

ALKALOIDS FROM NUPHAR LUTEUM. PART IV. MASS SPECTROSCOPY OF  
THIOBINUPHARIDINE, NEOTHIOBINUPHARIDINE AND THEIR  
DESULPHURATION PRODUCTS

O. Achmatowicz, H. Banaszek, G. Spitteller, and J.T. Wróbel

Department of Organic Chemistry, Warsaw University  
Institute of Organic Synthesis, Polish Academy of Sciences,  
Warsaw

Institute of Organic Chemistry, Vienna University

(Received 7 March 1964)

The assumption<sup>1)</sup> of a relationship between thiobinupharidine and neothiobinupharidine - the two crystalline sulphur alkaloids from Nuphar Luteum and deoxynupharidine has now been confirmed by mass spectroscopy. The spectra of thiobinupharidine and neothiobinupharidine (Fig.1) differ only in their intensities. Thus it may be concluded that the compounds in question are stereoisomers. The spectra indicate the molecular weight  $M = 494$ , which agrees with that obtained from analytical data.

Both alkaloids show beside the strong peaks of the molecular ions key fragments at masses 359, 230, 178, 136, and 94 (cf. Fig.1). Interpretation of the peaks was based upon an analysis of the mass spectrum of the deoxynupharidine (I), Fig.2. The spectrum contains key fragments at masses 94, 98 and 136. The presence of those fragments may be understood on

