SUMMARY

1. From nine species of plants of the family Boraginaceae we have isolated and identified 11 compounds, nine of which have proved to be previously known naphthoquinones in the form of shikonin derivatives.

2. The structure of the previously unknown δ-lactone of 5-(5',8'-dihydroxy-1',4'-naphthoquinon-2'-yl)-5-hydroxy-2-methylpent-2-enoic acid has been established.

3. The qualitative and quantitative compositions of the pigments of the species and groups of plants of the family Boraginaceae studied have been determined.

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MIGRATION OF THE EXOCYCLIC DOUBLE BOND IN TERPENOID COUMARINS OF THE IRESANE SERIES

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In terpenoid coumarins of the iresane series with an exocyclic double bond, migration of the double bond into the ring with the retention of the configuration of the substituent in position 1 is observed in an acid medium. The reaction has been performed in CF_3COOH and has been monitored by the PMR method. Badrakemin has yielded conferol, badrakemone has yielded conferone, badrakemin acetate has yielded conferol acetate, colladonin has yielded moschatol, and farnesiferol A and gummosin have yielded the corresponding isomers with endocyclic double bonds. The rate of the reaction is affected by the nature of the substituent at C-6. The presence of a keto group increases the time of isomerization to 1.5 h as compared with the 5-10 min for compounds with an OH group at C-6. The increase in the time of the reaction leads to the formation of byproducts. The reaction does not take place in CH_3COOH.

The action of an acid on farnesiferol A and its stereoisomers (I) containing an exocyclic double bond leads to the migration of the double bond with the formation of the corresponding compounds (III) containing the double bond in the ring:

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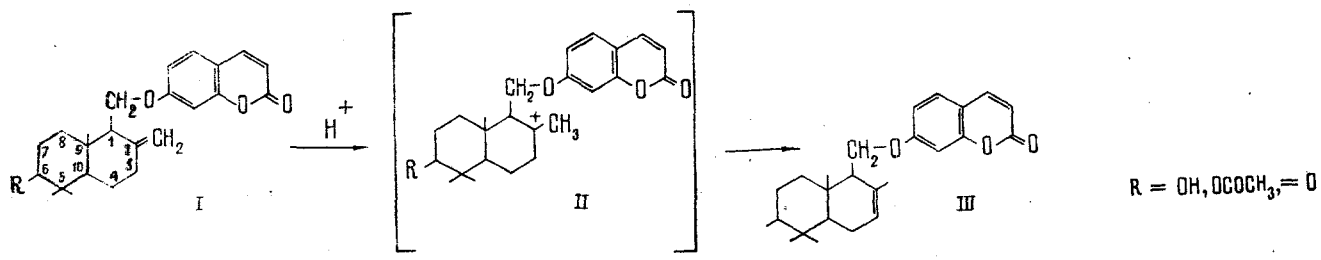


The conversion of terpenoid coumarins takes place readily in trifluoroacetic acid solution. In the PMR spectra of these solutions recorded at an interval of 4-15 min after the dissolution of the sample, there are no signals of an exocyclic methylene group (two broad singlets at 4.6-5.1 ppm, $W_{1/2}$ ~ 4 Hz, 1 H each) in the region of the resonance of olefinic protons, and a broadened one-proton signal appears with δ 5.63-5.80 ppm, $W_{1/2}$ ~ 8 Hz, similar to the signal of the olefinic proton in the PMR spectrum of conferol. In the strong-field region a broadened singlet appears with δ 1.75-1.82 ppm which is characteristic for a methyl group on a double bond (Table 1 and Fig. 1).

Preparative isolation of the reaction products and their subsequent comparison with authentic samples showed that badrakemin acetate (IV) is converted into conferol acetate (V), badrakemin (VI) into conferol (VII), colladonin (VIII) into moschatol (IX), and badrakemone (X) into conferone (XI). This shows that the intermediate carbocation selectively splits out a proton from position 3 of the iresane nucleus and the transformation is not accompanied by other isomerization processes. In agreement with this, farnesiferol A (XII) gives compound (XIII) and gummosin (XIV) gives (XV).

The PMR spectra of terpenoid coumarins with an exocyclic double bond are characterized by the presence of an unresolved signal of the cyclic olefinc proton located in the 5.55-5.69 ppm region ($W_{1/2} \approx$ 8-10 Hz), a multiplet or octet of the CH_2OAr group in the 4.0-4.4 ppm region, and a broadened signal of a CH_3 group at a double bond with δ 1.67-1.89 ppm (Table 1).

