

Cochliodinol

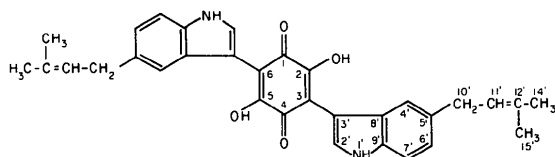
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Abstract. $C_{32}H_{30}N_2O_4$, F.W. 506.6; monoclinic, $P2_1/n$; $a = 17.14$ (1), $b = 7.386$ (4), $c = 10.291$ (5) Å, $\beta = 93.6$ (1)° at 20°C; $D_m = 1.293$, $Z = 2$, $D_x = 1.294$ g cm⁻³. Molecular symmetry centre. The compound is confirmed to be 2,5-dihydroxy-3,6-bis[5'-(2"-methylbut-1,2"-enyl)-3-indolyl]cyclohexadiene-1,4-dione.

Introduction. The molecular structure of the purple antibiotic metabolite cochliodinol (I) has been established by chemical and spectroscopic methods (Jerram, McInnes, Maass, Smith, Taylor & Walter, 1975).



However, the mass spectra obtained in this study were anomalous, suggesting a compound of mass two units greater than that proposed. It was considered desirable to confirm the proposed formulation by X-ray analysis of the crystal structure. The sample provided consisted of opaque brown needles elongated along **b**. The space group was determined from single-crystal photographs (systematic absences: $h0l$ for $h + l$ odd, $0k0$ for k odd). The specimen used for intensity measurements was a fragment of a needle ($0.13 \times 0.17 \times 0.5$ mm). This was mounted on a Picker four-circle diffractometer, with **b** parallel to the φ axis. The intensities of the 2207 independent reflexions within the limiting sphere $2\theta = 130^\circ$ were measured with Ni-filtered Cu $K\alpha$ radiation and a scintillation counter. The θ - 2θ scan mode was used, with scans of 2° for $2\theta < 100^\circ$, and 3° otherwise. Background intensities were estimated from an experimentally derived function of θ . For 239 reflexions the net count was less than 30, and these were treated as unobserved. No correction was made for absorption ($\mu = 8.1$ cm⁻¹).

The structure was readily determined by symbolic-addition procedures, with all non-hydrogen atoms appearing in the first E map. Refinement was by block-diagonal least squares, minimizing $\sum w\Delta F^2$. The H atoms were located in a ΔF synthesis and were included in the refinement. A correction for extinction

was applied to the 28 most intense reflexions, the largest correction being 10% of F_o . The weighting scheme used in the final stages was $w = 2.5 \sin^2 \theta$ for $\sin^2 \theta < 0.4$, and $w = 1$ otherwise. With this scheme there was no obvious systematic dependence of the weighted residual on either F_o or θ . On termination of refinement, R (for observed reflexions only) was 0.032. On the final cycle the largest coordinate shift of a non-hydrogen atom was less than one quarter of the corresponding e.s.d. of 0.002 Å. The final ΔF synthesis contained no electron density outside the limits -0.12

Table 1. Final atomic coordinates ($\times 10^4$ for hydrogen atoms; $\times 10^5$ otherwise)

