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CIRCULAR DICHROISM OF THE ALKALOIDS OF *Petilium raddeanum*

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The circular dichroism (CD) method has been used for studying the stereochemistry of steroid alkaloids containing an azomethine ring — petiline and petisine. In the CD spectrum of petiline a Cotton effect (CE) is observed in the 235 nm region which is due to a $n \rightarrow \pi^*$ transition in the azomethine chromophore. The negative sign of this CE shows the 25S configuration in petiline. An analysis of CD spectra has shown that the 25S configuration is retained when petiline is oxidized to petisine.

In order to determine the absolute configuration of the asymmetric center at C_{25} in the steroid alkaloids containing an azomethine ring, petiline (I) and petisine (II) [1, 2], we have considered their circular dichroism (CD) spectra and also, the CD spectra of 0,0^1—diacetyl-23-pseudosolasodine (III), and 0,0'-diacetyl-23-oxopseudosolasodine (IV) [3]. In their CD spectra, cyclic azomethines have a Cotton effect (CE) in the 230-250 nm region which is due to a $n \rightarrow \pi^*$ transition in the C=N chromophore, the sign of which has enabled the conformation of the ring and the configuration of the asymmetric center at C_{25} to be determined.

Figure 1 shows the two chiral conformations of the azomethine ring with the 25R (a) and 25S (b) configurations, which exhibit positive and negative Cotton effects, respectively, in the CD spectra.

It can be seen from the figures given in Table 1 that there is a negative CE in the 240 nm region of the CD spectrum of petiline and, consequently, petiline can be assigned to the 25S series. In addition to petiline, the alkaloid petisine was isolated from *Petilium raddeanum*, and this, as has been established, is the 23-oxo derivative of petiline [2].

In the CD spectrum of petisine, the azomethine CE is shifted into the 280-290 nm region thanks to the conjugation of the azomethine with the carbonyl group. In petiline and petisine there is another carbonyl group, at C_6, which also absorbs in the 290 nm region. Consequently, in the CD spectrum of petisine, a broad intense CE is observed in the 280-300 nm region with an inflection at 291 nm. Petisine can be obtained by the oxidation of petiline with manganese dioxide [2]. In order to exclude the influence of a second carbonyl group in the CD spectrum, the oxidation of the known alkaloid 0,0'-diacetylpseudosolasodine, which does not contain a carbonyl group at C_6, was performed under the same conditions. The negative CE in the CD spectrum of the resulting 0,0'-diacetyl-23-oxopseudosolasodine observed in the 270-290 nm region can be assigned unambiguously to the absorption of the conjugated chromophore O=C—C=N.

It can be seen from Dreiding models that in the least strained conformation of the azomethine ring in compounds (II) and (IV) the azomethine bond and the carbonyl group are located in the same plane (Fig. 1c). Such types of arrangement have been reported previously for monocyclic α,β-unsaturated ketones [5]. With such an arrangement, the carbonyl group does not change the intrinsic conformation of the azomethine ring. It can be seen from the octant diagram for the azomethine ring (Fig. 1d) that the contribution to the rotational force of the $n \rightarrow \pi^*$ transition due to the chirality of the O=C—C=N chromophore is zero, since it has a planar arrangement and the value and sign of the CE are determined by the conformation of the ring and of the methyl group at C_{25}.

Thus, the negative CE in the CD spectra of compounds (II) and (IV) permits them to be assigned to the 25S series.

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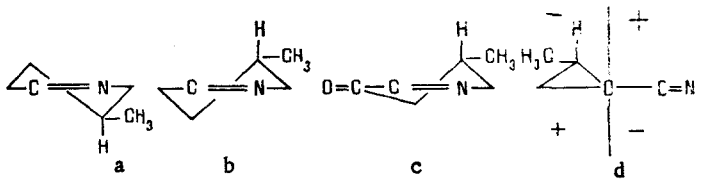
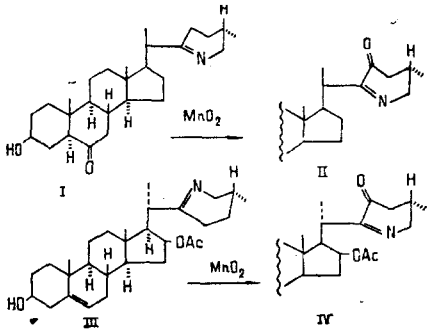


