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THE ABSOLUTE STRUCTURE OF PORANTHERINE

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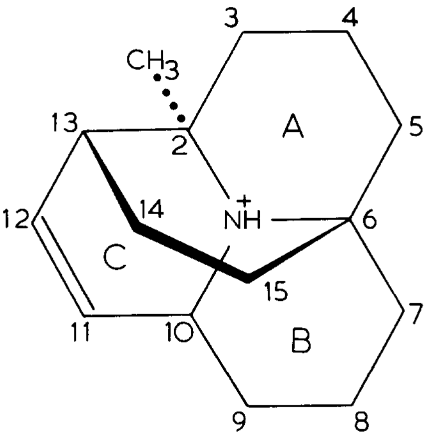
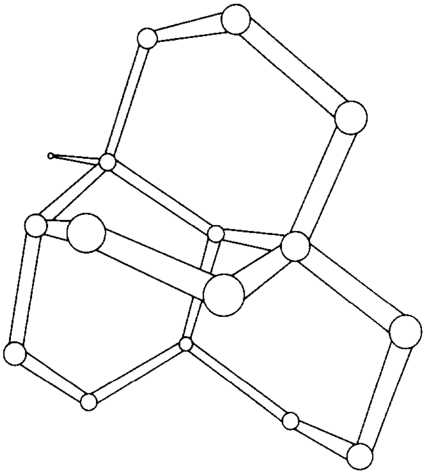
Porantherine, $C_{15}H_{23}N$, the major alkaloid of *Poranthera corymbosa* Brogn. (Family Euphorbiaceae) was isolated as colourless crystals, m.p. 36 - 40°C, $[\alpha]_D + 29^\circ$ (*c*, 0.35 in $CHCl_3$), M^+ at m/e 217, from plants collected near Torrington in northern New South Wales. Porantherine affords a crystalline hydrobromide, $C_{15}H_{23}N.HBr$, unmelted at 340°C, $[\alpha]_D - 13^\circ$ (*c*, 0.35 in ethanol). X-ray diffraction measurements showed these crystals belong to the orthorhombic space group $P2_12_12_1$ with lattice parameters, a = 11.689, b = 15.190 and c = 7.721 Å; 1203 independent intensities were measured on a diffractometer with CuK_α radiation. The structure was solved by the heavy atom method and the molecular skeleton I was found. Refinement defined unambiguously



I

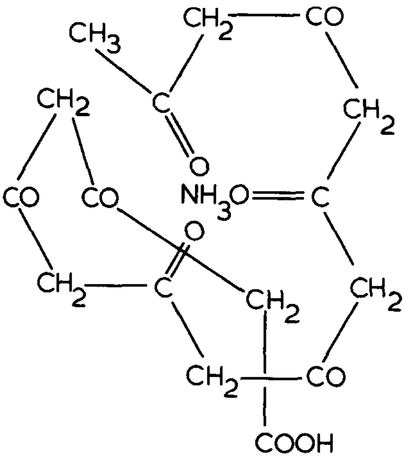


II

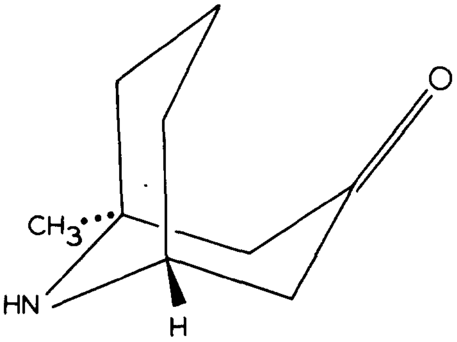
the location of the double bond and differentiated the N atom. Dimensions within the molecule are typical within the limits of experimental error. Examination of selected Bijvoet pairs determined the absolute configuration to be that in I. The 3-D shape of the molecule is shown in II.

Other spectroscopic data for porantherine are consistent with the structure I. In the 100 MHz n.m.r. spectrum of porantherine, a three-proton singlet at δ 1.13 can be assigned to the C-methyl group protons, a narrow two-proton multiplet at δ 5.69 to both double bond protons, and a broad one-proton singlet at δ 3.70 to C10-H, which is adjacent to both the nitrogen and the double bond.

It seems probable that porantherine is derived biosynthetically from condensation of a C_{16}-polyketide chain and one equivalent of ammonia, with appropriate cyclizations and loss of the terminal carboxyl group as in III. This mode of derivation resembles the postulated biosynthesis of (+)-9-aza-1 methylbicyclo(3,3,1) nonan-3-one (IV) (1) an alkaloid found in *Euphorbia atoto* which belongs to the same family as *P. corymbosa.*



III



IV

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