E.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-2858 (7)	-17687 (16)	-2846 (12)
O(1)	-4780 (6)	-33421 (12)	-4760 (11)
C(2)	5325 (7)	-14239 (17)	2663 (12)
O(2)	9672 (5)	-29103 (12)	4959 (11)
C(3)	8172 (7)	2435 (16)	5477 (12)
N(1')	26364 (6)	15252 (17)	23746 (12)
C(2')	18409 (8)	14845 (20)	21985 (14)
C(3')	16228 (7)	5816 (17)	10789 (13)
C(4')	24980 (7)	-8217 (19)	-6511 (13)
C(5')	32662 (8)	-10676 (20)	-9511 (14)
C(6')	38715 (8)	-4588 (21)	-666 (16)
C(7')	37320 (8)	4040 (20)	10736 (15)
C(8')	23323 (7)	563 (16)	5034 (13)
C(9')	29546 (7)	6768 (18)	13502 (13)
C(10')	34639 (10)	-19512 (25)	-22198 (16)
C(11')	41042 (9)	-33411 (24)	-20985 (15)
C(12')	40575 (10)	-49325 (24)	-15192 (15)
C(13')	47261 (13)	-62454 (30)	-14693 (20)
C(14')	33545 (12)	-55371 (29)	-8565 (20)
H(2)	698 (11)	-3792 (28)	306 (18)
H(1')	2896 (10)	1993 (25)	3012 (17)
H(2')	1520 (9)	2013 (23)	2844 (16)
H(4')	2070 (9)	-1275 (22)	-1243 (14)
H(6')	4412 (10)	-671 (25)	-314 (17)
H(7')	4152 (10)	829 (24)	1673 (16)
H(10')1	3617 (12)	-961 (29)	-2843 (20)
H(10')2	2987 (11)	-2527 (27)	-2599 (18)
H(11')	4601 (11)	-3040 (27)	-2486 (18)
H(13')1	5196 (12)	-5617 (30)	-1816 (20)
H(13')2	4584 (14)	-7339 (37)	-1984 (24)
H(13')3	4855 (14)	-6593 (35)	-548 (23)
H(14')1	3222 (15)	-6818 (37)	-1062 (25)
H(14')2	2892 (14)	-4763 (36)	-1078 (24)
H(14')3	3477 (14)	-5497 (35)	99 (24)

Table 2. Interatomic distances (Å) and bond angles (°)

Atoms designated $X(n)^i$ are related to $X(n)$ as $-x, -y, -z$; $X(n)^{ii}$ as $-x, -1-y, -z$.	
C(1)—O(1)	1.221 (2)
C(1)—C(2)	1.501 (2)
C(2)—O(2)	1.339 (2)
C(2)—C(3)	1.349 (2)
C(3)—C(1) ⁱ	1.463 (2)
C(3)—C(3')	1.474 (2)
N(1')—C(2')	1.365 (2)
C(2')—C(3')	1.363 (2)
C(3')—C(8')	1.439 (2)
C(8')—C(9')	1.411 (2)
C(9')—N(1')	1.369 (2)
C(4')—C(5')	1.383 (2)
C(5')—C(6')	1.410 (2)
C(6')—C(7')	1.370 (2)
C(7')—C(9')	1.395 (2)
C(4')—C(8')	1.398 (2)
C(5')—C(10')	1.517 (2)
C(10')—C(11')	1.502 (2)
C(11')—C(12')	1.323 (2)
C(12')—C(13')	1.500 (3)
C(12')—C(14')	1.490 (3)
O(2)—H(2)	0.81 (2)
N(1')—H(1')	0.84 (2)
C—H(mean)	0.99 (2)
C—H(range)	0.97–1.01
O(1) ... O(2)	2.632 (2)
O(1) ... O(2) ⁱⁱ	2.892 (2)
O(1) ... H(2)	2.15 (2)
O(1) ... H(2) ⁱⁱ	2.16 (2)
C(1)C(2)C(3)	123.5 (1)
C(2)C(3)C(1) ⁱ	116.8 (1)
C(3)C(1)C(2)	119.7 (1)
C(2)C(1)O(1)	117.3 (1)
C(3)C(1)O(1)	123.0 (1)
C(1)C(2)O(2)	115.1 (1)
C(3)C(2)O(2)	121.4 (1)
C(2)C(3)C(3')	123.5 (1)
C(1)C(3)C(3')	119.7 (1)
C(3)C(3)C(2')	126.7 (1)
C(3)C(3)C(8')	126.7 (1)
C(2)C(3)C(8')	106.6 (1)
C(3)C(8)C(9')	106.5 (1)
C(3)C(8)C(4')	134.2 (1)
C(4)C(8)C(9')	119.3 (1)
N(1')C(9)C(8')	107.6 (1)
N(1')C(9)C(7')	131.0 (1)
C(7)C(9)C(8')	121.5 (1)
C(2)N(1)C(9')	109.3 (1)
N(1)C(2)C(3')	110.0 (1)
C(5)C(4)C(8')	119.8 (1)
C(4)C(5)C(6')	119.1 (1)
C(4)C(5)C(10')	121.1 (1)
C(6)C(5)C(10')	119.8 (1)
C(5)C(6)C(7')	122.7 (1)
C(6)C(7)C(9')	117.6 (1)
C(5)C(10)C(11')	115.1 (1)
C(10)C(11)C(12')	125.4 (2)
C(11)C(12)C(13')	121.5 (2)
C(11)C(12)C(14')	123.1 (2)
C(13)C(12)C(14')	115.4 (2)
C(2)O(2)H(2)	108 (1)

