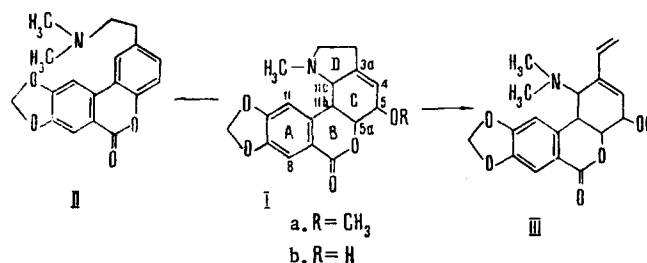


NMR-, MASS-, AND IR-SPECTROSCOPIC STUDY OF THE STRUCTURES OF 1-DES-N-METHYLUNGERINE AND 1-DES-N-METHYLHIPPEASTRINE*

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It has been shown previously [1, 2] that the Hofmann degradations of the alkaloids ungerine (Ia) and hippeastrine (Ib) take place differently in the first stage, as a result of which 1-des-N-methylungerine (II) and des-N-methylhippeastrine (III) are formed according to the two possible cleavages of a C-N bond in ring D.



It appeared of interest to study the structure of products (II) and (III) by the methods of NMR, mass, and IR spectroscopy (Figs. 1 and 2).

The integration of the areas of the signals in the NMR spectrum of 1-des-N-methylungerine (II) (Fig. 1a) shows that the substance contains 17 protons. In the aromatic part of the spectrum the signals of five protons appear clearly at τ 2.42 ppm (singlet, 2H), 2.66 ppm (singlet, 1H), and 2.83 ppm (singlet, 2H). The two aromatic protons H_4 and H_5 of ring C are equivalent and therefore give a singlet at 2.42 ppm, and the third (H_{11c}) is superposed on the signal of the H_{11} proton of ring A. As in ungerine [3], the protons of the methylenedioxy group of (II) are equivalent and are observed in the form of a two-proton singlet at 3.96 ppm, and the signals of the protons of the $N(CH_3)_2$ group are found in the form of a singlet at 7.75 ppm (6H). The signals of the methylene protons of the $N-CH_2-CH_2-Ar$ group are observed in the form of two multiplets in the regions of 7.25 ppm ($N-CH_2$) and 7.55 ppm ($-CH_2-Ar$).

In the NMR spectrum of 1-des-N-methylhippeastrine (III) (see Fig. 1b), unlike that of compound (II), there are only the signals of the two aromatic protons H_8 and H_{11} of ring A in the aromatic region - singlets at 2.54 and 2.99 ppm (1H each), the total intensity of all the signals of (III) amounting to 19 H. Furthermore, in the spectrum of compound (III) the clearly appearing signals of four olefinic protons [quartets at τ_1 5.25 ppm, $J_1^{cis} = 13$ Hz, $J_2^{gem} = 2.0$ Hz, and $\tau_2 = 4.94$ ppm, $J_1^{trans} = 14$ Hz, $J_2^{gem} = 2.0$ Hz, relating to the terminal methylene group $=CH_2$; broad signals at 4.29 ppm (1H) and 3.67 ppm (1H) due to the H_3 and H_4 protons] completely confirm the correctness of the proposed structure (III). What is unusual in the spectrum of (III) (See Fig. 1b) is the fact that the cis and trans spin-spin coupling constants of the $-CH=CH_2$ protons differ only slightly. In the NMR spectrum of (III), in addition to those mentioned, signals of

*The original nomenclature is used - translator.

