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Methyl Austrocorticinate†

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Abstract

The crystal and molecular structure of methyl austrocorticinate (methyl 3-ethyl-1-hydroxy-6,8-dimethoxy-9,10-dioxoanthracene-2-carboxylate, $C_{20}H_{18}O_7$) has been determined. Crystals of the naturally derived material were found to be twinned, whereas the crystals of the totally synthetic material showed no evidence of twinning. The three six-membered rings and the two methoxy groups are almost coplanar, while the orientation of the methyl ester group is almost perpendicular to the ring plane.

Comment

Austrocorticinic acid (3-ethyl-1-hydroxy-6,8-dimethoxy-9,10-dioxoanthracene-2-carboxylic acid) (1) is one of five unique anthraquinones isolated from the fruit bodies of an indigenous Australian toadstool that contain a C_2 side chain at C3 in the anthraquinone nucleus (Gill & Gimenez, 1988, 1990). The biogenetic origin of these quinones, which involves a propionate-initiated octaketide, has no precident in nature (Gill & Gimenez, 1990). While the natural product (1) did not form crystals suitable for X-ray analysis, its methyl ester, methyl austrocorticinate (methyl 3-ethyl-1-hydroxy-6,8-dimethoxy-9,10-dioxoanthracene-2-carboxylate), (2), gave orange-red needles, m.p. 483–485 K, from ethyl acetate–light petroleum. Methyl austrocorticinate (2) has also been prepared by total synthesis (Cotterill & Gill, 1994) and gave yellow–orange needles, m.p. 462–463 K, from ethyl acetate–light petroleum. Although the spectroscopic data (NMR, IR, UV, mass spectra) of the 'natural' and the 'synthetic' ester (2) were identical, there were clear differences between the colours and the melting

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† Part 35 in the series *Pigments of Fungi.*

points of the two samples. Therefore a crystal structure analysis was carried out on both samples of the ester (2) to confirm the assigned structure, and to see whether there were any differences between the two materials.

(1) R = H
(2) R = Me
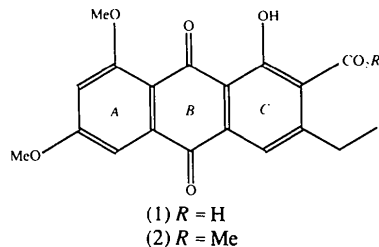
The intensity data collected from a crystal of the entirely synthetic material were found to have 2/m symmetry, despite β being close to 90°, and showed the systematic absences h0l: l = 2n + 1 and 0k0: k = 2n + 1, defining the space group as $P2_1/c$, for which a satisfactory solution was found. The crystals of the naturally derived material also showed the same systematic absences and gave similar cell parameters; however, intensity measurements indicated that many of the crystals were subject to varying degrees of twinning, including some where the intensity data showed almost *mmm* symmetry. Eventually, a crystal was found that showed only slight twinning, the intensity data giving an identical structure to that obtained from the totally synthetic material. Only the structure derived from the 'synthetic' crystal is reported.

The only difference between the two samples is that the crystals of the 'natural' material were found to be twinned, whereas the structural analysis, and intensity measurements on several other crystals of the 'synthetic' material, did not show any evidence of twinning. The bond lengths and angles found here compare well with those reported for similar structures, such as 7-methoxy-2-methyl-4,5-dihydroxy-9,10-anthracenedione (Ulický, Kožíšek & Ječný, 1991). In particular, O(9) is involved in a strong intramolecular hydrogen bond with O(1) [O(1)—H(O1) 0.96 (6), O(9)···H(O1) 1.72 (6) Å, O(1)—H(O1)···O(9) 138 (4)°] which results in the C(9)—O(9) distance being slightly longer than the C(10)—O(10) distance. Both methoxy groups lie almost in the plane of the aromatic ring A to which they are bonded, with C(6')—O(6)—C(6)—C(7) and C(8')—O(8)—C(8)—C(7) torsion angles of 10.5 (9) and 0.7 (9)°, respectively. In contrast, the plane of the methyl ester is almost perpendicular to the other aromatic ring C, with a torsion angle C(1)—C(2)—C(2')—O(2') of 103.8 (8)°. While the two six-membered aromatic rings show no significant deviation from planarity, the six atoms of the central ring B have a slightly less-planar relationship, with the greatest deviation from the plane being 0.030 (8) Å for C(10). Furthermore, the condensed-ring system is significantly

