INFLUENCE OF LIGHT ON COUMARINS OF THE KHELLACTONE GROUP

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Recently, there have been many reports of the interaction of light and coumarins, and also reports on the structure of the products formed in this interaction – photodimers, derivatives of coumaric acid, etc. [1, 2].

The present paper gives the results of investigations of the influence of light on some acylated dihydropyranocoumarins of the khellactone group.

In 1970, free cis and trans khellactones were isolated from the herb Seseli tenuisectum [3]. On studying the same species, we found that these hydroxycoumarins are present in the bound state in the form of esters. We isolated and identified the diangelic ester (anomalin) [4], 4-angeloyloxy-3-isovaleryloxydihydroseselin, and the 3'- and 4'-monoangelates of khellactone [5].

The considerable degree of contradiction in the information on the compositions of the coumarins that we found and of those isolated by other authors could not be a consequence of ecological or genetic factors, since in both cases plants growing in one region and collected in the same vegetation period were investigated. This circumstance impelled us to make a more detailed study of the cause of these divergences.

When ethanolic extracts obtained from the herb freshly dried in the shade were chromatographed on paper, it was found that they contained components with high R_f values corresponding to acyl derivatives of khellactone.

After the prolonged drying of the raw material in the sun, we were unable to find these components in its composition but we detected substances remaining at the start on chromatography. This difference in the qualitative composition of the coumarins forced us to turn our attention to the conditions of drying the raw material and, in particular, to the action of UV radiation. We irradiated six individual coumarins of the khellactone group and an ethanolic extract of the plant with UV rays (mercury lamp and sunlight). The substances were irradiated in a film for 36 h, samples being taken every 4 h which were evaluated by thin-layer chromatography. In addition, the R_f values of the individual spots were determined and their intensities were estimated roughly (Table 1).

The figures in the table show that the irradiation of the pyranocoumarins with UV light causes destructive changes in them accompanied by the formation of components with lower R_f values. By eluting these products from chromatograms and recording their UV spectra, it was found that the positions of their maxima had remained unchanged. Consequently, the chromophoric groups of the substances studied, unlike those of the furocoumarins and simple coumarins [1], undergo no change under the given conditions, and degradation takes place at the expense of the substituents at C_7 and C_8. The pyranocoumarins considered differ in relation to their stability to the action of light, and therefore their stability is determined by the nature and positions of the substituents.

In order to determine the structure of the substances formed and the nature of the changes taking place, we separated the products of the photolysis of anomalin by thin-layer chromatography. Elution with methanol gave the components with R_f 0.60 and 0.02. The first substance, with M^+ 344, which was formed

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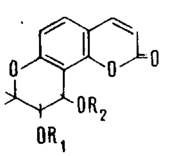
TABLE 1. R_f* Values of the Samples Investigated after Irradiation



Time of irradiation, h	Pteryxin, $R_1 = CO-CH_3$, R_2 = angeloyl			R_1 = angeloyl, $R_2 = OH$		$R_1 = OH$, R_2 = angeloyl		Anomalin, $R_1 = R_2$ = angeloyl			Vishadin, R_1 = α-Me-butyryl, $R_2 = CO-CH_3$			Dihydrosamidin, R_1 = isovaleryl, $R_2 = CO-CH_3$		
0,0	0,60‴			0,60‴		0,58‴		0,70‴			0,60‴			0,60‴		
4	0,60″	0,40′		0,60‴		0,58″	0,02′	0,70″	0,60′		0,60″	0,30′		0,60‴		
8	0,60′	0,40′	0,02′	0,60″	0,02′	Tr.	0,02″	0,70″	0,60′		0,60″	0,30′	0,02′	0,60″	0,30′	
16	Tr.	—	0,02‴	0,60′	0,02″	—	0,02‴	0,70′	0,60′	0,02′	0,60′	0,30′	0,02″	0,60′	0,30″	0,02′
24	—	—	0,02‴	—	0,02‴			Tr.	Tr.	0,02″	Tr.	—	0,02″	0,60′	0,30′	0,02″
30								—	—	0,02‴			0,02‴	Tr.		0,02‴
36														Tr.	—	0,02‴

