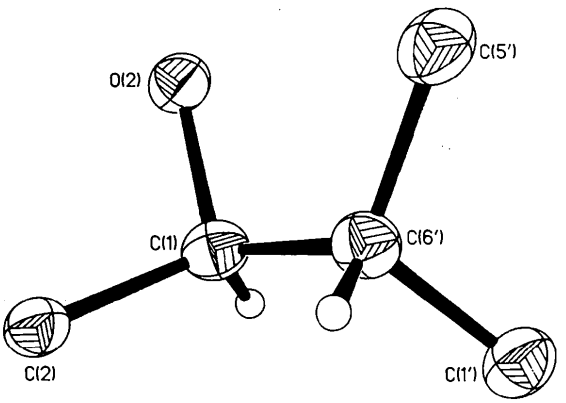


Fig. 2. The stereochemistry at the asymmetric centers C(1) and C(6').

an excellent plane (maximum deviation 0·005 Å), with C(5') lying 0·570 Å out of the plane. Atom C(6'), however, sits only 0·075 Å above this four-atom plane. Alternatively, if we view the ring as an envelope conformation we calculate a plane through the five atoms C(6'), C(1'), C(2'), C(3') and C(4'); the maximum deviation from this plane is 0·022 Å, and C(5') lies 0·617 Å below the plane.

Our principal interest in the title compound is in the configuration at the asymmetric carbon centers C(1) and C(6'), since we were unsure with which diastereomer we were dealing. The geometry at C(1) and C(6') is shown in Fig. 2. As can be seen in that figure, the configuration in the molecule shown is C(1)*S*, C(6')*S*; naturally, in this centrosymmetric crystal there are an equal number of the enantiomeric C(1)*R*, C(6')*R* species, but no other diastereomers.

KMC gratefully acknowledges the receipt of a Kuehn fellowship from the University of Wyoming and the E. R. Schierz Award from the Wyoming Section of the American Chemical Society. BAB acknowledges the support of the American Cancer Society through grant No. IN-160A.

References

BROWN, D. W., CAMPBELL, M. M., TAYLOR, A. P. & ZHANG, X. (1987). *Tetrahedron Lett.* **28**, 985.

EVANS, D. A. (1984). In *Asymmetric Synthesis*, edited by J. D. MORRISON, Vol. 3, pp. 1–110. New York: Academic Press.

HARTSHORN, M. P., MARTYN, R. J., ROBINSON, W. T. & VAUGHAN, J. (1986). *Aust. J. Chem.* **39**, 1609–1620.

HEATHCOCK, C. H. (1984). In *Asymmetric Synthesis*, edited by J. D. MORRISON, Vol. 3, pp. 112–212. New York: Academic Press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

SHELDRICK, G. M. (1987). *SHELXTL-PLUS Crystallographic System*, version 2. Nicolet XRD Corporation, Madison, Wisconsin, USA.

SINGH, P. & HODGSON, D. J. (1974). *Acta Cryst.* B**30**, 828–830.

STORK, G., KRAUS, G. A. & GARCIA, G. A. (1974). *J. Org. Chem.* **39**, 3459.

Acta Cryst. (1989). C**45**, 628–632

Structure of Elsinochrome A: a Perylenequinone Metabolite

BY STEFANO V. MEILLE, LUCIANA MALPEZZI, GIUSEPPE ALLEGRA AND GIANLUCA NASINI

Dipartimento di Chimica e Centro di Studio del CNR per le Sostanze Organiche Naturali, Politecnico di Milano, Piazza Leonardo da Vinci 32, *I*- 20133 *Milano, Italy*

AND ULRICH WEISS

Laboratory of Chemical Physics, National Institutes of Health, Bethesda, Maryland 20892, *USA*

(*Received* 3 *October* 1988; *accepted* 21 *October* 1988)

Abstract. *trans*-1,2-Diacetyl-1,2-dihydro-5,10-dihydroxy-3,7,8,12-tetramethoxybenzo[*ghi*]perylene-4,11-dione, $C_{30}H_{24}O_{10}$, $M_r = 544{\cdot}51$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 12{\cdot}428$ (3), $b = 13{\cdot}048$ (3), $c = 14{\cdot}933$ (3) Å, $V = 2421{\cdot}5$ (9) Å^3, $D_x = 1{\cdot}494$, D_m (by flotation) $= 1{\cdot}48$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 1{\cdot}057$ cm^{-1}, $F(000) = 1136$, $T = 293$ K, $R = 0{\cdot}046$ (2065 observed reflections). Elsinochrome A is shown to exist in the solid state as a non-planar quinone tautomer; the pigment adopts a helical conformation, in analogy with the related cercosporin, but the perylenequinone moiety in elsinochrome A appears to be significantly less skewed.