Similar changes in the spectrum of compound (X) take place considerably more slowly, and it requires approximately 1.5 h for the signals of the exocyclic CH_2 group to disappear completely (Fig. 2).

Since the transformation of the terpenoid coumarins of the iresane series with an exocyclic double bond into isomers with an endocyclic double bond takes place via the protonation of the exocyclic methylene with the formation of a carbocation followed by deprotonation at another center (C-3), the fall in the rate of isomerization of badrakemone is apparently connected with the competing reaction of the protonation of the carbonyl oxygen.

When terpenoid coumarins were dissolved in glacial acetic acid and the solutions were then heated to 100°C no isomerization was observed (monitoring by the PMR method), apparently because acetic acid is weaker than trifluoroacetic acid. An increase in the time of the treatment of the compounds described with trifluoroacetic acid or a rise in the temperature led, according to the PMR spectra, to the appearance of byproducts. Acylation of the hydroxy group in position 6 of the iresane nucleus probably took place.

Thus, in the PMR spectrum of farnesiferol A measured in CF_3COOH with heating to 60°C, after the end of isomerization the integral intensity of the signal of the proton geminal to the hydroxy group (δ 3.66) fell and a signal appeared with the same multiplicity at δ 4.9 ppm. The peak of the molecular ion with M^+ 478 of the reaction product (R_f 0.54, TLC, Silufol, ethyl acetate–petroleum ether (1:1)) isolated preparatively corresponded to the molecular weight of a trifluoroacetate of a product of the isomerization of farnesiferol A, $C_{26}H_{29}O_5F_3$ (XIII). In addition to this, the mass spectrum contained the strong peak of an ion $C_{17}H_{24}O_2F_3$ with m/e 317 apparently arising as the result of the splitting out of the umbelliferone fragment $C_9H_5O_3$ from the molecule of the trifluoroacetate.

TABLE 1. Characteristics of the PMR Spectra of the Terpenoid in $CDCl_3$ and CF_3COOH (chemical shifts, δ, ppm; multiplicities,

Compound	Solvent	$ArOCH_2-$	CH_3-C-
Badrakemin acetate (IV)	$CDCl_3$	4,21 d	0,86,s; 0,88,s; 0,91,s; 2,08,s (CH_3CO)
Conferol acetate (V) (transformation prod-	CF_3COOH	4,32, m	0,98,s; 1,06, s, 1,09,s; 2,24,s (CH_3CO)
uct of IV)	$CDCl_3$	4,14, m	0,85,s; 0,91,s; 0,97,s
Badrakemin (VI)	$CDCl_3$	4,20, m	0,83, s; 0,97,s
Conferol (VII) (transformation product of (VI))	CF_3COOH	4,35, m	1,02, us
Colladonin (VIII)	$CDCl_3$	4,18, d	0,88, s; 0,92 s; 1,00, s
Moschatol (IX) (transfor-	CF_3COOH	4,33, m	1,09, s; 1,03, s
mation product of (VIII))	$CDCl_3$	4,13, m	0,90, s; 1,02, s
Badrakemone (X)	$CDCl_3$	4,22, d	1,00, s; 1,04, s; 1,10, s
	CF_3COOH	4,44, d	1,18, s; 1,21, s; 1,24, s
Conferone (XI) (transformation product of X)	CF_3COOH	4,39, m	1,25, s; 1,33, s
Farnesiferol A (XII)	$CDCl_3$	4,02, q, $J_1 = 10,0$ Hz, $J_2 = 6,5$ Hz; 4,31, q, $J_1 = 10,0$ Hz $J_2 = 6,0$ Hz.	0,80, s; 0,97, s; 1,02, s
(XIII) (transformation product of (XII))	CF_3COOH	4,15, m	0,99, s; 1,05, s; 1,10, s
	$CDCl_3$	4,00, m	0,91, s; 1,02, s; 1,06, s
Gummosin (XIV)	$CODl_3$	4,12, q: $J_1=10,0$ Hz $J_2=7,0$ Hz; 4,44, q, $J_1=10,0$ Hz, $J_2= 6,0$ Hz	0,88, s; 1,00, s
(XV) (transformation	CF_3COOH	4,15, m	1,07, s; 1,14, s
product of (XIV))	$CDCl_2$	4,09, q, $J_1 = 11,0$ Hz $J_2 = 6,0$ Hz; 4,39, q $J_1 = 11,0$ Hz $J_2 = 3,0$ Hz	1,00, s, 1,04, s; 1,07, s;

Note. The following abbreviations are used in the table: s) signal appearing in the form of a singlet.

