CIRCULAR DICHROISM OF SOME PHTHALIDE-ISOQUINOLINE ALKALOIDS

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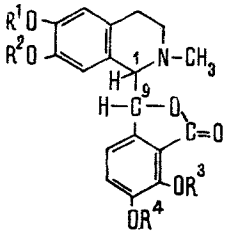
In the present paper we consider some difference in the CD spectra of the threo and erythro forms of the phthalide-isoquinoline alkaloids corledine (I), severtzine (II), *l*-adlumine (III), adlumidine (IV), d-α-hydrastine (V), d- and *l*-β-hydrastines (VI and VII), *l*-bicuculline (VIII), and corlumine (IX).

It has been established [1] that the configuration of the asymmetric center at C_1 can be determined from the Cotton effects (CE's) in the 290 and 205 nm regions which are due, respectively, to the ^1L_b and ^1B aromatic transitions of the tetrahydroisoquinoline moiety ("T" system) and the C_9 center, and from the CE's in the 320 and 225 nm regions, which are connected with the analogous transitions of the phthalide moiety of the molecule ("P" system) and it has been observed that the CD spectra of the phthalide-isoquinolines do not change appreciably on protonation.

Our measurements have shown that the latter conclusion is not quite accurate.

As can be seen from Fig. 1 and the results given in Table 1, on acidification in the case of the erythro isomers (VI-IX) there is in fact a change only in the amplitude of the CE's, while in the case of the threo compounds (I-V) the signs of the Cotton effects in the 290 and 200 nm regions connected with the C_1 center change. After neutralization, the original signs of the CE's are restored, i.e., the process is reversible. This fact must be borne in mind in determining the configurations of the C_1 center in hydrochlorides of phthalide-isoquinoline alkaloids.



I.	R^1=H;	R^2=CH_3;	R^3+R^4=CH_2
II.	R^1=CH_3;	R^2=H;	R^3+R^4=CH_2
III,IX.	R^1=R^2=CH_3;		R^3+R^4=CH_2
IV, VIII.	R^1+R^2=CH_2;		R^3+R^4=CH_2
V—VII.	R^1+R^2=CH_2		R^3=R^4=CH_3

Since in 1-benzyltetrahydroisoquinolines the signs of the CE's are retained on protonation [2], the inversion of the signs of the CE's in compounds (I-V) can be explained only by conformational changes that are more substantial for the threo form than for the erythro form. Another difference between the erythro and threo isomers must also be mentioned. In the erythro compounds (VI-IX) in an alcoholic solution, of the two ^1L_b CE's the most pronounced is that in the 320 nm region, and in the case of the threo isomer it is that in the 290 nm region, which reflects a difference in the nature of the disturbance of the ^1L_b transition of the "T" and "P" systems for these two forms. This is probably explained by the fact that in the threo isomers in the preferred conformation the aromatic nucleus of the "T" system and the lactone groups [3] are spatially close, which permits the existence of homoconjugation, i.e., the partial overlapping of the π orbitals of the aromatic ring and of the lactone group, and enhances the ^1L_b CE in the 290 nm region.

In the case of the erythro compounds, the conformation in which the two aromatic nuclei [3] are spatially close is the more stable, the interaction between them again increasing the intensities of the CE's due to the aromatic transition of the "P" system (CE's at 320 and 220 nm). For the erythro form (VI-IX) it is difficult to estimate the intensity of the CE at 290 nm which is located between CE's of opposite signs and appears in the form of a trough.

In the case of α- and β-hydrastines (V-VII), thanks to the replacement of the methylenedioxy group by two methoxy groups, the ^1L_b Cotton effect of the "P" system is shifted hypsochromically to 300 nm and is super-

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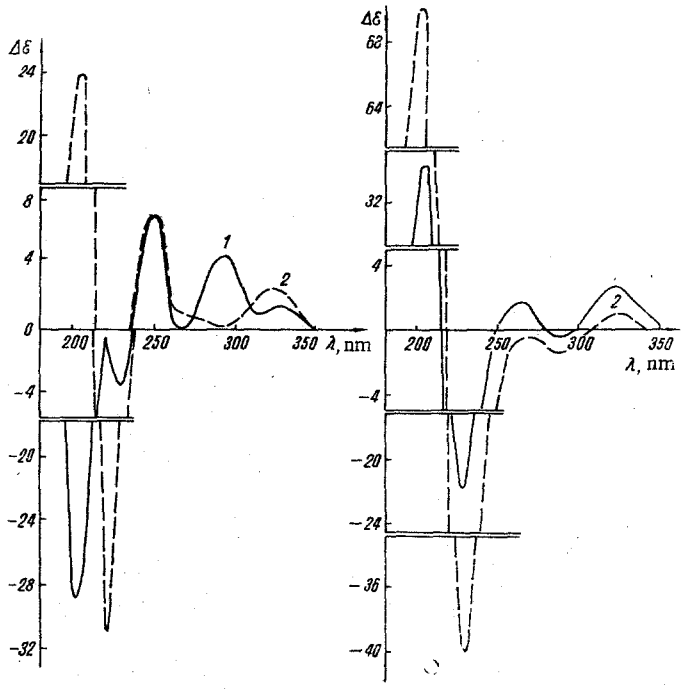

Fig. 1. CD spectra of the threo form (corledine) and of the erythro form (corlumine) in CH_3OH (1) and $CH_3OH+HCl$ (2).

