

THE STRUCTURES OF α - AND β -OBSCURINE

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OBSCURINE, a minor alkaloid occurring in several species of Lycopodium, including L. obscurum L. var. dendroideum, was first isolated in 1942 by Manske and Marion¹. Later², it was shown that obscurine is actually a mixture of two bases, α -obscurine ($C_{17}H_{26}ON_2$) and β -obscurine ($C_{17}H_{24}ON_2$). We now wish to report evidence which allows us to propose complete structures for these two alkaloids. Analytical results have confirmed the molecular formulas and have shown that, contrary to a previous report², both α - and

¹ R. H. F. Manske and L. Marion, Canad. J. Research B. 20, 87 (1942).

² B. P. Moore and L. Marion, Canad. J. Chem. 31, 952 (1953).

β -obscurine have an N-methyl group. Calc. for $C_{17}H_{26}ON_2$ (α -obscurine): C, 74.41; H, 9.55; N, 10.21; 1N-CH₃, 5.48; 1C-CH₃, 5.48%. Found: C, 74.43; H, 9.51; N, 10.27; N-CH₃, 5.49; C-CH₃, 3.03%. Calc. for $C_{17}H_{24}ON_2$ (β -obscurine): C, 74.96; H, 8.88; N, 10.29; 1N-CH₃, 5.52%. Found: C, 74.88; H, 8.74; N, 10.13; N-CH₃, 5.21, 5.42%.

Initial structural studies² on β -obscurine established the presence of an α -pyridone ring in the alkaloid and later work³ indicated that the basic nitrogen is tertiary.

α -Obscurine does not exhibit the spectral properties of an α -pyridone, but shows instead a maximum in the ultraviolet at 255 m μ ($\log \epsilon$, 3.75)² and bands in the infrared (measured in CCl₄ solution) at 1675 cm⁻¹ (strong, amide C=O) and 1700 cm⁻¹ (medium intensity, C=C). However palladium-charcoal dehydrogenation of α -obscurine yields 6-methyl- α -pyridone², suggesting the presence of a partially reduced α -pyridone ring in the alkaloid. Attempted acetylation of α -obscurine with refluxing acetic anhydride-pyridine yielded starting material as the only isolable product, confirming the tertiary nature of the

³ F. A. L. Anet and C. R. Eves, Canad. J. Chem. 36, 902 (1958).

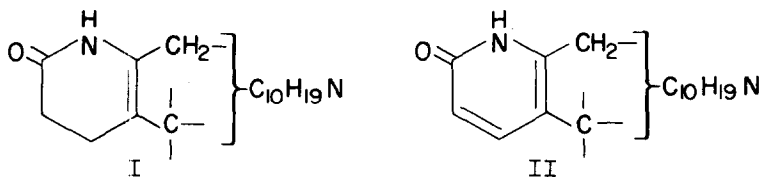
basic nitrogen. Since both α - and β -obscurine show an N-H stretching band in the infrared, the non-basic nitrogen must be secondary.

The possibility that α -obscurine contains a 5,6-dihydro- α -pyridone ring is ruled out by the spectral data already presented. The ultraviolet spectrum does not agree well with that of 6-methyl-5,6-dihydro- α -pyridone ($\lambda_{\text{max.}}$ 241, $\log \epsilon$ 3.17)⁴ and the high infrared frequency of the C=C stretching vibration suggests that the double bond is not conjugated to the carbonyl group but, by analogy with the structurally similar enol δ -lactones⁵, is attached directly to the amide nitrogen. The nuclear magnetic resonance spectrum of α -obscurine shows that it carries no vinylic hydrogens, whereas that of β -obscurine shows two doublets (each corresponding to one hydrogen) in the double-bond region. The formation of 6-methyl- α -pyridone on dehydrogenation, together with other data outlined above and the fact that α -obscurine contains only one C-methyl group (Kuhn-Roth determination) present in the grouping $>\text{CHCH}_3$ (NMR), may be interpreted in terms of partial structures I and II for α - and β -obscurine,

⁴ O. E. Edwards and T. Singh, Canad. J. Chem. 32, 683 (1954).

⁵ R. N. Jones and B. S. Gallagher, J. Amer. Chem. Soc. 81, 5242 (1959).

respectively.



It was now necessary to prove unambiguously that α -obscurine is simply dihydro- β -obscurine.

