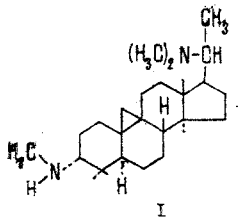

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IOLANTINE — A QUATERNARY BASE FROM *Merendera iolantae*

Kh. Turdikulov, Nguen van Dau, and M. K. Yusupov

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By chromatography on a column of alumina of the mixture of nonphenolic bases from *Merendera iolantae* E. Czerniak [1], we have isolated, in addition to iolantamine [2] and iolantimine [3], a new base with the composition $C_{20}H_{27}O_4N$, mp 269-270°C (acetone–methanol), which we have called iolantine.

From the nature of the UV spectrum, with absorption maxima at 210 and 285 nm, we can suggest for iolantine the carbon–nitrogen skeleton of homoproaporphine or proaporphine [4]. Its IR spectrum contains absorption bands corresponding to a hydroxy group (3400 cm^{-1}), a carbonyl group conjugated with a double bond (1650, 1630 cm^{-1}), the C=C bonds of a benzene ring (1600 cm^{-1}), and methylene groups (1460 cm^{-1}). The mass spectrum shows the peaks of ions with m/e 313, 312, 298, 285, 270, 244, 214, and 205, and the PMR spectrum (Fig. 1) shows the resonance signals of one methoxy group (three-proton singlet at 3.47 ppm), two N-methyl groups (three-proton singlets at 2.56 and 2.90 ppm), an AB quartet of two ortho olefinic protons with centers at 5.81 and 6.82 ppm, and of one aromatic proton (one-proton singlet at 6.34 ppm).

In its spectral characteristics, iolantine is close to the homoproaporphine alkaloids dihydrokreysiginone [5], bulbocodine [6], crociflorinone [7], and iolantanine, which have a spirocyclohexenone system in their molecule. At the same time, the presence of two N-methyl groups permits its assignment to the quaternary bases. The resonance signals of the methyl groups and of the aromatic and olefinic protons in iolantine and iolantamine [2] correlate with one another, with the exception of the presence of the second N-methyl group (2.90 ppm) in the former. On the basis of what has been said above we have suggested that iolantine has the structure of a quaternary base derived from iolantamine (I). To confirm this, the methiodide of iolantamine was treated with freshly-precipitated solver hydroxide. A strongly colored mixture of three substances was obtained — with R_f 0.5 (the main product),

V. I. Lenin Tashkent State University.

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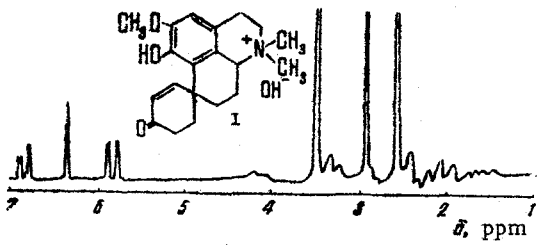

Fig. 1. PMR spectrum of iolantine (in CF_3COOOH).

0.30, and 0.38 [PC; n-butanol—5% acetic acid (1:1)]. The first of them apparently consists of the product of oxidation of the phenolic group, and the third was identical with iolantine.

For a definitive confirmation of the structure, we methylated iolantine and iolantamine with methyl iodide in the presence of potassium carbonate. In both cases we isolated the methiodides of their O-methyl ethers with mp 270-271°C, and these were identical with crocifiorinone methiodide.

This is the first time that a quaternary isoquinoline base has been isolated from colchicine-containing species of Liliaceae.

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THE STRUCTURE OF DIPTHOCARPAINE

S. F. Aripova, O. Abdulalimov, V. M. Malikov, and S. Yu. Yunusov

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Continuing a study of the alkaloids of *Dipthychocarpus strictus* [1], we have studied the structure of dipthocarpaine, $C_8N_{18}N_2O_2S$ (I), mp 124-125°C, (acetone—methanol), $[\alpha]_D^{23}$ −80.33° (ethanol). In the IR spectrum of the base there are the bands of active hydrogen (3220, 3380 cm^{-1}), of an amide carbonyl group (1660 cm^{-1}), and of a S→O bond (1035 cm^{-1}).

The NMR spectrum of (I) (JNM-4H-100/100 MHz in $CDCl_3$ with HMDS as internal standard) has the following signals (ppm): δ 1.1-1.8 (8H, m, methylene protons), 2.25 (3H, $S\overset{O}{\rightarrow}CH_3$); 2.73 (2H, t, CH_2—S); 3.03 (2H, q, CH_2—H); 5.38 (1H, t, NH), and 4.39 (2H, —CO—NH_2).

The mass spectrum of the base gives the peak of the molecular ion with m/e 206 and the peaks of ions with m/e 162, 143 ($M - S\overset{O}{\rightarrow} - CH_3$), 129, 119, 100, 73, 61, 44. As mentioned previously [1], in the reduction of the alkaloid with lithium tetrahydroaluminate, and also with zinc and hydrochloric acid, an optically inactive substance (II) with mp 118-

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