Acta Cryst. (1989). C45, 2004–2006

Structure of 5a,11a-Epoxy-5a,6a,7,10,10a,11a-hexahydro-7-acetoxy-5,6,11,12-naphthacenetetrone*

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(*Received* 10 *March* 1989; *accepted* 26 *June* 1989)

Abstract. $C_{20}H_{14}O_7$, $M_r = 366{\cdot}33$, monoclinic, $P2_1/a$, $a = 7{\cdot}352\ (2)$, $b = 19{\cdot}658\ (5)$, $c = 11{\cdot}338\ (3)$ Å, $\beta = 92{\cdot}37\ (2)^\circ$, $V = 1637\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}49$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}06$ cm^{-1}, $F(000) = 760$, $T = 296$ K, $R = 0{\cdot}041$, 1197 unique observed reflections. The compound was prepared by Diels–Alder reaction of 1,4,9,10-anthracenetetrone with 1-acetoxybutadiene. The molecule is a linearly annelated tetracycle having an acetoxy group at C7 and an epoxide at C5a,C11a. *cis* stereochemistry exists between the O atoms of the epoxide ring at C5a and C11a, and the H atoms at C6a and C10a.

Table 1. *Positional and equivalent isotropic thermal parameters and their e.s.d.'s*

$$B_{eq} = (8\pi^2/3)[U_{22} + (1/\sin^2\beta)(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

	x	y	z	B_{eq}(Å^2)*
O(1)	0·4618 (5)	−0·0637 (2)	0·5788 (3)	5·5 (2)
O(2)	0·7700 (5)	0·0116 (2)	0·6599 (3)	5·6 (2)
O(3)	0·3183 (4)	0·1319 (2)	0·9533 (3)	4·3 (2)
O(4)	0·0563 (4)	0·0410 (2)	0·8761 (3)	5·2 (2)
O(5)	0·5087 (4)	−0·0205 (2)	0·8783 (2)	3·6 (2)
O(6)	0·3924 (4)	0·1287 (2)	0·6504 (2)	3·3 (1)
O(7)	0·3402 (5)	0·1982 (2)	0·4958 (3)	6·3 (2)
C(1)	0·0060 (8)	−0·1042 (3)	0·8513 (5)	4·5 (3)
C(2)	−0·0226 (8)	−0·1701 (3)	0·8141 (5)	5·0 (3)
C(3)	0·0916 (9)	−0·1982 (3)	0·7330 (5)	5·1 (3)
C(4)	0·2325 (8)	−0·1619 (3)	0·6889 (5)	4·1 (3)
C(5)	0·2634 (6)	−0·0965 (2)	0·7291 (4)	3·5 (2)
C(6)	0·4110 (6)	−0·0551 (2)	0·6770 (4)	3·5 (2)
C(7)	0·4921 (6)	−0·0004 (2)	0·7566 (3)	3·0 (2)
C(8)	0·6588 (7)	0·0390 (3)	0·7168 (4)	3·5 (2)
C(9)	0·6757 (7)	0·1124 (3)	0·7569 (4)	3·5 (3)
C(10)	0·5720 (7)	0·1609 (3)	0·6726 (5)	4·0 (3)
C(11)	0·5540 (7)	0·2298 (3)	0·7229 (6)	4·8 (3)
C(12)	0·5942 (7)	0·2449 (3)	0·8336 (6)	5·2 (3)
C(13)	0·6517 (8)	0·1939 (3)	0·9262 (6)	5·0 (3)
C(14)	0·6196 (7)	0·1214 (3)	0·8851 (4)	3·6 (2)
C(15)	0·4243 (7)	0·0993 (2)	0·8985 (4)	3·2 (2)
C(16)	0·3730 (6)	0·0304 (2)	0·8470 (4)	3·0 (2)
C(17)	0·1788 (6)	0·0045 (3)	0·8473 (4)	3·5 (2)
C(18)	0·1495 (6)	−0·0675 (3)	0·8105 (4)	3·4 (2)
C(19)	0·2931 (7)	0·1514 (3)	0·5552 (4)	4·1 (3)
C(20)	0·1278 (9)	0·1092 (4)	0·5350 (6)	5·3 (4)
H(1)	−0·070 (6)	−0·086 (2)	0·898 (4)	4 (1)
H(2)	−0·124 (7)	−0·191 (2)	0·844 (4)	6 (1)
H(3)	0·072 (5)	−0·241 (2)	0·713 (3)	2 (1)
H(4)	0·301 (7)	−0·181 (3)	0·620 (5)	7 (2)
H(5)	0·800 (5)	0·122 (2)	0·757 (3)	1·7 (8)
H(6)	0·636 (6)	0·164 (2)	0·591 (4)	5 (1)
H(7)	0·505 (7)	0·267 (3)	0·663 (5)	6 (1)
H(8)	0·586 (6)	0·292 (3)	0·860 (4)	5 (1)
H(9)	0·783 (7)	0·198 (3)	0·946 (4)	6 (1)
H(10)	0·589 (6)	0·203 (2)	1·002 (4)	6 (1)
H(11)	0·694 (5)	0·090 (2)	0·925 (3)	2 (1)
H(12)	0·076 (6)	0·099 (2)	0·600 (4)	4 (1)
H(13)	0·04 (1)	0·139 (4)	0·501 (7)	12 (3)
H(14)	0·14 (1)	0·077 (4)	0·473 (7)	13 (3)

