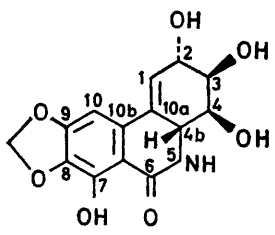
The Crystal and Molecular Structure of Narciclasine Tetra-acetate

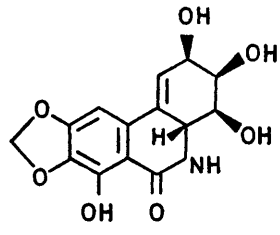
By A. IMMIRZI*
(*Istituto di Chimica delle Macromolecole del CNR, via A. Corti* 12, 20133 *Milano, Italy*)
and C. FUGANTI
(*Istituto di Chimica del Politecnico di Milano, Centro del CNR per la chimica delle sostanze organiche naturali, Milano, Italy*)

Summary We report the results of a single-crystal *X*-ray analysis of narciclasine tetra-acetate.

THE stereochemistry reported here for narciclasine (I) differs from that previously suggested, (II),[1] on the basis of a reinterpretation of the ^{1}H n.m.r. spectrum of the *O*-methyltriacetyl derivative.



(I)



(II)

Crystal data: $C_{22}H_{21}NO_{11}$, $M = 475{\cdot}4$, $a = 39{\cdot}09(2)$, $b = 8{\cdot}09(1)$, $c = 6{\cdot}91(1)$ Å, $D_m = 1{\cdot}5$, $D_c = 1{\cdot}44$, $Z = 4$, $F(000) = 992$, space group $P2_12_12_1$, Cu-K_α radiation, ($\lambda = 1{\cdot}5418$ Å).

Integrated intensities were measured on an AED Siemens single-crystal diffractometer for 2444 unique reflexions having $\sin\theta/\lambda \leqslant 0{\cdot}60$, and 2109 were considered observable. No absorption correction has been introduced ($\mu R < 0{\cdot}02$).

The initial phases were determined by using the computer program MULTAN[2] and 372 reflexions, $E(hkl) \geqslant 1{\cdot}4$. The weighted *E*-map gave the correct positions for 31 of the 34 independent non-hydrogen atoms and also had 5 spurious maxima. The structure analysis was completed by a Fourier synthesis phased with the contributions of the 31 atoms above. Isotropic least-squares refinement has reduced *R* to a current value of 0·12.

The Figure shows the molecular structure in the correct *absolute* configuration: for, on biosynthetic grounds, the configuration of C(4b) is that of (+)-crinane.[3] All the bond lengths and angles (mean standard deviations 0·02 Å and 0·6°) have acceptable values; for bond lengths the maximum deviation from the expected values is 0·04 Å.

Both the five-membered and the aromatic rings are essentially planar (maximum torsion angle 5°). The six-membered heterocyclic ring is near to the *boat* conformation: the torsion angles about C(6b)–C(10b), C(10b)–C(10a), *etc.* are, in order, −11, −22, 45, −40, 10, 18°. The cyclohexene ring has a distorted *half-chair* conformation: the angles about C(1)–C(2), C(2)–C(3), . . . *etc.* are 8, 40, −62, 52, −20°. The greatest torsion angles are observed for the bonds bearing two bulky groups in *cis* relation.

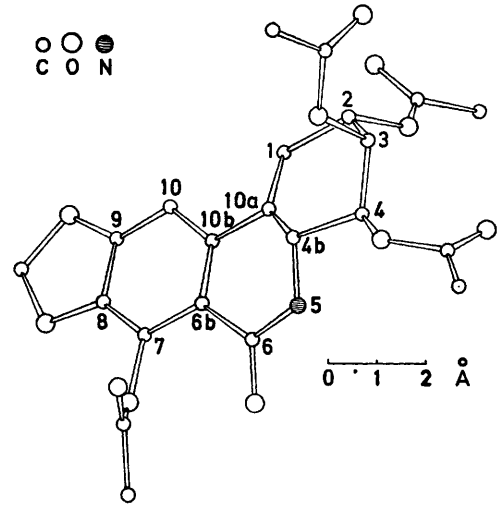


FIGURE. *Molecular structure of narciclasine tetra-acetate in its absolute configuration.*

The oxygen atoms bonded to carbon atoms 2, 3, and 4 are *trans,cis,cis* related to the hydrogen atom at C(4b). This confirms all details of the earlier suggested structure (II) except for the orientation of the oxygen function at C(2). As narciclasine can be regenerated from this derivative by mild basic treatment, we infer that a similar stereochemistry occurs in narciclasine and represent it as (I).

We thank Prof. M. Nardelli and Dr. A. Chiesi for help in data collection on the Siemens diffractometer.

(*Received, 29th December* 1971; *Com.* 2200.)

[1] A. Mondon and K. Krohn, *Chem. Ber.*, 1970, **103**, 2729.
[2] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.
[3] C. Fuganti and M. Mazza, preceding communication.