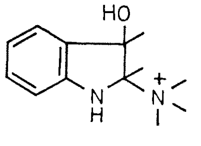
Hunteracine: the Crystal Structure of a Quaternary Alkaloid from *Hunteria eburnea* Pichon

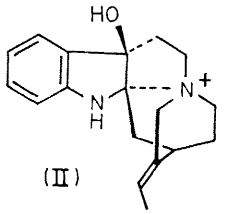
By R. H. BURNELL,* A. CHAPELLE, and M. F. KHALIL
(*Département de Chimie, Université Laval, Québec, Canada*)
and P. H. BIRD
(*Chemistry Department, Sir George Williams University, Montreal, Canada*)

Summary The Hunteracine cation has been shown by *X*-ray crystallographic analysis to have the structure given in the Figure.

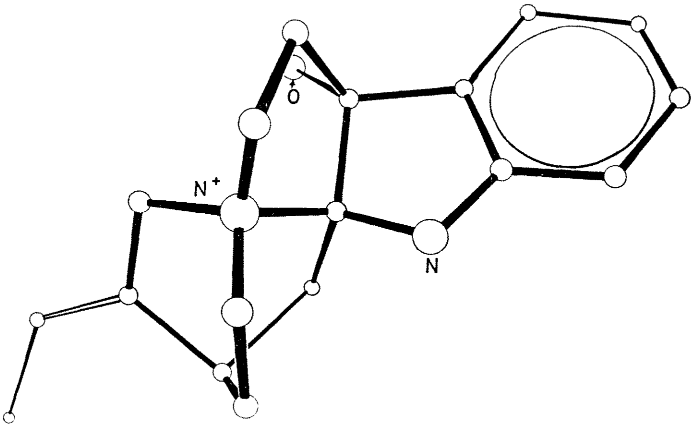
Hunteria eburnea PICHON has been a rich source of alkaloids including a series of quaternary bases some of which had been characterized but for which no structures were postulated usually through lack of material.[1] Among the latter, hunteracine chloride presented certain interesting features since it was claimed (and we have since verified) that although quaternary it contains no *N*-alkyl residue and the dihydroindole moiety has a hydroxyl group at the β-position. We have recently isolated more hunteracine and while most of the physical properties agree with those of previous authors, classical elemental analysis fitted $C_{18}H_{23}N_2OCl$ rather than the C_{20} formula preferred earlier. The molecular ion observed at 283 *m/e* in the mass spectrum confirms our findings. Other peaks in the mass spectrum (130, 124, 122, and 108 *m/e*) have obvious interpretations but the over-all fragmentation is reminiscent of no well-known group of alkaloids. The n.m.r. spectrum (in D_2O) shows peaks for four aromatic protons (δ 6·7—7·5) and an exocyclic ethylidene group [δ 5·20 (m, 1H) and 1·66 (d, 3H)]. No other methyl signals are present.



(I)



(II)



FIGURE

Hunteracine chloride, which sublimes without decomposition, is stable to most degradative methods but is converted by alkoxides into a pseudoindoxyl as shown by the u.v. and i.r. spectra. This behaviour and other spectral evidence suggest the partial formula (I) but after exchanging the anion for bromide it was felt that *X*-ray diffraction would provide the only unambiguous structure.

The compound crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 18{\cdot}00$, $b = 9{\cdot}662$, $c = 9{\cdot}645$ Å. The observed density ($D_m = 1{\cdot}42 \pm 0{\cdot}02$ g cm^{-3}) is in reasonable agreement with the density calculated for $C_{18}H_{23}N_2OBr$, *M* 363·10, $Z = 4$. ($D_c = 1{\cdot}437$ g cm^{-3}). The structure was solved by conventional Patterson, Fourier, and least-squares refinement procedures. Refinement using isotropic thermal parameters and anomalous dispersion correction reduced the discrepancy index to 16·5% with the absolute configuration of the cation as indicated in the Figure. The final (isotropic) discrepancy index using the enantiomeric ion was 17·1%. Anisotropic refinement using the original molecule is continuing; the present discrepancy index is $R = 8{\cdot}4\%$ for 1136 independent non-zero reflections collected on a fully automated Picker four-circle diffractometer. The nitrogen and oxygen atom positions were assigned on the basis of chemical evidence substantiated by the behaviour of the atomic thermal parameters on least-squares refinement.

Biogenetically hunteracine (II) could arise from stemmadenine[2] with loss of the two oxygen bearing carbon atoms and a mode of cyclisation such as suggested for the formation of rhazidine from rhazidigenine.[3]

We thank the National Research Council of Canada for operating and equipment grants.

(*Received, May 1st,* 1970; *Com.* 648.)

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[2] A. A. Qureshi and A. I. Scott, *Chem. Comm.*, 1968, 948.

[3] S. Markey, K. Biemann, and B. Witkop, *Tetrahedron Letters*, 1967, 157.