CIRCULAR DICHROISM OF SOME CAROTANES

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The circular dichroism method has been used to study the stereochemistry of the carotanes. An analysis of the results obtained has shown that an α-oriented ester group at C_6 corresponds to a positive Cotton effect (CE) in the 240-260-nm region. A link has been established between the position of the carbonyl group in the ring B and the sign of a CE in the 340-nm region. Hydrolysis of an ester group at C_6 takes place more readily in an alkaline medium than in an acid medium, and in the case of carbonyl-containing carotanes dehydration takes place as well as hydrolysis.

Continuing a study of the stereochemical features of the structures of sesquiterpenes [1], we have considered the circular dichroism (CD) spectra of unsaturated esters of the carotane series. In the scientific literature, information on the use of chiroptic methods for carotanes relate mainly to determining the orientation of the angular methyl group [2].

We have reported the CD spectra of epoxydihydrolapidin (I), lapiferin (II), lapidolin (III), pallinin (IV), lapiferinin (V), lapidolinin (VI), palliferidin (VII), ferutinin (VIII), lapidin (IX), palliferinin (X), the ketone of ferutinol (XI), lapidol (XII), and anhydrolapidol (XIII) in neutral, acidic, and alkaline media. The structures of these compounds have been determined previously [3-5].

Analysis of the results obtained has shown that in the CD spectra of compounds (I-VIII) the Cotton effect (CE) due to the n → π* transition of a conjugated ester group appears in the 240-nm region (for esters of α,β-unsaturated aliphatic acids) and in the 260-nm region (for esters of hydroxy- and methoxyaromatic acids). It is positive for an α-oriented ester group. A double bond at C_8—C_9 does not affect the sign of the ester CE at 263 nm, as can be seen from a comparison of the CD spectra of compound (V) and compounds (VII) and (VIII). In the CD spectra of (VII) and (VIII) a positive CE is observed in the 210-nm region which is due to a π → π* transition in the C_8—C_9 double bond. Measurement of the CD of the carotanes (I-VIII) in acid and alkaline media showed that hydrolysis takes place far faster in an alkaline medium than in an acid one. Thus, when the esters (I-VIII) were treated with 5% ethanolic caustic soda without heating, the Cotton effects connected with the ester groups decreased to zero after only an hour, while in an acid medium only a slight decrease in the intensity of the corresponding CE was observed even after 24 hours. In Table 1, only the results of acid hydrolysis are given for compounds (I-VIII), since after treatment with alkali the Cotton effect observed in the CD spectra of the initial compound disappears.

In the CD spectra of the carbonyl-containing carotanes (IX-XII) there are powerful Cotton effects in the 330- and 240-nm regions due to n π* and π → π* transitions of the α,β-unsaturated carbonyl chromophore. In the case of the trans linkage of rings A/B, these Cotton effects are, respectively, negative and positive when the carbonyl group is located at C_{10} (compounds (IX) and (X)) and of the opposite signs when the C=O group is present at C_6 (compound XI) (see Table 1). These characteristics can be used to prove the structures of such compounds. The Cotton effect due to the n → π* transition of the conjugated ester group, being superposed on the π → π* Cotton effect of the α,β-unsaturated carbonyl chromophore, increases its intensity. In addition to the superposition of these two effects, here the homoconjugation factor is also acting, substantially increasing the intensity of the CEs under consideration. That the two groups do interact is also confirmed by the fact that in the ketone of ferutinol, which lacks an ester group, the intensities of the carbonyl Cotton effects have their usual values, and the CEs of ester groups do not exceed $\Delta\varepsilon \sim 4$ in the absence of a carbonyl group (see Table 1, compounds (I-VIII)).

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TABLE 1. Results of CD Measurements of Carotanes in Neutral and Acid Media