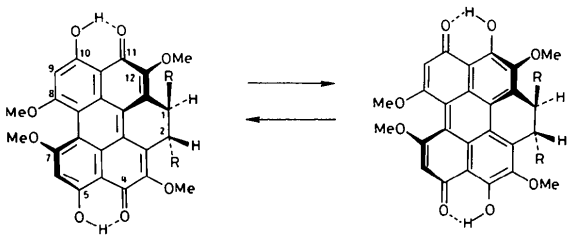
Introduction. Perylenequinones form a group of chemically interesting biologically active (especially photosensitizing) pigments obtainable from natural sources (Weiss, Merlini & Nasini, 1987); almost all the

0108-2701/89/040628-05$03.00

metabolites of this class are produced by a wide variety of moulds (*e.g.* cercosporins from *Cercospora* spp.), most of which are phytopathogens. It seems that the plant diseases are caused by the photodynamic action of these perylenequinoes (Arnone, Assante, Caronna, Di Modugno & Nasini, 1988). Furthermore, interest in new photochemically active compounds is increasing because of their possible applications in the phototherapy of cancer (Bonnet, Berenbaum & Knaur, 1983).

The red pigment elsinochrome A (1*a*, 1*b*) is produced together with elsinochromes B, C and D by a large number of moulds of the ascomycetous genus *Elsinoë* (asexual stage *Sphaceloma*). It was first examined by one of us (Weiss, Flon & Burger, 1957), and recognized as a perylenequinone derivative, for which the complete chemical structure was established subsequently (Lousberg, Salemink, Weiss & Batterham, 1969).

It has been shown earlier (Weiss, Merlini & Nasini, 1987) that, like most other natural perylenequinones, elsinochrome A exists in solution as a mixture of roughly equal amounts of the tautomers (1*a*) and (1*b*).



(1*a*) R = COMe (1*b*)

Furthermore, compound (1) is optically active. This property could be caused by asymmetric carbons C(1) and C(2), by a fixed non-coplanarity of the extended chromophore as in cercosporin (Merlini, Nasini, Andreetti, Bocelli & Sgarabotto, 1982), or by a combination of both factors. Inspection of the CD curve of compound (1) shows close similarity in the signs and positions of most peaks with the curve of cercosporin, but with large differences in intensity in the 250–300 nm region (Arnone, Merlini, Mondelli, Nasini & Weiss, 1989) and, because the CD is mainly due to the inherently dissymmetrical perylenequinone chromophore, it follows that (1) has the same axial chirality (*R*) as cercosporin, which was established by X-ray diffraction (Merlini *et al.*, 1982). The knowledge of the axial chirality of the system allows us to determine the absolute configuration of the asymmetric carbons of elsinochrome A.

Experimental. Ruby-red transparent single crystals, prismatic in habit, from CH_2Cl_2–heptane solution; crystal dimensions 0·5 × 0·4 × 0·3 mm; Nonius CAD-4 diffractometer (graphite-monochromated Mo $K\alpha$ radiation); cell constants refined from angular setting values of 18 reflections with $2\theta > 18°$; intensity measurements with $6 \le 2\theta \le 56°$; *hkl* ranges: $0 \le h \le 16$, $0 \le k \le 17$, $0 \le l \le 19$; $\omega/2\theta$ scan mode, scan width $(1{\cdot}20 + 0{\cdot}35\tan\theta)°$; three standard reflections (307, $\bar{3}07$, $\bar{3}0\bar{7}$) monitored every 2 h to check crystal stability and experimental conditions, no significant decay; 3309 independent reflections collected, 2065 [with $I > 2\sigma(I)$] were considered observed; Lorentz and polarization but no absorption correction applied.