* All H-atom *B*'s are isotropic.

Experimental. General synthesis procedure originally employed by Jackson & Stoodley (1981) in their preparation of 4-demethoxy-7-*O*-methyldaunomycinone. Title compound prepared from a solution of 1,4,9,10-anthracenetetrone (0·508 g, 2 mmol) and 1-acetoxybutadiene (0·138 ml, 3 mmol). Mixture heated under reflux in benzene, after 4 h the solvent was evaporated, crystallized with hexane/dichloromethane to yield pale-brown crystals. Crystal used for data collection 0·10 × 0·10 × 0·39 mm, pale-brown, transparent, broken fragment. Rigaku AFC5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, scan speed 3° min^{-1}, maximum of three scan repetitions to obtain $\sigma F/F < 0{\cdot}10$. Lattice parameters from least-squares fit of 25 strong reflections in 2θ range 20–37°. A total of 2886 reflections measured (h 0 to 8, k 0 to 23, l −13 to 13), 1689 reflections considered unobserved with $I < 3\sigma(I)$, data set composed of 1197 unique reflections, $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}60$ Å^{-1}. Three standard reflections ($1\bar{2}\bar{1}$,111,$1\bar{1}0$) changed by 0·0, 0·4, and 0·0%, respectively; no decay correction applied. Data corrected for Lorentz and polarization; no correction for absorption. Direct methods provided the locations of 19 of the 27 non-H atomic positions, remaining eight sites obtained from difference Fourier synthesis. Full-matrix least-squares refinement was performed to minimize $\sum w(|F_o| - |F_c|)^2$ where $w = [1/\sigma^2(|F_o|)]$ and $p = 0{\cdot}05$ [details of σ^2 calculation given in Robinson, Hinckley & Kibala (1988)]. A difference Fourier synthesis revealed the positions of all H atoms. Final stage of refinement performed with 300 variables including all positional parameters, anisotropic thermal parameters for the non-H atoms, isotropic thermal parameters for the H atoms, and one scale factor. Large *B*'s for two of the methyl H atoms

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* 5a,6a,7,10,10a,11a-Hexahydro-5,6,11,12-tetraoxo-5a,11a-epoxy-7-naphthacenyl acetate.

