Structure Analysis of *p*-Bromobenzoate of Sterigmatocystin by X-ray Diffraction Method

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Sterigmatocystin, a metabolite of Aspergillus versicolor (Vuillemin) Tiraboshi, is a natural product containing the dihydrofurobenzofuran system. The structure was postulated by means of spectrometry and various chemical methods.[1,2] In order to establish the structure, *p*-bromobenzoate of sterigmatocystin was investigated by X-ray diffraction method.

TABLE 1. CRYSTAL AND PHYSICAL DATA

Molecular weight:	$C_{25}H_{15}O_7Br$ 507.31
Melting point :	260°C
Monoclinic :	$a=13.01\pm0.04$ Å
	$b=9.03\pm0.03$ Å
	$c=8.93\pm0.03$ Å
	$\beta=102.5\pm0.5°$
Space group :	$P2_1$
Density (by flotation) :	1.640 g/cm^3
Density (calculation) :	1.645 g/cm^3
Two molecules per unit cell.	
Volume of the unit cell :	1023.8 Å^3

The compound was obtained by the reaction between sterigmatocystin and *p*-bromobenzoylchloride. The crystal grown from acetone solution was light brown needles elongated along the *b* axis. The unit cell dimensions shown in Table 1 were obtained from NaCl-calibrated Weissenberg and rotation photographs about the *b* and c axes. Intensities of 1545 independent reflections were measured visually from equi-inclination Weissenberg photographs of 0—6 layers around the *b* axis.

The bromine atom was easily located as $x=-0.06$, $y=0.25$(arbitrary chosen) and $z=0.16$ from the Harker peak of a sharpened three-dimensional Patterson function. The nine atoms were assigned in the benzoyl group near the bromine atom, though the first Fourier map based on the bromine atom alone was confused by false symmetry. The whole structure of the molecule was revealed after five successive structure factor and Fourier synthesis calculations.

Refinement of the structural parameters was carried out by the block-diagonal least-squares method. The discrepancy factor was reduced to 0.168 after six cycles of the refinement with the isotropic thermal parameters. The average standard deviation of the bond length is 0.041 Å. The current three-dimensional electron density distribution viewed along the *b* axis is shown in Fig. 1. The structure of sterigmatocystin in this molecule is in agreement with that proposed by Bullock *et al.*[2]

Further refinement of the structure and determination of the absolute configuration will be published later.

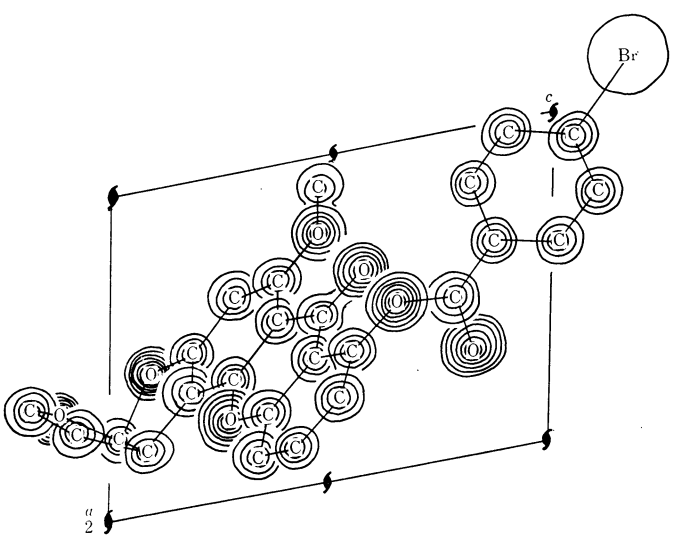

Fig. 1. Electron density distribution viewed along the *b* axis

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2) E. Bullock, J.C. Roberts and J.G. Underwood, *J. Chem. Soc.*, **1962**, 4179.