The differences found are possibly due to the variety of characteristics of the plant. For the N-acyllyso-PEs the structure of 2-acylglycerophosphoryl-N-acylethanolamines has been established.

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THE TRANSFORMATION PRODUCTS OF SOME NATURAL COUMARINS

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The natural coumarins osthole (I) and oxypeucedanin hydrate (II) are the main components of the species of the genus *Prangos* and possess a high hypotensive activity [1, 2]. Consequently, a chemical and pharmacological study of these compounds and also of their analogs is of great interest for practical medicine. The present paper gives the results of a study of new transformation products of (I) and (II) and of decursinol (III).

We have established that when (I) reacts with a mixture of concentrated acetic and hydrochloric acids at room temperature, the main products are two substances: (IV), $C_{15}H_{17}O_3Cl$, mp 89-91°C, M^+ 280; and (V) $C_{15}H_{16}O_4$, mp 69-70°C, M^+ 262.

On the basis of a study of IR, PMR, and mass spectra it has been shown that (IV) is 8-(3'-chloroisopentyl)-7-methoxycoumarin, and (V) is 8-(3'-hydroxyisopentyl)-7-methoxycoumarin. Consequently, under the reaction conditions hydrogen chloride adds to the double bond in the side chain of (I) in accordance with Markownikoff's rule [3]. On reaction with ethanol, compound (IV) formed the ethoxy derivative (VI), $C_{17}H_{22}O_4$, M^+ 290, and on acetylation with acetic anhydride in the presence of pyridine, (V) gave the acetate (VII), $C_{17}H_{20}O_5$, mp 61-62°C, M^+ 304.

We have shown previously [4] that when (II) is treated with 20% sulfuric acid in ethanol, in addition to other coumarin derivatives a new compound is formed, namely: the ethyl ether of (II). It was later shown that the reaction of (II) with acetone in an acid medium forms an acetonide (VIII) with the composition $C_{19}H_{20}O_6$, mp 161-163°C, M^+ 344, and the dehydration of (II) with thionyl chloride gives its 2",3"-sulfinyldioxy derivative (IX) ($C_{16}H_{14}O_7S$, mp 181-183°C, M^+ 350), isoimperatorin (X), and gosferol (XI). Details of the PMR spectra of some of the compounds investigated are given in Table 1.

Decursinol (III) is one of the components of the roots of *Seseli grandivittatum* and contains one secondary hydroxy group in position 3', which was confirmed by the production of the monoacetate [5]. Likewise, on dehydration with 20% H_2SO_4, compound (III) gives xanthyletin. However, the oxidation of (III) with chromium trixoide in acetic acid and in acetone took place in an unusual fashion, and instead of the expected ketone (XII) the dicarboxylic acid (XIII), $C_{14}H_{12}O_7$, mp 225-227°C, M^+ 292, and substance (XIV), with mp 205-207, M^+ 304, were formed. The PMR spectrum of (XIII) taken in dimethyl sulfoxide showed signals with chemical shifts of 6.31 and 7.98 ppm (d, J = 10 Hz, 1H each) and of 8.02 and 6.65 ppm (s, 1H each) due to the protons in positions 3, 4, 5, and 8 of the coumarin nucleus, respectively. A