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0108-2701/89/122004-03$03.00

Table 2. *Selected bond distances* (Å), *bond angles* (°), *torsion angles* (°), *and their e.s.d.'s*

O(1)	C(6)	1·201 (5)	C(11)	C(12)	1·311 (8)
O(2)	C(8)	1·192 (5)	C(12)	C(13)	1·501 (9)
O(3)	C(15)	1·202 (5)	C(13)	C(14)	1·514 (8)
O(4)	C(17)	1·207 (5)	C(14)	C(15)	1·514 (6)
O(5)	C(7)	1·435 (5)	C(15)	C(16)	1·516 (6)
O(5)	C(16)	1·446 (5)	C(16)	C(17)	1·516 (6)
O(6)	C(19)	1·352 (5)	C(17)	C(18)	1·489 (7)
O(6)	C(10)	1·476 (5)	C(19)	C(20)	1·481 (8)
O(7)	C(19)	1·200 (6)	C(1)	H(1)	0·87 (4)
C(1)	C(18)	1·374 (7)	C(2)	H(2)	0·93 (5)
C(1)	C(2)	1·375 (8)	C(3)	H(3)	0·88 (4)
C(2)	C(3)	1·386 (8)	C(4)	H(4)	1·01 (5)
C(3)	C(4)	1·369 (8)	C(9)	H(5)	0·94 (3)
C(4)	C(5)	1·380 (7)	C(10)	H(6)	1·05 (4)
C(5)	C(18)	1·394 (6)	C(11)	H(7)	1·06 (5)
C(5)	C(6)	1·497 (6)	C(12)	H(8)	0·98 (5)
C(6)	C(7)	1·511 (6)	C(13)	H(9)	0·98 (5)
C(7)	C(16)	1·503 (6)	C(13)	H(10)	1·01 (5)
C(7)	C(8)	1·534 (6)	C(14)	H(11)	0·93 (4)
C(8)	C(9)	1·516 (7)	C(20)	H(12)	0·87 (4)
C(9)	C(10)	1·531 (7)	C(20)	H(13)	0·95 (8)
C(9)	C(14)	1·538 (6)	C(20)	H(14)	0·96 (8)
C(10)	C(11)	1·478 (7)			

