Stereochemistry at C-3 of Evernitrose: a Fallacy in the Determination of Stereochemistry at Quaternary Centres using Nuclear Magnetic Resonance Spectroscopy. *X*-Ray Crystal Structure of Methyl 3-Acetamido-2,3,6-trideoxy-3-*c*,4-*O*-dimethyl-L-*xylo*-hexopyranoside

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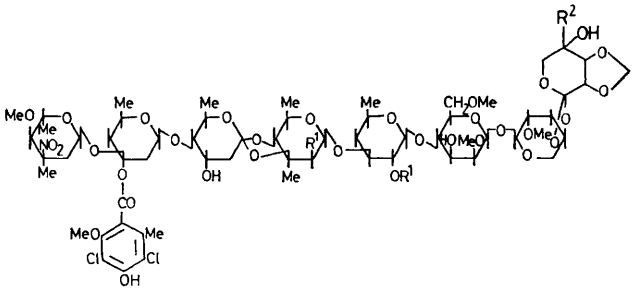
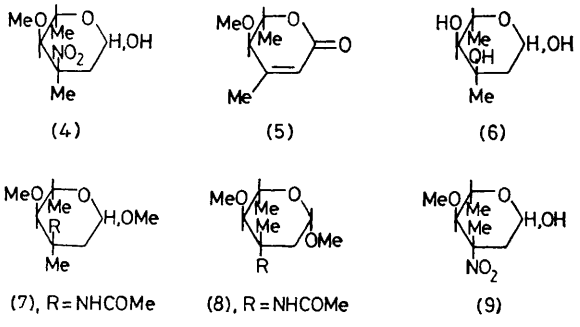
Summary Single crystal *X*-ray analysis of the title compound (**8**) is reported which establishes the stereochemistry at C-3 of evernitrose.

EVERNINOMICIN B[1] (**1**), C[2] (**2**), and D[3] (**3**) are oligosaccharide antibiotics containing many structurally novel features one of which is the presence of evernitrose. The structure and relative stereochemistry of evernitrose, the first naturally occurring nitro-sugar to be isolated, was deduced[4] earlier as (**4**) from spectroscopic evidence and chemical degradations. Correlation[4] of (**4**) with mycarose[5] (**6**), a compound of known absolute configuration, through their conversion into the same α,β-unsaturated δ-lactone (**5**) unambiguously established the absolute stereochemistry at C-4 and C-5. The axial nature of the nitro-function at C-3 in (**4**) could only be tentatively assigned on the basis of the chemical shift (δ 1·95) for the acetamido methyl group in (**7**) [prepared in three steps[4] from (**4**)], which agreed well with that (δ 1·93–1·86) predicted[6] for an axially oriented acetamido methyl group on a fully substituted carbon atom but lay outside the range (δ 1·87—1·78) for the corresponding equatorial substituent. It was recognized,[4] however, that such an assignment could not be regarded as being firmly established since there was a lack of any suitable example. We



(**1**); R^1 = OH, R^2 = CH(Me)(OMe)
(**2**); R^1 = R^2 = H
(**3**); R^1 = H, R^2 = CH(Me)(OMe)



(4) (5) (6)

(7), R = NHCOMe (8), R = NHCOMe (9)

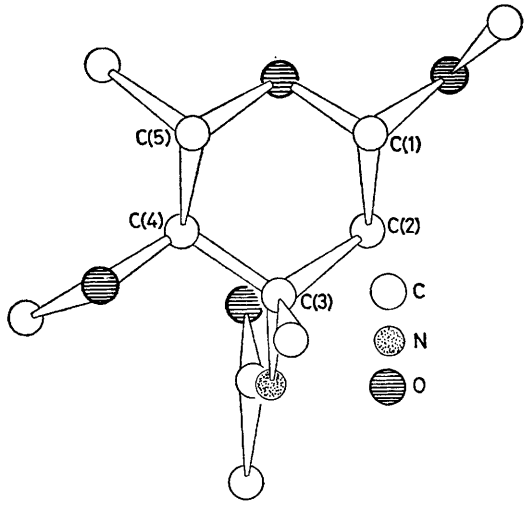


FIGURE. Solid-state conformation of (**8**).

have now resolved this point by single crystal *X*-ray analysis of (**8**).†

Crystals of (**8**) are orthorhombic, space group $P2_12_12_1$, $a = 12{\cdot}960(6)$, $b = 13{\cdot}944(6)$, $c = 6{\cdot}949(4)$ Å, $Z = 4$. Intensity data to θ 67°, recorded on an Enraf-Nonius CAD 3 diffractometer (Ni-filtered Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, θ-2θ scans), yielded 699 statistically significant [$I > 2{\cdot}0\sigma(I)$] reflections. The structure was solved by direct methods by use of MULTAN.[7] Full-matrix least-squares refinement of atomic positional and thermal (anisotropic C, N, and O; isotropic H) parameters has converged at R 0·050. The solid-state conformation, illustrated in the Figure, clearly shows that the ring adopts a chair form with an equatorially oriented C-3 acetamido-function from which it follows that the structure of evernitrose must be revised to (**9**). Thus, it is clear that the assignment of stereochemistry of an acetamido-function on a fully substituted carbon atom could not be made unequivocally on the basis of the predicted[6] chemical shift values of the acetamido methyl group.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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