STRUCTURE OF TRISPHAERIDINE

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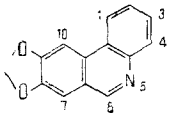
The structure of the alkaloid trisphaeridine has been established with the aid of IR and UV spectroscopy, high-resolution mass spectroscopy, and PMR and ^{13}C NMR spectroscopy.

The isolation from the leaves of *Ungernia trisphaera* Bunge, growing in the foothills of the Kopet-Dagh of the Ashkhabad region of the Turkman SSR, of the new optically inactive alkaloid trisphaeridine, $C_{14}H_{11}NO_3$, mp 140-141°C (acetone), mol. wt. 261, has been reported previously [1]. This alkaloid has also been isolated from *U. spiralis* Proskor, collected in the Kara-Kal region of the Turkman SSR and from the epigeal part (leaves and flowers) of *Galanthus plicatus* MB (family Amaryllidaceae) growing close to the village of Kochuliya, Moldavian SSR.

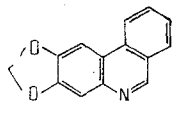
We give the results of an investigation of the structure of trisphaeridine (I).

The composition of (I) was established with the aid of high-resolution mass spectrometry: $C_{14}H_9NO_2$. M^+ 223 (100%). The IR spectrum of (I) contains bands in the 1500-1620 cm^{-1} region that are characteristic for the skeletal stretching vibrations of aromatic rings and at 765-860 cm^{-1} of ortho-disubstituted and 1,2,4,5-tetrasubstituted benzene rings [2]. There are no absorption bands corresponding to the vibrations of C=O, NH, and OH groups at 1700-1750 and 3100-3800 cm^{-1} respectively. The UV spectrum of (I) has three absorption maxima with $\lambda_{max}^{C_2H_5OH}$ 253, 280, and 309 nm (log ε 4.52, 4.06, and 3.60, respectively) showing the presence of an aromatic chromophore.

The PMR spectrum of (I) (Fig. 1) shows the following signals: at 5.98 ppm — a two-proton singlet corresponding to the CH_2 protons of an aromatic methylenedioxy group; at 7.13, 7.66, and 8.92 ppm — one-proton singlets, corresponding to isolated protons of aromatic and heteroaromatic rings; and 7.53 and 8.10 ppm — two-proton multiplets of aromatic protons. A weak-field one-proton broadened singlet at 8.92 ppm shows the presence in compound (I) of a N-heteroaromatic ring. Analysis of the characteristics of the IR, UV, and, especially, PMR spectra taking the composition of trisphaeridine into account permits two possible variants of the structure (I and II) to be suggested



I



II

For an unambiguous selection of the position of the nitrogen atom we performed experiments using the method of INDOR double resonance and of the NOE, which showed the existence of long-range spin—spin coupling of the protons with 8.92 and 7.66 ppm, and also their spatial propinquity, since on additional irradiation with a strong radiofrequency field having ν_2 = 766 Hz the signal of the proton with δ 8.92 contracted and its intensity rose. This fact gives grounds for selecting position 5 of the nitrogen atom, and structure (I) for trisphaeridine. Thus, trisphaeridine belongs to the alkaloids of the isoquinoline series, which is in harmony with biogenetic laws, since other alkaloids consisting of isoquinoline derivatives have been isolated from the family Amaryllidaceae [3].

Structure (I) for trisphaeridine was confirmed completely by the features of the ^{13}C NMR spectrum where signals appear in the 153-100 ppm region from 13 sp^2-hybridized aromatic and

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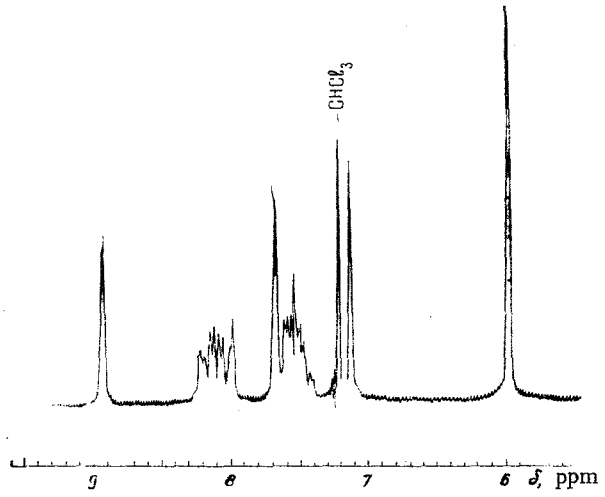

Fig. 1

heteroaromatic carbon atoms which in the "off-resonance" spectrum give six singlets and seven doublets, and also one triplet at 99.6 ppm relating to the carbon atom of an aromatic OCH_2O group. No signals were detected in the 100-0 ppm region apart from the signals of the solvent $CDCl_3$.

EXPERIMENTAL

The UV spectrum of (I) was obtained on a EPS-3T spectrometer in C_2H_5OH, the IR spectrum on a UR-20 spectrophotometer in paraffin oil, the high-resolution mass spectrum on a MKh-1310 spectrometer and the PMR spectrum on JNM-4H-100/100 MHz and Varian-XL-100-15 spectrometers in $CDCl_3$ with 0 — HMDS. The ^{13}C NMR spectrum of (I) was obtained on a Varian-CF T-20 instrument at a frequency of 20 MHz, $CDCl_3$, 0 — TMS, pulsed regime, Fourier transformation, under the conditions of complete and partial "off-resonance" decoupling from protons.

SUMMARY

The structure of the alkaloid trisphaeridine has been established on the basis of an analysis of IR, UV, and high-resolution PMR spectra and ^{13}C NMR spectra.

LITERATURE CITED

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