The Crystal Structure of Showdomycin and their Derivatives

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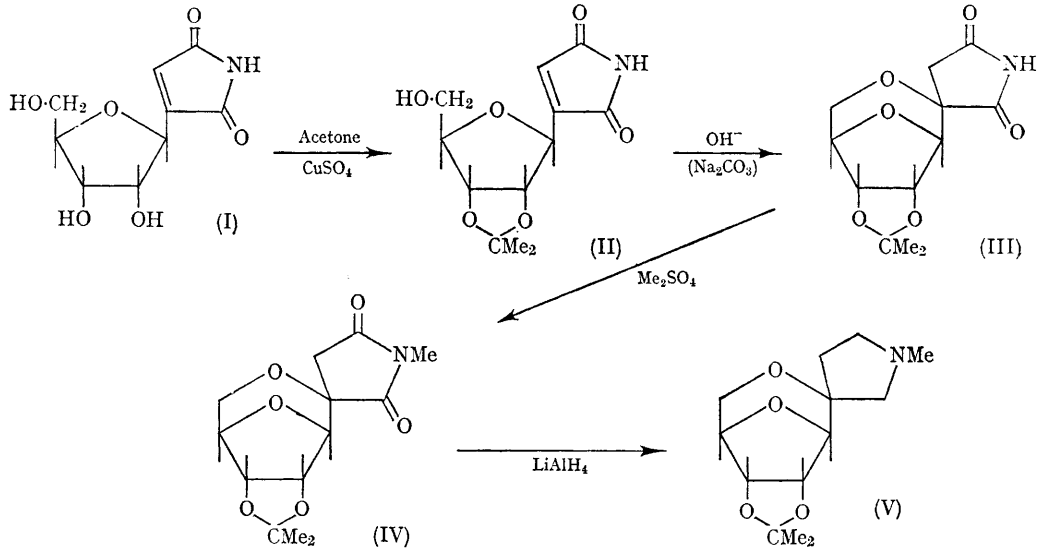
SHOWDOMYCIN, which was isolated from *Streptomyces showdoensis* by Nishimura[1] and his collaborators in 1964, is a white needle crystalline antibiotic with the empirical formula $C_9H_{11}NO_6$. Based on the results of *X*-ray structure analysis of *N*-methylbisdeoxo-cycloshowdomycin acetonide hydrobromide (V) and various chemical information, we recently reported[2] that showdomycin must be represented by formula (I), 3-β-D-ribofuranosylmaleimide, shown in the Scheme.



Here we report the crystal data of showdomycin and the molecular structure of *N*-methylbisdeoxo-cycloshowdomycin acetonide hydrobromide elucidated by three-dimensional *X*-ray structure analysis.

The following data were obtained using Cu-K_α radiation:

(a) Showdomycin, $C_9H_{11}NO_6$, $M = 229{\cdot}2$, m.p. 153—154°. *Monoclinic*, $a = 15{\cdot}52$, $b = 6{\cdot}57$, $c = 11{\cdot}52$ Å, $\beta = 121°10'$, $U = 1005$ Å^3, $D_m = 1{\cdot}526$ g.cm.$^{-3}$, $Z = 4$, $D_c = 1{\cdot}514$ g.cm.$^{-3}$, Space group, *C*2.

(b) *N*-Methylbisdeoxocycloshowdomycin acetonide hydrobromide, $C_{13}H_{21}NO_4$, HBr, $M = 336{\cdot}2$, m.p. 275°. *Monoclinic*, $a = 11{\cdot}01$,

$b = 7{\cdot}17$, $c = 10{\cdot}98$ Å, $\beta = 118°45'$, $U = 760{\cdot}6$ Å, $D_m = 1{\cdot}465$, g.cm.$^{-3}$, $Z = 2$, $D_c = 1{\cdot}467$ g.cm.$^{-3}$, Space group, $P2_1$.

The crystal structure of (b) has been determined and the structure analysis of (a) is in progress. The intensities of 1020 significantly non-zero reflexions (larger than the standard deviation of its measurements) were measured with an automatic diffractometer (with Mo-K_α radiation) equipped with SrO–ZrO_2 balanced filters. The structure was solved by the heavy-atom method and refined by the least-squares method based on 769 exact reflexions (rejecting the intensities of lower indices with extremely strong extinction effect and those smaller than three times of the standard deviation of total counts). At this time, anisotropic temperature factors have been used for Br^- ion only and no hydrogen atoms have been included.