Compound	CH_3OH		$CH_3OH+HCl$	
	λ_{max}, nm	Δε	λ_{max}, nm	Δε
I. Epoxydihydrolapidin	243	+1,70	243	+1,39
	218	−1,18	218	−1,37
II. Lapiferin	240	+1,89	241	+1,70
	223	−2,07	220	−1,84
III. Lapidolin	243	+1,92	243	+1,70
	220	−2,50	218	−1,98
IV. Pallinin	250	+1,12	248	+0,95
	210	−51,4	210	−47,8
V. Lapiferinin	263	+2,20	260	+0,71
	238	−1,24	239	−1,20
VI. Lapidolinin	263	+1,19	262	+1,17
	242	−1,35	243	−1,23
VII Palliferidin	265	+2,47	265	+2,15
	238	−0,35	239	−0,30
	210	+10,7	213	+10,1
VIII. Ferutinin	258	+4,49	258	+4,31
	228	−2,92	228	−2,78
	209	+2,82	209	+2,62
IX. Lapidin	333	−3,57	345	−4,55
	240	+23,9	295	+8,74
	214	−2,33	246	+2,05
			220	−7,77
X. Palliferinin	330	−3,50	345	−4,55
	255	+18,8	290	+7,40
	233	+17,4	265	+7,25
	214	−7,25	213	−4,93
XI. Ketone of ferutinol	338	+1,24	338	+1,12
	240	−7,05	240	−6,60
	215	−3,34	210	−3,10
XII. Lapidol			395	+0,46
	350	−5,75	348	−4,46
	294	+10,6	295	+8,34
	214	−10,1	220	−7,03
XIII Anhydrolapidol	386	+13,2	385	+12,2
	329	−6,69	330	−5,50
	250	+4,08	287	+1,24
	221	+25,3	250	+3,55
			222	−21,6

TABLE 2. Results of CD Measurements of Carbonyl-Containing Carotanes in an Alkaline Medium.

Compound	5% KOH*		5% KOH†	
	λ_{max}, nm	Δε	λ_{max}, nm	Δε
Lapidin			384	+5,41
	349	−5,92	326	−2,50
	293	+10,4	290	+0,85
	250	+1,77	260	+1,21
	218	−9,82	222	−6,21
Palliferinin			382	+7,05
	345	−4,95	327	−1,98
	295	+1,99	290	+0,73
	249	+8,15	263	+1,81
	218	−1,99	223	−13,0
Ketone of ferutinol	338	+0,43	330	+0,29
	290	+0,25	290	+0,20
	240	−0,99	238	−0,35
Lapidol	389	+2,07	386	+6,05
	340	−4,13	327	−2,28
	294	+6,15	290	+1,78
	253	+2,23	260	+2,45
	218	−10,2	223	−11,2
Anhydrolapidol	386	+14,2	385	+7,03
	329	−6,09	330	−2,40
	250	+2,08	289	+1,40
	221	−22,3	250	+0,60
			220	−12,8

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*The measurements were made immediately after the sample had been dissolved in alkali.

†The measurements were made 24 hours after the dissolution of the sample.

The presence of a carbonyl group in ring B considerably accelerates the hydrolysis of the ester group in compounds (IX) and (X) both in alkaline and in acid media; in an alkaline medium hydrolysis takes place practically instantaneously. Immediately the carotanes (IX) and (X) have been dissolved in an alkaline solution, and it is possible to see in their spectra the appearance of Cotton effects in the 350- and 290-nm regions that are characteristic for lapidol (XII) and a decrease in the ester band in the 250-260 nm region (Table 2). Similar changes in the CD spectra of acidified solutions of (IX) and (X) can be observed only after 24 hours (Fig. 1). In alkaline solutions of compounds (IX), (X), and (XII) that have been left at room temperature for a day, the hydroxyl at C_6 formed as the result of the hydrolysis of the ester group undergoes dehydration.

Another double bond appears in ring B, lengthening the chain of conjugation, and causing the appearance in the long-wave region of the spectrum of another CE at 390 nm (see Fig. 1), which is characteristic for anhydrolapidol. The high intensities of the Cotton effects observed in the spectrum of anhydrolapidol, in spite of the decrease in the number asymmetric centers as the result of dehydration, are due to the formation of an internally dissymmetric chromophore in ring B.

The dehydration reaction can be accelerated by heating an alkaline solution of a carbonyl-containing carotane to the boil.