Moiety of the Coumarins of the Iresane Series Investigated
J, Hz; 0 — TMS)

=CH_2	=CH–3	H-6	CH_3–C=
4,57,s, $W_{1/2}$ = 4 Hz		4,72,m $W_{1/2}$ = 6 Hz	
4,94,s, $W_{1/2}$ = 4 Hz	—		—
	5,66, us	3,90, us	1,75, us
—	$W_{1/2}$ = 9 Hz	$W_{1/2}$ = 6 Hz	
—	5,59, us	4,80,m	1,67, us
	$W_{1/2}$ = 9 Hz	$W_{1/2}$ = 6 Hz	
4,54,s, $W_{1/2}$ = 4 Hz			
4,90,s, $W_{1/2}$ = 4 Hz	—	3,46,m, $W_{1/2}$ = 6Hz	—
—	5,69, us	3,87, us	
	$W_{1/2}$ = 9 Hz	$W_{1/2}$ = 6 Hz	1,75,us
4,55,s, $W_{1/2}$ = 4 Hz	—	3,32,q, ΣJ = 16,0 Hz	
4,92,s, $W_{1/2}$ = 4 Hz			—
—	5,66, us	3,68, t, ΣJ = 16,0Hz	1,75, us
	$W_{1/2}$ = 9 Hz		
—	5,55, us	3,33, t, ΣJ = 16,0 Hz	1,69,us
	$W_{1/2}$ = 9Hz		
4,60, s, $W_{1/2}$ = 4 Hz	—	—	—
4,97, s, $W_{1/2}$ = 4 Hz			
4,71,s, $W_{1/2}$ = 4Hz	—	—	—
5,08,s, $W_{1/2}$ = 4 Hz			
—	5,72, us	—	1,77,us
	$W_{1/2}$ = 10 Hz		
4,72,m, $W_{1/2}$ = 4Hz	—	3,27, t, ΣJ = 16,0Hz	—
4,82,m, $W_{1/2}$ = 4Hz			
—	5,63, us	3,58, q, ΣJ = 16,0Hz	1,78,us
	$W_{1/2}$ = 9 Hz		
—	5,58, us	3,30, t, ΣJ = 16,0 Hz	1,83, us
	$W_{1/2}$ = 8 Hz		
4.74,m, $W_{1/2}$ = 4 Hz			
4,84,m, $W_{1/2}$ = 4Hz	—	3,48, m, $W_{1/2}$ = 6Hz	—
—	5,80, us	3,80, us, $W_{1/2}$ = 6Hz	1,82, us
	$W_{1/2}$ = 8Hz		
—	5,69, us	3,66,m, $W_{1/2}$ = 6 Hz	1,89,us
	$W_{1/2}$ = 8 Hz		