C(7)	O(5)	C(16)	62·9 (3)	O(4)	C(17)	C(18)	122·7 (5)
C(19)	O(6)	C(10)	116·4 (4)	O(4)	C(17)	C(16)	121·0 (5)
C(18)	C(1)	C(2)	120·1 (6)	C(18)	C(17)	C(16)	116·3 (4)
C(1)	C(2)	C(3)	119·3 (6)	C(1)	C(18)	C(5)	119·9 (5)
C(4)	C(3)	C(2)	121·5 (6)	C(1)	C(18)	C(17)	120·6 (5)
C(3)	C(4)	C(5)	118·8 (6)	C(5)	C(18)	C(17)	119·4 (4)
C(4)	C(5)	C(18)	120·3 (5)	O(7)	C(19)	O(6)	122·8 (5)
C(4)	C(5)	C(6)	119·3 (5)	O(7)	C(19)	C(20)	126·6 (5)
C(18)	C(5)	C(6)	120·2 (4)	O(6)	C(19)	C(20)	110·6 (5)
O(1)	C(6)	C(5)	123·2 (4)	H(1)	C(1)	C(18)	120 (3)
O(1)	C(6)	C(7)	121·6 (4)	H(1)	C(1)	C(2)	119 (3)
C(5)	C(6)	C(7)	115·2 (4)	H(2)	C(2)	C(1)	115 (3)
O(5)	C(7)	C(16)	58·9 (2)	H(2)	C(2)	C(3)	125 (3)
O(5)	C(7)	C(6)	113·2 (4)	H(3)	C(3)	C(4)	121 (3)
O(5)	C(7)	C(8)	112·6 (3)	H(3)	C(3)	C(2)	117 (3)
C(16)	C(7)	C(6)	117·9 (4)	H(4)	C(4)	C(3)	120 (3)
C(16)	C(7)	C(8)	119·5 (4)	H(4)	C(4)	C(5)	121 (3)
C(6)	C(7)	C(8)	119·0 (4)	H(5)	C(9)	C(8)	106 (2)
O(2)	C(8)	C(9)	122·9 (5)	H(5)	C(9)	C(10)	110 (2)
O(2)	C(8)	C(7)	120·3 (5)	H(5)	C(9)	C(14)	106 (2)
C(9)	C(8)	C(7)	116·7 (4)	H(6)	C(10)	O(6)	108 (2)
C(8)	C(9)	C(10)	111·9 (4)	H(6)	C(10)	C(11)	110 (2)
C(8)	C(9)	C(14)	111·8 (4)	H(6)	C(10)	C(9)	110 (2)
C(10)	C(9)	C(14)	111·8 (4)	H(7)	C(11)	C(12)	121 (3)
O(6)	C(10)	C(11)	111·4 (4)	H(7)	C(11)	C(10)	115 (3)
O(6)	C(10)	C(9)	105·0 (4)	H(8)	C(12)	C(11)	120 (3)
C(11)	C(10)	C(9)	112·3 (5)	H(8)	C(12)	C(13)	116 (3)
C(12)	C(11)	C(10)	123·8 (6)	H(9)	C(13)	H(10)	106 (4)
C(11)	C(12)	C(13)	124·3 (6)	H(9)	C(13)	C(12)	110 (3)
C(12)	C(13)	C(14)	112·2 (5)	H(9)	C(13)	C(14)	106 (3)
C(13)	C(14)	C(15)	112·1 (4)	H(10)	C(13)	C(12)	111 (3)
C(13)	C(14)	C(9)	110·8 (5)	H(10)	C(13)	C(14)	111 (3)
C(15)	C(14)	C(9)	110·8 (4)	H(11)	C(14)	C(13)	113 (2)
O(3)	C(15)	C(14)	122·4 (4)	H(11)	C(14)	C(15)	108 (2)
O(3)	C(15)	C(16)	121·3 (4)	H(11)	C(14)	C(9)	102 (2)
C(14)	C(15)	C(16)	116·1 (4)	H(12)	C(20)	H(13)	99 (5)
O(5)	C(16)	C(7)	58·2 (2)	H(12)	C(20)	H(14)	123 (6)
O(5)	C(16)	C(17)	114·1 (4)	H(12)	C(20)	C(19)	112 (3)
O(5)	C(16)	C(15)	111·4 (4)	H(13)	C(20)	H(14)	102 (6)
C(7)	C(16)	C(17)	116·2 (4)	H(13)	C(20)	C(19)	106 (5)
C(7)	C(16)	C(15)	118·7 (4)	H(14)	C(20)	C(19)	112 (5)
C(17)	C(16)	C(15)	121·2 (4)				

O(1)	C(6)	C(7)	O(5)	−143·5 (4)	C(7)	C(16)	C(15)	C(14)	−18·8 (6)
O(2)	C(8)	C(9)	H(5)	−24 (2)	C(7)	C(8)	C(9)	C(14)	40·0 (5)
O(2)	C(8)	C(9)	C(10)	95·6 (6)	C(8)	C(7)	C(16)	C(17)	156·6 (4)
O(2)	C(8)	C(7)	O(5)	102·3 (5)	C(8)	C(7)	C(16)	C(15)	−1·4 (6)
O(3)	C(15)	C(14)	H(11)	114 (2)	C(9)	C(14)	C(15)	C(16)	49·0 (6)
O(3)	C(15)	C(16)	O(5)	−129·7 (4)	H(5)	C(9)	C(10)	H(6)	48 (3)
O(4)	C(17)	C(16)	O(5)	146·1 (4)	H(5)	C(9)	C(14)	H(11)	−60 (3)
O(6)	C(10)	C(9)	H(5)	163 (2)	H(6)	C(10)	C(11)	H(7)	46 (4)
O(6)	C(10)	C(9)	C(8)	46·5 (5)	H(7)	C(11)	C(12)	H(8)	−3 (5)
C(5)	C(6)	C(7)	C(16)	−28·7 (6)	H(8)	C(12)	C(13)	H(9)	−75 (4)
C(6)	C(7)	C(16)	C(17)	−1·6 (6)	H(8)	C(12)	C(13)	H(10)	42 (4)
C(6)	C(7)	C(16)	C(15)	−159·7 (4)	H(9)	C(13)	C(14)	H(11)	35 (4)
C(7)	C(16)	C(17)	C(18)	31·1 (5)	H(10)	C(13)	C(14)	H(11)	−80 (4)

