Chemical Structure of Deoxynupharidine, the Alkaloid Obtained from Nuphar Japonicum

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Hofmann degradation and subsequent ozonolysis of deoxynupharidine, $C_{15}H_{23}NO$ (I), the alkaloid obtained from the roots of *Nupher Japonicum* afforded 3-furaldehyde (Dimedone derivative, m. p. 167–170°, Found: C, 70.35; H, 7.18. Calcd. for $C_{21}H_{26}O_5$: C, 70.39; H, 7.26), which was identified by silver oxide oxidation to 3-furoic acid (m. p. 122–123°. Found: C, 53.89; H, 3.47. Calcd. for $C_5H_4O_3$: C, 53.57; H, 3.57), and characterization of the latter by means of mixed melting point and infrared spectrum. Compound I which gives an orange colored Ehrlich reaction, has a λ_{max} at 213 mμ ($\log \varepsilon=3.9$), and shows infrared absorptions at 873, 1500, and 3120 cm^{-1} corresponding to a furan ring; these absorption maxima and coloration dissappear upon conversion into tetrahydrodeoxynupharidine by catalytic reduction of I.

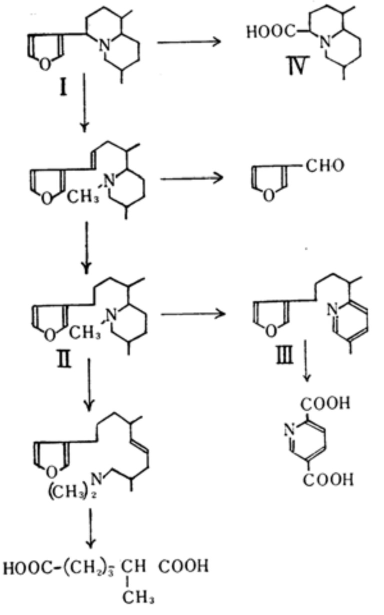
Palladium dehydrogenation of I, or dehydrogenation of $C_{15}H_{24}NO\cdot CH_3$, (II) (Perchlorate, m. p. 97–98°) resulting from Hofmann degradation and catalytic reduction of (I), afforded $C_{15}H_{19}ON$ (III) (Platinum chloride complex, m. p. 155–160°); potassium permanganate oxidation of (III) yielded pyridine 2, 5-dicarboxylic acid (Dimethylester, m. p. 163–164°. Found: C, 55.36; H, 4.39; N, 7.24. Calcd. for $C_9H_9NO_4$: C, 55.33;

H, 4.56; N, 7.11), which was identified through a mixed melting point test and infrared absorption comparison with an authentic sample.

Further Hofmann degradation and ozonolysis of II gave a dicarboxylic acid, m. p. 84.5–85° (Found: C, 52.78: N, 7.22. Calcd. for $C_7H_{12}O_4$: C, 52.50; H, 7.50.), which was shown to be α-methyladipic acid from the infrared spectra of its dimethyl ester and *p*-bromophenancyl ester (measured in chloroform).

An acid, m. p. 181–183° (Found: C, 68.07; H, 9.85; N, 6.53. Calcd. for $C_{12}H_{21}NO_2$: C, 68.25; H, 10.02; N, 6.64.), resulting from the nitric and chromic acid oxidation of I, and the two pK_a' values at 2.0 and 10.8 suggested that it is presumably an α-amino acid of formula IV.

The mentioned facts point to the proposed structure I, and the reactions involved may be represented by the following scheme:



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