X-Ray Crystallographic Determination of the Structure of Stemonamine, a New Alkaloid from *Stemona japonica* Miq.: Isolation of Isostemonamine

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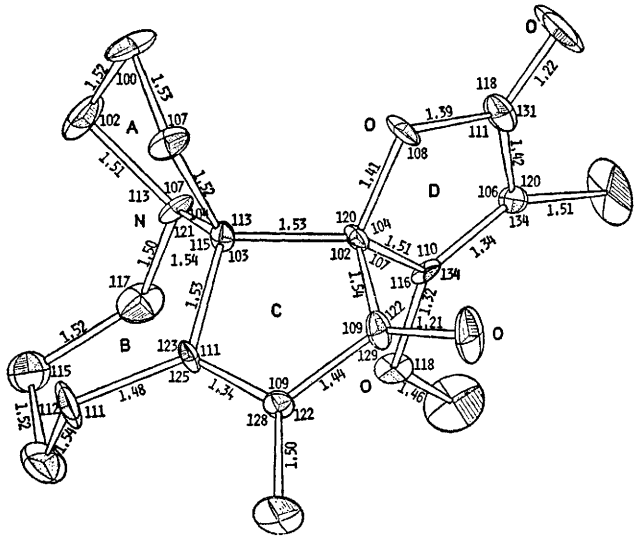
Summary The structure of stemonamine (I) isolated from *Stemona japonica* Miq. has been determined by *X*-ray crystal-structure analysis of its hydrochloride and the structure (II) is suggested for isostemonamine occurring in the same plant.

FROM the basic fraction of the extracts of the roots of *Stemona japonica* Miq. of the family *Stemonaceae*, we have isolated small amounts of two new racemic alkaloids which we have named stemonamine, $C_{18}H_{23}NO_4$, m.p. 172—174°, and isostemonamine, $C_{18}H_{23}NO_4$, m.p. 165—169°. Stemonamine showed the following spectral data: λ_{max} (EtOH) 239 nm (ϵ 22,500), ν_{max} (KBr disc) 1760, 1710, 1660, and 1620 cm^{-1}, δ ($CDCl_3$) 4·00 (3H, s, OMe) and 2·02 and 1·78 (3H, s, two vinyl Me's), and $M^+ = 317$. Due to shortage of material, we decided to undertake the structure determination by *X*-ray crystallographic analysis using single crystals of stemonamine hydrochloride dihydrate $C_{18}H_{24}NO_4Cl,2H_2O$, m.p. 148–151°, which crystallised from acetone in the triclinic space group, $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 14{\cdot}62$, $b = 9{\cdot}29$, $c = 7{\cdot}75$ Å; $\alpha = 69{\cdot}6°$, $\beta = 99{\cdot}7°$, $\gamma = 101{\cdot}9°$; $D_m = 1{\cdot}31$, $D_c = 1{\cdot}35$ g cm^{-3}. Crystals of stemonamine hydrobromide dihydrate, m.p. 184—190° are isomorphous with $a = 14{\cdot}76$, $b = 9{\cdot}35$, $c = 7{\cdot}67$ Å; $\alpha = 69{\cdot}1°$, $\beta = 100{\cdot}5°$, $\gamma = 102{\cdot}1°$. The structure was solved by Woolfson's modified Fourier technique,[1] based on the heavy-atom positions obtained from a difference Patterson map based on data from the isomorphous crystals mentioned above. The intensity data were obtained by visual estimation from *a*-axis Weissenberg and



FIGURE

c-zone precession photographs, taken with Cu-K_α and Mo-K_α radiations, respectively. Refinement by block-

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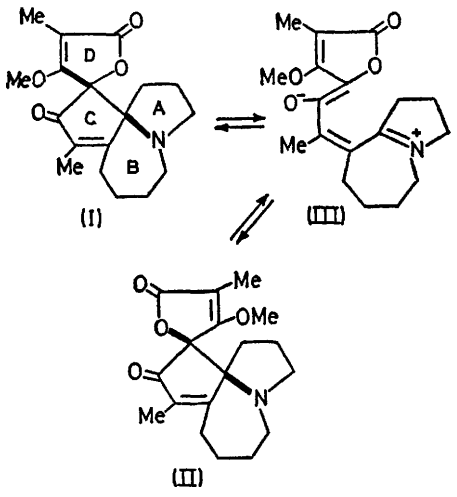
diagonal least-squares with anisotropic temperature factors for non-hydrogen atoms reduced the *R*-factor to 0·108.



The molecular structure (I) so derived is composed of racemic pairs of molecules. A perspective view along with bond lengths and angles of one of the molecules of stemonamine is shown in the Figure. Isostemonamine had i.r. bands similar to but not superimposable upon those of stemonamine. The n.m.r. spectrum of isostemonamine was very similar to that of stemonamine and the mass spectrum (M^+ 317) was virtually identical. These spectral properties suggested that the alkaloids are stereoisomers. We therefore suggest structure (II) for isostemonamine. Perhaps the most intriguing feature of the chemistry of stemonamine and isostemonamine is that they are optically inactive and isomeric with respect to their spiro-structures which are expected to be interconvertible in acid or base through the intermediate (III) which has no asymmetric centres. Precedents for this are found in the pairs of oxindole alkaloids[2] such as rhyncophylline, and isorhyncophylline, uncarine-A and uncarine-B, and mitraphylline and isomitraphylline.

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[1] M. M. Woolfson, 'An Introduction to X-ray Crystallography,' University Press, Cambridge, 1970.
[2] J. E. Saxton in 'The Alkaloids,' vol. 8, ed. R. H. F. Manske, Academic Press, New York, London, 1965, p. 59.