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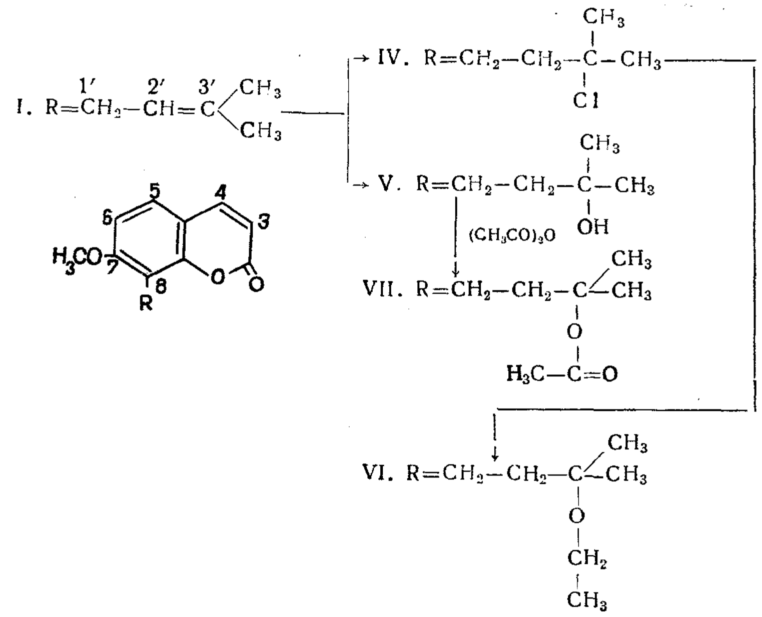
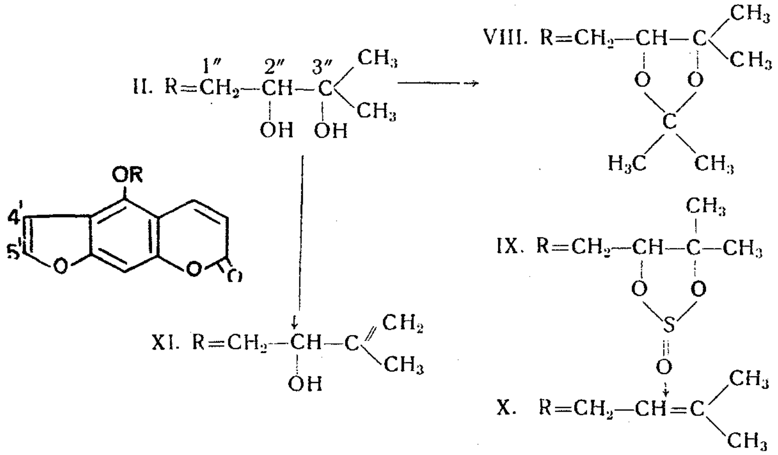
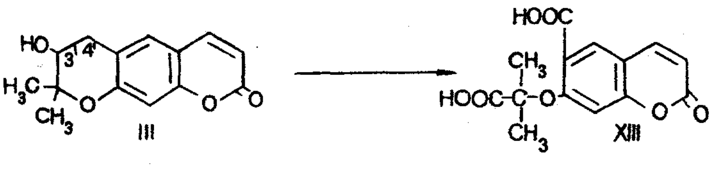
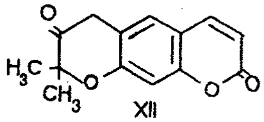




six-proton singlet at 1.60 ppm is due to the protons of the two methyl groups. The detection of the signals from the latter and from the H_5 proton in a weaker field than usual is connected with the presence adjacent to them of carboxy groups the signals of which do not appear in the spectrum because of exchange reactions. The structure of (XIV) has not yet been determined.





EXPERIMENTAL

The PMR spectra were taken on a Brüker HX-90 instrument, and the mass spectra on a Hewlett-Packard 5980 A chromatomass spectrometer. The melting points were determined on a Kofler block. The elementary analyses of all the compounds corresponded to the calculated figures.

TABLE 1. Details of the PMR Spectra of the Compounds Investigated in $CDCl_3$, δ, ppm (multiplicity, J, Hz)

Compound	Assignment											
	$H_{3,4}$	$H_{5,6}$	H_8	$H_{4',5'}$	$H_{1',2'}$	$H_{1'',2''}$	OCH_3	OH	$C\langle^{CH_3}_{CH_3}$	$OCOCH_3$	$-\underset{\vert}{C}\langle^{CH_3}_{CH_3}$	$O-CH_2-CH_3$
I	6,27; 7,60 (d, 10)	7,40; 6,89 (d, 8,5)			3,47 (d, 8), 5,14 (m)		3,94 (s)		1,60; 1,78 (s)			
II	6,14; 8,23 (d, 10)		6, 92 (s)	7,08; 7,64 (d, 2,5)		3,70 4,70 (m)		2,44 (s)			1,24; 1,29 (s)	
IV	6,14; 7,52 (d, 10)	7,22; 6,74 (d, 9,5)			2,96; 1,88 (m)		3,84 (s)				1,62 (s)	
V	6,03; 7,50 (d, 10)	7,17; 6,70 (d, 9,0)			2,96; 1,62 (m)		3,79 (s)	2,73 (s)			1,26 (s)	
VI	6, 19; 7,65 (d, 10)	7,42; 6,80 (d, 9,5)			2,81; 1,74 (m)		3,89 (s)				1,20 (s)	3,42 (q, 6; 10) 1,08 (t, 6)
VII	6,13; 7,56 (d, 10)	7,22; 6,76 (d, 9,5)			2,85; 2,05 (m)		3,89 (s)			1,85 (s)	1,40 (s)	
VIII	6,20; 8,05 (d, 10)		7,05 (s)	6,93 7,53 (d, 2,5)		4,20 – 4,65 (m)					1,22; 1,42; 1,49 (s)	
IX	6,27; 8,05 (d, 10)		7,05 (s)	6,87; 7,60 (d, 2,5)		4,75 (d, 6) 5,05 (t, 6)					1,36; 1,76 (s)	

