

COUMARINS OF THE ROOTS OF ANGELICA SAXATILIS

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In the roots and stem roots of Angelica saxatilis Turcz. collected in the Khabarovsk territory in the surroundings of a mixture of the village of Ayan there is 1.09% of lactones altogether, consisting of a mixture of six compounds with  $R_f$  0.92, 0.89, 0.82, 0.59, 0.15, and 0.03 [hexane-benzene-methanol (5:4:1) system; Leningrad type "B" paper previously impregnated with a 10% solution of formamide in methanol].

By the chromatographic separation of a methanolic extract of the roots on a column of acidic alumina we have isolated the lactones  $C_{16}H_{14}O_4$ , mp 108-109° C,  $R_f$  0.92, yield 0.1% (A);  $C_{16}H_{14}O_4$ , mp 101-102° C,  $R_f$  0.89, yield 0.23% (B);  $C_{12}H_8O_4$ , mp 188-190° C,  $R_f$  0.82, yield 0.017% (C);  $C_{11}H_6O_4$ , mp 245-247° C,  $R_f$  0.1 (D); and  $C_{16}H_{16}O_6$ , mp 129-130° C,  $[\alpha]_D^{21} + 24^\circ$  (c 0.94; acetone),  $R_f$  0.03, yield 0.08% (E).

On the basis of their physicochemical constants, IR spectra, and the absence of a depression of the melting point in mixtures with authentic samples, the lactones A, B, C, D, and E have been identified as isoimperatorin, imperatorin, bergapten, xanthotoxol, and (+)-oxypeucedanin hydrate, respectively.

Paper chromatography shows that xanthotoxol is not present in the plant and is probably formed as the result of the decomposition of the imperatorin on the alumina.

In addition to the coumarins mentioned,  $\beta$ -sitosterol,  $C_{29}H_{50}O$ , mp 138-140° C, yield 0.05%, identified by its IR spectrum and a mixed melting point, was isolated as an accompanying substance.

(+)-Oxypeucedanin hydrate has been isolated previously from the closely related species A. gmelinii (DC.) M. Pimen. [1], and isoimperatorin and imperatorin from species of the Angelica section A. sylvestris L. [2] and A. genuflexa Nutt. [3]. Thus a study of the chemical composition of the roots confirms the chemosystematic characteristics found previously in an investigation of the coumarins of the fruit of A. saxatilis [4], a species occupying an intermediate position between the sections Coelopleurum and Angelica.

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HERNIARIN FROM ARTEMISIA DIFFUSA

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It is known [1] that the flower heads of Artemisia diffusa contain a large amount (3.8%) of santonin. We have studied this species of wormwood, collected in the northern part of the Golodnaya steppe (UzSSR), in the early vegetation periods. We found no  $\alpha$ - or  $\beta$ -santonin or other  $\gamma$ -lactones either in the epigeal part of the early crop (April) or in the flower heads in the beginning of September.

From the epigeal part of this wormwood collected in May, extraction with hot water and subsequent chromatography of the neutral fraction of the extract on a column of alumina yielded a crystalline substance  $C_{10}H_8O_3$  with mp 117° C (from ether) with the characteristic properties of coumarin compounds—it fluoresced lilac in UV radiation and was shown up by diazotized sulfanilic acid. IR spectrum,  $cm^{-1}$ : 1715 (C=O of a coumarin), 1610, 1505 (aromatic double bonds).

When the substance was heated with hydriodic acid, a methyl group was split off and the compound  $C_9H_6O_3$  was formed, which was identified as umbelliferone. The action of diazomethane on umbelliferone yielded the initial coumarin compound. Consequently, the substance isolated from *Artemisia diffusa* is the methyl ether of umbelliferone, i. e., herniarin [2]; this is the first time that it has been obtained from this plant.

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#### COUMARINS AND ACIDS OF THE FRUIT OF *ANETHUM GRAVEOLENS*

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The fruit of *A. graveolens* (common dill) is a source of the composite preparation Anethine, which is used for the treatment of chronic coronary insufficiency, for the prophylaxis of attacks of angina pectoris, and in spastic states of the musculature of the organs of the peritoneal cavity [1]. Information on the chemical composition of the fruit of the dill is fairly limited and relates mainly to a study of the composition of the essential oils. Only recently has a paper appeared on the presence in the fruit of coumarin derivatives—bergapten, umbelliprenin [2], scopoletin, and a new compound of this series—8,8-dimethyl-6,7-dihydro-2H,8H-benzof[1,2-b;5,4-b']dipyran-2,6-dione [3].

By paper chromatography in several systems of solvents, we detected in an ethanolic (60°) extract no less than 14 coumarin derivatives. On the basis of color reactions, the paper chromatography of mixtures with known substances, and UV spectroscopy, five of them were identified as bergapten, umbelliprenin, scopoletin, esculentin, and umbelliferone. This is the first time that the last two compounds have been found in dill. By chromatography on polyamide we isolated a substance which has been assigned preliminarily to the hydroxycoumarin derivatives (mp 276–277° C; UV spectrum  $\lambda_{max}$ , m $\mu$ : 243, 330, 345; IR spectrum,  $cm^{-1}$ : 1730, 1610, 1570, 3090, 3210).

In addition to coumarin derivatives, phenolcarboxylic acids have been detected in the fruit of the dill. The acids were isolated by preparative paper chromatography (2% acetic acid) from the fraction obtained in the following way: an aqueous extract of the evaporated ethanolic extract was treated with ethyl acetate, the phenolic acids were extracted from the ethereal phase with half-saturated aqueous sodium carbonate solution, and the extract was acidified with sulfuric acid to pH 3 and treated with ethyl acetate. The ethyl acetate extract yielded caffeic, ferulic, and chlorogenic acids.

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