singlet; d) doublet; t) triplet; q) quartet; us) unresolved

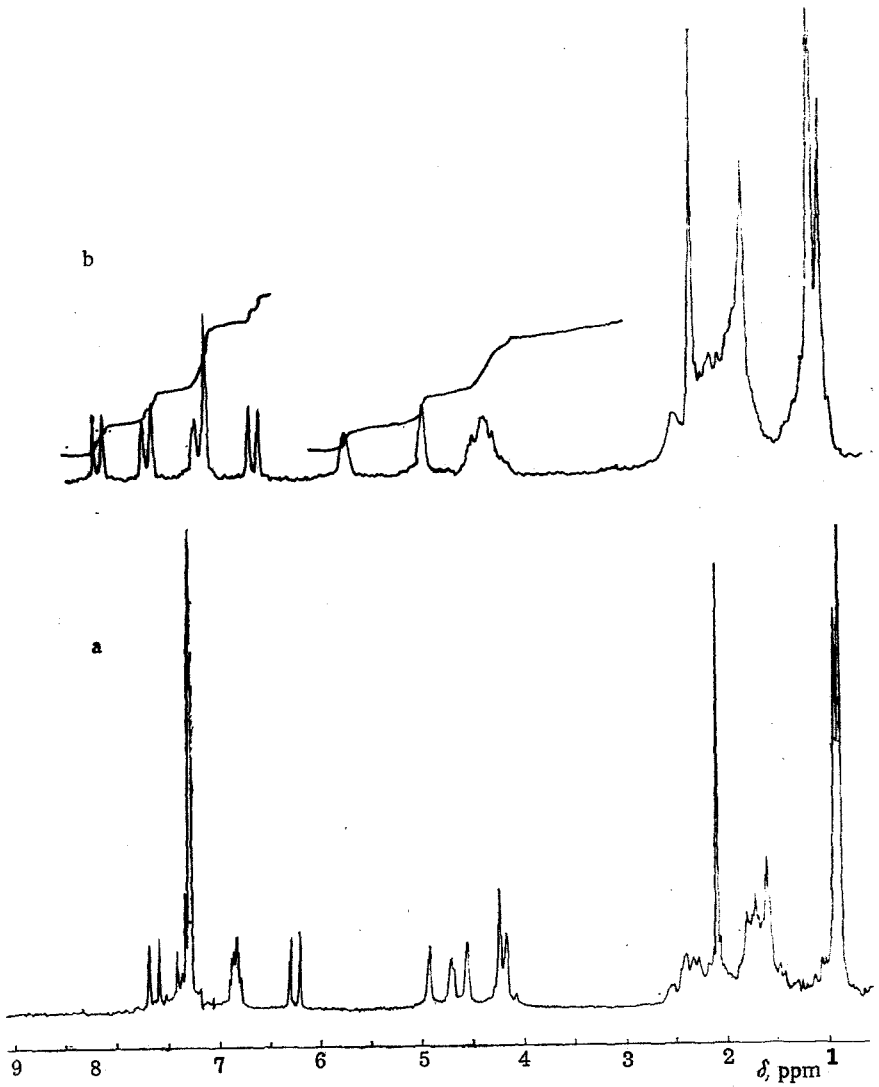
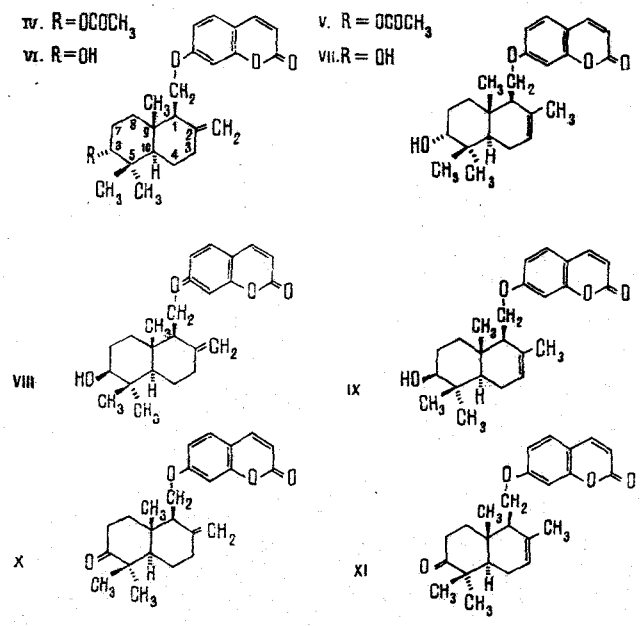


Fig. 1. PMR spectra of badrakemin acetate: a) in $CDCl_3$; b) in CF_3COOH.



