The Crystal Structure of Viomycidine

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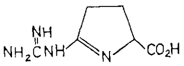
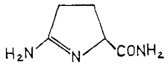
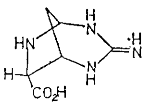
ACID hydrolysis of the antibiotic viomycin yields carbon dioxide, urea, L-$\alpha\beta$-diaminopropionic acid, L-β-lysine, L-serine, and a guanidino-amino-acid, which has been named viomycidine.[1,2] Based on the physical properties, colour tests, and observed chemical reactions [fusion with alkali yielded 2-aminopyrimidine and glycine; hydrolysis with aqueous barium hydroxide gave pyrrole-2-carboxylic acid; acetylation (pyridine, acetic anhydride) followed by ozonolysis, oxidative work-up, and hydrolysis yielded aspartic acid and guanidine] the structure 2-guanidino-1-pyrroline-5-carboxylic acid (I) was suggested for viomycidine.[2]

To confirm this structure a synthesis of (I) was planned. 2-Amino-1-pyrroline-5-carboxamide (II) was obtained by rational synthetic reactions. The n.m.r. spectrum of (II) was radically different from that reported for viomycidine.[2] For this reason,


(I)


(II)


(III)

the suggested structure for viomycidine seemed to be in question, and we initiated an X-ray crystallographic structure determination using crystalline viomycidine hydrobromide.

Crystals of the compound ($C_6H_{10}N_4O_2$,HBr) are orthorhombic, space group $C222_1$, $a = 9{\cdot}36 \pm 0{\cdot}01$, $b = 12{\cdot}47 \pm 0{\cdot}01$, $c = 15{\cdot}29 \pm 0{\cdot}01$ Å, $Z = 8$, $D_c = 1{\cdot}87$, D_m (by flotation) $= 1{\cdot}85$. The bromide ions were located by a three-dimensional Patterson synthesis and the structure was solved by successive Fourier syntheses. Using full-matrix least-squares refinement with isotropic temperature factors and individual layer scale factors, the R index converged to 0·090 for 397 independent non-zero reflections (Mo-K_α, precession camera data).

The most important details of the geometry of the structure obtained for viomycidine, 2,4,6-triaza-3-iminobicyclo[3,2,1]octane-7-carboxylic acid (III), are shown in the Figure, which represents the protonated viomycidine cation. The values for the angles shown are ±3°. The bridgehead angle, C(3)–C(4)–C(5), which is 99°, can be compared with the value of 97° found in the tricyclo[3,2,1,$0^{2,4}$]octane nucleus.[3] All other bond angles and all bond lengths show normal values.

This crystal structure determination of viomycidine fully supports the recent suggestion[4] for this structure.

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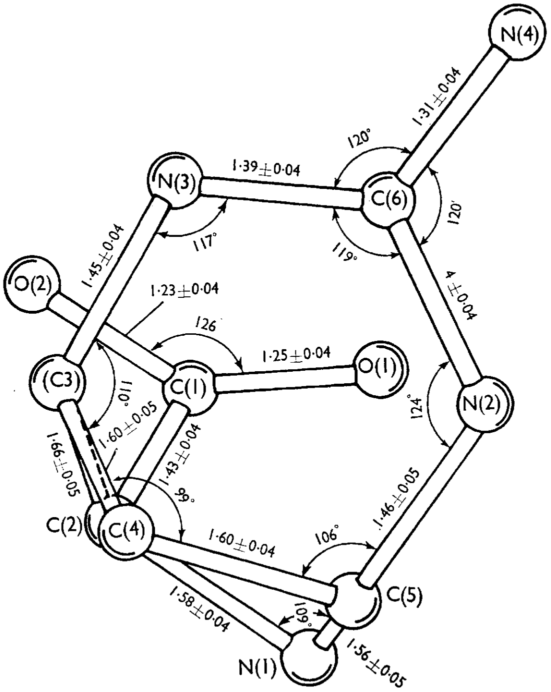

FIGURE. *Bond distances* (Å) *and representative bond angles for the viomycidine cation.*

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[3] A. C. McDonald and J. Trotter, *Acta Cryst.*, 1965, **18**, 243.

[4] Private communication from Professor G. Büchi to Professor A. W. Johnson; B. W. Bycroft, D. Cameron, L. R. Croft, A. W. Johnson, T. Webb, and P. Coggon, *Tetrahedron Letters*, 1968, 2925.