non-planar, with the dihedral angle between the two aromatic rings A and C being 7.2°, while the dihedral angles between the central ring B and the aromatic rings A and C are 3.9 and 3.4°, respectively.
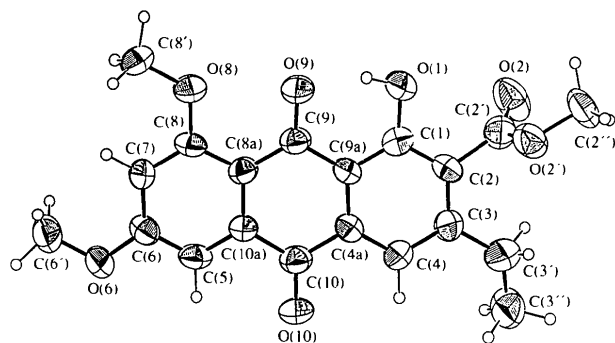

Fig. 1. *ORTEP*II (Johnson, 1976) diagram of methyl austrocorticinate showing the labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was synthesized as described by Cotterill & Gill (1994).

Crystal data

$C_{20}H_{18}O_7$	Mo $K\alpha$ radiation
$M_r = 370.3$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 14.565$ (3) Å	$\theta = 7-14°$
$b = 15.359$ (3) Å	$\mu = 0.10$ mm^{-1}
$c = 7.883$ (2) Å	$T = 293$ (1) K
$\beta = 90.08$ (2)°	Thin needle
$V = 1764$ (1) Å^3	$0.53 \times 0.09 \times 0.07$ mm
$Z = 4$	Yellow–orange
$D_x = 1.394$ Mg m^{-3}	
$D_m = 1.39$ (1) Mg m^{-3}	
D_m measured by flotation	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.024$
MachS diffractometer	$\theta_{max} = 25°$
$\omega-2\theta$ scans	$h = -17 \rightarrow 17$
Absorption correction:	$k = -1 \rightarrow 18$
none	$l = -1 \rightarrow 9$
4278 measured reflections	3 standard reflections
3085 independent reflections	frequency: 160 min
1064 observed reflections	intensity decay: 11%
$[I \geq 2\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.01$
$R = 0.063$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
$wR = 0.043$	$\Delta\rho_{min} = -0.31$ e Å^{-3}
$S = 1.876$	Extinction correction: 020
1062 reflections	and 210 omitted