may indicate minor rotational disorder. Convergence yielded $R = 0{\cdot}041$, $wR = 0{\cdot}047$, $S = 1{\cdot}17$ and $(\Delta/\sigma)_{\max} = 0{\cdot}01$. Final difference synthesis produced $\Delta\rho_{\max} = 0{\cdot}15$ and $\Delta\rho_{\min} = -0{\cdot}16$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974). Positional and isotropic thermal parameters are listed in Table 1, selected interatomic distances and angles are given in Table 2.* Fig. 1 shows the IUPAC atom-numbering scheme, Fig. 2 illustrates the molecular configura-

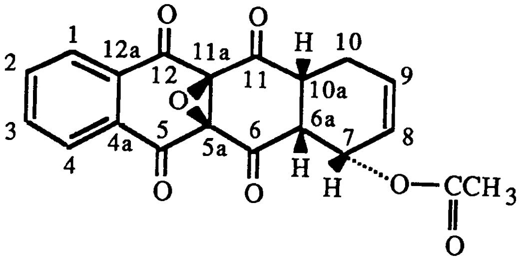

Fig. 1. IUPAC atom designations.

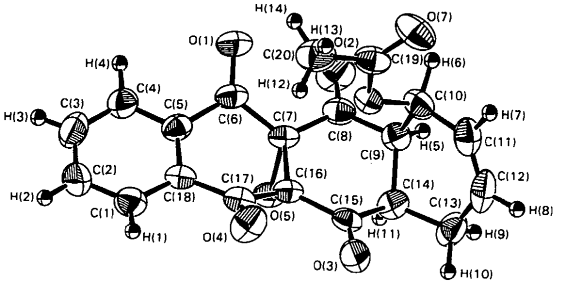

Fig. 2. Molecular structure and numbering scheme, thermal ellipsoids at the 50% probability level. H atoms shown with isotropic *B*'s of 1·0 Å^2.

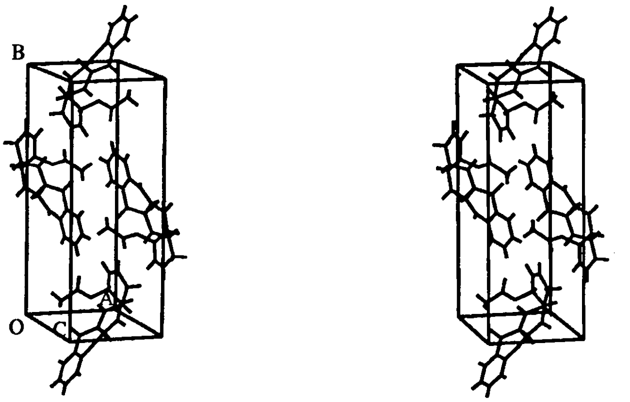

Fig. 3. Stereoscopic illustration of the molecular packing.

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* Lists of structure factors, intermolecular distances, torsion angles, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52074 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tion, thermal motion and our atom-numbering scheme, and Fig. 3 displays the molecular packing. All computer programs from the *TEXSAN* crystal-structure-analysis package (Molecular Structure Corporation, 1985).