The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined with *SHELX*76 (Sheldrick, 1976). The blocked full-matrix least-squares refinement was carried out with isotropic temperature factors for the atoms belonging to the condensed ring system in order to keep the data/parameter ratio at an acceptable value (7·6). Exocyclic non-hydrogen atoms were refined anisotropically; H atoms were finally located on difference Fourier maps. Convergence was reached with a final disagreement factor $R = 0{\cdot}046$, $wR = 0{\cdot}046$, unit weights, $(\Delta/\sigma)_{max} = 0{\cdot}3$, no peak absolute value in the final Fourier synthesis exceeding 0·15 e Å^{-3}, atomic scattering factors incorporated in *SHELX*76, geometrical calculations with *PARST* (Nardelli, 1983).*

Discussion. An arbitrary *PLUTO* (Motherwell, 1978) view of elsinochrome A, with the referenced atomic labeling scheme, is presented in Fig. 1. Final positional

* Lists of observed and calculated structure factors, H-atom positional parameters, anisotropic thermal parameters and details of least-squares-planes calculation have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51530 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

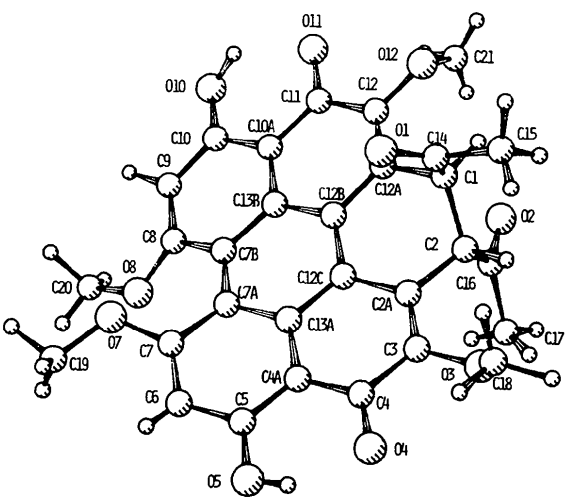


Fig. 1. A *PLUTO* (Motherwell, 1978) view of elsinochrome A.

parameters and equivalent isotropic temperature factors are reported in Table 1, while bond distances, bond angles and selected torsion angles are listed in Table 2.

Bond lengths and angles of the perylenequinone moiety are in good agreement with the values reported for cercosporin (Mentzafos, Terzis & Filippakis, 1982) and derivatives (Merlini *et al.*, 1982); in particular, the pattern of alternation of short and long bond lengths is similar, even if somewhat less clear. Furthermore all the bond-length data and the intramolecular hydrogen-bonding geometry (Table 3) consistently indicate that tautomer (1*a*) prevails in the solid-state structure of elsinochrome A, in analogy with cercosporin. On the other hand the values of the phenolic and quinonic C—O bond lengths are respectively shorter and longer than in cercosporin and other pertinent systems (Brown & Colclough, 1983), suggesting that minor amounts of tautomer (1*b*) might coexist with tautomer (1*a*) also in the crystal structure of elsinochrome A.

Assignment of axial chirality *R* to the molecule, in agreement with CD results (Arnone, Merlini *et al.*, 1989) allows us to determine as *S* the absolute configuration of carbons C(1) and C(2). The *trans* diaxial arrangement of the acetyl groups on the hydroaromatic ring is also apparent. These results are in complete agreement with the findings based on ^{1}H NMR spectroscopy of the title compound (Arnone, Merlini *et al.*, 1989).

The elsinochrome A molecule is compatible in principle with a twofold rotation axis through the midpoints of the C(1)–C(2), C(12*B*)–C(12*C*) and C(7*A*)–C(7*B*) bonds. Actually, the molecule approaches non-crystallographic symmetry around this pseudo-C_2 axis: while the deviations from such symmetry are hardly significant in the central region of the molecule, they become more important on the peripheral rings and even more pronounced in the acyclic portions. In fact, while the conformations of the two pairs of methoxy side chains related by the pseudo-axis nearly respect the C_2 symmetry, the two *trans* diaxial acetyl substituents adopt clearly distinct conformations, as apparent from the values of torsion angles C(15)–C(14)–C(1)–C(12*A*) = −165·3 (4) and C(17)–C(16)–C(2)–C(2*A*) = 50·2 (5)°.

Of the five perylenequinone rings, the central one deviates most from planarity, its conformation closely approaching an ideal twist boat with total puckering amplitude of 0·169 (4) Å (Cremer & Pople, 1975). The conformations of the other four aromatic rings are also distorted, although to a lesser extent; they can be described in terms of the internal rotation angles reported in Table 2.