Reaction of Osthole (I) with a Mixture of Acids. With stirring, 40 ml of concentrated hydrochloric acid was added to a solution of 3.5 g of natural (I) in 15 ml of glacial acetic acid. This led to a precipitate consisting of two substances which was filtered off and chromatographed on a column (3.0 × 50 cm) of alumina (300 g, activity grade II). Elution was performed with petroleum ether (fractions 1-15) and with petroleum ether—chloroform (2:1) (fractions 16-25), 50-ml fractions being collected. After evaporation of the solvent and recrystallization from petroleum ether—chloroform (1:1), fractions 3-14 yielded 1.8 g of 8-(3'-chloroisopentyl)-7-methoxycoumarin (IV), $C_{15}H_{17}O_3Cl$, mp 89-91°C, M^+ 280, and from the subsequent fractions (fractions 18-25), when they were concentrated by evaporation, crystals of 8-(3'-hydroxyisopentyl)-7-methoxycoumarin (V), $C_{15}H_{16}O_4$, mp 69-70° (from benzene), M^+ 262, deposited (0.95 g).

Reaction of (IV) with Ethanol. A solution of 0.5 g of (IV) in 30 ml of ethanol was heated at 100-105°C under reflux for 4 h. After the ethanol had been distilled off and the reaction mixture had been subjected to preparative separation in a thin layer of alumina (Al_2O_3, activity grade II, $CHCl_3$), 0.31 g of a liquid substance (VI) with the composition $C_{17}H_{22}O_4$, M^+ 290, was obtained.

Acetylation of (V). Compound (V) (0.27 g) was acetylated with acetic anhydride (15 ml) in the presence of pyridine (1.5 ml) at 90-100°C for 6 h. Then the reaction mixture was diluted with water, and the reaction product was extracted with chloroform (3 × 30 ml). After the solvent had been distilled off, the reaction mixture was separated preparatively under the conditions described above [see (VI)]. This gave 0.25 g of the acetyl derivative (VII) $C_{17}H_{20}O_5$, mp 61-62°C (from petroleum ether). M^+ 304.

Reaction of (II) with Acetone. A solution of 2.0 g of (II) in 30 ml of acetone was treated with 0.5 ml of concentrated sulfuric acid and the mixture was left for a day. After the acetone had been distilled off and the residue had been recrystallized from ethanol, 1.25 g of the acetonide (VII) was obtained, $C_{19}H_{20}O_6$, mp 161-163°C, M^+ 344.

Dehydration of Oxypeucedanin Hydrate (II) with Thionyl Chloride. A solution of 2.7 g of natural (II) in 20 ml of thionyl chloride was heated at 80-95°C for 5 h. Then the excess of thionyl chloride was distilled off in vacuum, and the reaction mixture was chromatographed on a column (3.5 × 80 cm) of alumina (500 g, activity grade II) under the conditions described above [see (I)]. This gave 0.5 g of isoimperatorin (X), $C_{16}H_{14}O_4$, mp 106-108°C (from petroleum ether), 0.8 g of gosferol (XI), $C_{16}H_{14}O_5$, mp 137-138°C (from ethanol), and 0.96 g of substance (IX) with the composition $C_{16}H_{14}O_7S$, mp 181-183°C (from acetone). M^+ 350.

Oxidation of Decursinol (III) with Chromium Trioxide. With constant stirring, 0.83 g of chromium trioxide in 10 ml of 20% sulfuric acid was added to a solution of 0.62 g of natural (III) in 25 ml of acetone, and the mixture was left for a day. The removal of the acetone by distillation and recrystallization from suitable solvents gave 0.25 g of (XIII), $C_{14}H_{12}O_7$, mp 225-227°C (from ethyl acetate), M^+ 292, and 0.12 g of substance (XIV), with mp 205-207°C (from ethanol), M^+ 304.

SUMMARY

Products of the reactions of natural coumarins have been studied for the first time: the products of the reaction of osthole with a mixture of concentrated acetic and hydrochloric acid, of oxypeucedanin hydrate with acetone and thionyl chloride, and of decursinol with chromium trioxide. A total of eight new compounds not previously described in the literature has been obtained.

The structures of seven of the substances have been established on the basis of their IR, PMR, and mass spectra and chemical reactions.

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