

POLYOXYGENATED XANTHONES FROM *CENTAURIUM ERYTHRAEA* ROOTS

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*Centaureum erythraea* Rafn. (Gentianaceae) is a folk medicinal herb whose underground parts have not been previously investigated. We report here that the *n*-hexane extract of the roots contains six 1-hydroxy-3-methoxyxanthones identified by their spectral data and those of the acetylated derivatives. They are, in order of elution from the silica column, 1,8-dihydroxy-3,5-dimethoxyxanthone (methylbellidifolin) (1,4), 1,8-dihydroxy-3,5,6,7-tetramethoxyxanthone (8-desmethyleustomin) (1, 4-6), 1-hydroxy-3,5,6,7-tetramethoxyxanthone (6, 7), 1-hydroxy-3,5,6-trimethoxyxanthone (9), 1-hydroxy-3,7,8-trimethoxyxanthone (decussatin) (7), and 1-hydroxy-3,5,6,7,8-pentamethoxyxanthone (eustomin) (7). With the exception of methylbellidifolin and 8-desmethyleustomin, the other xanthones found in the roots of *C. erythraea* have not been previously reported from the aerial parts of this species (1-3).

When the xanthonic compositions of *C. erythraea* aerial parts and roots are compared, on the basis of the identified compounds, it is clearly shown that three oxygenated derivatives (tetra-, penta-, and hexa-oxygenation) were obtained from both aerial and underground parts, that hexa-oxygenated compounds are the most abundant in both, and that aerial parts generally contain more hydroxylated compounds than roots.

In the family Gentianaceae, the genus *Centaureum* (1-6) is characterized by xanthones with a single aromatic ring (1-OH, 3-OMe), by the absence of the usual trioxygenation in favor of a new oxidative step, hexa-oxygenation, previously found only in the genus *Eustoma* (7), and by the xanthone compound 8-desmethyleustomin, only found previously in *Centaureum cacahanlabuen* (4), *C. erythraea* (1-3), and *Centaureum linarifolium* (5,6).

## EXPERIMENTAL

PLANT MATERIAL.—*C. erythraea* was collected in July 1983, in Macedonia, Greece; a voucher specimen is deposited at Laboratoire de Pharmacognosie de Grenoble, Domaine de La Merci, F-38700 La Tronche.

EXTRACTION AND ISOLATION OF XANTHONES.—Air-dried, powdered roots of *C. erythraea* (130 g) were extracted at room temperature with *n*-hexane (4 × 500 ml). The extract (0.61 g) was separated by column chromatography (SiO<sub>2</sub>), affording four fractions eluted by a gradient from C<sub>6</sub>H<sub>6</sub> up to CHCl<sub>3</sub>. Repeated SiO<sub>2</sub> cc of fraction 1 gave methylbellidifolin (5 mg); fraction 2, also purified by the same procedure, yielded 8-desmethyleustomin (12 mg), while fraction 3 afforded 1-hydroxy-3,5,6,7-tetramethoxyxanthone (10 mg), 1-hydroxy-3,5,6-trimethoxyxanthone (3.5 mg), and fraction 4 gave decussatin (3.5 mg), and eustomin (25 mg) by preparative tlc on silica gel F-254 with several developments in *n*-hexane-CHCl<sub>3</sub> (60:40).

Acetylation was performed with C<sub>5</sub>H<sub>5</sub>N and Ac<sub>2</sub>O in the usual way, with purification by chromatography on SiO<sub>2</sub>.

Identification of the isolated xanthones was made from their spectral data (uv, ir, ms, <sup>1</sup>H nmr) and those of their acetylated derivatives, in comparison with published data (1), (4-10). Details are available from the senior author.

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