The close contact between the two methoxy oxygens at C(7) and C(8) [O(7)···O(8) 2·497 (4) Å] induces larger deviations from planarity than in the corresponding portion of the cercosporin molecule, where the two O atoms are included in a seven-membered ring. Thus the values of torsion angles O(8)–C(8)–C(7*B*)–C(7*A*), C(8)–C(7*B*)–C(7*A*)–C(7) and O(7)–C(7)–C(7*A*)–C(7*B*) are −15·9 (6), −23·9 (7) and −16·2 (6)° in compound (1*a*, 1*b*), while the values of the corresponding angles are −4·2 (5), −10·0 (5), and 8·2 (5)° in cercosporin (Merlini *et al.*, 1982).

Conversely, in elsinochrome A the cyclohexadiene ring, having a half-chair conformation, allows for a more nearly planar arrangement than in the corresponding portion of the cercosporin molecule where the most important steric conflict arises from the non-connected analogues of C(1) and C(2). The different modes of distortion from planarity of the perylenequinone moiety in elsinochrome A and in cercosporin can be appreciated by considering as a probe the distances of atoms C(7), C(8), C(2*A*) and C(12*A*) from the least-squares planes of the perylenequinones: they are 0·436 (5), −0·417 (4), −0·302 (4) and 0·264 (4) Å respectively in (1) and 0·210, −0·255, −0·671 and 0·592 Å for the corresponding atoms in cercosporin (Mentzafos *et al.*, 1982). The degree of distortion can also be evaluated from the average

Table 1. *Fractional atomic coordinates* (× 10^4) *for non*-H *atoms and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
O(1)	9434 (3)	304 (3)	6816 (2)	4·0 (3)
O(2)	7386 (4)	−793 (3)	9612 (3)	5·5 (3)
O(3)	8301 (3)	2706 (2)	8938 (2)	3·1 (2)
O(4)	7250 (3)	4053 (2)	7809 (2)	3·5 (2)
O(5)	5875 (3)	4402 (2)	6603 (2)	4·1 (3)
O(7)	4768 (3)	1640 (2)	4796 (2)	3·4 (3)
O(8)	3646 (2)	289 (3)	5524 (2)	3·5 (2)
O(10)	5209 (3)	−2993 (3)	5800 (3)	4·4 (3)
O(11)	6836 (3)	−3215 (2)	6730 (3)	4·3 (3)
O(12)	8440 (2)	−2424 (2)	7791 (2)	3·2 (2)
C(1)	8574 (4)	−319 (3)	8154 (3)	2·5 (1)
C(2)	8115 (3)	561 (3)	8722 (3)	2·5 (1)
C(2*A*)	7558 (3)	1327 (3)	8126 (3)	2·4 (1)
C(3)	7679 (4)	2348 (3)	8242 (3)	2·7 (1)
C(4)	7111 (3)	3087 (3)	7688 (3)	2·6 (1)
C(4*A*)	6391 (3)	2710 (3)	7020 (3)	2·5 (1)
C(5)	5806 (4)	3391 (4)	6483 (3)	3·0 (1)
C(6)	5195 (4)	3039 (4)	5766 (3)	3·4 (1)
C(7)	5143 (4)	2004 (3)	5584 (3)	2·8 (1)
C(7*A*)	5568 (3)	1253 (3)	6200 (3)	2·4 (1)
C(7*B*)	5389 (4)	170 (3)	6150 (3)	2·6 (1)
C(8)	4482 (4)	−328 (3)	5709 (3)	2·8 (1)
C(9)	4456 (4)	−1366 (4)	5563 (3)	3·2 (1)
C(10)	5257 (4)	−1999 (4)	5925 (3)	3·1 (1)
C(10*A*)	6073 (4)	−1580 (3)	6468 (3)	2·7 (1)
C(11)	6838 (4)	−2245 (4)	6877 (3)	3·1 (1)
C(12)	7665 (4)	−1791 (3)	7443 (3)	2·8 (1)
C(12*A*)	7698 (4)	−768 (3)	7585 (3)	2·5 (1)
C(12*B*)	6905 (3)	−97 (3)	7193 (3)	2·4 (1)
C(12*C*)	6892 (3)	945 (3)	7400 (3)	2·3 (1)
C(13*A*)	6267 (3)	1633 (3)	6874 (3)	2·3 (1)
C(13*B*)	6116 (3)	−491 (3)	6595 (3)	2·5 (1)
C(14)	9506 (3)	127 (3)	7602 (3)	2·7 (3)
C(15)	10523 (4)	348 (4)	8114 (3)	3·8 (4)
C(16)	7390 (4)	120 (4)	9465 (3)	3·1 (3)
C(17)	6779 (4)	871 (4)	10024 (3)	4·5 (4)
C(18)	9274 (4)	3221 (4)	8671 (4)	4·6 (4)
C(19)	4132 (4)	2302 (4)	4240 (3)	4·4 (4)
C(20)	2717 (4)	−129 (4)	5089 (3)	3·7 (4)
C(21)	8049 (5)	−3096 (4)	8480 (3)	4·5 (4)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