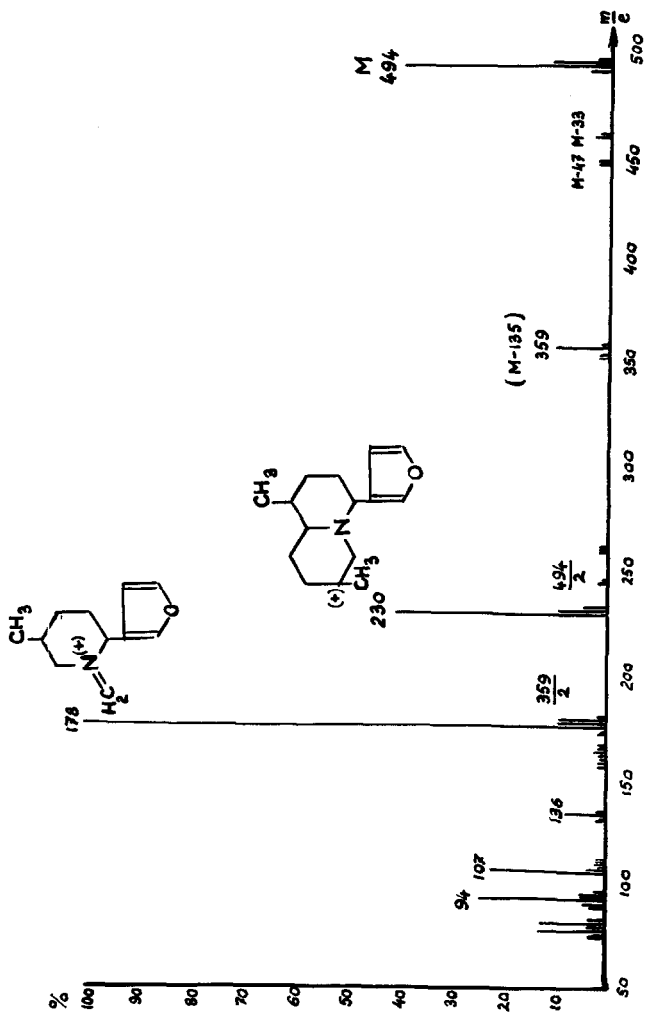


FIG. 1

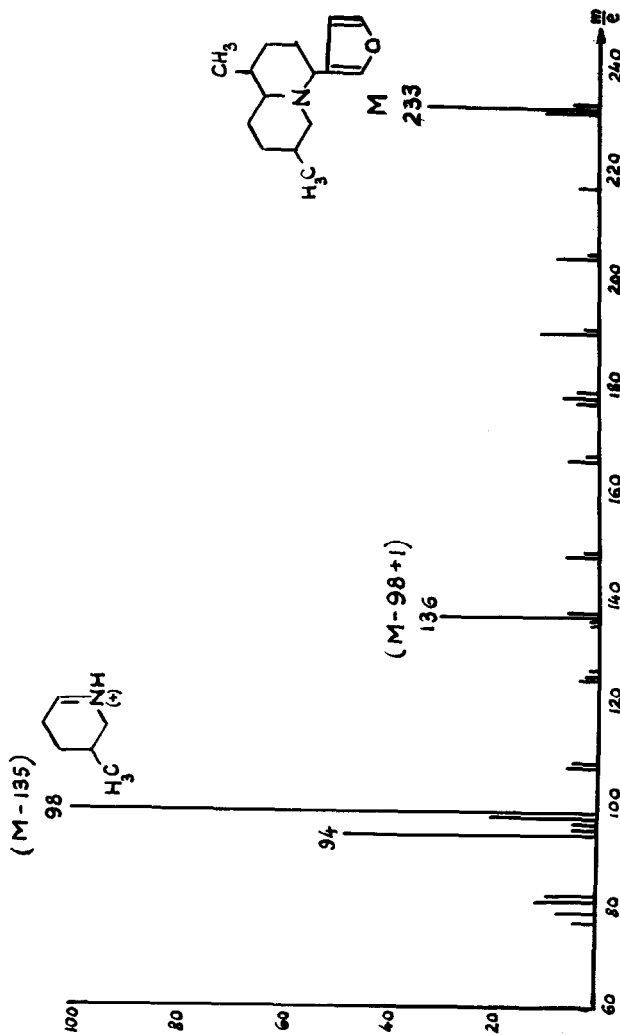
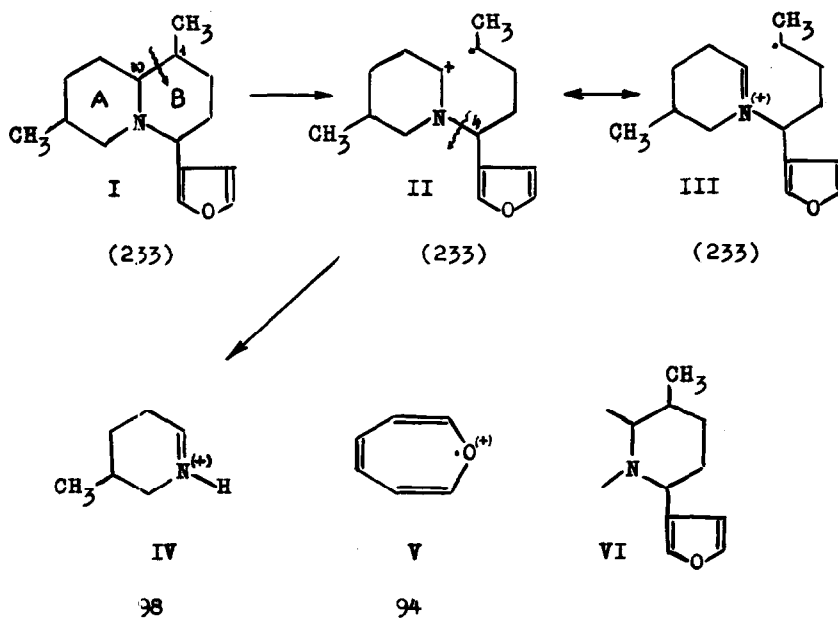


Fig. 2

the following basis: Cleavage of a carbon-carbon bond next to a nitrogen is strongly favoured, because the electron pair of a nitrogen atom may stabilise a positive charge of a neighbouring carbon. Further stabilisation of the positive charge



obtained by hyperconjugation makes a preliminary fission of the bond between carbons 1 and 10 understandable. Ion (III), still having the mass of the molecular ion 233 (II) is now cleaved between the nitrogen and C-4 with a simultaneous shift of the hydrogen atom resulting in the appearance of the key fragment of the mass 98 (IV). The preliminary fission combined with this shift seems to be possible in this case owing only to the presence of the furan ring, because other quinolizidine alkaloids are usually cleaved between C-3 and C-4<sup>2)</sup>.

