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RETAMINE N-OXIDES

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We report on the preparation, identification and structural studies of not only the monoamine oxides but also the diamine oxide of the Lupine alkaloid, retamine. So far only monoamine oxides of a few related species such as sparteine (1) have been prepared.

Treatment of retamine with an excess of 30% (by weight) Merck perhydrol in methanol for two days at room temperature gave a mixture of three products (t.l.c.). Component (A) (m.p., 184°C), with the lowest Rf value, was effectively separated from the faster moving components by trituration with $CHCl_3$. Careful column chromatography on basic "Woelm" alumina, activity IV, gave components (C) (m.p., 195°C) and (B) (m.p., 179°C) consecutively. Products (A), (B) and (C) were obtained in the approximate ratio 3:1:1:

Mass spectrometry (2) of the three compounds, using direct insertion, showed molecular ions consistent with components (A) and (C) being monoamine oxides of retamine (m/e 266), and with component (B) being a diamine oxide (m/e 282). Elemental analyses obtained on samples dried at room temperature under high vacuum were correct for monoamine oxide (C), and for monoamine oxide (A) and diamine oxide (B) containing 1.3 and 1.7 moles of water, respectively.

The above results are consistent with the structure of retamine being 12a-Hydroxy-(+)-sparteine (3,4) with ring C in the boat form.

In order to establish the structure of the above N-oxides the IR spectra (5) of these compounds were measured in chloroform solution dried over Molecular Sieve 5A. The IR spectrum of the diamine oxide showed no Bohlman's bands in the 2840-2600 cm^{-1} region suggesting that the lone pair of the nitrogen atoms have been utilised for bond formation with oxygen (6). The OH stretching frequency indicated intramolecular hydrogen bonding between the N-O and the O-H groups. The above results are consistent with the ring C of diamine oxide of retamine being in the boat form as is the case with retamine itself.

The IR spectrum of the monoamine oxide (C) showed the presence of two bands at 2805 and 2765 cm^{-1}, the former being more intense. This suggests a cis-fused rings C and D with the former being in a boat and the latter in the chair form (7). This thus indicates that the N-oxide function is at N_1. Hydrogen bonding between the hydroxyl group and the N_{16} lone pair supports this view. The conversion of this amine oxide to the diamine oxide with hydrogen peroxide lends further support to the view that ring C is in the boat form.

IR bands at 2805 and 2765 cm^{-1} and a broad -OH band in the spectrum of the monoamine oxide (A) suggested a structure similar to monoamine oxide (C) but the fact that the monoamine oxide (A) could not be converted into the diamine oxide (B) on further treatment with hydrogen peroxide implied that ring C could not be in the boat form (8).

Further support for the structures of monoamine oxides (A) and (C) and diamine oxide (B) was obtained by pyrolysis of the N-oxides in vacuum followed by borohydride reduction of the resulting products.

Monoamine oxide (A) and diamine oxide (B) gave a mixture of three main compounds (t.l.c.). The fastest moving component was identified as retamine (t.l.c.) and the slowest moving component as 12e-Hydroxy-α-isosparteine (9) (t.l.c. and mass spectra (10)). The third component was presumably 12a-Hydroxy-α-isosparteine (Fig. 1). Monoamine oxide (C) gave only retamine.

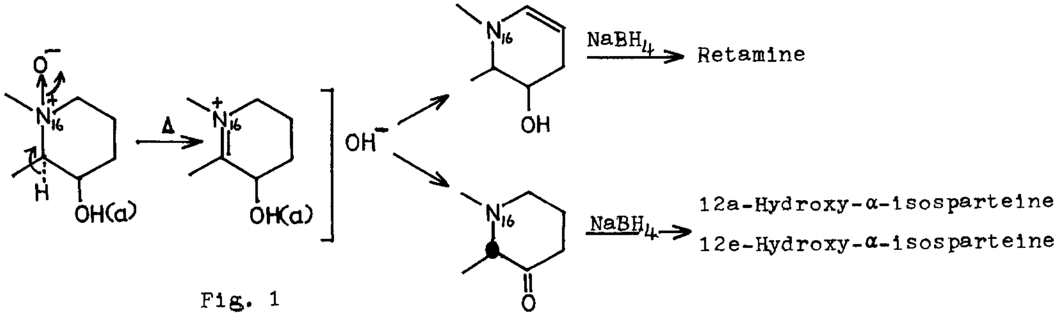
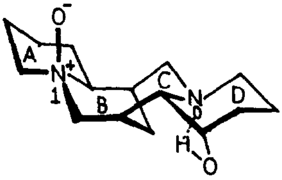
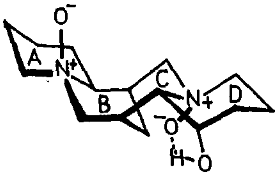


Fig. 1

The above results suggest that N-oxides (B) and (C) possess structures (I) and (II) respectively and we believe that N-oxide (A) is an N_{16}-oxide with ring C in the chair form. The possibility of inversion of N_{16} in compound (A) has been considered in the literature for the sparteine nucleus.



II



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