X-Ray Determination of the Structure of Capaurimine

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Summary An *X*-ray analysis of capaurimine mono-*p*-bromobenzoate has confirmed that capaurimine is 5,6,13,13a-tetrahydro-1,10-dihydroxy-2,3,9-trimethoxy-8*H*-dibenzo[*a*,*g*]quinolizine.

CAPAURIMINE, one of the protoberberine alkaloids isolated from *Corydalis* species,[1] had been assigned structure (I) through chemical degradations by Manske,[2] but compound (I) synthesised by one of the present authors was not identical with natural capaurimine.[3] We have therefore reinvestigated capaurimine and found that it is 5,6,13,13a-tetrahydro-1,10-dihydroxy-2,3,9-trimethoxy-8*H*-dibenzo-[*a*,*g*]quinolizine (II).[4] It was predicted that on account of a non-bonded interaction of the hydroxy-group at the 1-position with the hydrogens at the 13-position, a *cis*-quinolizidine conformation would be preferred.[4] We have now undertaken an *X*-ray analysis of capaurimine mono-*p*-bromobenzoate (III) in order to determine its three-dimensional molecular structure.

Treatment of capaurimine, isolated from *C. pallida var. tenuis* Yatabe by us,[5] with *p*-bromobenzyl chloride in pyridine gave its mono-*p*-bromobenzoate (III), which was recrystallised from methanol as pale yellow plates. $C_{27}H_{26}O_6NBr$, M.W. = 540·402, m.p. 177—178°, [D_c = 1·483

(I) $R^1 = R^3 = H, R^2 = R^4 = Me$
(II) $R^1 = R^4 = H\ R^2 = R^3 = Me$
(III) $R^1 = H, R^2 = R^3 = Me, R^4 = CO{\cdot}C_6H_4Br$
(IV) $R^1 = H, R^2 = R^3 = R^4 = Me$
(V) $R^1 = R^4 = Me, R^2 = R^3 = H$

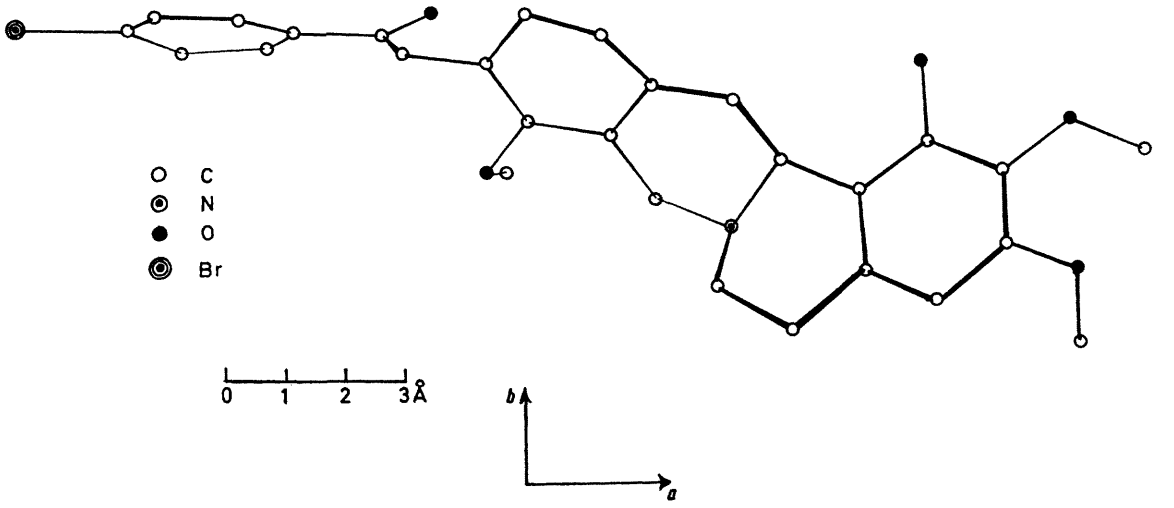
g cm^{-3}, D_m = 1·499 g cm^{-3}, monoclinic, a = 13·182, b = 7·705, c = 13·369 Å, β = 117·0°, space group $P2_1$, Z = 2.

The intensity data were collected by multiple-film equi-inclination Weissenberg photographs using Cu-K_α radiation.

Relative intensities were estimated visually. The structure was solved by the heavy-atom method. In spite of a disturbance by a false mirror plane at $y = 0$, it was possible to pick out the atoms in the *p*-bromobenzoyl group. Two successive three dimensional Fourier syntheses showed clearly the whole molecule.

The structure was refined by least-squares method. After three cycles of refinements, the discrepancy factor was reduced to 0·12. Further refinements are in progress.

The molecular structure of capaurimine mono-*p*-bromobenzoate as projected along the *c*-axis is shown in the Figure. As shown in the Figure, three methoxyl groups exist at the 2, 3, and 9-positions and *p*-bromobenzoyl group exists at the 10-position. Furthermore, the B/C ring junction is *cis*-fused as those of the hydrobromide of capaurine (IV)[6] and the position isomer of capaurimine (V).[7] On the basis of this result, the correctness of the structure of capaurimine (II) suggested by us[4] has been confirmed.



FIGURE

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