OPTICAL ROTATORY DISPERSION OF SOME THALICTRUM ALKALOIDS

G. P. Moiseeva, Z. F. Ismailov,
and S. Yu. Yunusov

UDC 547.944/945+541.653

A simple connection between the absolute configuration of the asymmetric center and the rotatory dispersion (RD) curves has been established for the 1-benzyltetrahydroisoquinoline alkaloids. All the compounds belonging to the S series have RD curves with two positive Cotton effects (CE), while the enantiomeric R compounds show two negative CEs in the 300-240 nm region [1]. In the case of the bisbenzyltetrahydroisoquinoline alkaloids, the pattern is more complex. The rule of optical superposition is not observed for them, since a contribution to the optical rotation is made not only by the two asymmetric centers but also by the conformational changes around the mobile ether and methylene bonds.

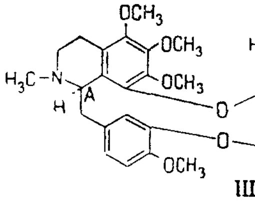
In order to establish definite laws connecting the stereochemistry and nature of the optical rotatory dispersion of the bisbenzyltetrahydroisoquinoline alkaloids, we have recorded the RD curves of thalsimidine (I), thalsimine (II), hernandezine (III), thalisopine (IV), thalmine (V), O-methylthalicberine (VI), thalfoetidine (VII), the benzylisoquinoline-aporphine alkaloid foetidine (VIII), and the aporphine thalicmidine (IX). The configurations of all these alkaloids have been established by chemical methods [3, 4, 6, 8, 13, 14].

The bisbenzyltetrahydroisoquinoline alkaloids possess anomalous RD curves with CEs in the 320-240 nm region (Figs. 1 and 2). The UV spectra of the bisbenzyltetrahydroisoquinolines have two absorption bands due to the presence of the aromatic chromophore: the first of medium intensity (ε 6,000-10,000) at 282 nm and the second, stronger, band, that of an allowed $\pi \rightarrow \pi^*$ transition at 206 nm (ε 80,000-130,000) with a shoulder at about 225-238 nm.

The first CE is connected with the aromatic absorption band at 282 nm. Craig et al. [2] considered a connection of the second CE with the UV absorption in the 230 nm region more likely than with the strong band at 206 nm, as suggested by Battersby [1]. Craig based his conclusion on information from circular dichroism. We have succeeded in recording the first extremum of the second CE only for certain alkaloids.

From the nature of their rotatory dispersions, thalsimidine (I) and thalsimine (II) may be considered as simple benzyltetrahydroisoquinolines for which the positive CE confirms the S configuration. The C = N chromophoric group increases absorption in the region of the first optically active band because of the $\pi \rightarrow \pi^*$ transition in the benzene ring with the $n \rightarrow n^*$ transition of the C =N bond. Because of the small angles of rotation and the strong absorption, their RD curves were recorded only down to 290 nm (see Fig. 1).

Hernandezine (III) is fairly easily obtained from substance II. Thus, both the dimensions and the configuration of the dioxide ring do not change in this process and the increase in the molecular rotation of hernandezine as compared with II shows that the second asymmetric center also has the S configuration.



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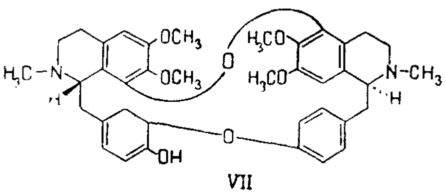

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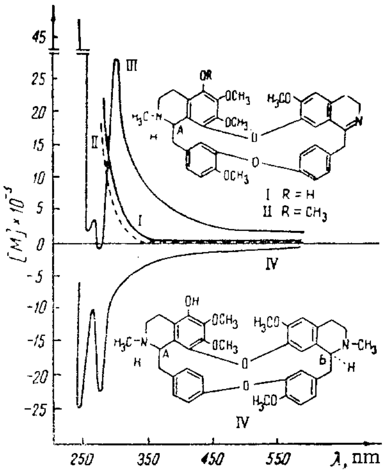
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 705-708, November-December, 1970. Original article submitted June 19, 1970.



