

mation and configuration resemble those of molecule I most closely. In this orientation, it appears in II as if the phenyl group and the methoxycarbonyl group have interchanged positions between C(4) and C(6) as compared to I.

Fig. 3 shows the close resemblance between the values of the bond lengths, bond angles and torsional angles associated with the dithiin rings in I and II. The only major difference is at C(5) where the methoxycarbonyl side group flips over by nearly 160° . The remaining bond lengths and angles for molecule II, listed in Tables 3 and 4, are also very nearly equal to those observed in molecules IA and IB.

These are the first 1,3-dithiins whose structure have been determined, although the structures of a number of 1,4-dithiins have appeared in the literature (see *e.g.* Levi & Doedens, 1980). In the three molecules in this paper, the C—S bond adjacent to the double bond has an average value of $1.747(5) \text{ \AA}$ as compared to an average of $1.820(5) \text{ \AA}$ for the nine single C—S bonds. The CSC angle adjacent to C=C has an average value of $105.5(6)^\circ$ while the CSC angle surrounded by saturated carbon atoms has an average value of $98.9(6)^\circ$.

In the packing in crystals I and II there are only van der Waals contacts between molecules. In both crystals the nearest approaches are between molecules related

by centers of symmetry. In crystal I the nearest approaches between non-hydrogen atoms are S(3)A...O(2)'A at $3.12(1)$, S(3)B...O(2)'B at $3.27(1)$, O(1)A...C(14)'A at $3.32(1)$ and O(1)B...C(14)'B at $3.42(1) \text{ \AA}$. In crystal II the closest contact is between O(1)...O(1)' at $3.06(1) \text{ \AA}$. All other distances between non-hydrogen atoms have considerably greater values.

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Methyl (\pm)-5 α -Acetoxymethyl-4 β -methoxy-1-oxo-1,2,3,4,4a β ,5,6,7,8,8a α -decahydronaphthalene-4a β -carboxylate, C₁₆H₂₄O₆

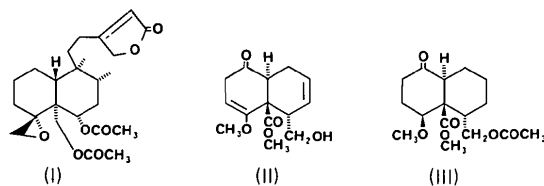
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(Received 26 May 1982; accepted 14 October 1982)

Abstract. $M_r = 312.4$, monoclinic, $P2_1/c$, $a = 8.479(6)$, $b = 17.225(10)$, $c = 11.411(8) \text{ \AA}$, $\beta = 102.64(5)^\circ$, $V = 1626(2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.27$, $D_m = 1.25(2) \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 0.059 \text{ mm}^{-1}$, $T = 296 \text{ K}$. The structure, which was refined to $R = 0.068$ using 2263 observed reflections, has a *cis* relationship between the methoxy and ring-junction ester function.

Introduction. Ajugarin I, (I), isolated from *Ajuga remota* (Labiatae) (Kubo, Lee, Balogh-Nair, Nakanishi & Chayya, 1976), shows significant antifeeding activity against African army worms, *Spodoptera exempta*, and has been well characterized (Hosazawa, Kato, Munakato & Chen, 1974).



In designing the *de novo* synthesis of this natural product, it was essential to establish the stereochemistry of several intermediates along the synthetic pathway. The structure reported here is one of these intermediates.

The title compound, (III), whose synthesis is described elsewhere (Goldsmith & Thottathil, 1982)

results from the acetylation and subsequent hydrogenation of compound (II). The stereochemical result of this reduction was uncertain and the X-ray crystal structure was undertaken to determine its stereochemistry.

