

associate *via* a complex network of N—H...O hydrogen bonds and dipolar attractions, utilizing most of the available amide and carbonyl functional groups.

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Structure of Demethylsterigmatocystin

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Abstract. C₁₇H₁₀O₆, $M_r = 310.3$, monoclinic, C_2 , $a = 16.359$ (3), $b = 7.099$ (1), $c = 12.150$ (1) Å, $\beta = 107.71$ (1)°, $D_x = 1.53$ Mg m⁻³ for $Z = 4$. The structure was refined by the block-diagonal least-squares method to $R = 0.068$ for 962 non-zero reflections. The xanthone skeleton is slightly twisted to take a propeller-like form.

Introduction. The title compound was isolated from *Aspergillus versicolor* (Vuillemin) Tiraboschi, and was shown to be a demethyl derivative of sterigmatocystin (Elsworthy, Holker, McKeown, Robinson & Mulheirn, 1970). The present X-ray analysis was undertaken to reveal the conformation of the dihydrofuro[2,3-*b*]furan moiety which is a common structural unit in toxic metabolites of the genus *Aspergillus*.

Pale yellow needle-shaped crystals elongated along the b axis were obtained from acetone solution. The systematic absences uniquely characterized the space group as C_2 , since the compound has optical activity. The unit-cell constants were obtained by least-squares refinement of the setting angles measured on a four-circle diffractometer. The intensities were measured on a Rigaku computer-controlled four-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation from a crystal cut to approximate dimensions of $0.1 \times 0.3 \times 0.1$ mm. The θ – 2θ scan technique was employed with a scan speed of 4° min^{-1} in 2θ . The scan range for θ was calculated as $1.0^\circ + 0.15^\circ \tan \theta$. The backgrounds were counted for 10 s at both sides of the scan range. The intensities of 1081 reflections were measured within the range $2\theta \leq 120^\circ$; 962 of these were non-zero, and corrected for Lorentz and polarization factors only. The structure was solved by interpretation of the Patterson function, and refined by block-diagonal least-squares calculations (Ashida, 1973) with anisotropic temperature factors for heavy atoms and fixed isotropic temperature factors (4.0 \AA^2)

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for H atoms, where unit weight was applied for each reflection. The final R value was 0.068 for all non-zero reflections. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates are given in Table 1.*

Discussion. The molecular structure is shown in Fig. 1, together with the atomic numbering used in this paper; the configurations around C(14) and C(17) were assumed to be the same as those in related molecules established by the X-ray method (Fukuyama, Hamada, Tsukihara & Katsube, 1978; Bear, Waters & Waters, 1970). The bond lengths and angles for non-hydrogen atoms are shown in Table 2, and the equations of least-squares planes and the deviations of atoms from each plane are in Table 3.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34174 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates* ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms)

	x	y	z
C(1)	1274 (5)	2641 (18)	1115 (7)
C(2)	1047 (5)	2723 (16)	2105 (7)
C(3)	1662 (5)	2610 (16)	3219 (6)
C(4)	1418 (5)	2641 (18)	4256 (7)
C(5)	2114 (5)	2491 (15)	5342 (6)
C(6)	1974 (5)	2544 (15)	6432 (6)
C(7)	2638 (6)	2507 (16)	7427 (7)
C(8)	3473 (6)	2360 (15)	7386 (7)
C(9)	3658 (6)	2314 (16)	6337 (7)
C(10)	2972 (5)	2400 (16)	5349 (6)
C(11)	2532 (5)	2351 (15)	3286 (6)
C(12)	2775 (5)	2155 (15)	2305 (7)
C(13)	2136 (6)	2286 (15)	1259 (6)
C(14)	3352 (7)	1452 (17)	792 (8)
C(15)	4226 (7)	4030 (17)	1160 (9)
C(16)	4151 (6)	3688 (16)	2182 (8)
C(17)	3639 (6)	1860 (16)	2121 (7)
O(1)	212 (4)	3034 (12)	2006 (5)
O(2)	658 (4)	2824 (13)	4252 (5)
O(3)	1158 (4)	2710 (13)	6496 (5)
O(4)	3168 (3)	2283 (10)	4319 (4)
O(5)	2453 (4)	2002 (12)	347 (4)
O(6)	3841 (4)	2733 (16)	321 (5)