Attempts to selectively remove two hydrogen atoms from α -obscurine by hydrogen exchange with chloranil were unsuccessful. However, treatment of α -obscurine with N-bromosuccinimide in refluxing carbon tetrachloride containing a trace of benzoyl peroxide, followed by chromatography of the basic products over alumina, gave, in about 30% yield, β -obscurine (m.p. 316° (dec.), m.m.p. undepressed). The infrared and ultraviolet spectra were identical with those of an authentic sample. Inspection of the ultraviolet spectrum of the crude products indicated that dehydrobromination had occurred prior to chromatography.

Palladium dehydrogenation of α -obscurine gives, besides 6-methyl- α -pyridone, 7-methylquinoline². Assuming that no rearrangement of the carbon skeleton has occurred during the dehydrogenation, and that the tertiary N-methyl must be eliminated to allow aromatization of the

quinoline ring, these fragments account for all the carbon, nitrogen and oxygen atoms of α -obscurine.

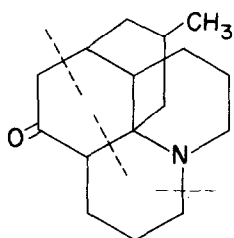
The Lycopodium alkaloid lycopodine (III)⁶ also yields 7-methylquinoline on dehydrogenation with supported palladium⁷, presumably by cleavage as indicated by the dashed lines in III. If we make the likely assumption that both lycopodine and the obscurines arise from the same biogenetic precursor, such as IV, then condensation of IV with ammonia, or its biological equivalent, at the oxygenated carbons, followed by N-methylation, leads to structure V and VI for α - and β -obscurine, respectively.

Structure V and VI explain all the known chemistry of the obscurines. Thus, partial structures I and II are incorporated and dehydrogenation with cleavage (dashed lines in V) analogous to that in lycopodine leads to 6-methyl- α -pyridone and 7-methyl-quinoline.

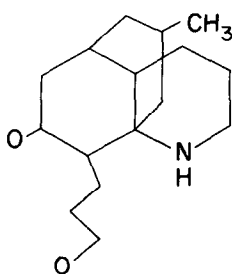
The NMR spectrum of β -obscurine is somewhat anomalous in that the $>\text{CHCH}_3$ peak (at 9.17 ppm relative to tetramethyl silane as an internal standard) is unsplit, whereas in α -obscurine the peak (at 9.14 ppm) is split.

⁶ D. B. MacLean and W. A. Harrison, in the press. We would like to thank Dr. MacLean for a copy of this paper previous to its appearance in print.

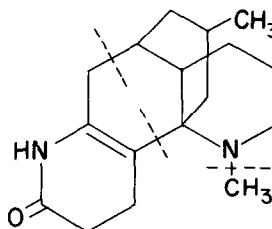
⁷ L. Marion and R. H. F. Manske, Canad. J. Research, B, 20, 153 (1942).



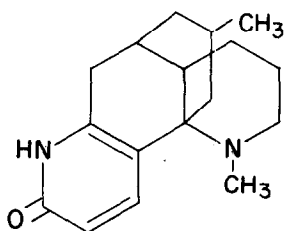
III



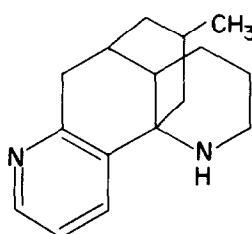
IV



V



VI



VII

The Lycopodium alkaloid lycodine³ appears to be closely related to the obscurines. It has been shown³ that lycodine contains a 2,3-disubstituted pyridine ring fused to a cyclohexane ring, a C-methyl group, and a secondary amino group. The analytical results quoted³ do not exclude a molecular formula $C_{16}H_{22}N_2$ for lycodine and it is attractive to speculate that this alkaloid is formed by the same biogenetic path as the obscurines,

except that N-methylation has not occurred, and that lycodine is represented by structure VII.

Further support for the α -obscurine structure is provided by the recent elucidation⁸ of the structure of selagine, a very closely related α -pyridone type of Lycopodium alkaloid.

This work was supported by a grant from the National Research Council of Canada.

⁸ Z. Valenta, H. Yoshimura, E. R. Rogers, M. Ternbah and K. Wiesner. Tetrahedron Letters No. 10, 26 (1960), following paper.