272 parameters
$w = 2.793/[\sigma^2(F) + 0.00005F^2]$

Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0.4071 (3)	0.4553 (3)	0.1798 (7)	0.067 (2)
O(2)	0.3360 (4)	0.6339 (3)	0.3143 (7)	0.094 (2)
O(2')	0.3918 (3)	0.6674 (3)	0.0604 (7)	0.074 (2)
O(6)	0.0855 (3)	0.0278 (3)	-0.1463 (7)	0.066 (1)
O(8)	0.3665 (3)	0.1272 (3)	0.1105 (6)	0.064 (2)
O(9)	0.3886 (3)	0.2944 (3)	0.1348 (7)	0.073 (2)
O(10)	0.0713 (3)	0.3442 (3)	-0.1972 (7)	0.073 (2)
C(1)	0.3266 (5)	0.4637 (5)	0.0960 (9)	0.052 (2)
C(2)	0.2926 (5)	0.5470 (5)	0.0776 (10)	0.055 (2)
C(3)	0.2105 (5)	0.5624 (5)	-0.0081 (10)	0.070 (3)
C(4)	0.1630 (5)	0.4910 (5)	-0.0738 (11)	0.068 (3)
C(4a)	0.1957 (4)	0.4080 (5)	-0.0524 (9)	0.049 (2)
C(5)	0.1201 (5)	0.1750 (5)	-0.1283 (10)	0.055 (2)
C(6)	0.1451 (5)	0.0902 (5)	-0.0958 (10)	0.051 (2)
C(7)	0.2282 (5)	0.0728 (5)	-0.0169 (10)	0.049 (2)
C(8)	0.2845 (4)	0.1415 (5)	0.0321 (9)	0.046 (2)
C(8a)	0.2597 (5)	0.2286 (5)	0.0037 (9)	0.047 (2)
C(9)	0.3140 (5)	0.3031 (5)	0.0594 (10)	0.049 (2)
C(9a)	0.2787 (4)	0.3912 (5)	0.0317 (9)	0.047 (2)
C(10)	0.1419 (5)	0.3318 (5)	-0.1171 (10)	0.055 (2)
C(10a)	0.1745 (5)	0.2426 (5)	-0.0801 (10)	0.046 (2)
C(2')	0.3419 (5)	0.6205 (5)	0.1658 (12)	0.061 (3)
C(2'')	0.4404 (5)	0.7419 (5)	0.1360 (11)	0.083 (3)
C(3')	0.1725 (9)	0.6527 (7)	-0.029 (2)	0.131 (4)
C(3''A)†	0.0938 (11)	0.6734 (13)	-0.099 (4)	0.087 (6)
C(3''B)‡	0.162 (2)	0.6866 (15)	-0.174 (3)	0.117 (8)
C(6')	0.1014 (4)	-0.0600 (4)	-0.0917 (10)	0.074 (3)
C(8')	0.3955 (4)	0.0386 (4)	0.1411 (10)	0.069 (2)

† Site occupancy = 0.52.
‡ Site occupancy = 0.48.

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(1)	1.351 (9)	C(3)—C(3')	1.502 (14)
O(2)—C(2')	1.192 (11)	C(4)—C(4a)	1.371 (11)
O(2')—C(2')	1.319 (10)	C(4a)—C(9a)	1.402 (9)
O(2')—C(2'')	1.471 (9)	C(4a)—C(10)	1.498 (10)
O(6)—C(6)	1.353 (9)	C(5)—C(6)	1.376 (11)
O(6)—C(6')	1.434 (8)	C(5)—C(10a)	1.360 (10)
O(8)—C(8)	1.362 (8)	C(6)—C(7)	1.386 (10)
O(8)—C(8')	1.445 (8)	C(7)—C(8)	1.391 (10)
O(9)—C(9)	1.245 (9)	C(8)—C(8a)	1.404 (11)
O(10)—C(10)	1.221 (9)	C(8a)—C(9)	1.458 (11)
C(1)—C(2)	1.379 (11)	C(8a)—C(10a)	1.421 (10)
C(1)—C(9a)	1.408 (10)	C(9)—C(9a)	1.464 (11)
C(2)—C(3)	1.393 (11)	C(10)—C(10a)	1.479 (10)
C(2)—C(2')	1.507 (11)	C(3')—C(3''A)	1.31 (2)
C(3)—C(4)	1.396 (11)	C(3')—C(3''B)	1.27 (3)
C(2')—O(2')—C(2'')	115.8 (5)	O(10)—C(10)—C(4a)	119.6 (5)
C(6)—O(6)—C(6')	118.3 (4)	O(10)—C(10)—C(10a)	121.1 (5)
C(8)—O(8)—C(8')	118.9 (4)	C(4a)—C(10)—C(10a)	119.3 (5)
O(1)—C(1)—C(2)	116.8 (5)	C(5)—C(10a)—C(8a)	121.5 (5)
O(1)—C(1)—C(9a)	122.0 (5)	C(5)—C(10a)—C(10)	117.7 (5)
C(2)—C(1)—C(9a)	121.2 (5)	C(8a)—C(10a)—C(10)	120.8 (5)
C(1)—C(2)—C(3)	121.1 (6)	O(2)—C(2')—O(2')	124.4 (5)
C(1)—C(2)—C(2')	118.4 (6)	O(2)—C(2')—C(2)	123.2 (6)
C(3)—C(2)—C(2')	120.3 (6)	O(2')—C(2')—C(2)	112.4 (5)
C(1)—C(9a)—C(9)	120.2 (5)	C(3)—C(3')—C(3''A)	126.3 (12)
C(4a)—C(9a)—C(9)	122.9 (5)	C(3)—C(3')—C(3''B)	121.5 (12)