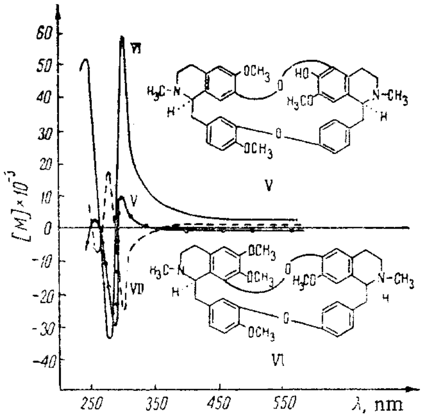


Fig. 1 Fig. 2

Fig. 1. RD curves of thalsimidine (I), thalsimine (II), hernandezine (III), and thalisopine (IV).

Fig. 2. RD curves of thalmine (V), O-methylthalicberine (VI), and thalfoetidine (VII).

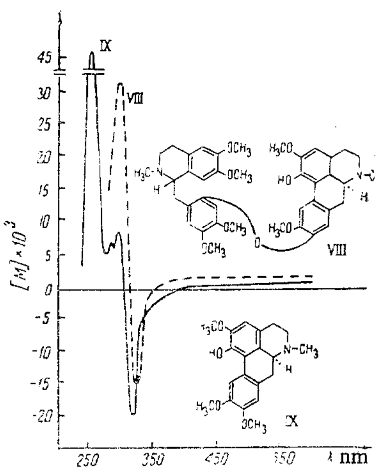


Fig. 3. RD curves of foetidine (VIII) and thalicmidine (IX).

The cleavage of thalisopine (IV) with sodium in liquid ammonia showed that the asymmetric center B has the S configuration, and the S configuration has been ascribed to the second center of asymmetry, A, on the basis of NMR spectra [6]. A measurement of the ORD of IV showed that in the 275 and 245 nm regions (see Fig. 1) there are two negative CEs, although, according to Battersby [1], in alkaloids of the type of oxyacanthine with an SS configuration there should be two positive CEs on a negative background.

The RS configuration has been proposed for thalmine (V) [7] and the SS configuration for O-methylthalicberine (VI) on the basis of NMR spectroscopy. In a study of the cleavage products, the SS configuration was found for V and VI. From the nature of the RD curve, the SS configuration is more likely for thalmine. Both alkaloids (V and VI) have RD curves with positive CEs differing only in amplitude (see Fig. 2). The considerable increase in the amplitude of the CE of VI as compared with V is possibly connected with a decrease in the size of the internal dioxide ring from 21- to 19-membered.

A Cotton effect of approximately the same amplitude as in thalmine but of opposite sign appears in thalfoetidine (VII) in the 290 nm region. The RS configuration has been proposed for this [11].

We have measured the ORD of foetidine (VIII) (Fig. 3), the aporphine fragment of which can be regarded as thalicmidine (IX). The latter has an RD curve with a negative CE in the 306 nm region (see Fig. 3) and, consequently, the S configuration [12]. Foetidine also has a negative CE in the same region, but its amplitude is larger than in thalicmidine. The increase in the amplitude of the CE could have been expected, since the benzylisoquinoline fragment in foetidine possesses the R configuration [13, 14]; a negative CE is also characteristic for this.

EXPERIMENTAL

The optical rotatory dispersions were measured on a VNIÉKIPRODMASh [All-Union Scientific-Research Experimental Design Institute for Food Machinery] SPU-M spectropolarimeter; cells with thicknesses of 1, 0.5, and 0.1 dm were used. The concentrations were varied between 1.0 and 0.01 mg/ml. The solvent was methanol.

SUMMARY

For all the bisbenzyltetrahydroisoquinoline alkaloids considered except thalisopine, positive CEs are found in the case of the SS configuration and negative CEs in the case of the RS configuration.

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