

that it has been found in nature. The IR and PMR spectra of (I) and of a known sample coincide completely which shows their identity.

The IR spectra were taken on a UR-20 spectrometer (in paraffin oil), the PMR spectra on a Varian HA-100 spectrometer, and the mass spectra on a Hewlett-Packard chromatomass spectrometer. The melting points were determined on a Kofler block.

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PHOTOREACTION OF OSTHOLE

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Thanks to their specific structural features [1], derivatives of 5,6-benzo- α -pyrone (coumarins and furocoumarins) undergo various chemical transformations under the action of sunlight [2]. Coumarins may dimerize [3], oxidize, isomerize, etc. [4, 5]. The action of light on the furocoumarin peucedanin leads to chemical changes going as far as the cleavage of the furan ring [6]. In a study of the photolysis of dihydropyrancoumarins definite laws of the dependence of this reaction on the structure of the substituent in position 4' of the pyran ring have been found [7].

Some workers consider that the biosynthesis of 7-methoxycoumarin (herniarin) is catalyzed by light [8]. Italian workers explain the biological action of the furocoumarins xanthotoxin and bergapten by the photoreaction of these compounds with natural DNA [9]. We have shown experimentally that 8-isopentyl-7-methoxycoumarin (osthole) undergoes a photoreaction in just the same way as 6-isopentyl-7-methoxycoumarin (suberosin).

We left chloroform solutions of osthole in quartz and ordinary glass vessels for 4, 6, 16, and 26 h. An experiment with a solution of suberosin was performed in parallel. The reaction was monitored by thin-layer chromatography (TLC) on Silufol plates (solvent: chloroform) and by gas-liquid chromatograph (GLC). After only 4 h, the color of the solution of osthole changed to faint crimson. After 6-16 h the color deepened and it then changed to yellow. TLC showed the appearance, first, of three fluorescing spots and towards the end of the experiment (after 26 h) of six spots together with unchanged osthole. Three reaction products were identified by TLC with authentic samples; merancin, isomerancin, and merancin hydrate, i.e., epoxy, oxo, and dihydroxy derivatives of osthole.

The IR spectrum of the products of the photoreaction of osthole showed new absorption bands and, in particular, the band of OH groups at $3460-3510\text{ cm}^{-1}$. On a gas chromatogram (Fig. 1), it can clearly be seen that, in addition to the osthole remaining unchanged at the end of the experiment (peak 1), new peaks (2-7) appeared. Peaks 3, 4, and 5 correspond on the chromatogram to merancin, isomerancin, and merancin hydrate.

The preliminary results that we have obtained on the action of light on osthole show that the photoreaction takes place with differently substituted coumarin derivatives. Naturally, the reaction took place more intensively both with osthole and with suberosin in the quartz glass vessels.

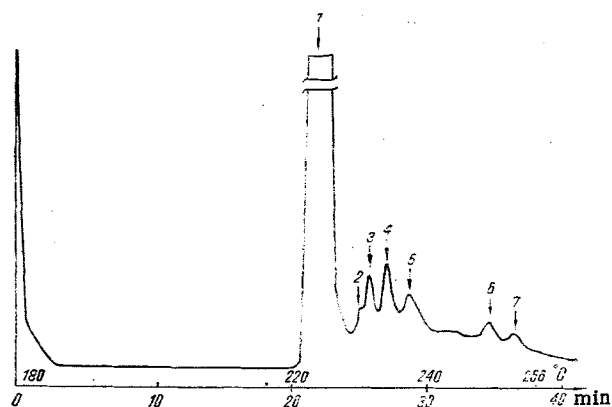


Fig. 1. Chromatogram of the products of the photo-reaction of osthole: 1) osthole; 2) unidentified compound; 3-5) merancin + isomerancin + merancin hydrate; 6, 7) unidentified compounds. GLC was carried out on a column 1.5 m long with OV-17 (3%) as the stationary phase and Chromosorb W (70-80 mesh) as the support; the temperature was programmed at 2 deg/min from 180 to 256°C. The rate of flow of the carrier gas, argon, was 30 ml/min.

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