O(1)–C(14)	1·199 (5)	C(4A)–C(13A)	1·429 (6)	C(18)–O(3)–C(3)–C(4)	−71·0 (5)
O(2)–C(16)	1·210 (6)	C(5)–C(6)	1·391 (7)	C(19)–O(7)–C(7)–C(6)	−18·0 (6)
O(3)–C(3)	1·376 (5)	C(6)–C(7)	1·380 (6)	C(20)–O(8)–C(8)–C(9)	−5·3 (6)
O(3)–C(18)	1·440 (6)	C(7)–C(7A)	1·444 (6)	C(21)–O(12)–C(12)–C(11)	−71·2 (5)
O(4)–C(4)	1·284 (5)	C(7A)–C(7B)	1·433 (6)	C(2)–C(1)–C(14)–O(1)	−105·2 (5)
O(5)–C(5)	1·334 (5)	C(7A)–C(13A)	1·419 (6)	C(2)–C(1)–C(14)–C(15)	73·9 (4)
O(7)–C(7)	1·352 (5)	C(7B)–C(8)	1·459 (6)	C(2)–C(1)–C(12A)–C(12B)	38·2 (5)
O(7)–C(19)	1·436 (6)	C(7B)–C(13B)	1·414 (6)	C(2)–C(1)–C(12A)–C(12)	−142·2 (4)
O(8)–C(8)	1·343 (5)	C(8)–C(9)	1·372 (7)	C(12A)–C(1)–C(2)–C(16)	71·9 (4)
O(8)–C(20)	1·432 (6)	C(9)–C(10)	1·401 (7)	C(12A)–C(1)–C(2)–C(2A)	−53·9 (4)
O(10)–C(10)	1·313 (6)	C(10)–C(10A)	1·410 (6)	C(14)–C(1)–C(2)–C(16)	−165·1 (3)
O(11)–C(11)	1·284 (6)	C(10A)–C(11)	1·424 (6)	C(1)–C(2)–C(16)–O(2)	11·0 (6)
O(12)–C(12)	1·371 (5)	C(10A)–C(13B)	1·435 (6)	C(1)–C(2)–C(16)–C(17)	−173·6 (4)
O(12)–C(21)	1·437 (6)	C(11)–C(12)	1·457 (6)	C(1)–C(2)–C(2A)–C(3)	−137·2 (4)
C(1)–C(2)	1·538 (6)	C(12)–C(12A)	1·352 (6)	C(1)–C(2)–C(2A)–C(12C)	41·6 (5)
C(1)–C(12A)	1·500 (6)	C(12A)–C(12B)	1·444 (6)	C(2)–C(2A)–C(3)–O(3)	−2·0 (6)
C(1)–C(14)	1·536 (6)	C(12B)–C(12C)	1·395 (6)	C(2)–C(2A)–C(12C)–C(12B)	−9·1 (6)
C(2)–C(2A)	1·507 (6)	C(12B)–C(13B)	1·422 (6)	C(12C)–C(2A)–C(3)–C(4)	3·5 (6)
C(2)–C(16)	1·541 (6)	C(12C)–C(13A)	1·424 (6)	C(2A)–C(3)–C(4)–O(4)	−179·4 (4)
C(2A)–C(3)	1·352 (6)	C(14)–C(15)	1·505 (6)	C(2A)–C(3)–C(4)–C(4A)	1·4 (6)
C(2A)–C(12C)	1·452 (6)	C(16)–C(17)	1·495 (7)	C(3)–C(4)–C(4A)–C(13A)	−2·6 (6)
C(3)–C(4)	1·453 (6)			C(4)–C(4A)–C(5)–O(5)	−2·5 (7)
C(4)–C(4A)	1·428 (6)			C(4)–C(4A)–C(13A)–C(12C)	−1·1 (6)
C(4A)–C(5)	1·401 (6)			C(13A)–C(4A)–C(5)–C(6)	−6·1 (7)
				C(4A)–C(5)–C(6)–C(7)	1·1 (7)
C(3)–O(3)–C(18)	114·9 (3)	C(7B)–C(8)–C(9)	122·0 (4)	C(5)–C(6)–C(7)–C(7A)	10·1 (7)
C(7)–O(7)–C(19)	118·8 (4)	O(8)–C(8)–C(9)	122·8 (4)	O(7)–C(7)–C(7A)–C(7B)	−16·2 (6)
C(8)–O(8)–C(20)	119·2 (4)	C(8)–C(9)–C(10)	120·2 (4)	C(6)–C(7)–C(7A)–C(13A)	−15·4 (6)
C(12)–O(12)–C(21)	113·7 (4)	O(10)–C(10)–C(9)	119·7 (4)	C(7)–C(7A)–C(13A)–C(4A)	10·1 (6)
C(12A)–C(1)–C(14)	113·1 (3)	C(9)–C(10)–C(10A)	120·3 (4)	C(7)–C(7A)–C(7B)–C(8)	−23·9 (7)
C(2)–C(1)–C(14)	107·0 (3)	O(10)–C(10)–C(10A)	119·8 (4)	C(7B)–C(7A)–C(13A)–C(12C)	8·9 (6)
C(2)–C(1)–C(12A)	109·6 (4)	C(10)–C(10A)–C(13B)	119·1 (4)	C(13A)–C(7A)–C(7B)–C(13B)	−16·9 (6)