The second fragment formed by the cleavage of the deoxynupharidine molecular ion has 136 mass units; no suggestions are made concerning its structure, since the character of the rearrangement which must occur to stabilise the fragment is not known.

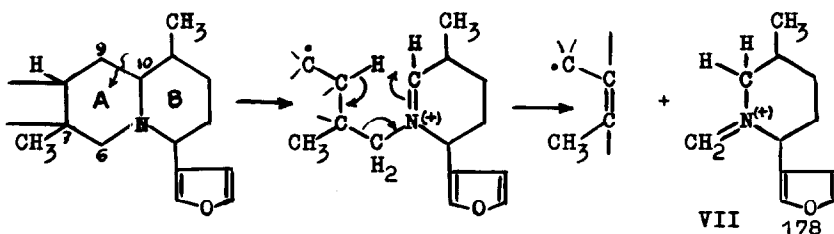
The third key peak in the deoxynupharidine spectrum corresponds to the mass 94. Fragments of this mass are often found in the spectra of compounds containing a furan ring with a side chain. Its structure may be of the type represented by (V). Thus the peak at mass 94 in the spectrum of neothio- and thiobinupharidine independently confirms the presence of a furan ring previously indicated by IR and NMR spectra.

The peak observed at mass 98 in the deoxynupharidine spectrum corresponds to the loss of 135 mass units from the molecular ion. In the neothio- and thiobinupharidine spectra, peaks are observed at mass 359, corresponding to the same loss of mass. This seems to indicate the presence of the system (VI) in neothio- and thiobinupharidine, further confirmed by the peak at mass 136, which also is present in the spectrum of deoxynupharidine.

The mixture of bases obtained by desulphuration of neothio- and thiobinupharidine under very drastic conditions (ethanolic solution, 200°C, 100 atm) was investigated by mass spectrometry. The spectrum obtained by fractional evaporation of each sample within the ion source was identical with that of deoxynupharidine. Therefore it was deduced that each of the two alkaloids consists of two deoxynupharidine skeletons linked by one C-C and one C-S-C bond: 494 (molecular weight of

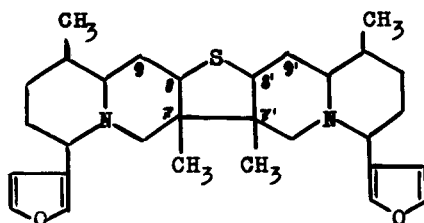
neothio- and thiobinupharidine) =  $2 \times 233$  (molecular weight of deoxynupharidine) + sulphur (32) - 4 H (4). The bonds between the two deoxynupharidine skeletons are not possible at any position of either ring B, or the furan ring, because otherwise the fragments of mass 136 and M-135 would not be found. Therefore the bonds linking the two deoxynupharidine skeletons must be situated in rings A, causing their easier cleavage.

Thus it seems that the presence of the fragment of mass 178 (VII) can be explained by cleavage of the bond C9 - C10 followed by fission of the bond C6 - C7 and by a shift of one hydrogen from C8 to C10.



Kuhn-Roth determination yields results corresponding to  $2 \text{ } \overset{\cdot}{\text{C}}\text{-CH}_3$  groups. This means that there are three or four of these groups excluding at the same time the linking of the two skeletons by methylene groups. Therefore the bonds between the two deoxynupharidine skeletons can only be situated in positions 7, 8 or 9. Moreover the C-C bond is likely to be at carbons 7, 7' because the presence of methyl groups on a quaternary carbon was shown by NMR spectra, and the Kuhn-Roth determination of this grouping yields usually too low results.