Related literature. In a similar compound (5a,11a-epoxy-5a,6a,7,10,10a,11a-hexahydro-7-methoxy-5,6,-9,11,12-naphthacenepentone), the same *cis* stereochemistry exists between the O atoms of the epoxide ring at C5a and C11a, and the H atoms at C6a and C10a (Gupta, Jackson & Stoodley, 1985).

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Acta Cryst. (1989). C45, 2006–2010

Structures of Three Pseudoguaianolides: Parthenin, Hymenolin (11β,13-Dihydroparthenin) and Bipinnatin

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(*Received* 27 *December* 1988; *accepted* 3 *July* 1989)

Abstract. Parthenin, $C_{15}H_{18}O_4$, $M_r = 262{\cdot}3$, tetragonal, $P4_1$, $a = 6{\cdot}862\,(1)$, $c = 28{\cdot}681\,(8)$ Å, $V = 1350{\cdot}5\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}290$ g cm^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}54184$ Å, $\mu = 7{\cdot}25$ cm^{-1}, $F(000) = 560$, $T = 298$ K, $R = 0{\cdot}036$ for 1316 observations with $I > 1\sigma(I)$. Hymenolin (11β,13-dihydroparthenin), $C_{15}H_{20}O_4$, $M_r = 264{\cdot}3$, monoclinic, $P2_1$, $a = 6{\cdot}495\,(1)$, $b = 28{\cdot}380\,(6)$, $c = 7{\cdot}587\,(1)$ Å, $\beta = 102{\cdot}90\,(1)°$, $V = 1363{\cdot}2\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}288$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 0{\cdot}86$ cm^{-1}, $F(000) = 568$, $T = 297$ K, $R = 0{\cdot}060$ for 1757 observations with $I > 0{\cdot}5\sigma(I)$. Bipinnatin, $C_{15}H_{20}O_4$, $M_r = 264{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}231\,(1)$, $b = 9{\cdot}713\,(2)$, $c = 15{\cdot}453\,(2)$ Å, $V = 1385{\cdot}5\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}267$ g cm^{-3}, μ(Cu $K\alpha$) $= 7{\cdot}07$ cm^{-1}, $F(000) = 568$, $T = 299$ K, $R = 0{\cdot}058$ for 1145 observations with $I > 3\sigma(I)$. The seven-membered ring of parthenin has a chair conformation with a pseudo mirror passing through C10, and asymmetry parameter $\Delta C_s = 4{\cdot}3°$. The cyclopentenone and lactone rings both have envelope conformations with C5 at the flap, $\Delta C_s = 5{\cdot}2°$ and C7 at the flap, $\Delta C_s = 0{\cdot}7°$, respectively. Molecules are linked in chains along the symmetry axis by hydrogen bonds involving the hydroxyl group and lactone carbonyl, O···O distance 2·805 (5) Å. The crystal structure of hymenolin contains two independent molecules. In both, the five-membered rings are in conformations closely resembling those of parthenin. The seven-membered ring of one molecule has a twist-chair conformation with C10 lying on the pseudo diad, and asymmetry parameter $\Delta C_2 = 3{\cdot}9°$, while the other molecule has an asymmetric seven-membered ring. Molecules are linked in chains of alternating molecule types, by hydrogen bonds involving hydroxy groups and lactone carbonyl O atoms. O···O distances are 2·855 (5) and 2·878 (5) Å. Hymenolin was isolated from *Hymenoclea salsola* T. and G. with unresolved stereochemistry at C11 [Toribio & Geissman (1968). *Phytochemistry*, 7, 1623–1630]. The seven-membered ring of bipinnatin also has two conformations in the crystal, but both exist at the same site as a *ca* 70–30% disorder of atoms C8 and C9. The seven-membered ring of the major conformer has the parthenin conformation, with $\Delta C_s = 6{\cdot}1°$, while the minor conformer has the twist-chair

0108-2701/89/122006-05$03.00