C(1)–C(2)–C(16)	109·6 (4)	C(10)–C(10A)–C(11)	119·4 (4)	C(7A)–C(7B)–C(8)–O(8)	−15·9 (6)
C(1)–C(2)–C(2A)	109·9 (3)	C(11)–C(10A)–C(13B)	121·5 (4)	C(7A)–C(7B)–C(13B)–C(12B)	9·8 (6)
C(2A)–C(2)–C(16)	113·9 (4)	O(11)–C(11)–C(10A)	121·8 (4)	C(8)–C(7B)–C(13B)–C(10A)	11·6 (6)
C(2)–C(2A)–C(12C)	118·4 (4)	C(10A)–C(11)–C(12)	118·1 (4)	C(13B)–C(7B)–C(8)–C(9)	−13·8 (6)
C(2)–C(2A)–C(3)	121·8 (4)	O(11)–C(11)–C(12)	120·0 (4)	C(7B)–C(8)–C(9)–C(10)	7·0 (7)
C(3)–C(2A)–C(12C)	119·8 (4)	O(12)–C(12)–C(11)	118·1 (4)	C(8)–C(9)–C(10)–C(10A)	2·4 (7)
O(3)–C(3)–C(2A)	119·6 (4)	C(11)–C(12)–C(12A)	120·9 (4)	O(10)–C(10)–C(10A)–C(11)	−0·1 (7)
C(2A)–C(3)–C(4)	121·8 (4)	O(12)–C(12)–C(12A)	120·9 (4)	C(9)–C(10)–C(10A)–C(13B)	−4·3 (7)
O(3)–C(3)–C(4)	118·5 (4)	C(1)–C(12A)–C(12)	119·8 (4)	C(10)–C(10A)–C(11)–O(11)	3·4 (7)
O(4)–C(4)–C(3)	120·4 (4)	C(12)–C(12A)–C(12B)	121·0 (4)	C(11)–C(10A)–C(13B)–C(12B)	−4·2 (6)
C(3)–C(4)–C(4A)	118·2 (4)	C(1)–C(12A)–C(12B)	119·2 (4)	C(13B)–C(10A)–C(11)–C(12)	0·9 (7)
O(4)–C(4)–C(4A)	121·4 (4)	C(12A)–C(12B)–C(13B)	120·4 (4)	C(10A)–C(11)–C(12)–C(12A)	0·8 (7)
C(4)–C(4A)–C(13A)	120·9 (4)	C(12A)–C(12B)–C(12C)	120·6 (4)	O(11)–C(11)–C(12)–C(12A)	178·2 (4)
C(4)–C(4A)–C(5)	120·4 (4)	C(12C)–C(12B)–C(13B)	119·0 (4)	O(12)–C(12)–C(12A)–C(1)	−1·8 (6)
C(5)–C(4A)–C(13A)	118·7 (4)	C(2A)–C(12C)–C(12B)	119·6 (4)	C(11)–C(12)–C(12A)–C(12B)	1·0 (7)
O(5)–C(5)–C(4A)	121·2 (4)	C(12B)–C(12C)–C(13A)	119·9 (4)	C(1)–C(12A)–C(12B)–C(12C)	−5·6 (6)
C(4A)–C(5)–C(6)	121·0 (4)	C(2A)–C(12C)–C(13A)	120·4 (4)	C(12A)–C(12B)–C(12C)–C(2A)	−10·5 (6)
O(5)–C(5)–C(6)	117·6 (4)	C(7A)–C(13A)–C(12C)	120·3 (4)	C(12A)–C(12B)–C(13B)–C(10A)	6·0 (6)
C(5)–C(6)–C(7)	120·0 (4)	C(4A)–C(13A)–C(12C)	118·4 (4)	C(12C)–C(12B)–C(13B)–C(7B)	5·8 (6)
O(7)–C(7)–C(6)	122·1 (4)	C(4A)–C(13A)–C(7A)	121·2 (4)	C(13B)–C(12B)–C(12C)–C(13A)	−14·0 (6)
C(6)–C(7)–C(7A)	121·4 (4)	C(10A)–C(13B)–C(12B)	117·8 (4)	C(2A)–C(12C)–C(13A)–C(4A)	6·1 (6)
O(7)–C(7)–C(7A)	116·3 (4)	C(7B)–C(13B)–C(12B)	121·0 (4)	C(12B)–C(12C)–C(13A)–C(7A)	6·6 (6)
C(7)–C(7A)–C(13A)	116·0 (4)	C(7B)–C(13B)–C(10A)	121·2 (4)		
C(7)–C(7A)–C(7B)	125·4 (4)	O(1)–C(14)–C(1)	122·8 (4)		
C(7B)–C(7A)–C(13A)	118·5 (4)	C(1)–C(14)–C(15)	115·7 (4)		
C(7A)–C(7B)–C(13B)	118·5 (4)	O(1)–C(14)–C(15)	121·5 (4)		
C(7A)–C(7B)–C(8)	125·7 (4)	O(2)–C(16)–C(2)	120·1 (4)		
C(8)–C(7B)–C(13B)	115·8 (4)	C(2)–C(16)–C(17)	117·0 (4)		
O(8)–C(8)–C(7B)	115·1 (4)	O(2)–C(16)–C(17)	122·8 (4)		