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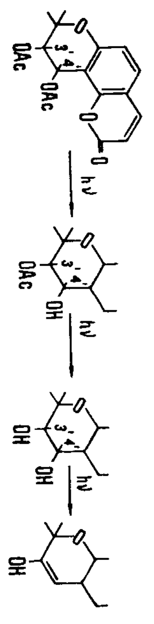
* The estimated intensities are given on a three-point scale: ‴) considerable amount, ″) moderate amount, ′) small but appreciable amount. Tr.) present in the form of traces; —) absent.

after irradiation for 4 h, proved to be identical, according to its IR spectrum, with khellactone monoangelate, which we have previously isolated as a natural product from Seseli tenuisectum [4, 5]. In the mass spectrum of the second product, formed on more prolonged irradiation (16 h) there were the peaks of two molecular ions with M^+ 262 and 244, which showed the presence in this fraction of two substances, which were then separated by thin-layer chromatography on silica gel. Two compounds were obtained with R_f 0.2, M^+ 262, and R_f 0.05, M^+ 244. From the nature of its fragmentation in the mass spectrum the first compound corresponded to khellactone, the fragmentation of which has been described previously [8], and the second to 3'-hydroxyseselin. This means that when anomalin is irradiated with UV light changes take place according to the following scheme: the splitting off of the acyl residue at C_4' and then the one at C_3' with the subsequent dehydration of the diol so formed and the formation of 3'-hydroxyseselin.



Thus, the nature of the changes taking place on the irradiation of the pyranocoumarins recalls their fragmentation under the influence of electron impact in mass spectrometry, in particular the splitting off of the acid residues from the C_4' position.

The results of chromatographic analysis showed that similar changes are observed on the UV irradiation of other pyranocoumarins. Some difference is observed only in the rates of the reactions taking place. Among the monoesters of khellactone, the 4'-monoangelate is cleaved faster than its 3' isomer. Among the diesters, pteryxin and anomalin, which are characterized by the presence of a voluminous substituent at C_4', are the most sensitive, and dihydrosamidin, containing an acetyl group at C_4', is the most stable. An increase in the length of the chain of carbon atoms in the acyl residue at C_4' of khellactone possibly decreases the stability of these substances to UV light.

When plant extracts and raw material are irradiated the same changes take place as in the pure substances. The presence of chlorophyll somewhat retards this process, and in natural solar radiation a greater effect is shown than on irradiation with a quartz mercury lamp.

EXPERIMENTAL

The UV spectra were taken on a Hitachi instrument (in ethanol), the IR spectra on a UR-20 spectrophotometer (KBr), and the mass spectra on an MKh-1303 mass spectrometer. The source of UV light was a "Medicor Q-250" quartz mercury lamp with a power of 500 W and sunlight

(June, July). The materials studied were six khellactone derivatives, including three isolated from the plant mentioned.

About 0.1 g of the coumarin under investigation was dissolved in 5 ml of methanol and the solution was evaporated in the open air in a Petri dish (d=9 cm). The dishes with the films of substances formed were arranged 40 cm from the lamp (perpendicular luminous flux) or in natural daylight. Every 4 h, samples of the substances were chromatographed on "Silufol" plates in the ether–petroleum ether (3 : 1) system and on paper impregnated with a 10% solution of formalin in methanol in the hexane–benzene–methanol (5 : 4 : 1) system.

The spots were revealed by the treatment of the chromatograms with a 10% solution of caustic soda in methanol followed by heating to 105°C for 1 min and spraying with a solution of diazotized sulfanilamide [7]. For the preparative isolation of the substances we used chromatography in a thin nonfixed layer of KSK silica gel with benzene–methanol (8 : 2) as the stationary phase, the spots being detected by their fluorescence in UV light. The separated adsorbent with the appropriate substance was transferred to a flask and covered with methanol; the mixture was heated in the water bath for 5 min. The eluate was filtered and the filtrate was evaporated to dryness. The chromatographically homogeneous residue was investigated by UV, IR, and mass spectra.

SUMMARY

The results of experiments on the UV irradiation of six coumarins and the study of the products formed have shown that acylated derivatives of khellactone undergo photolysis with the successive splitting out of acyl residues at C_4', and then at C_3', followed by the dehydration of the resulting diol and the formation of 3'-hydroxyseselin. The hypothesis has been put forward that dihydrocoumarins containing a more voluminous substituent in the 4' position are the most sensitive to light.

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