and $+0.18 e \text{ \AA}^{-3}$. The final atomic positions are given in Table 1.*

The computer programs used were those of Ahmed, Hall, Pippy & Huber (1966). Scattering factors were taken from Stewart, Davidson & Simpson (1965) for H, and from Hanson, Herman, Lea & Skillman (1964).

Discussion. The analysis confirms the proposed structure. Bond lengths and angles are given in Table 2, details of some mean planes are given in Table 3, and the crystal and molecular structures are illustrated in Fig. 1. The molecule is defined by three planes. The first contains the cyclohexadiene ring, the O atoms, and the bridgehead atom of the indole nucleus. The second contains the indole nucleus and the bridgehead atom of the cyclohexadiene ring. The third contains the 2-methyl-2-butene group. The second is inclined at 56.3° to the first, and the third at 87.6° to the second. Some torsion

* Lists of atomic thermal-motion parameters (anisotropic for the non-hydrogen atoms) and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32130 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Distances ($\text{\AA} \times 10^3$) of some atoms from certain mean planes

An asterisk indicates an atom not used to define the plane. Symmetry-related atoms are designated as in Table 2.

Plane	Distances ($\text{\AA} \times 10^3$)
Plane 1	C(1) 8 [C(1) ⁱ -8]; C(2) 11 [C(2) ⁱ -11]; C(3) 0 [C(3) ⁱ 0]; O(1) -4 [O(1) ⁱ 4]; O(2) -6 [O(2) ⁱ 6]; *C(3') 14.
Plane 2	*C(3) -1; N(1') 5; C(2') 26; C(3') -7; C(4') -5; C(5') 24; C(6') 6; C(7') -12; C(8') -23; C(9') -14; *C(10') 97.
Plane 3	C(10') 8; C(11') -12; C(12') 3; C(13') 4; C(14') -3.

Dihedral angles: 1-2 56.3° ; 2-3 87.6° .

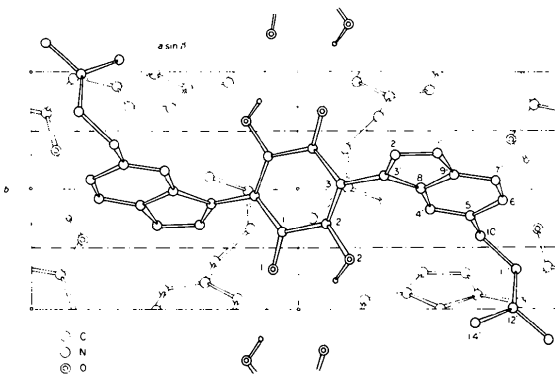


Fig. 1. The structure viewed along c . H atoms not involved in hydrogen bonding have been omitted.

angles of interest are: C(1)ⁱC(3)—C(3')C(2') 56.8° ; C(6)C(5')—C(10)C(11') 45.5° ; C(5)C(10')—C(11')C(12') 68.1° . Molecules related by the b translation are linked by OH...O bonds to form endless chains parallel to the needle axis. The hydroxyl proton is also coordinated to the carbonyl O of the same molecule, and thus participates in a bifurcated bonding system. The remaining contacts are consistent with van der Waals interactions.

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