Experimental. Crystals from ether, colorless prisms, 0.3 × 0.3 × 0.4 mm, density determination by flotation, preliminary characterization by precession photography, systematic absences: $h0l, l = 2n + 1; 0k0, k = 2n + 1$, Syntex P2₁ four-circle diffractometer, graphite monochromator, $2\theta_{\max} = 12.2^\circ$; cell dimensions from 15 reflections centered by machine, unconstrained least-squares refinement of lattice parameters and orientation matrix, $2\theta/\theta$ scans, width minimum 2° , variable scan rate: 4.02 to $29.3^\circ \text{ min}^{-1}$, $2\theta_{\max} = 50^\circ$, $\pm h, +k, +l$, 2878 unique reflections, standard reflections 400, 040, 004 monitored every 100 reflections, less than 5% variation in intensity, background/scan time = 1; no absorption correction, structure solution by direct methods, full-matrix anisotropic least squares on $|F|$, $F > 2\sigma(F)$; programs: *SHELX 76* (Sheldrick, 1977) and *ORTEP* (Johnson, 1965), H atoms from difference electron density Fourier synthesis, $R_w = 0.076$, $w = 2.483/(2\sigma|F| + 0.001026|F|^2)$ (Grant, Killeen & Lawrence, 1969), maximum final electron density difference peak $0.55e \text{ \AA}^{-3}$, $F(000) = 672$, atomic scattering factors from analytical approximation in *International Tables for X-ray Crystallography* (1974).

Discussion. The observed bond distances and selected angles are presented in Fig. 1 and the refined positional

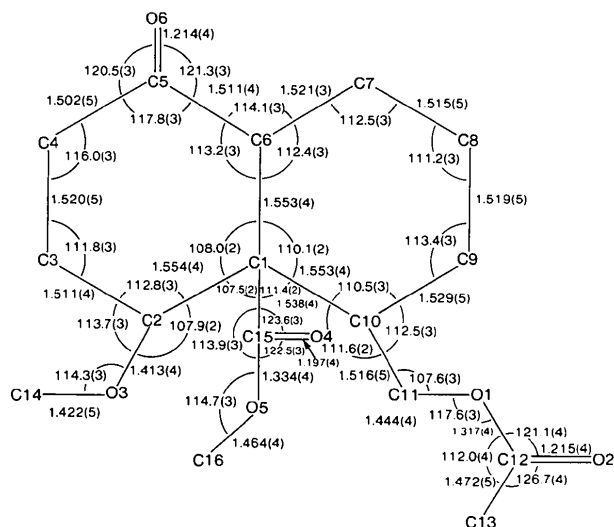


Fig. 1. Bond distances (Å) and bond angles ($^\circ$). The estimated error in the least significant digit is shown parenthetically.

Table 1. Atomic positional parameters and isotropic temperature factors with e.s.d.'s in parentheses