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). Refinement was carried out by a full-matrix least-squares method using *SHELX*76 (Sheldrick, 1976) with anisotropic displacement factors for all non-H atoms. The

terminal atom of the ethyl group appeared to be disordered and was refined over two sites with occupancies of 0.52 and 0.48. The occupancy factors were not refined in the final cycles as there were strong correlations with the position and displacement parameters of these atoms. All the partially occupied H atoms on the ethyl group were fixed on the basis geometrical estimates, while the other methyl H atoms were included at calculated positions and refined using a riding model, with a common isotropic displacement factor for each group. All other H atoms were refined with individual isotropic displacement factors.

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Diels–Alder Products of the Alkaloid (−)-Thebaine with α-Chloroacrylnitrile and 1-Methoxy-1,3-cyclohexadiene with Tetracyanoethene

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Abstract

(5R,6S,7R,9R,13S,14R)-7-Chloro-7-cyano-4,5-epoxy-3,6-dimethoxy-N-methyl-6,14-ethenoisomorphinane, (1), C22H23ClN2O3, and 1-methoxy-5,5,6,6-tetracyano-

bicyclo[2.2.2]oct-2-ene, (2), C13H10N4O, which had not been convincingly characterized before by any other analytical method due to possible existence of several isomers, were obtained from the Diels–Alder reactions of (−)-thebaine [for compound (1)] and 1-methoxy-1,3-cyclohexadiene [for compound (2)]. The X-ray structural results provided reliable information on the stereochemical course of Diels–Alder reactions of (−)-thebaine and 1-methoxy-1,3-cyclohexadiene with α-chloroacrylnitrile and tetracyanoethene, respectively.

Comment

Diels–Alder reactions of the electron-rich opium alkaloid (−)-thebaine, as well as of related compounds also possessing 1,3-cyclohexadiene subunits, with acceptor-substituted dienophiles are of general interest in the development of new analgesic drugs (Bentley, 1954). The previously reported structural data on cycloadducts of thebaine and related systems (Bentley, 1971) is not completely convincing because of the possible existence of several stereoisomers. Therefore, reinvestigations of several Diels–Alder reactions of (−)-thebaine and related dienes, and detailed structural analysis of reaction products is still necessary (Pindur & Keilhofer, 1993; Pindur, Keilhofer & Schollmeyer, 1994) in order to carry out reliable studies on structure–activity relationships in medicinal chemistry.

(1)   (2)
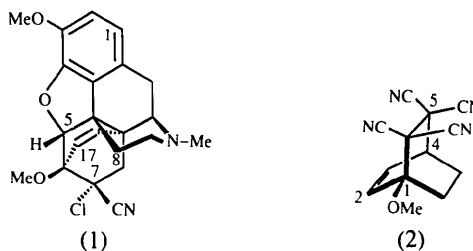
The results of the X-ray structure determination of the title compounds (1) and (2) gave very detailed information concerning the course of the Diels–Alder reactions of (−)-thebaine with α-chloroacrylnitrile, and of 1-methoxy-1,3-cyclohexadiene, as a subunit model for thebaine, with tetracyanoethene. In the case of the [4 + 2] cycloaddition of (−)-thebaine with α-chloroacrylnitrile, a reliable determination of the configuration of the newly formed stereocentres was not possible previously (Pindur & Keilhofer, 1993) and has been the subject of some controversy (Hua, Jung, Ostrander & Takusagawa, 1987; Lewis, Readhead, Selby, Smith & Young, 1971). However, applications of several high-resolution NMR techniques were not able to clarify the regio- and stereo-chemistry of cycloadduct (1) (Pindur & Keilhofer, 1993) because of missing selective probes in the molecule to discriminate from eight different isomeric Diels–Alder products. We have now clarified unambiguously the