TABLE 1

Compound	Configuration	CH_3OH		$CH_3OH+HCl$		Compound	Configuration	CH_3OH		$CH_3OH+HCl$	
		λ^*_{max}, nm	$\Delta\varepsilon$	λ_{max}, nm	$\Delta\varepsilon$			λ_{max}, nm	$\Delta\varepsilon$	λ_{max}, nm	$\Delta\varepsilon$
I	1R,9R	325	+ 1,43	323	+ 2,68	VI	1S,9R	310	+ 3,09	308	+ 1,85
		292	+ 4,35	292	tr†			290	tr	290	— 3,32
		247	+ 6,98	245	+ 6,98			265	+ 1,82	—	—
		228	— 3,82	220	—31,0			216	— 16,3	220	—17,0
		205	—29,2	206	+24,0			200	+40,1	200	+78,0
II	1R,9R	324	+ 1,85	320	+ 2,34	VII	1R,9S	310	— 3,26	309	— 2,09
		293	+ 2,40	290	tr			290	tr	289	+ 3,40
		245	+ 8,20	240	+10,2			265	— 1,98	—	—
		220	— 7,35	220	—38,8			215	+10,4	222	+5[illegible],7
		205	—11,7	205	+36,7			200	—46,1	204	—81,0
III	1R,9R	320	+ 2,08	320	+ 2,67	VIII	1R,9S	321	— 3,25	321	— 1,28
		290	+ 4,16	290	tr			290	tr	292	+ 1,92
		245	+ 9,15	245	+ 9,80			248	— 4,02	—	—
		225	— 1,82	220	—26,7			223	+16,5	223	+27,3
		203	—28,4	205	+ 32,4			202	—21,2	204	—48,6
IV	1S,9S	327	— 0,72	318	— 1,54	IX	1S,9R	325	+ 2,62	330	+ 0,82
		295	— 2,60	290	tr			290	— 0,40	285	— 1,42
		248	— 4,25	248	— 4,48			268	+ 1,80	—	—
		228	— 7,10	220	+13,9			226	—22,4	228	—40,2
		204	+18,10	205	—10,2			205	+35,1	205	+69,0
V	1S,9S	302	— 3,44	302	— 2,79						
		278	+ 1,21	—	—						
		255	— 1,02	250	— 2,79						
		213	+27,0	213	+35,0						
		206	+13,5	203	—27,0						

* The main characteristics of the CE's are given.

† The CE at 290 nm located between positive CE's appears in the form of a trough (tr).

posed on the CE at 290 nm. Consequently, the configuration of the C_1 center is determined only from the CE in the 200 nm region, an inversion of the sign of which on acidification is suffered by the threo form in α-hydrastine (V). In the erythro compounds d and l-β-hydrastines (VI, VII) the sign of the CE's in the 200 nm region does not change.

The assignment of the two new phthalide-isoquinoline alkaloids corledine and severtzine [4, 5] to the 1R,9R series has been confirmed by their CD spectra.

EXPERIMENTAL

The CD spectra were recorded on a JASCO J-20 spectropolarimeter. The concentration of the solutions was 1 mg/ml and the cell thicknesses 0.05 and 0.01 cm. Methanol was used as the solvent. On acidification, a drop of concentrated hydrochloric acid was added to 2 ml of a methanolic solution of the base. The changes in CD took place within an hour after the addition of the hydrochloric acid.

SUMMARY

1. It has been established that on protonation the threo isomers of phthalide-isoquinolines undergo an inversion of the signs of the CE's in the 290 and 200 nm regions, while in the case of the erythro compounds only the amplitudes of the corresponding CE's in the CD curves change.

2. An interconnection has been established between the preferred conformations of the threo and erythro forms and the relative intensities of the ^1L_b CE's in the CD curves of the phthalide-isoquinolines.

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ALKALOIDS OF *Delphinium biternatum*

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We have studied the epigeal part and roots of the plant *Delphinium biternatum* Huth collected in the budding-flowering stage on the slopes of the Fergana range at the Alchamaidan landmark. Iliensine has previously been isolated from the epigeal part of this plant [1, 2].

By chloroform extraction of the epigeal part of the plant we obtained 1.3% of the combined alkaloids from which, together with iliensine, we obtained five known alkaloids and three new ones. The constants and compositions of these bases are given below:

Alkaloid	Composition	mp, °C	$[\alpha]_D$, deg
Iliensine	$C_{24}H_{37}NO_7$	202—203	41
Acomonine	$C_{25}H_{41}NO_7$	208—210	25
Delphatine	$C_{26}H_{43}NO_7$	107	38,4
Anthranoyllycoctonine	$C_{32}H_{46}N_2O_8$	166	51
Browniine (I)	$C_{25}H_{41}NO_7$	110—112	33
Dehydrobrowniine (II)	$C_{25}H_{39}NO_7$	176—178	32
10-Benzoylbrowniine (VII)	$C_{32}H_{45}NO_8$	114—116	53
10-Benzoyliliensine (VIII)	$C_{31}H_{43}NO_8$	147—149	50
10-Dehydroiliensine (III)	$C_{24}H_{37}NO_7$	208—210	26

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