Bonded to	x	y	z	
H(1)	C(1)	88 (6)	175 (18)	39 (8)
H(2)	O(1)	15 (6)	293 (19)	246 (8)
H(3)	O(3)	94 (6)	287 (20)	591 (8)
H(4)	C(7)	259 (6)	233 (19)	807 (8)
H(5)	C(8)	390 (6)	224 (19)	799 (8)
H(6)	C(9)	427 (6)	213 (19)	633 (8)
H(7)	C(14)	341 (7)	15 (19)	56 (9)
H(8)	C(15)	457 (7)	509 (19)	103 (9)
H(9)	C(16)	433 (6)	470 (18)	277 (9)
H(10)	C(17)	400 (7)	44 (19)	263 (9)

There are two intramolecular hydrogen bonds: O(1)—H(2)···O(2) and O(3)—H(3)···O(2). The distances O(2)···H(2) and O(2)···H(3) are 2.08 and 1.93 Å, respectively, and the angles O(1)—H(2)···O(2) and O(3)—H(3)···O(2) are 148 and 161°. Comparison of the bond angles C(3)—C(2)—O(1) and C(5)—C(6)—O(3) with those of related compounds has shown that the angle involving the hydroxyl group as a side chain is larger by a few degrees than that involving the methoxy group. The same effect has been observed in other compounds, and interpreted by Coppens & Schmidt (1965). The other bond lengths and angles in the xanthone skeleton seem to be the same as those

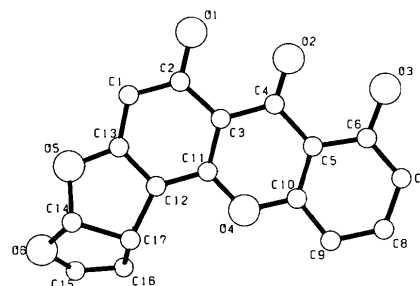


Fig. 1. Molecular structure of demethylsterigmatocystin plotted by a local version of PLUTO (Motherwell, 1976).

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

C(1)—C(2)	1.365 (17)	C(1)—C(13)	1.390 (17)
C(2)—C(3)	1.421 (16)	C(2)—O(1)	1.352 (14)
C(3)—C(4)	1.433 (17)	C(3)—C(11)	1.414 (15)
C(4)—C(5)	1.461 (16)	C(4)—O(2)	1.248 (15)
C(5)—C(6)	1.413 (15)	C(5)—C(10)	1.402 (15)
C(6)—C(7)	1.358 (16)	C(6)—O(3)	1.365 (14)
C(7)—C(8)	1.386 (16)	C(8)—C(9)	1.397 (16)
C(9)—C(10)	1.373 (16)	C(10)—O(4)	1.386 (13)
C(11)—C(12)	1.374 (15)	C(11)—O(4)	1.366 (13)
C(12)—C(13)	1.382 (15)	C(12)—C(17)	1.511 (16)
C(13)—O(5)	1.373 (14)	C(14)—C(17)	1.565 (17)
C(14)—O(5)	1.458 (15)	C(14)—O(6)	1.440 (17)
C(15)—C(16)	1.307 (17)	C(15)—O(6)	1.376 (17)
C(16)—C(17)	1.534 (16)		

