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Structure of α-Santonin

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Abstract. $C_{15}H_{18}O_3$, $M_r = 246{\cdot}1$, orthorhombic, $P2_12_12_1$, $a = 34{\cdot}575\,(7)$, $b = 10{\cdot}705\,(1)$, $c = 6{\cdot}991\,(1)$ Å, $V = 2587{\cdot}5\,(7)$ Å^3, $Z = 8$, $D_x = 1{\cdot}264$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}94$ cm^{-1}, $F(000) = 1056$, $T = 294$ K, $R = 0{\cdot}051$ for 3129 observed reflections. The unit cell contains two crystallographically independent molecules of similar conformations. In the packing structure, the dienone rings are nearly stacked parallel along the *b* axis with an interplanar angle of 28°, and their carbonyl O atoms are surrounded by short intermolecular contacts.

Introduction. The stereochemistry of α-santonin has been established both by chemical methods (Nakazaki & Arakawa, 1962; Cocker & McMurry, 1960) and by the X-ray structure analyses of its derivatives (Inayama, Shimizu, Hori, Ohsaka, Hirose, Shibata & Iitaka, 1982; White & Sim, 1975; Asher & Sim, 1965). However, the crystal structure of α-santonin itself has not yet been determined. Santonin undergoes photoinduced rearrangement in solution to give lumisantonin (Kropp, 1967), while in the solid state a cyclopentadienone derivative is obtained (Matsuura, Sata, Ogura & Mori, 1968). The photochemical rearrangement of α-santonin in solution accompanies a large movement of atoms, while in the solid state it results in the migration of an H atom from C(1) to the neighboring C(10). These facts agree with the general rule that the photochemical reaction in the solid state proceeds with a minimum amount of atomic movements from the starting material (Cohen & Schmidt, 1964). The crystal-structure analysis of α-santonin has been undertaken to give a structural basis to the understanding of its photochemical reaction in the solid state.

Experimental. Crystals of α-santonin by slow evaporation from ethanol solution. Crystal dimensions 0·5 × 0·5 × 0·5 mm. Intensity data from Rigaku C–5 automated four-circle diffractometer equipped with graphite-monochromated Mo *K*α radiation from a rotating anode. Lattice parameters refined using 31 reflections measured in 2θ range 20–40°. 3399 unique reflections measured to the limit $2\theta < 55°$ using ω–2θ scans; range of *hkl*: $0 \le h \le 44$, $0 \le k \le 13$, $0 \le l \le 9$; 3129 significant with $I > 2\sigma(I)$; three standard reflections monitored periodically showed no systematic variation in intensity during course of data collection; Lorentz–polarization corrections, no absorption corrections applied. Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Difference electron density maps used to locate all 36 H atoms; anisotropic block-diagonal least-squares refinement for 36 non-H atoms, isotropic for 36 H atoms; final $R = 0{\cdot}051$ and $wR = 0{\cdot}064$ for 3129 significant reflections, $\sum w(F_o - F_c)^2$ minimized where $w = 1/[\sigma^2(F) + 0{\cdot}002F^2]$, $(\Delta/\sigma)_{\max} = 0{\cdot}6$, largest features in $\Delta\rho$ map 0·2 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computations performed on an ACOS S-850 computer.

Discussion. The final parameters for the non-H atoms are given in Table 1.* The cornformation of the molecules and the numbering of the atoms are shown in

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42403 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Fig. 1. The absolute configuration of the molecule was chosen to be the same as that determined for 2-bromo-6-epi-α-santonin (White & Sim, 1975). Selected molecular dimensions are listed in Table 2. The corresponding bond distances and angles of the two independent molecules, *A* and *B*, agree well with maximum differences of 0·02 Å and 0·9° respectively. The dienone rings are only approximately planar with maximum deviations of atoms from the mean planes of

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å²) *for the non*-H *atoms*

$$B_{eq} = \tfrac{4}{3}(\beta_{11}^2 a^2 + \beta_{22}^2 b^2 + \beta_{33}^2 c^2).$$

