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THE MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF PORANTHERICINE AND PORANTHERIDINE

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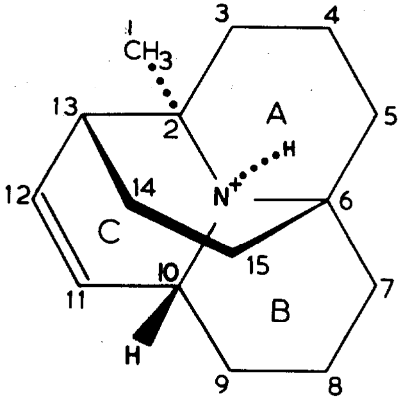
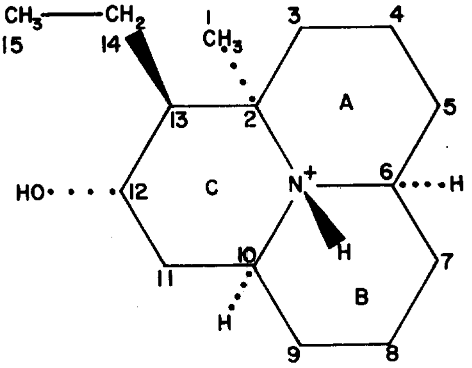
The structure of porantherine I, the major alkaloid of *Poranthera corymbosa* Brogn. (Family Euphorbiaceae), has already been established by x-ray crystal structure analysis (1). A number of other alkaloids, two of which have been named poranthericine and porantheridine, have now been isolated from *P. corymbosa.*

Poranthericine, a colourless oil, $[\alpha]_D$ -20° (*c*, 0.45 in $CHCl_3$) was found to have the molecular formula $C_{15}H_{27}NO$ by microanalysis of a crystalline hydrobromide, m.p. 308° (decomp.), $[\alpha]_D$ -8° (*c*, 0.5 in MeOH), and by the presence of a very weak molecular ion peak at m/e 237 in the mass spectrum. Poranthericine has a secondary alcohol grouping, ν max. 3710 cm^{-1} (CCl_4), C<u>H</u>-OH multiplet at δ 3.93 in $CDCl_3$, and on acetylation is converted into O-acetyl poranthericine, a colourless oil, $[\alpha]_D$ + 2° (*c*, 1.6 in $CHCl_3$), which is identical with another alkaloid from *P. corymbosa.* Mild alkaline hydrolysis of the naturally occurring O-acetylporanthericine, a colourless oil, $[\alpha]_D$ + 2° (*c*, 1.6 in $CHCl_3$), ν max. 1720 cm^{-1} (CCl_4), 3H singlet at δ 2.02 ($\underline{CH_3}CO$) and 1H multiplet at δ 4.97 (C<u>H</u>.OAc) in $CDCl_3$, afforded poranthericine, $[\alpha]_D$ -20° (*c*, 1.2 in $CHCl_3$), hydrobromide salt, m.p. 308° (decomp.), $[\alpha]_D$ -9° (*c*, 0.5 in MeOH), identical with the naturally occurring alkaloid.

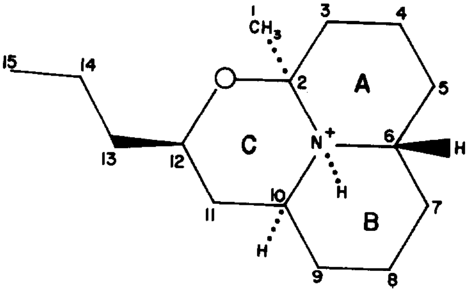
Crystals of poranthericine hydrobromide, $C_{15}H_{27}NO.HBr$, belong to the orthorhombic space group $P2_12_12_1$ with lattice parameters, $\underline{a}$ = 12.761, $\underline{b}$ = 15.144, $\underline{c}$ = 8.030 Å; the structure was solved by the heavy atom method with 1276 independent intensities measured by diffractometer with CuK_α radiation. The absolute configuration was determined from the anomalous scattering of the bromine atom and the resulting molecular skeleton is shown in II. A three-dimensional representation is given in IV.



I



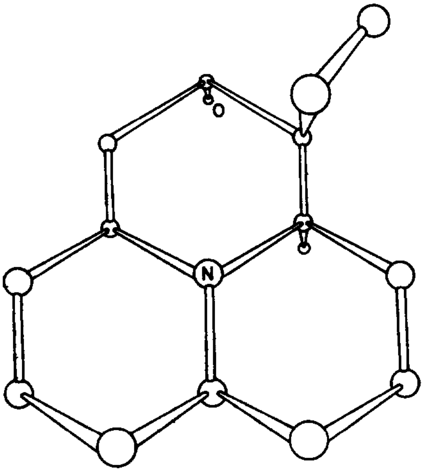
II



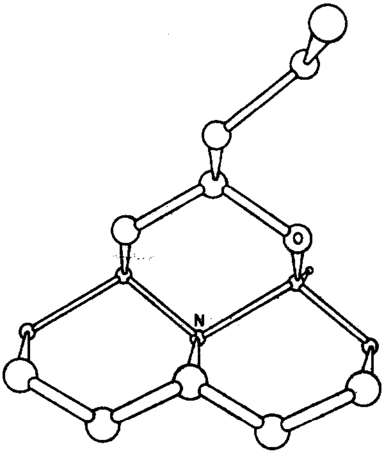
III

Porantheridine, a colourless gum, $[\alpha]_D$ -26° (*c*, 0.57 in $CHCl_3$), was also found to have the molecular formula $C_{15}H_{27}NO$ from microanalysis of a crystalline hydrobromide, m.p. 165-166°, $[\alpha]_D$ -19° (*c*, 0.89 in MeOH) and from a weak molecular ion peak at m/e 237 in the mass spectrum. The absence of hydroxyl or carbonyl bands from the i.r. spectrum indicated that the oxygen was probably contained in an ether linkage.

Crystals of porantheridine hydrobromide, $C_{15}H_{27}NO.HBr$, were found from x-ray measurements to belong to the orthorhombic space group $P2_12_12_1$ with $\underline{a}$ = 10.059, $\underline{b}$ = 16.704, $\underline{c}$ = 9.629 Å; the structure was solved by the heavy atom method using 624 independent intensities measured by diffractometer with MoK$_{\alpha}$ radiation. The absolute configuration was determined from the anomalous scattering of the bromine atom and the resulting molecular skeleton is shown in III. A three-dimensional representation is given in V. The dimensions found in both molecules were consistent with accepted bond lengths and angles.



IV



V

The structures of the new alkaloids are in accordance with the postulated biosynthesis of porantherine (1) by cyclization of a polyketide chain and condensation with one equivalent of ammonia. The 15-carbon atom chain is very evident in porantheridine and the C(1) methyl is shown to be a chain-ending as surmised in the porantherine case. The 15-carbon atom chain can also be traced in poranthericine, again with the methyl as a terminal group. The constancy of the configuration at the C(2) centre carrying the methyl group and the variety of skeletal arrangements at the other points along the designated carbon chain suggests that the biosynthesis may proceed through a common intermediate in which the configuration at C(2) is fixed and that the stereochemistry at the other centres is then established at successive condensations.

1. Denne, W. A., Johns, S. R., Lamberton, J. A. and Mathieson, A. McL., *Tetrahedron Letters*, 3107 (1971).