

CRYSTAL STRUCTURE AND ABSOLUTE CONFIGURATION OF FUMITREMORGIN B,
A TREMORGENIC TOXIN FROM ASPERGILLUS FUMIGATUS FRES .

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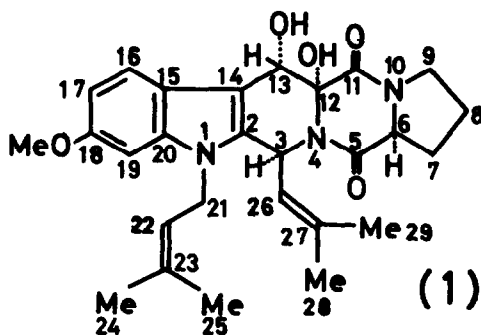
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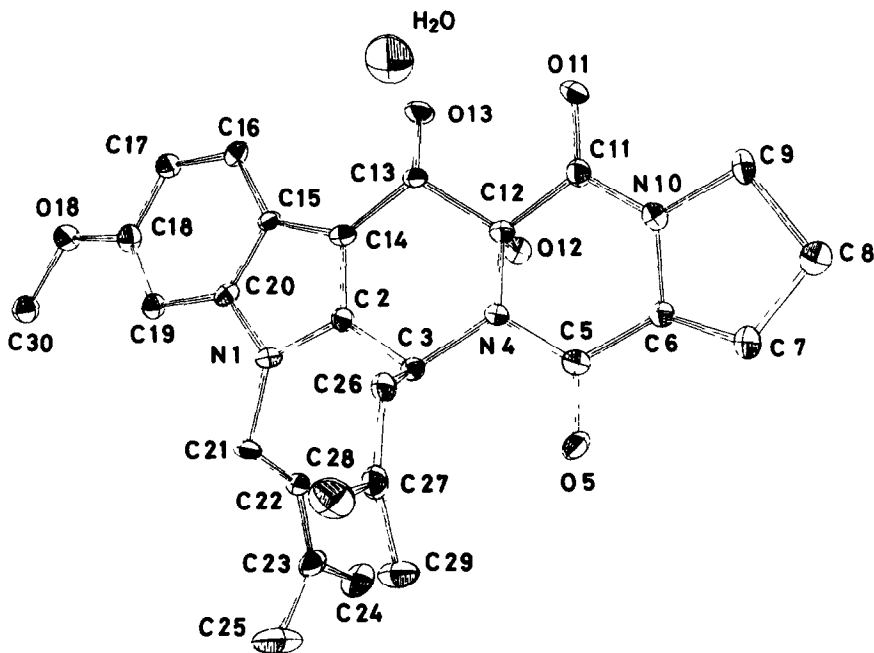
In regard to tremorgenic and neurotropic metabolites, four fumitremorgins were isolated from Aspergillus fumigatus Fres. growing on home made "miso".^{1,2)} We have previously proposed a structure (1) without discussion on the stereochemistry for fumitremorgin B (FTB) on the basis of spectral studies on FTB and its hydrogenated derivatives.²⁾ This communication describes the stereostructure and the absolute configuration of FTB. The relative stereochemical structure was determined by the X-ray analysis of FTB itself, and its absolute configuration was determined based on that of proline obtained by the hydrolysis of FTB.



Crystals of FTB recrystallized from MeOH are orthorhombic, space group $P2_12_12_1$ with 4 molecules in a unit cell of dimensions $a=14.771$ $b=24.925$, $c=7.321$ (Å). A total of 2011 (1699 observed) independent structure factors were collected with a Rigaku 4 circle diffractometer using $\text{CuK}\alpha$ radiation. The structure was solved by means of the MDKS and triple product formulae

of Hauptman,^{3,4)} and application of the tangent formula. The E-map of the solution giving the lowest R-value (Karle) revealed the whole skeletal atoms. Refinement by least squares techniques followed by difference Fourier syntheses gave the location of the missing atoms including the water of crysta-

lization. The structure has been refined by block-matrix least squares to an R factor of 0.11 with anisotropic thermal parameters for C, O and N atoms.



2)

As previously reported proline was obtained by the hydrolysis of FTB with 6N-HCl and purified by preparative paper chromatography using a solvent system of n-BuOH-AcOH-H₂O (4:1:1). The optical rotatory dispersion of proline obtained as above showed a minus plain curve which is identical with that of the authentic sample of L-(-) proline (S-configuration). Therefore, the absolute configuration of FTB is established as shown in the figure.

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- 4) One of the authors (T.A.) is grateful to Dr. J. V. Silverton of N.I.H. in U.S.A. for the calculation of the formulae.