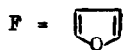
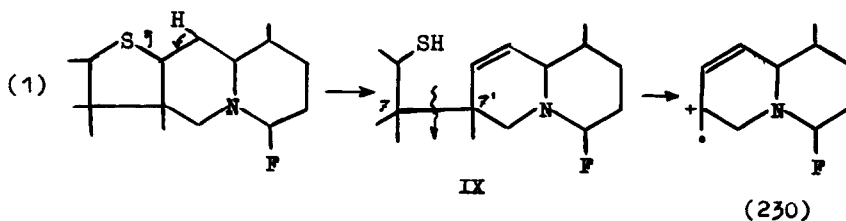
The above data lead to the structure (VIII) of neothio- and thiobinupharidine, as a working hypothesis:



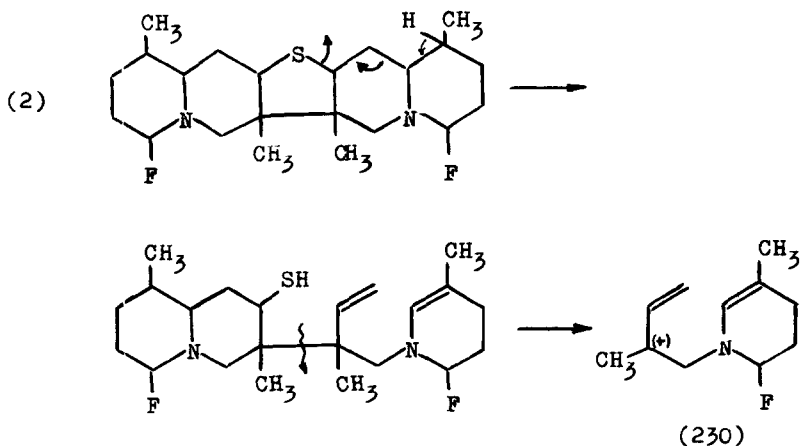
VIII

The possibility of the two skeletons being linked in positions 7,7' and 9,9' simultaneously is excluded owing to steric reasons. Neither is there a possibility of linkages between carbons 8,8' and 9,9' since the molecule would then contain 4  $-\overset{\text{O}}{\underset{|}{\text{C}}}\text{H}-\text{CH}_3$  groups and this is ruled out by the NMR spectrum. From the steric point of view there are no objections to the sulphur being situated between 7,7' or 7,8' atoms.

The proposed structure accounts for the presence of the peak at mass 230. If a hydrogen shift over a 4 membered transition state (eq.1)<sup>3)</sup> is assumed an intermediate (IX) results in which the C7 - C7' bond may be easily broken, owing to the activating influence of the allylic group:



An alternative mechanism involving a 6 membered transition state (eq.2) may also be taken into account:



Reactions of this type are well known for compounds having a double bond, but it was only recently shown that they occur in the same manner in the decomposition of alcohols, thiols and ethers<sup>4</sup>).

The spectra were made on the Atlas CH4 mass spectrometer, using a direct inlet system. The compounds were evaporated at 70° - 80°; the mass spectrum of deoxynupharidine was obtained as hydrochloride, according to the procedure described earlier<sup>5</sup>).

#### References

- 1) O.Achmatowicz and J.T.Wróbel *Tetr. Letters* 1964, 129
- 2) G.Spiteller and N.Neuer-Jehle - to be published
- 3) F.W.Mc Lafferty, *Analyt. Chem.* 29, 1782 (1957)
- 4) G.Spiteller and M.Spiteller-Friedmann *Mh. chem.* 95, (1964) February - in print.
- 5) G.Spiteller and M.Spiteller-Friedmann *Mh.chem.* 94, 742 (1963)