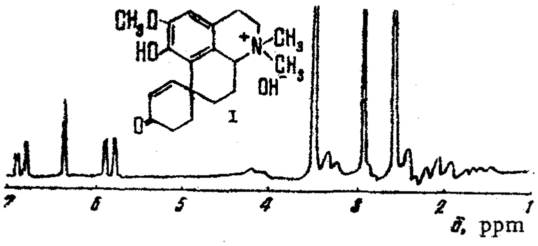

Fig. 1. PMR spectrum of iolantine (in CF_3COOOH).

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 crociflorinone 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

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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 $S \rightarrow O$ 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, $\overset{\overset{O}{\nearrow}}{S}—CH_3$); 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 2.06 and the peaks of ions with m/e 162, 143 $(M - \overset{\overset{O}{\nearrow}}{S} - CH_3)$, 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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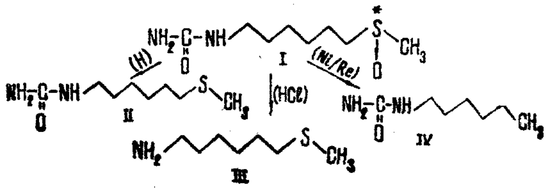
119°C, mol. wt. 190 (mass spectrometrically) was obtained. The IR spectrum of (II) differed from that of the initial base only by the absence of a band at 1035 cm^{-1} (sulfoxy group). In a comparative study of the NMR spectra of (I) and (II) it was found that the signal of the protons of the methyl group attached to the sulfur had undergone a diamagnetic shift by 0.5 ppm. The difference in the molecular weights of (I) and (II) of 16 m/e also shows that in this process the sulfoxy group was apparently reduced.

Dipthocarpaine gives the biuret reaction for urea derivatives and, consequently, it is an N-alkyl derivative of the latter. When dipthocarpaine was heated in 6 N hydrochloric acid in a sealed tube (110°C), an amorphous substance (III) was isolated with mp 90-92°C, mol. wt. 147 (mass spectrometrically). The IR spectrum of (II) lacked the absorption bands of an amide carbonyl group. The mass spectrum gave the peaks of ions with m/e 147 (M^+), 117 $(M - CH_2NH_2)$, 103 $(117 - CH_2)$, 100 $(M - S - CH_3)$, 61 $(CH_3{-}S{-}CH_2{-})$, and 86 $(100 - CH_2)$.

The hydrogenation of dipthocarpaine in the presence of Raney nickel [1] gave an optically inactive substance of neutral character with mp 108-109°C (IV). The IR spectrum of this differed from that of (I) by the absence of a band at 1035 cm^{-1}. In the NMR spectrum of (IV) in the strong-field region a triplet appeared at δ 0.83 ppm (3H) from the protons of the methyl of an ether group, and the signals of the protons of the $CH_2{-}\overset{O}{\overset{\nearrow}{S}}{-}CH_3$ group had appeared. The mass spectrum showed the peaks of the molecular ion with m/e 144 and the peaks of ions with m/e 129, 115, 101, 87, and 73 corresponding to the successive splitting out of 14 m/e. In all its properties, (IV) is similar to the N-n-hexylurea described in the literature [2].

Thus, the facts given permit the assumption that dipthocarpaine has the structure of N-(6-methylsulfinylhexyl)urea (I):



The presence of optical activity in dipthocarpaine and the absence of it in the products of its reduction are explained by the presence of the sulfoxy group in the molecule, where the sulfur atom bound to two nonequivalent radicals and one electron pair playing the role of fourth substituent is asymmetric [3].

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