OPTICAL ROTATORY DISPERSION OF THE SPARTEINE ALKALOIDS

S. Iskandarov and S. Yu. Yunusov

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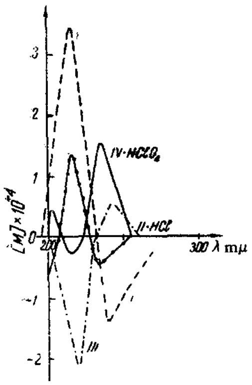
In a study of the IR and NMR spectra of the quinolizidine alkaloids, some characteristic parameters have been established which give information on the absolute configuration of these alkaloids [1, 2].

We have studied the possibility of applying the method of optical rotatory dispersion (OR) to the alkaloids of the sparteine series, which are characterized by the position of an amide carbonyl in a heterocyclic system. The curves of (–)-α-isolupanine (I), (+)-aphylline (II), (+)-17-oxosparteine (III), and (+)-aphyllidine (IV) were recorded (on a Cary 60 spectropolarimeter) in methanol, water, and tetrahydrofuran (figure). No substantial changes in the sign, shape, or amplitude of the curves were observed. These alkaloids have strong absorption in the UV spectrum in the 210 mμ region, with the exception of aphyllidine, in which the absorption maximum is shifted by 30 mμ in the long-wave direction due to the presence of a double bond conjugated with the carbonyl through the nitrogen atom.



OR curves of the sparteine alkaloids: I) (–)-α-isolupanine, II) (+)-aphylline, III) (+)-17-hydroxysparteine, and IV) (+)-aphyllidine.

Comparison of the OR curves shows that because of its low absorption coefficient the optically active band is not seen in the UV spectrum. These alkaloids, apart from IV, give curves with a simple Cotton effect at about 230 mμ. The signs of rotation change according to whether the carbonyl is present in a cis- or trans-quinolizidine system and do not depend on whether the carbonyl is in the outer or the inner ring, although the latter circumstance has a marked effect on the magnitude of the molecular amplitude of the rotation. Whether the quinolizidine part is cis or trans also affects the molecular amplitude of the rotation [I) 48 260°, II) 30 770°, and III) 18 000°].

The observed changes in the zero point of the extremum as a function of the conformation of the lactam ring are in agreement with chemical information concerning the relative stability of III [I and II) 232 mμ, III) 227 mμ] [3]. Although aphyllidine has intense absorption in the UV spectrum at 240 mμ, which is characteristic for the chromophore $-\overset{|}{C}=\overset{|}{C}-\overset{|}{N}-\overset{|}{C}=O$ [4], its optically active absorption is shifted 16 mμ and is fairly clearly determined because of its high rotation. In this case, the curves consist of three extrema. The rotation of the first extremum is far higher than that of the second, which has not been observed in the other spectra. When the OR curves of these alkaloids were recorded in an acid medium, no appreciable shift in the optically active rotation was recorded, but the molecular amplitude rose at the expense of the second extremum. Thus, the sign and amplitude of the rotation vary according to the configuration of the adjacent asymmetric centers.

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Institute of the Chemistry of Plant Substances, AS UzSSR