C(2)—C(1)—C(13)	115.8 (11)	C(1)—C(2)—C(3)	122.2 (11)
C(1)—C(2)—O(1)	117.8 (11)	C(3)—C(2)—O(1)	119.9 (10)
C(2)—C(3)—C(4)	122.0 (10)	C(2)—C(3)—C(11)	118.1 (10)
C(4)—C(3)—C(11)	119.8 (10)	C(3)—C(4)—C(5)	116.3 (10)
C(3)—C(4)—O(2)	122.8 (11)	C(5)—C(4)—O(2)	120.9 (11)
C(4)—C(5)—C(6)	122.7 (10)	C(4)—C(5)—C(10)	120.9 (10)
C(6)—C(5)—C(10)	116.3 (10)	C(5)—C(6)—C(7)	121.3 (10)
C(5)—C(6)—O(3)	119.8 (10)	C(7)—C(6)—O(3)	118.9 (10)
C(6)—C(7)—C(8)	120.0 (11)	C(7)—C(8)—C(9)	121.6 (10)
C(8)—C(9)—C(10)	116.8 (10)	C(5)—C(10)—C(9)	123.9 (10)
C(5)—C(10)—O(4)	120.2 (10)	C(9)—C(10)—O(4)	115.8 (10)
C(3)—C(11)—C(12)	121.0 (10)	C(3)—C(11)—O(4)	122.0 (9)
C(12)—C(11)—O(4)	117.0 (9)	C(11)—C(12)—C(13)	117.0 (10)
C(11)—C(12)—C(17)	132.3 (10)	C(13)—C(12)—C(17)	110.7 (9)
C(1)—C(13)—C(12)	125.6 (11)	C(1)—C(13)—O(5)	122.9 (10)
C(12)—C(13)—O(5)	111.5 (9)	C(17)—C(14)—O(5)	106.6 (9)
C(17)—C(14)—O(6)	105.4 (10)	O(5)—C(14)—O(6)	107.7 (10)
C(16)—C(15)—O(6)	115.2 (11)	C(15)—C(16)—C(17)	108.6 (10)
C(12)—C(17)—C(14)	100.2 (9)	C(12)—C(17)—C(16)	113.4 (9)
C(14)—C(17)—C(16)	101.2 (9)	C(10)—O(4)—C(11)	120.5 (8)
C(13)—O(5)—C(14)	109.0 (9)	C(14)—O(6)—C(15)	108.2 (10)

Table 3. *Least-squares planes and deviations (Å) of atoms from each plane*

The e.s.d.'s of the deviations are ~ 0.015 Å.

(a) Xanthone skeleton

$$0.100X + 0.995Y + 0.005Z = 1.982^*$$

C(1)	-0.06	C(2)	-0.05
C(3)	-0.03	C(4)	0.02
C(5)	0.04	C(6)	0.06
C(7)	0.01	C(8)	-0.03
C(9)	-0.06	C(10)	-0.03
C(11)	0.01	C(12)	0.08
C(13)	0.06	O(2)	0.01
O(4)	-0.02	O(1)†	-0.13
O(3)†	0.08	C(14)†	0.43
C(17)†	0.14	O(5)†	0.18

(b) Five-membered ring comprising C(12), C(13), C(14), C(17), and O(5)

$$0.219X + 0.973Y - 0.073Z = 2.153^*$$

C(12)	0.05	C(13)	0.02
C(14)	0.08	C(17)	-0.09
O(5)	-0.05		

(c) Five-membered ring comprising C(14), C(15), C(16), C(17), and O(6)

$$0.793X - 0.573Y + 0.206Z = 3.793^*$$

C(14)	0.08	C(15)	0.01
C(16)	0.03	C(17)	-0.06
O(6)	-0.06		

* X , Y , and Z are defined as $ax + cz \cos \beta$, by , and $cz \sin \beta$ respectively.

† Not included in the least-squares calculations.

found in related molecules. The skeleton of the present molecule is slightly twisted along its longitudinal axis to take a propeller-like form, while the skeleton in the *p*-bromobenzoate ester of sterigmatocystin took a bent form (Fukuyama, Tsukihara, Katsube, Tanaka, Hamasaki & Hatsuda, 1975). The conformation of the ring C(12)–C(13)–O(5)–C(14)–C(17) approximates

a half-chair with C(14) and C(17) displaced on opposite sides of the plane through C(12), C(13), and O(5), while that of C(14)–C(17)–C(16)–C(15)–O(6) is an envelope with C(14) displaced from the plane through C(15), C(16), C(17), and O(6). C(12)–C(17)–C(14)–O(5) and C(16)–C(17)–C(14)–O(6) torsion angles are 13.6 and 11.2° , respectively, each of which is the largest of the values in related molecules so far determined (Fukuyama, Ashida, Katsube & Kakudo, 1979). The molecules related by screw symmetry are stacked with respect to each other along the *b* axis at the xanthone moieties with a dihedral angle of about 11° . The intermolecular short contact (2.83 Å) between O(3) and O(2) of an adjacent molecule seems to be a van der Waals contact.

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