ON THE STRUCTURE OF DIOSCORINE

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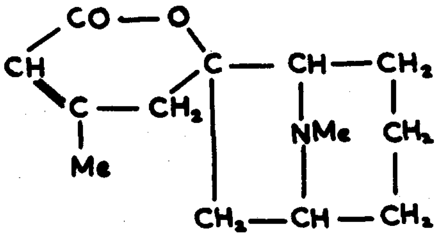
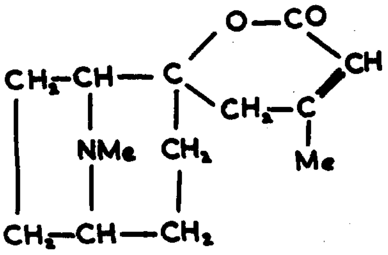
AFTER investigations by Pinder [2-7] had shown that the alkaloid Dioscorine has either structure I or II, Büchi et al.[8] presented evidence in favour



I



II

of I. It was subsequently shown by Pinder [9] that this cannot be correct, and that the correct structure must be II.

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[1] I.C.I. Fellow.

[2] A.R. Pinder, Nature Lond. **168**, 1090 (1951).

[3] A.R. Pinder, J. Chem. Soc. 2236 (1952).

[4] A.R. Pinder, J. Chem. Soc. 1825 (1953).

[5] A.R. Pinder, J. Chem. Soc. 1577 (1956).

[6] A.R. Pinder, Chem. & Ind. 1240 (1957).

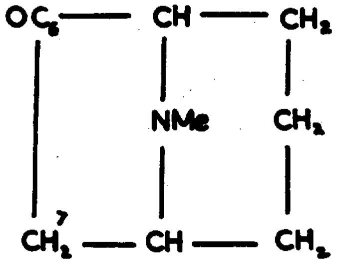
[7] A.R. Pinder, Tetrahedron **1**, 301 (1957).

[8] G. Büchi, D.E. Ayer and D.M. White, XVIth International Congress of Pure and Applied Chemistry, Paris, July 1957.

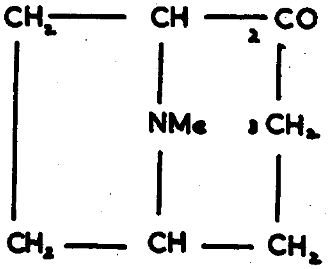
[9] J.B. Jones and A.R. Pinder, Chem. & Ind. 1000 (1958).

This structure is now supported by Büchi.[10] His earlier evidence [8] in favour of structure I was as follows:

(1) That the ketone derived by degradation of the lactone ring (i.e., III or IV) had a carbonyl band in the infra-red at 1730 cm^{-1}, 1723 cm^{-1} (CS_2) [10] and that this was in better agreement with a <u>cyclo</u>pentanone than with a <u>cyclo</u>hexanone structure. Pinder has already pointed out [9] that this is not so; in fact, accepted ranges [11] are 1720-1706 cm^{-1} for <u>cyclo</u>hexanones and 1749-1745 cm^{-1} for <u>cyclo</u>pentanones. It is relevant to consider more closely related compounds: the carbonyl frequency in tropinone (3-oxotropane) is at 1722 cm^{-1} (Nujol), and in 6-hydroxytropinone [12] at 1705 cm^{-1} (Nujol), 1715 cm^{-1} (CCl_4). This clearly supports the <u>cyclo</u>hexanone structure (IV) for the ketone, and is confirmed by the position of the carbonyl band in 6-oxotropane (III),[9] which is at 1750 cm^{-1}, as expected for a <u>cyclo</u>pentanone.



III



IV

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[10] D.E. Ayer, G. Büchi, P. Reynolds-Warnhoff and D.M. White, <u>J. Amer. Chem. Soc.</u> **80**, 6146 (1958).

[11] L. J. Bellamy, <u>The I.R. Spectra of Complex Molecules.</u> Methuen, London (1958).

[12] Samples were generously provided by Professor A. Stoll and Dr. N. Clauson-Kaas.

(2) That Hofmann degradation of the oxotropane (now known to be IV) methiodide occurred very readily (aqueous sodium bicarbonate at 30°). This is not referred to in Büchi's more recent communication,[10] although it becomes even more curious since 6-oxotropane, which, of the two compounds, should eliminate more readily, is unaffected by the same reagent.[9]

Thus, although the weight of the evidence [13] definitely supports Pinder's structure (II) for Dioscorine, there remains an anomalous piece of evidence against it.

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[13] The degradation product, 2-oxotropane, has been synthesised [M.R. Bell and S. Archer, J. Amer. Chem. Soc. **80**, 6147 (1958)].