At the present stage of refinement, the R-factor was 9·1%. At the final step in the analysis the absolute configuration of the molecule was determined by the anomalous dispersion method.[3] The final three-dimensional electron-density distribution over one molecule of N-methylbisdeoxocycloshowdomycin acetonide hydrobromide is shown, together with the true absolute configuration of the molecule, in the Figure. The standard deviations in the intramolecular bond distances and angles are ~0·03 Å and ~2·2° respectively. Full details will be published later.

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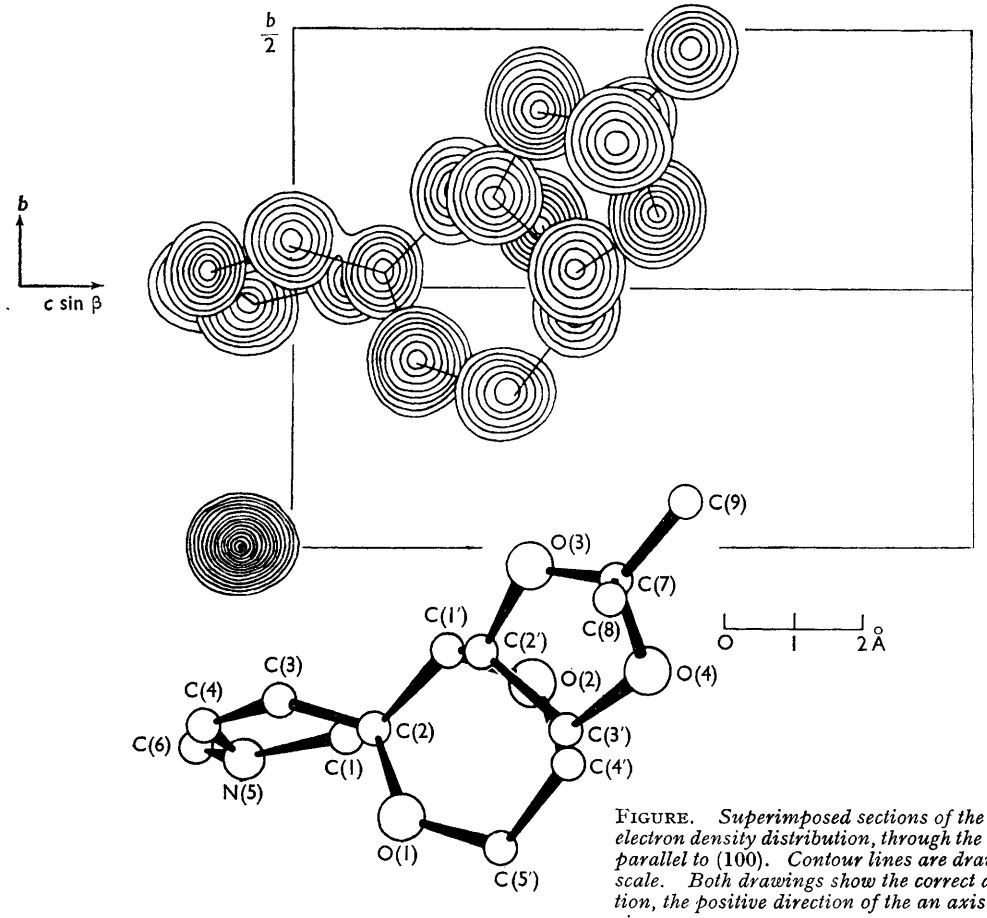

FIGURE. *Superimposed sections of the three-dimensional electron density distribution, through the atomic centres and parallel to* (100). *Contour lines are drawn on an arbitrary scale. Both drawings show the correct absolute configuration, the positive direction of the an axis being opposite the viewer.*

[1] H. Nishimura, M. Mayama, Y. Komatsu, H. Kato, N. Shimaoka, and Y. Tanaka, *J. Antibiotics, Ser. A*, 1964, **17**, 148.

[2] Y. Tsukuda, Y. Nakagawa, T. Sato, M. Shiro, H. Kano, and H. Koyama, Abstracts of the 20th annual meeting of the Chemical Society of Japan, 1967, Ser. 1, 76.

[3] J. M. Bijvoot, A. F. Peerdeman, and A. J. van Bommel, *Nature*, 1951, **168**, 271.