Communications to the Editor

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The Absolute Configuration of Desacetylaustin isolated from *Emericella nidulans* var. *dentata*

Desacetyl derivative of austin has newly been isolated from *Emericella nidulans* var. *dentata*. The X-ray difraction analysis has revealed that the absolute configuration of this compound is antipodal to that of austin previously reported.[1]

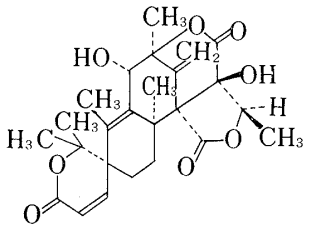
Keywords——fungal metabolite; *Emericella nidulans* var. *dentata*; desacetylaustin; austin; absolute configuration

In the course of investigation of the productivity of sterigmatocystin, two new metabolites, ED-1, colorless needles, mp>300°, $C_{25}H_{28}O_8$ and ED-2, amorphous, $C_{25}H_{30}O_8$, were isolated from a strain of *Emericella nidulans* var. *dentata*. One of them, ED-2 was hydrogenated with H_2/PtO_2 and afforded a crystalline dihydro derivative (ED-2H), colorless needles (from methanol), mp 280—283°, $C_{25}H_{32}O_8$.

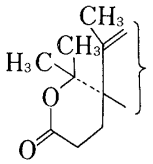
The present X-ray diffraction study of ED-2H has revealed the absolute configuration of ED-2 and that ED-2 is the desacetyl derivative of austin previously isolated from *Aspergillus ustus* however the figure given to austin in the previous report[1] represents the antipode of austin.

The crystals of ED-2H were orthorhombic, space group $P2_12_12_1$, with a=11.261 (4), b=8.144 (3), c=24.867 (5) Å, Z=4. Intensities were measured on a Rigaku computer-controlled four-circle diffractometer with Ni-filtered Cu$K\alpha$ radiation and the θ-2θ scan technique. The intensities of 2154 independent reflections were measured within the range $0<2\leqq127°$, and corrected for the Lorentz and polarization factors.

The structure was solved by MULTAN[2] followed by Fourier synthesis. The positional and anisotropic temperature factors for non-hydrogen atoms were refined by the block-diagonal least-squares method.[3] All hydrogen atoms were located in a different electron density map, and included in the subsequent refinement with isotropic temperature factors. The weighting scheme used in the final refinement was: w=0.28 for F_o=0, w=1.0 for $0<F_o\leqq20$, and w=$[1.0+0.21(F_o-20)]^{-1}$ for $20<F_o$. However, the six strongest reflections were ommitted from the later stage of the refinement. The final R value was 0.044 for 2148 independent reflections (R=0.038 for non-zero reflections).



desacetylaustin (ED-2)



ED-2H

Chart 1

The absolute configuration was determined by the Bijvoet method by utilizing the anomalous scattering of light-atoms for Cu$K\alpha$ radiation.[4,5] Twelve sets of Bijvoet pairs and reference pairs were chosen according to BA_{th}'s and intensities. A specimen of size *ca.* 0.2×0.4×0.2 mm was mounted with its b axis parallel to the ϕ axis of the diffractometer. The intensities

1) K.K. Chexal, J.P. Springer, J. Clardy, R.J. Cole, J.W. Kirksey, J.W. Dorner, H.G. Cutler, and B.J. Strawter, *J. Am. Chem. Soc.*, **98**, 6748 (1976).
2) G. Germain, P. Main, and M.M. Woolfson, *Acta Cryst.*, **A27**, 368 (1971).
3) T. Ashida, HBLS-V, The Universal Crystallographic Computing System-Osaka, pp. 55—61. The Computation Center of Osaka University (1973).
4) D.W. Engel, *Acta Cryst.*, **B28**, 1496 (1972).
5) K. Fukuyama, K. Hamada, T. Tsukihara, and Y. Katsube, *Bull. Chem. Soc. Japan*, **51**, 37 (1978).

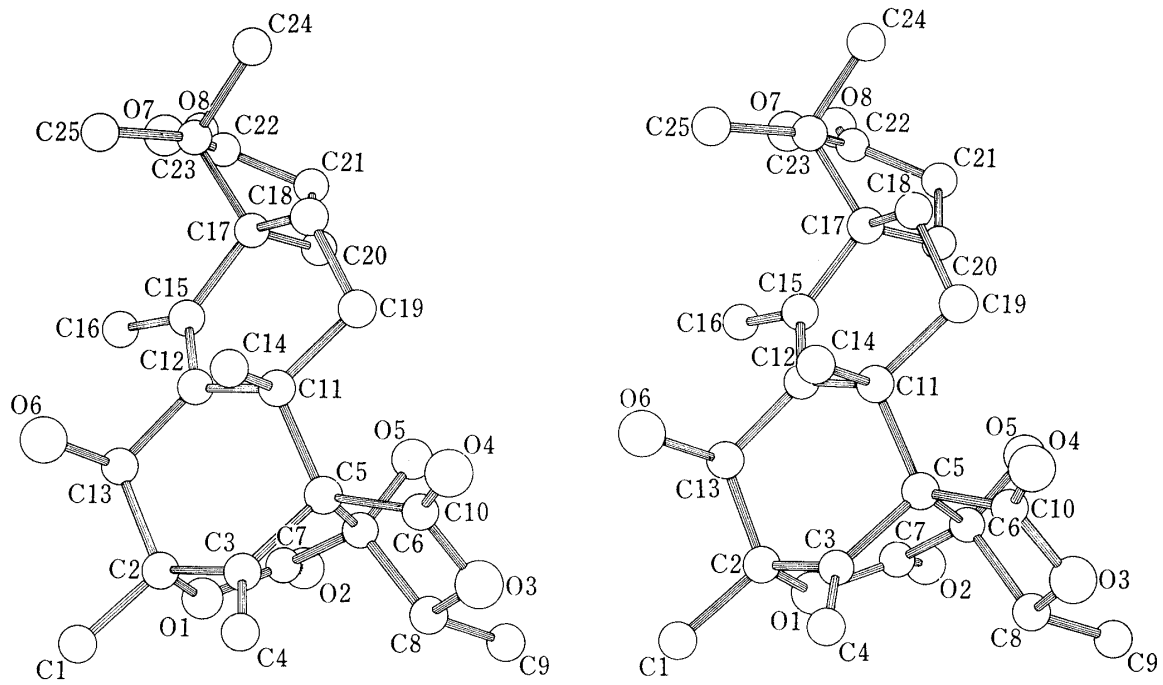


Fig. 1. Stereoscopic View of Dihydrodesacetylaustin

The figure is drawn with the correct absolute configuration. The hydrogen atoms are omitted from the figure for the sake of clarity.

of Bijvoet pair and its reference pair were measured alternately at least 10 times with Ni-filtered Cu$K\alpha$ radiation. The scan speed was 0.5° min^{-1} and the background was counted for 25 s at each side of the scan range. Figure 1 is a computer generated stereoscopic view[6] of ED-2H drawn on the basis of the Bijvoet measurement. The probability that the absolute configuration shown in Fig. 1 is wrong estimated to be less than 0.01 assuming t-distribution of DELA's; the ratio of the mean DELA and its standard derivation was 3.48. The imaginary components used in this calculation were $\Delta f''_{O}=0.02$ and $\Delta f''_{C}=\Delta f''_{H}=0.0$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[7]

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6) S. Motherwell, PLUTO, A program for plotting molecular, and crystal structures. University of Cambridge, 1976.
7) "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham, 1974.