Table 3. *Geometry* (Å,°) *of the observed hydrogen bonds* (*e.s.d.'s in parentheses*)

Donor–H	Donor···Acceptor	H···Acceptor	Donor–H···Acceptor
O(5)–H(5)	O(5)···O(4)	H(5)···O(4)	O(5)–H(5)···O(4)
0·82 (5)	2·524 (5)	1·79 (5)	149 (5)
O(10)–H(10)	O(10)···O(11)	H(10)···O(11)	O(10)–H(10)···O(11)
0·99 (5)	2·471 (5)	1·73 (5)	129 (4)

distance of the 20 perylenequinone C atoms from the perylenequinone least-squares plane: 0·251 Å in cercosporin [calculated from the data of Mentzafos *et al.* (1982)] and 0·181 Å in (1). The lower degree of skewedness of elsinochrome A is consistent with the lower overall intensity of its CD spectrum compared with that of cercosporin (Arnone, Merlini *et al.*, 1989).

References

ARNONE, A., ASSANTE, G., CARONNA, T., DI MODUGNO, V. & NASINI, G. (1988). *Phytochemistry*, **27**, 1669–1674.

ARNONE, A., MERLINI, L., MONDELLI, R., NASINI, G. & WEISS, U. (1989). In preparation.

BONNET, R., BERENBAUM, M. C. & KNAUR, H. (1983). *Porphyrins Tumor Phototherapy*, edited by A. ANDREONI & R. CUBEDDU. New York: Plenum.

BROWN, C. J. & COLCLOUGH, M. L. (1983). *Acta Cryst.* C**39**, 300–302.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

LOUSBERG, J. J. CH., SALEMINK, C. A., WEISS, U. & BATTERHAM, T. J. (1969). *J. Chem. Soc. C*, pp. 1219–1227.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
MENTZAFOS, D., TERZIS, A. & FILIPPAKIS, S. E. (1982). *Cryst. Struct. Commun.* **11**, 71–74.
MERLINI, L., NASINI, G., ANDREETTI, G. D., BOCELLI, G. & SGARABOTTO, P. (1982). *Tetrahedron*, **38**, 2787–2796.
MOTHERWELL, W. D. S. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
WEISS, U., FLON, H. & BURGER, W. C. (1957). *Arch. Biochem. Biophys.* **69**, 311–319.
WEISS, U., MERLINI, L. & NASINI, G. (1987). *Progress in the Chemistry of Natural Products*, Vol. 52, edited by W. HERZ, H. GRISEBACH, G. W. KIRBY & CH. TAMM, pp. 1–71. Vienna, New York: Springer Verlag.