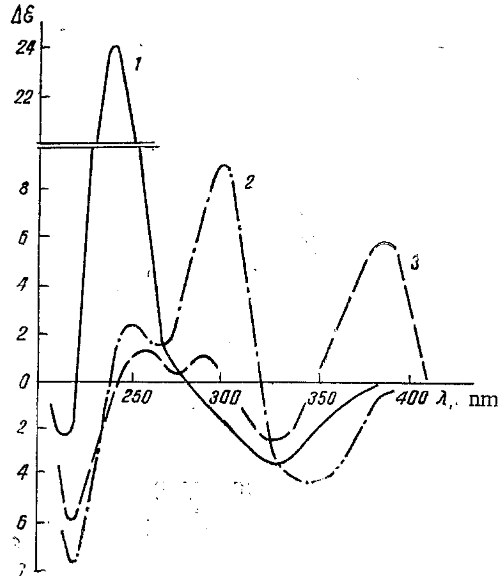
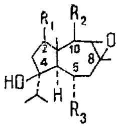
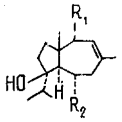


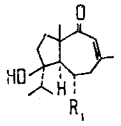
Fig. 1. Circular dichroism spectra of lapidin in CH_3OH (1) in $CH_3OH + HCl$ (2), and in 5% KOH (3).



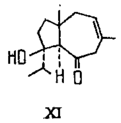
	R₁	R₂	R₃
I	H	OH	$OCO-C(CH_3)=CH(CH_3)$
II	H	$OCOCH_3$	$OCO-C(CH_3)=CH(CH_3)$
III	$OCOCH_3$	$OCOCH_3$	$OCO-C(CH_3)=CH(CH_3)$
V	$OCOCH_3$	H	$OCO-C_6H_4(OCH_3)_2$
VI	$OCOCH_3$	$OCOCH_3$	$OCO-C_6H_4(OCH_3)_2$



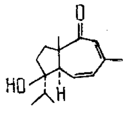
IV	$OCO-C(CH_3)=CH(CH_3)$	$OCO-C(CH_3)=CH(CH_3)$
VII	H	$OCO-C_6H_3(OCH_3)_3$
VIII	H	$OCO-C_6H_5OH$



IX	$OCO-C(CH_3)=CH(CH_3)$
X	$OCO-C_6H_3(OCH_3)_3$
XII	OH



XI



XIII

The ease of dehydration of the hydroxy groups in compounds (IX, X, XII) is due to the presence of the hydroxy group in the β position with respect to the conjugated carbonyl [6]. This feature has been reported in the study of sesquiterpene lactones having a dienone grouping [7].

EXPERIMENTAL

CD spectra were recorded on a JASCO J-20 spectropolarimeter. The concentration of the solutions was 1 mg/ml and the cell thicknesses 0.1, 0.05, 0.02, and 0.01 cm. Methanol was used as solvent. For acidification, 3 drops of concentration hydrochloric acid was added to 1 ml of methanolic solution. Table 1 gives the results of the CD measurements made 24 hours after the addition of the acid. Alkaline solutions were obtained by dissolving a weighed amount of a carotane in a 5% methanolic solution of potassium hydroxide. Table 2 gives the results of CD measurements of alkaline solutions of carbonyl-containing carotanes made immediately after and 24 hours after the dissolution of weighed amounts of the carotanes.

SUMMARY

1. It has been established from CD-spectroscopic characteristics that in trans-carotane derivatives a positive Cotton effect in the 260-249 nm region corresponds to an ester group at C_6.

2. A link has been established between the position of the carbonyl groups and the sign of the Cotton effect in the 340-nm region.

3. It has been established that the hydrolysis of an ester group at C_6 takes place more readily in an alkaline medium than in an acid medium, and that in carbonyl-containing carotanes dehydration takes place as well as hydrolysis.

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PHOTOSENSITIZED OXIDATION OF ISOCEMBROL.

VII. PRODUCTS OF REACTION AT THE C_{11} DOUBLE BOND

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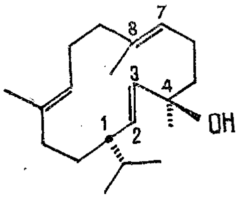
It has been established that in the photooxidation of isocembrol, in addition to other compounds, five products of oxidation at the C_{11} double bond are formed, and their structures and stereochemistry have been established by chemical transformations and physicochemical methods. In the stereochemical respect, the photooxidation of isocembrol at the C_{11} double bond is similar to its epoxidation at the same bond.

Continuing a study of the oxidation of cembrane diterpenoids by singlet oxygen [1], we have investigated the products of the photosensitized oxidation of isocembrol (I) — a component of the oleoresin of coniferous plants [2], tobacco [3], and soft corals [4]. The structure [2] and stereochemistry [5] of this alcohol have been established previously with the aid of chemical and spectral methods.



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