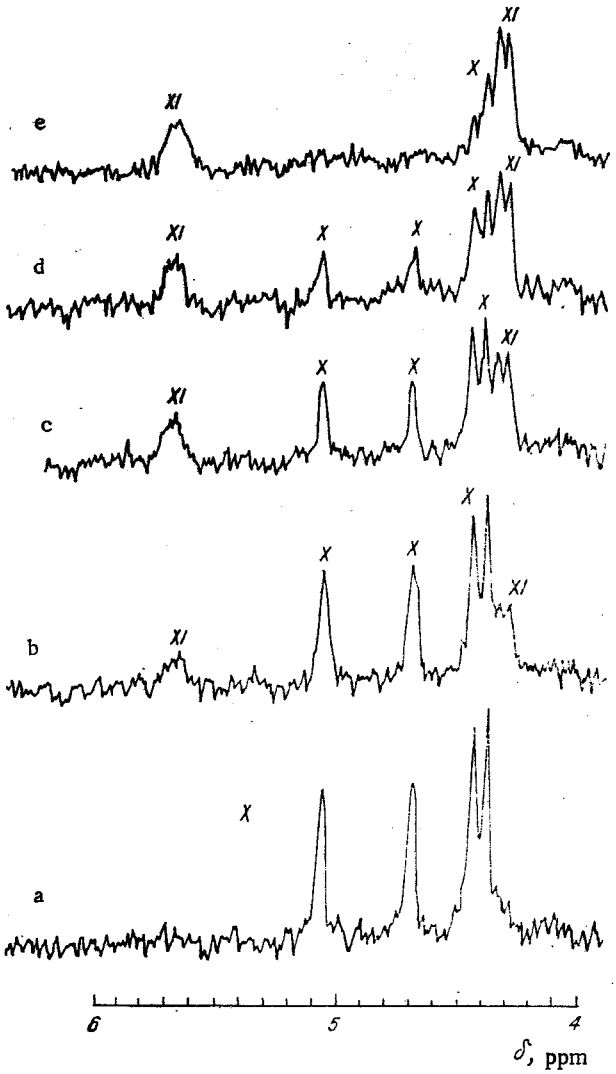
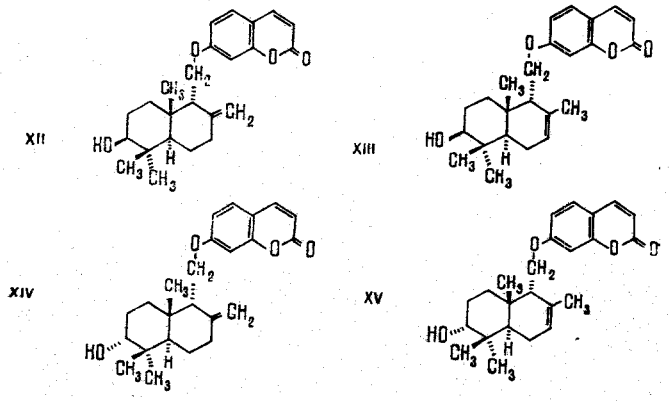


Fig. 2. Fragments of the PMR spectra of badrakemone (X) in CF_3-COOH: a) recorded immediately after the dissolution of the sample; b) after 15 min; c) after 30 min; d) after 45 min; e) after 1 h 20 min.



EXPERIMENTAL

Conditions for Recording the PMR Spectra. The PMR spectra of solutions of the substances in trifluoroacetic acid ch.d.a. ["pure for analysis"] (standard — TMS) and in $CDCl_3$ (0 — TMS) were recorded on a Varian HA-100D instrument at a sample temperature of 25°C. In the investigation we used authentic samples of acetylbadrakemin [1-4], badrakemin [1, 3, 5, 11], badrakemone [1, 3, 4, 6], farnesiferol A [3, 7-9, 11], colladonin [10, 11], and gummosin [9, 11], corresponding in melting points and PMR spectra [4, 11] to those given in the literature. For studying the transformations by PMR spectroscopy we used 10% solutions of the substances.

Preparative Isolation of the Reaction Products. Isolation of the Isomerization Products. Each of the initial coumarin derivatives (30-60 mg) was dissolved in 2-3 ml of CF_3COOH, and the solution was kept at 20°C for 15 min and was poured into 30-50 ml of water. The resulting precipitate was filtered off, washed with water to neutrality, and dried, after which the constants were determined and the PMR spectrum was recorded in $CDCl_3$. For comparison we used authentic samples of conferol acetate [12], moschatol [13], conferol [14], and conferone [14].

Isolation of the trifluoroacetate of the product of the isomerization of farnesiferol A. An authentic sample of farnesiferol A (58 mg) was dissolved in 0.5 ml of CF_3COOH. The reaction took place in the sensor of the NMR spectrometer at a sample temperature of 60°C and was stopped after the disappearance of the signals of the $=CH_2$ group of the initial substance (δ 4.72, m; 4.82, m), a decrease in the integral intensity of the H-6 signal (3.66, m) and the appearance of a signal with the same multiplicity at 4.9 ppm. The reaction mixture was diluted with water (30 ml) and the reaction product that had deposited was separated off, washed with water, and dried. According to TLC (Silufol, ethyl acetate—petroleum ether (1:1)), the resulting material contained, in addition to the isomerization product (XIII) and umbelliferone (identification with markers), an unknown substance with the lowest polarity having R_f 0.54, which was isolated preparatively on plates of silica gel 5/40 μ in the petroleum ether—ethyl acetate (1:1) system. The molecular weight determined by mass spectrometry was 478.

SUMMARY

In terpenoid coumarins of the iresane series having an exocyclic double bond, the double bond migrates into the ring in an acid medium.

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