n-1-ALKANOLS OF *HYPERICUM PERFORATUM*

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Several species of the genus *Hypericum* have been shown to produce antibacterial constituents (1-5), and in the case of *Hypericum perforatum* L. (St. John's wort), extracts have been utilized clinically in Russia to treat infections (6) and in the United States as a food preservative (3). Recently, we reported on the stereochemistry (7) of the antibiotic hyperforin, which is present in *H. perforatum* (6) and on the *n*-alkanes occurring in this plant (8). As part of our study on the constituents of *H. perforatum*, which is commercially available as dried plant material from Scandinavian drugstores, we have examined the saturated long-chain alcohols present in an acetone extract of this plant.

Previously, dodecanol (9), 1-tetracosanol (10), 1-hexacosanol (10-11), and 1-octacosanol (10) have been identified as constituents of *H. perforatum*. By gc-ms and co-chromatography with authentic *n*-alkanols, the present study showed that, based on the acetone extract, the content of long-chain alkanols was 4.3 g in 1 kg of dried plant material. The mixture of alkanols consisted of 1-tetracosanol (9.7%), 1-hexacosanol (27.4%), 1-octacosanol (39.4%), and 1-triacontanol (23.4%). The amount of 1-triacontanol is noteworthy because this constituent had not previously been identified in *H. perforatum*. The discrepancy between the former and the present investigations could possibly be explained by the development in gc-columns. The high-temperature fused silica column used in the present work would be expected to be better suited for compounds of low volatility.

EXPERIMENTAL

PLANT MATERIAL.—Dried leaf material of *H. perforatum* (*Herba hyperici*) was purchased from Norsk Medisinaldepot, Oslo. A voucher specimen is deposited at the Department of Pharmacy, University of Oslo.

EXTRACTION AND IDENTIFICATION.—Dried, powdered plant material (1 kg) was extracted with acetone (3 liters) in a Soxhlet apparatus for 3 h. The acetone extract was stored at $-10°$ for 24 h. The precipitate that appeared was collected by filtration and was washed with methanol until coloured material could no longer be removed. The remainder of the precipitate was fractioned on a silica gel column (120 g) and, on elution with benzene, a fraction (4.3 g) corresponding to saturated alkanols was obtained. This fraction was examined using gas chromatography with a Chrompack CP-Sil 5 column (25 m, id 0.22 mm) and gas chromatography in combination with mass spectroscopy. The identity of the *n*-1-alkanols was confirmed by observing no separation on co-chromatography with authentic *n*-1-alkanols.

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

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CONSTITUENTS OF *ANTENNARIA DIOICA*

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Antennaria dioica grows in the northeast region of Turkey (1) and is used for the ailments of bile, bronchitis, phythisis, and coughs (2,3). A chromatographic research is reported for *A. dioica* (4), and luteolin, luteolin 7-glucoside, and luteolin 4′-glucoside are recorded to be present in the plant (5). In this work, apigenin, apigenin 7-glucoside, apigenin 4′-glucoside, luteolin 7,4′-diglucoside, ursolic acid, and chlorogenic acid have been isolated from *A. dioica* for the first time.

EXPERIMENTAL

PLANT MATERIAL.—*Antennaria dioica* (L.) Gaertner (syn. *Gnaphalium dioicum* L.) was collected from Zigana Pass between Trabzon and Gümüşhane in June 1980 (voucher 44674) and identified by Prof. Dr. A. Baytop (Department of Pharmaceutical Botany, Faculty of Pharmacy, University of Istanbul).

EXTRACTION AND ISOLATION OF SUBSTANCES.—The dried and powdered herb (400 g) was worked up by standard procedures (6,7). The compounds obtained were apigenin (13 mg), luteolin (22 mg), a mixture of apigenin 7-glucoside and luteolin 7-glucoside (34 mg), apigenin 4′-glucoside (8 mg), luteolin 4′-glucoside (65 mg), luteolin 7,4′-diglucoside (11 mg), as well as ursolic acid (17 mg) and chlorogenic acid (6 mg). Caffeic acid was also obtained from the plant with preparative pc, and β-sitosterol and lupeol were identified chromatographically.

The substances were identified with authentic samples and spectral analysis. The glycosides were subjected to acid hydrolysis. Ursolic acid was identified by its melting point and ir spectra. Full details of the isolation and identification are available on request to the author.

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