	x	*y*	*z*	B_{eq}
Molecule *A*				
O(1)	0·30958 (7)	0·5012 (3)	0·1108 (5)	6·04
O(2)	0·38589 (6)	0·1047 (2)	0·3208 (4)	4·11
O(3)	0·44524 (7)	0·0360 (3)	0·3905 (4)	5·72
C(1)	0·26197 (7)	0·3273 (3)	0·4692 (5)	3·98
C(2)	0·26992 (8)	0·4213 (3)	0·3535 (6)	4·25
C(3)	0·30326 (8)	0·4174 (3)	0·2256 (5)	3·80
C(4)	0·33004 (7)	0·3091 (3)	0·2404 (4)	3·10
C(5)	0·32267 (7)	0·2183 (3)	0·3663 (4)	2·85
C(6)	0·34896 (7)	0·1097 (3)	0·4156 (5)	3·18
C(7)	0·35915 (7)	0·1116 (3)	0·6288 (4)	2·99
C(8)	0·32307 (9)	0·0868 (3)	0·7455 (5)	3·94
C(9)	0·29467 (7)	0·1925 (3)	0·7028 (5)	3·94
C(10)	0·28585 (7)	0·2114 (3)	0·4865 (5)	3·37
C(11)	0·39426 (8)	0·0239 (3)	0·6332 (5)	3·50
C(12)	0·41240 (8)	0·0523 (3)	0·4392 (5)	3·90
C(13)	0·42152 (9)	0·0382 (4)	0·8011 (6)	4·81
C(14)	0·36395 (9)	0·3200 (4)	0·1059 (5)	4·35
C(15)	0·26005 (8)	0·1024 (4)	0·4094 (7)	5·02
Molecule *B*				
O(1)	0·30406 (6)	0·7943 (3)	0·3798 (5)	5·93
O(2)	0·44935 (6)	0·7407 (3)	0·1777 (3)	4·35
O(3)	0·49939 (7)	0·8486 (3)	0·0641 (4)	6·28
C(1)	0·35748 (9)	0·6014 (4)	0·6940 (5)	4·28
C(2)	0·32776 (8)	0·6645 (4)	0·6196 (6)	4·68
C(3)	0·33096 (7)	0·7325 (3)	0·4411 (5)	3·97
C(4)	0·36858 (7)	0·7293 (3)	0·3380 (5)	3·25
C(5)	0·39926 (7)	0·6692 (3)	0·4174 (4)	2·90
C(6)	0·44062 (7)	0·6703 (3)	0·3487 (4)	3·15
C(7)	0·46674 (7)	0·7291 (3)	0·5003 (4)	2·83
C(8)	0·46779 (8)	0·6482 (3)	0·6764 (5)	3·45
C(9)	0·42608 (8)	0·6390 (3)	0·7537 (4)	3·47
C(10)	0·39660 (7)	0·5927 (3)	0·6030 (4)	3·22
C(11)	0·50290 (7)	0·7561 (3)	0·3860 (5)	3·55
C(12)	0·48547 (8)	0·7886 (4)	0·1928 (5)	4·28
C(13)	0·52853 (8)	0·8604 (4)	0·4654 (6)	4·74
C(14)	0·36797 (9)	0·7952 (4)	0·1502 (5)	4·48
C(15)	0·40386 (9)	0·4531 (3)	0·5625 (5)	4·32

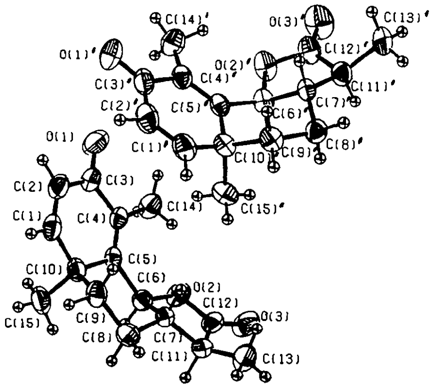

Fig. 1. View (*ORTEP*, Johnson, 1971) of α-santonin molecules *A* and *B* (primed) in the asymmetric unit. Thermal ellipsoids are plotted at the 50% probability level. H atoms are depicted as 0·1 Å radius spheres.

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
C(1)–C(2)	1·320 (5)	1·335 (5)
C(2)–C(3)	1·460 (5)	1·449 (5)
C(3)–C(4)	1·487 (4)	1·487 (4)
C(4)–C(5)	1·336 (4)	1·359 (4)
C(5)–C(10)	1·527 (4)	1·537 (4)
C(1)–C(10)	1·496 (5)	1·498 (4)
C(5)–C(6)	1·516 (4)	1·509 (4)
C(6)–C(7)	1·531 (4)	1·528 (4)
C(7)–C(8)	1·514 (4)	1·507 (4)
C(8)–C(9)	1·528 (5)	1·543 (4)
C(9)–C(10)	1·556 (4)	1·547 (4)
C(6)–O(2)	1·440 (4)	1·445 (4)
O(2)–C(12)	1·357 (4)	1·354 (4)
C(11)–C(12)	1·524 (5)	1·519 (4)
C(7)–C(11)	1·535 (4)	1·511 (4)
C(3)–O(1)	1·223 (4)	1·219 (4)
C(4)–C(14)	1·507 (4)	1·491 (4)
C(10)–C(15)	1·564 (5)	1·542 (4)
C(11)–C(13)	1·514 (5)	1·530 (5)
C(12)–O(3)	1·198 (4)	1·206 (4)
C(1)–C(2)–C(3)	121·2 (3)	122·1 (3)
C(2)–C(3)–C(4)	118·1 (3)	118·2 (3)
C(3)–C(4)–C(5)	119·6 (3)	119·7 (3)
C(4)–C(5)–C(10)	123·9 (3)	123·4 (2)
C(5)–C(10)–C(1)	112·0 (3)	112·3 (2)
C(10)–C(1)–C(2)	124·6 (3)	124·1 (3)
C(10)–C(5)–C(6)	109·7 (2)	109·2 (2)
C(5)–C(6)–C(7)	110·4 (2)	110·0 (2)
C(6)–C(7)–C(8)	109·4 (2)	110·1 (2)
C(7)–C(8)–C(9)	107·1 (3)	107·5 (2)
C(8)–C(9)–C(10)	114·3 (3)	113·4 (2)
C(9)–C(10)–C(5)	112·2 (2)	111·4 (2)
C(7)–C(6)–O(2)	104·2 (2)	103·6 (2)
C(6)–O(2)–C(12)	109·5 (2)	109·0 (2)
O(2)–C(12)–C(11)	110·3 (3)	110·4 (3)
C(12)–C(11)–C(7)	100·7 (2)	100·7 (2)
C(11)–C(7)–C(6)	101·1 (2)	101·6 (2)

