

COUMARINS FROM THE FRUIT OF PRANGOS FERULACEA

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We have previously reported [1-5] the isolation of a number of coumarin derivatives from the roots of Prangos ferulacea (L.) Lindl. (family Umbelliferae) collected in the Bichenak mountains of the Nakhichevan Autonomous Soviet Socialist Republic.

According to chromatography on paper treated with a 20% aqueous solution of ethylene glycol (mobile phase petroleum ether) [6] and in a thin layer of alumina [ethyl acetate-benzene (1 : 6) and (1 : 2) systems;  $Al_2O_3$  of activity grade II], the fruit of the plant studied contains nine substances of a coumarin nature, of which two—a compound  $C_{15}H_{12}O_3$  (I) with mp 82.5° C and a compound  $C_{15}H_{14}O_4$  (II) with mp 108° C—were identified with osthol and isoimperatorin, respectively.

Substance (III),  $C_{16}H_{14}O_5$ , with mp 115-117° C, from its IR spectrum and its  $R_f$  value, corresponds to the known furocoumarin oxypeucedanin, which we have previously isolated from the roots of Prangos ferulacea [1, 3, 4].

When III was isomerized in 20% sulfuric acid, an isomer of oxypeucedanin  $C_{16}H_{16}O_5$  (IV) with mp 146° C (from ethanol) was obtained. A mixture of isomerized III with an authentic sample of isomerized oxypeucedanin likewise gave no depression of the melting point. Nevertheless, the melting point of III did not correspond to any of the known forms of oxypeucedanin. Since the dextrorotatory form of oxypeucedanin (Prangolarin), which has been isolated from the roots of Prangos pabularia (L.) Lindl., has mp 104-105° C,  $[\alpha]_D^{20} +20.1^\circ$  (chloroform) [7], and the optically inactive form (racemate) has mp 141-142° C [1], substance III is obviously the levorotatory form of oxypeucedanin. Substance III was isolated in very small amount.

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FLAVONOIDS OF POLYGONUM PERSICARIA

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We give the results of a study of the flavonoids of the leaves of Polygonum persicaria L. (spotted ladysthumb) collected in the botanical garden of the Academy of Sciences of the Kazakh SSR in May, 1966.

The flavonoids were separated by chromatography of a methanolic extract on a column containing Kapron and by preparative paper chromatography.

Repeated recrystallization from aqueous ethanol gave quercetin, isoquercitrin, and hyperoside.

The substances obtained were identified on the basis of alkaline cleavage, acid and enzymatic hydrolysis, reduction with magnesium in concentrated hydrochloric acid, molecular rotation, and IR spectra, and also by comparing the products of these processes with reference samples in paper chromatography in various systems of solvents [1, 2].

The location of the hydroxy groups in the flavonoids was confirmed by measuring their absorption spectra with complex-forming and ionizing additives [3, 4].

The flavonoids were determined quantitatively by the spectrophotometric method from the maximum density of the spots directly on the chromatograms after staining with aluminum chloride. The measurements were carried out on a SF-4A spectrophotometer.

Found, %: quercetin 0.05, isoquercitrin 0.11, and hyperoside 0.03.

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#### OXYGEN-CONTAINING FRACTIONS OF THE ESSENTIAL OIL OF LIBANOTIS TRANSCAUCASICA. II

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We have continued our investigation [1] of the essential oils of Libanotis transcaucasica Schischk collected at various growth sites.

The essential oil of the fruit of this plant growing in the South Ossetin Autonomous Region (constants of the oil  $[\alpha]_D^{20} +2.6^\circ$ ,  $n_D^{20}$  1.4860,  $d_4^{20}$  0.8940, ester No. 36.0) [2], after saponification and elimination of the low-boiling fraction and the sesquiterpene hydrocarbons, was subjected to chromatography on  $Al_2O_3$  (activity grade III). By repeated chromatography, three compounds were isolated. The first of them, isolated in small amount, consisted of an aldehyde ( $[\alpha]_D^{20} -20.0^\circ$ ,  $n_D^{20}$  1.4890) the IR spectrum of which had a frequency at  $1728\text{ cm}^{-1}$ . The second compound was acorenone ( $[\alpha]_D^{20} -18.0^\circ$ ,  $n_D^{20}$  1.5040,  $d_4^{20}$  0.9568. Its 2,4-dinitrophenylhydrazone was prepared (mp  $149^\circ\text{C}$  from ethanol). The third compound amounted to about 50% of the oxygen-containing fraction of the essential oil. Its constants were: bp  $134^\circ\text{C}/3\text{mm}$ ,  $[\alpha]_D^{20} +53.0^\circ$ ,  $n_D^{20}$  0.9232, IR spectrum identical with that of bisabolol. The essential oil from the fruit of Libanotis collected in the foothills of the Elbrus had constants extremely similar to those of the oil mentioned above ( $[\alpha]_D^{20} 0^\circ$ ,  $n_D^{20}$  1.5540,  $d_4^{20}$  1.0764).

After similar treatment, from the oxygen-containing fraction of the essential oil we isolated isoelemicin (picrate, mp  $68^\circ\text{C}$ , from ethanol), which amounted to about 40% of this fraction.

The isoelemicin found in the ethereal oil after its saponification with ethanolic alkali is apparently a product of secondary origin, i.e., it is formed as a result of the isomerization of elemicin [1].

The oxygen-containing fraction also includes two sesquiterpene alcohols; farnesol and bisabolol, the presence of which was shown on the basis of their characteristic constants and IR spectra.

The essential oil from the fruit of Libanotis collected in the Stavropol region (village of Kardonikskaya) contained farnesol, bisabolol, acorenone, elemicin, and 3,4,5-trimethoxybenzaldehyde. The presence of these compounds was shown by the same methods of investigation as in the preceding case.

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