Fig. 1

TABLE 1

Compound	CH_3OH		$CH_3OH+HCl$	
	λ_{max}, nm	$\Delta\varepsilon$	λ_{max}, nm	$\Delta\varepsilon$
Petiline (I)	292	−1,74	292	−1,70
	236	3,55	210	+3,60
Petisine (II)	385	−0,11	325	+0,43
	291 shoulder	−1,83	292	−1,68
	285	−2,32	285	−1,46
	220	−1,97	245	+0,83
O,O'-Diacetylpseudosolasodine (III)	239	+1,96	—	—
	212	−0,56	216	−1,92
O,O'-Diacetyl-23-oxopseudo-solasodine (IV)	408	−0,21	320	−0,12
	280	−0,61	250	+0,25
	215 shoulder	+3,09	218	−1,32
	200	+4,01	200	+4,65

It must be mentioned that on the oxidation both of petiline (I), which belongs to the 25S series, and also of 0,0'-diacetylpseudosolasoline, having the 25R configuration (the azomethine CE at 239 nm is positive), a 23-oxo compound was obtained (II, IV) in the CD spectrum of which negative CEs were observed in the 270-290 nm region (see Table 1).



On protonation, in the CD spectra of the 23-oxo compounds (II and IV) a positive CE appeared in the 240-250 nm region which is obviously connected not only with salt formation but also with a change in the conformation and a disturbance of the planarity of the O=C–C=N chromophore.

EXPERIMENTAL

CD spectra were recorded on a JASCO-20 spectropolarimeter. The concentration of the solutions was 1 mg/ml and the thickness of the cells 0.5, 0.1, 0.05, and 0.01 cm. CD spectra were taken in methanol and in dioxane. The observed changes were similar in the two solvents, and therefore only the results for the methanol solutions are given in Table 1.

SUMMARY

The 25S configuration has been established in petiline and petisine by the CD method.

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MOLECULAR AND CRYSTAL STRUCTURE OF LUTEIDINE

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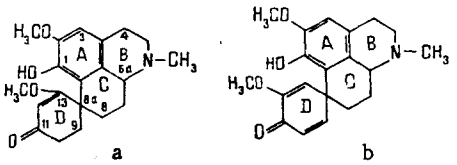
The crystal structure of luteidine has been deciphered by x-ray structural analysis; there are two molecules in the independent part of its elementary cell. These symmetrically independent molecules differ in structure. The position of the olefinic methoxy group of luteidine has been established. Its structure has been determined as 1-hydroxy-2,12-dimethoxy-9,10-dihydrohomoaporphine.

The present paper gives the results of an x-ray structural analysis of the alkaloid luteidine isolated previously [1] from the Central Asian species of the autumn crocus *Colchicum luteum* Baker. The structure of this alkaloid was determined as 1-hydroxy-2,13-dimethxy-9,10-dihydrohomoproaporphine (a) [2].



However, not all the questions relating to the structure of luteidine were resolved: The configurations of the C_{6a} and C_{8a} atoms were not elucidated and the positions of the olefinic methoxy group at C_{13} did not agree with the biogenetic scheme of the proaporphine and homoproaporphine alkaloids [3, 4]. Furthermore, it was necessary to determine how comparable are the configurations of this alkaloid and of the alkaloid kreysiginone (b) for which the results of an x-ray structural analysis have been given [5].

We have established that in the independent part of the elementary cell of luteidine there are two molecules of the substance which we shall subsequently denote by (I) and (II), and therefore in the figures and tables we give individual details for the molecules (I) and (II) of this compound. Figure 1 shows the conformation of luteidine, the methoxy group in ring D being located at the C_{12} atom, and not the C_{13} atom as was assumed previously, and ring D being oriented in such a way that this methoxy group is in the syn position relative to the H atom at C_{6a}. It has also been established that the N-methyl group (C_{18}) of the base is present in different positions in molecules (I) and (II): In (I) it is in the equatorial position and in (II) in the axial position to ring B (Fig. 1).

The conformations of the rings can be judged from the figures of Table 1, which gives the equations of the planes of fragments of the rings and the deviations of the atoms from these planes. The aromatic ring A is practically planar, the deviations of the atoms in it

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