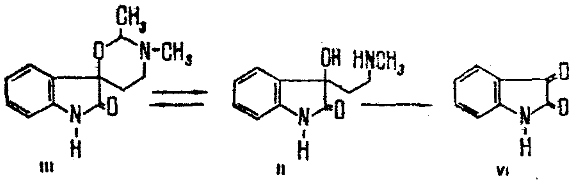

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CONFIGURATION OF *l*-CYCLOPROTOBUXINE-C

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We have previously reported the isolation of the new alkaloid *l*-cycloprotobuxine-C with mp 195-197°C, $[\alpha]_D - 62°$, $C_{27}H_{48}N_2$ (I), and we concluded that it was the levorotatory form of cycloprotobuxine-C (II) [1-3]. However, a comparison of (I) with an authentic sample of (II) (kindly given to us by J. Tomko, Bratislava) showed a difference in their physicochemical properties. Consequently, (I) is not the antipode of (II).

The mass-spectrometric decomposition of (I) takes place similarly to that of (II) but differs in the intensities of the peaks of the ions. In both (I) and (II) the maximum peak is that of the ion with m/e 72. On comparing the chemical shifts of the protons of the secondary and tertiary methyl groups in the NMR spectra of (I) and (II), a downfield displacement of the signal of the protons from the 18-CH_3 group in (I) by 4 Hz was found [4]. Such a displacement is connected with a configurational difference of the C_{20} asymmetric center and in (I), probably, the $N(CH_3)_2$ at C_{20} has the β orientation. A study of the rates of saponification of buxaline-C, baleabuxidine [5-7], and the N-acetyl derivative of (I) showed that buxaline-C (III) and baleabuxadine (IV) are readily hydrolyzed [(III) has a 3β-N-acetyl group and (IV) a 3β-N-isobutyryl group), while the N-acetyl and N-benzoyl derivatives of (I) do not undergo acid or alkaline hydrolysis under various reaction conditions. Such an inhibition of saponification is observed only when the N-acyl group at C_3 has the α-axial orientation (examined on models of (I) and (II)]. Consequently, in (I) the $NH-CH_3$ group at C_3 has the α-axial orientation.

On the basis of the facts given, it may be considered that the alkaloid (I) is a stereoisomer of (II) and has the most probable structure and configuration of 20β-dimethylamino-4,4,14α-trimethyl-3α-methylamino-9β,19-cyclo-5α-pregnane:

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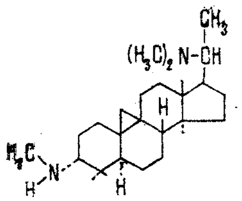

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IOLANTINE — A QUATERNARY BASE FROM *Merendera iolantae*

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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),

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