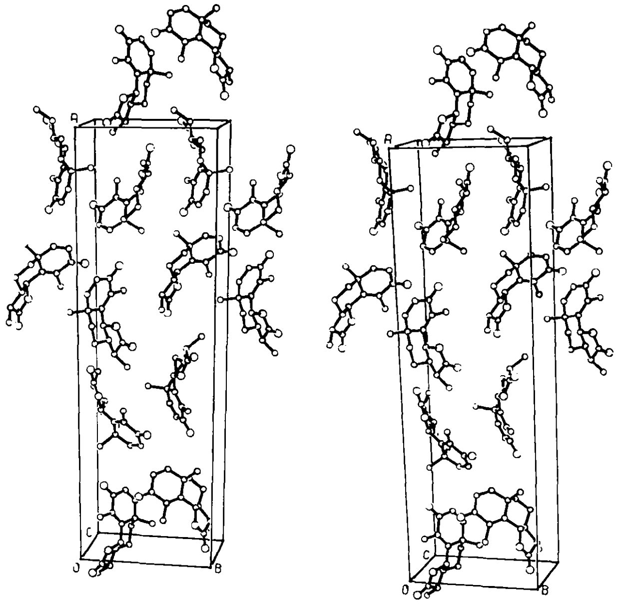

Fig. 2. Stereodrawing of the molecular packing viewed along the *c* axis in the crystal.

0·05 and 0·02 Å in molecules *A* and *B* respectively. This slight aplanarity is brought about by a distortion due to the fused ring structure as seen in the C(1)—C(10)—C(5)—C(4) torsion angles, −8·8 (4)° in molecule *A* and −5·0 (4)° in molecule *B*. The puckered central six-membered ring has a chair conformation, and the average endocyclic torsion angles, 56·7° in molecule *A* and 57·6° in *B*, are similar to those of photosantonin (Sheldon, Shaefer, Gulbis, Ruble, Burgstahler & Lee, 1982) and 14-chlorosantonin (Takayanagi, Ogura & Iitaka, 1978). As seen in Fig. 1, the dienone rings of the independent molecules lie close to each other with an interplanar angle of 28°. The molecules are nearly stacked parallel along the *b* axis in the crystal as shown in Fig. 2. Short intermolecular contacts less than 3·6 Å are seen involving the O atoms: C(1)···O(1) = 3·236 (3) Å and C(2)···O(1) = 3·388 (3) Å between molecules *A* at x, y, z and $\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$; O(1)···C(3′) = 3·466 (3) Å and O(1)···C(4′) = 3·556 (3) Å between molecules *A* and *B* in the same unit; O(3)···C(11′) = 3·536 (4) Å between molecules *A* at x, y, z and *B* at $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$. The carbonyl oxygen O(1) is in close contact with the —C(1)H=C(2)H— moiety in the dienone ring of the symmetry-related molecule. These short intermolecular contacts surrounding the dienone ring offer strong crystal fields permitting only restricted movements of atoms during photochemical reactions in the solid state.

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Structure of 1,4,9-Triazaphenoxathiin at 163 K

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Abstract. $C_9H_5N_3OS$, $M_r = 203·22$, orthorhombic, *Pbca*, $a = 14·892$ (5), $b = 15·778$ (4), $c = 7·1688$ (15) Å, $V = 1684·4$ (8) Å^3, $Z = 8$, $D_x = 1·603$, D_m(295 K) = 1·597 (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3·43$ cm^{-1}, $F(000) = 832$, $R = 0·0451$ for 1842 observed reflections. The molecule is composed of a planar pyridine ring and a planar pyrazine ring. The dihedral angle between the rings is 172·47 (8)°; 172·15 (5)° is obtained when S and O are included in the calculation of each plane. Both N atoms in the pyrazine ring have unsymmetrical bond lengths as do S and O in the central ring.

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