kaempferol 3-diglycoside yielded kaempferol and glucose (tlc comparison with authentic sample) and traces of what appeared to be another sugar, which was not identified. β-Glucosidase hydrolysis did not change the compound. The nmr spectrum indicated two sugar moieties were present in the molecule (broad group of signals between 3.4–3.9 integrating for about 10 protons) and confirmed the kaempferol skeleton. Ms (as PM derivative) was not successful. The lack of material prevented further studies on this compound.

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LITERATURE CITED

1. A. Ulubelen and S. Oksuz, *Lloydia*, **33**, 397 (1970).
2. A. Ulubelen and S. Oksuz, *Tetrahedron Letters*, 4455 (1971).
3. A. Ulubelen and N. Ates (unpublished notes).
4. A. Ulubelen, N. Ates and T. Nishida, *Phytochemistry*, **18**, 338 (1979).
5. A. Ulubelen, *Phytochemistry*, **11**, 2652 (1972).
6. T. J. Mabry, K. R. Markham and M. B. Thomas, "The Systematic Identification of Flavonoids, p. 16, Springer-Verlag, N. Y. (1970).