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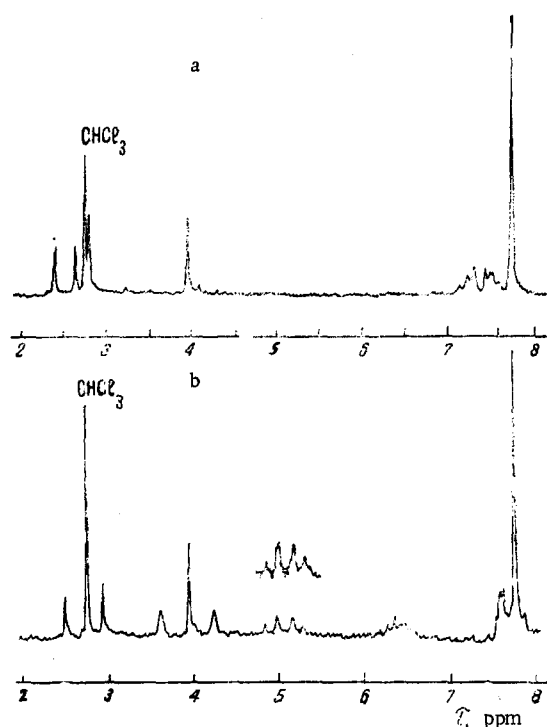


Fig. 1. NMR spectra of 1-des-N-methylungerine (a) and of 1-des-N-methylhippeastrine (b).

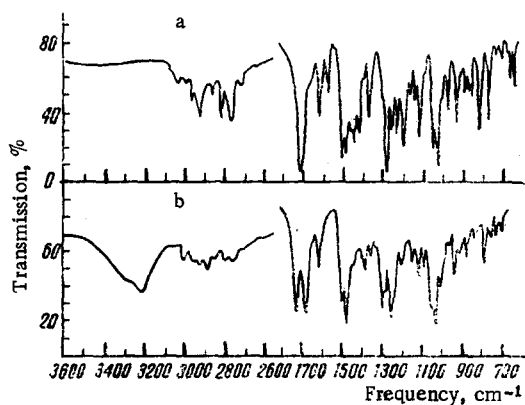


Fig. 2. IR spectra of 1-des-N-methylungerine (a) and of 1-des-N-methylhippeastrine (b).

OCH_2O are observed at 4.00 ppm (s, 2H), of $\text{N}(\text{CH}_3)_2$ at 7.67 ppm (s, 6H), of H_5 and H_{5a} in the 6.20–6.60 ppm range (m, 2H), and of H_{11b} , H_{11c} , and OH at 7.60 ppm (m, 3H).

The features of the NMR spectrum of 1-des-N-methylhippeastrine also agree with its molecular weight (329), determined mass spectrometrically. In the mass spectrum of (III) there is an intense peak of an ion with m/e 311 corresponding to the fragment $\text{M}-\text{H}_2\text{O}$.

Additional information on the structure of compounds (II) and (III) can be obtained by an analysis of their IR spectra (Fig. 2a and b). On comparing the IR spectra of (II) and (III) it can be seen that they differ fundamentally. The IR spectrum of (III) (see Fig. 2b), unlike that of (II), shows a well-defined broad band with a maximum at 3230 cm^{-1} due to the stretching vibrations of OH groups involved in intermolecular hydrogen bonds. The IR spectra of (II) and (III) also differ appreciably in the region of the stretching vibrations of the $\text{C}=\text{O}$ of the lactone ring B ($1730\text{--}1685\text{ cm}^{-1}$), in that of the skeletal vibrations of the aromatic ring ($1620\text{--}1500\text{ cm}^{-1}$), and in the "fingerprint" region ($1300\text{--}700\text{ cm}^{-1}$). Thus, it follows from the spectral characteristics given that the Hofmann degradation of alkaloids of the ungerine type takes place in two directions in the first stage: both with the aromatization of ring C (II) and without it (III).

EXPERIMENTAL

The NMR spectra (deuteriochloroform) were obtained on a JNM-4H-100 instrument with a working frequency of 100 MHz using HMDS as internal standard. The chemical shifts are given in the τ scale. The mass spectrum of (III) was taken on an MKh-1303 instrument fitted with a system for the direct introduction of the substance into the ion source. The IR spectra (tablets with KBr) were recorded on a UR-10 instrument.

SUMMARY

The results of a comparative study of the NMR, mass, and IR spectra have shown that the structures proposed previously for 1-des-N-methylungerine and 1-des-N-methylhippeastrine are correct.

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