Acta Cryst. (1989). C**45**, 632–634

Structure of Dimethyl 4-*O*-Methyltrioxanoate

BY NORIAKI HIRAYAMA,* TAKAO IIDA AND KUNIKATSU SHIRAHATA

Tokyo Research Laboratories, Kyowa Hakko Kogyo Co. Ltd, 3-6-6 *Asahimachi, Machida, Tokyo* 194, *Japan*

(*Received* 9 *August* 1988; *accepted* 1 *November* 1988)

Abstract. (2*R*,3a*S*,4*R*,9b*S*)-Dimethyl 2-dimethoxymethyl-4-methoxy-9-methyl-3a,9b-dihydrospiro(2,4-methano-4*H*-benzo[*b*][1,3]dioxolo[4,5-*d*]pyran-10,2′-oxiran)-6,7-dicarboxylate, $C_{21}H_{24}O_{11}$, $M_r = 452{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}333$ (1), $b = 23{\cdot}310$ (3), $c = 9{\cdot}029$ (2) Å, $Z = 4$, $D_x = 1{\cdot}382$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 9{\cdot}219$ cm^{-1}, $F(000) = 952$, $T = 293$ K, $wR = 0{\cdot}048$ for 2216 observed reflections. The molecule contains a unique tricyclo skeleton. The dioxabicycloheptane ring adopts a structure similar to that of norbornane. The dihydropyran adopts a twist conformation. The absolute configuration was determined by the Bijvoet method.

Introduction. Antibiotic trioxacarcin A which is isolated from the culture broth of *Streptomyces ochraceus* shows anticancer activity against mouse Sarcoma 180 and Leukemia P-388 and also antibacterial activity against both Gram-positive and Gram-negative bacteria (Tomita, Tamaoki, Morimoto & Fujimoto, 1981). The structural characteristics of the anticancer antibiotic have been studied by chemical and spectroscopic methods to show that it contains a relatively complex aglycone moiety the structure of which was difficult to determine unequivocally by these methods. To disclose its structure, we have undertaken the degradation of trioxacarcin A (Shirahata, Iida & Hirayama, 1981). After oxidation followed by methanolysis of trioxacarcin A, the title compound, which maintains the most complex moiety, was obtained. The present X-ray analysis was undertaken to establish the structure.

* Author to whom correspondence should be addressed.

0108-2701/89/040632-03$03.00

Experimental. Colourless crystals from a mixture of acetone and cyclohexane (2:1), dimensions 0·40 × 0·37 × 0·20 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Cell dimensions from setting angles of 21 independent reflections with $24{\cdot}0 \le \theta \le 34{\cdot}0°$. 2574 reflections surveyed in the range $4 \le 2\theta \le 150°$; $0 \le h \le 12$, $0 \le k \le 29$, $0 \le l \le 11$; 2233 independent reflections with $I > 3{\cdot}0\sigma(I)$. Three reference reflections monitored periodically showed no significant variation in intensity. Empirical absorption correction (North, Phillips & Mathews, 1968) was applied (transmission 0·873–0·999). A secondary-extinction correction (Zachariasen, 1963) was applied (refined coefficient $3{\cdot}8 \times 10^{-6}$). Structure solved using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier-map recycling. Refinement using the *SDP* package (Frenz, 1985), full-matrix least-squares refinement on F, with non-H atoms having anisotropic temperature factors and H atoms (located from a difference Fourier synthesis) having isotropic temperature factors. Weight $w = 4F_o^2/[\sigma(I_o)^2 + (0{\cdot}04I_o)^2]^{1/2}$/Lp, final $R = 0{\cdot}036$, $wR = 0{\cdot}048$, $S = 2{\cdot}04$, maximum shift/e.s.d. in the final least-squares cycle 0·14, maximum and minimum peaks in the final difference map 0·37(8) and −0·34(9) eÅ^{-3}, respectively. The absolute configuration was determined with Bijvoet differences (Bijvoet, Peerdeman & van Bommel, 1951) using the anomalous dispersion of O and N to Cu $K\alpha$ radiation. After structure refinement a set of reflections was chosen which were those the most sensitive to the anomalous-dispersion effects, based on the largest values for $||F^+| - |F^-||$calc./