A CHEMICAL STUDY OF PEUCEDANUM LITORALE

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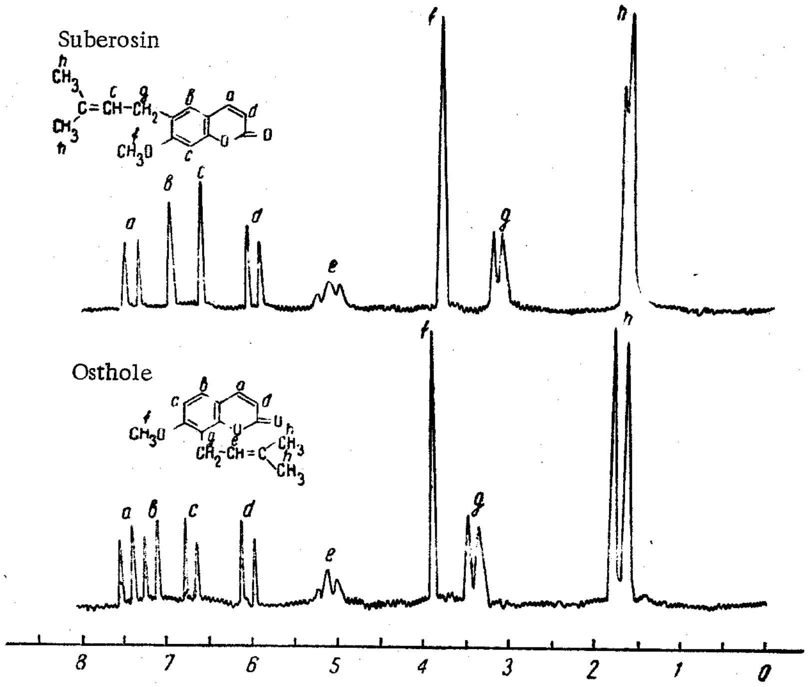
Pseucedanum litorale Worosch. et Gorovoi [1] collected in the extreme south of Primor'e (Cape Butakova) contains 0.55% of lactones consisting, according to the results of paper chromatography, of a mixture of four substances.

By subjecting a methanolic extract to chromatographic separation on a column of alumina (activity grade II; 90 × 6.5 cm), three individual substances have been isolated.

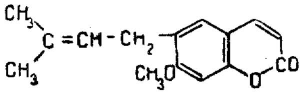
Elution of the column with benzene gave a crystalline substance $C_{15}H_{16}O_3$ with mp 87°–89° C (yield 0.05%) containing a methoxy and a $C-CH_3$ group. UV spectrum: λ_{max} 224, 255 and 330 mμ (log ε 4.32, 3.67, 4.22); IR spectrum: ν_{max} 1735, 1620, 1565, 1385, 1365 cm^{-1}. These results indicated a coumarin.

The NMR spectrum of the coumarin (figure) has doublets *a* (δ = 7.37, J = 10 Hz) and d (δ = 5.95, J = 10 Hz) due to protons in positions 4 and 3 of a coumarin nucleus [2]. The singlets b (δ = 6.93) and c (δ = 6.56) relate to the 5- and 8-protons. Thus, this lactone is a 6,7-disubstituted coumarin. The nature of the substituents in the molecule were also determined from the NMR spectrum. Singlet f (δ = 3.78) is characteristic for an aromatic methoxy group. The triplet e (δ = 5.09, J = 6.5 Hz) and the doublet g (δ = 3.14, J = 6.5 Hz) show that the molecule of the lactone contains a $CH-CH_2-$ grouping. The signals with δ = 1.70 and δ = 1.62 may be assigned to two methyl groups located at a double bond.



NMR spectra of suberosin and osthole.

The combination of these results permits the conclusion that the substituents in the lactone molecule are OCH_3 and $-CH_2-CH=C(CH_3)_2$ groups. Consequently, this substance is a structural isomer of osthole, which was confirmed also by comparing the NMR spectra of the coumarin isolated and that of osthole (cf. figure). The spectra of the two lactones differ only in the region of the aromatic protons, which shows that they differ only by the position of the substituents and, in fact, while in osthole the substituents are located in the 7, 8-positions, in the lactone isolated they are the 6, 7-positions. On the basis of biogenetic considerations (all natural coumarins are derivatives of 7-hydroxycoumarin) it may be assumed that the methoxy group is in position 7. Then the structural formula of the lactone must be as follows:



Suberosin

The lactone must be identical with suberosin, which is present in tropical species of Zanthoxylum (family Rutaceae) [3, 4].

The occurrence of suberosin in plants of the genus Peucedanum arouses great interest; it may be considered as one of the precursors in the biosynthesis of peucedanin and deltoin, which are found in some species of hogfennel [5-8].

Elution with a mixture of benzene and methanol (9:1) gave a hydroxycoumarin with the composition $C_9H_6O_4$, mp 227°-229° C, which was identified as umbelliferone; elution with a mixture of benzene and methanol gave β-sitosterol.

We established the presence of a glycoside whose hydrolysis gave 7-hydroxycoumarin in the water-soluble fraction

The microanalyses of the substances isolated were carried out by E. A. Nikonova, and the NMR spectra were taker by G. Yu. Pek.

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THE COUMARINS OF THE ROOTS OF HERACLEUM CYCLOCARPUM

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Sphondin, xanthotoxin, isopimpinellin, pimpinellin, bergapten, isobergapten, and angelicin have previously been isolated from certain species of Heracleum growing in the territory of the Soviet Union [1]. The study of the seeds of fourteen species of Heracleum [2] has shown that all these species contain substances of coumarinic nature.

The present paper gives information on the coumarinic composition of the endemic species Heracleum cyclocarpum C. Koch., collected in the Caucasus, which has not been investigated previously.

The coumarins were extracted from 0.85 kg of the comminuted roots with 96% alcohol, the solvent was distilled off, and the residue was dissolved in benzene and purified by passage through a layer of alumina. The evaporated filtrate was transferred to a column of alumina (65 × 5 cm) and eluted with diethyl ether. The separation of the coumarin on the column was followed in UV light. This process gave six substances: sphondin, isopimpinellin, bergapten, isobergapten, pimpinellin, and osthole.

Osthole has been isolated from the genus Heracleum for the first time. To identify this substance it was demethylated to give ostenol [7-hydroxy-8-(γ, γ-dimethylallyl) coumarin] with mp 123°-124° C of composition $C_{14}H_{14}O_3$.

Paper chromatography of the total coumarins of the roots of Heracleum cyclocarpum showed the presence of xanthotoxin and angelicin.