$$B_{eq} = \frac{8}{3}\pi^2 \sum_i U_{ii}$$

	x	y	z	$B_{eq}/B_{iso} (\text{Å}^2)$
C(1)	0.7485 (3)	0.1178 (2)	0.7860 (2)	3.94 (8)
C(2)	0.7099 (4)	0.1857 (2)	0.8649 (3)	4.26 (9)
C(3)	0.6015 (5)	0.1615 (2)	0.9475 (4)	5.23 (10)
C(4)	0.6720 (5)	0.0935 (2)	1.0268 (3)	5.42 (11)
C(5)	0.7469 (4)	0.0302 (2)	0.9667 (3)	4.52 (9)
C(6)	0.8360 (4)	0.0533 (2)	0.8711 (3)	4.26 (9)
C(7)	0.8865 (5)	-0.0148 (2)	0.8028 (4)	5.23 (11)
C(8)	0.9870 (5)	0.0101 (3)	0.7147 (3)	5.77 (11)
C(9)	0.9021 (4)	0.0733 (2)	0.6313 (3)	4.97 (10)
C(10)	0.8543 (4)	0.1435 (2)	0.6977 (3)	4.29 (9)
C(11)	0.9993 (5)	0.1906 (3)	0.7607 (3)	5.43 (11)
C(12)	1.1978 (5)	0.2685 (2)	0.7020 (4)	5.30 (10)
C(13)	1.2800 (7)	0.2861 (3)	0.6040 (5)	6.37 (14)
C(14)	0.6591 (9)	0.3216 (3)	0.8454 (5)	7.21 (17)
C(15)	0.5864 (4)	0.0836 (2)	0.7186 (3)	4.82 (9)
C(16)	0.3708 (5)	0.0868 (3)	0.5487 (4)	6.26 (14)
O(1)	1.0847 (3)	0.2154 (2)	0.6708 (2)	6.39 (7)
O(2)	1.2315 (4)	0.2943 (2)	0.08034 (3)	8.56 (11)
O(3)	0.6477 (3)	0.2479 (1)	0.7879 (2)	5.15 (7)
O(4)	0.5171 (3)	0.0325 (2)	0.7577 (2)	6.22 (8)
O(5)	0.5274 (2)	0.1170 (1)	0.6126 (2)	4.71 (6)
O(6)	0.7473 (3)	-0.0365 (2)	1.0016 (2)	6.22 (8)
H(2)	0.8100 (4)	0.207 (2)	0.913 (3)	4.8 (7)
H(31)	0.591 (4)	0.201 (2)	1.005 (3)	4.7 (7)
H(32)	0.500 (6)	0.155 (3)	0.893 (4)	8.7 (12)
H(41)	0.596 (5)	0.072 (2)	1.068 (3)	5.7 (8)
H(42)	0.760 (4)	0.117 (2)	1.084 (3)	5.1 (8)
H(6)	0.922 (4)	0.076 (2)	0.909 (3)	3.2 (6)
H(71)	0.798 (5)	-0.038 (2)	0.767 (4)	6.8 (11)
H(72)	0.960 (5)	-0.052 (2)	0.869 (4)	5.1 (9)
H(81)	1.103 (4)	0.028 (2)	0.764 (3)	4.6 (7)
H(82)	1.008 (4)	-0.039 (2)	0.663 (3)	5.9 (8)
H(91)	0.787 (4)	0.055 (2)	0.571 (3)	5.1 (7)
H(92)	0.963 (4)	0.095 (2)	0.580 (2)	5.7 (9)
H(10)	0.791 (4)	0.177 (2)	0.635 (3)	4.1 (7)
H(111)	1.070 (4)	0.166 (2)	0.821 (3)	4.8 (8)
H(112)	0.976 (4)	0.229 (2)	0.800 (4)	4.9 (10)
H(131)	1.315 (8)	0.323 (4)	0.622 (6)	10.9 (22)
H(132)	1.213 (9)	0.303 (4)	0.545 (7)	13.6 (22)
H(133)	1.352 (2)	0.246 (4)	0.580 (7)	13.7 (21)
H(141)	0.613 (5)	0.363 (3)	0.785 (4)	7.8 (11)
H(142)	0.783 (6)	0.331 (2)	0.883 (4)	8.6 (12)
H(143)	0.615 (6)	0.318 (3)	0.903 (5)	8.8 (14)
H(161)	0.345 (6)	0.126 (3)	0.473 (5)	10.4 (14)
H(162)	0.269 (7)	0.090 (3)	0.597 (5)	10.6 (14)
H(163)	0.369 (6)	0.034 (3)	0.539 (5)	10.7 (15)

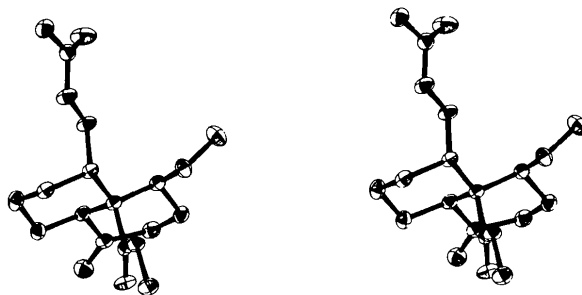


Fig. 2. Stereoview showing molecular configuration and thermal ellipsoids. Thermal ellipsoids are shown at the 33% probability level.

parameters and equivalent isotropic thermal parameters are listed in Table 1.* The *ORTEP* (Johnson, 1965) drawing in Fig. 2 shows the conformation of the rings and the extended disposition of the acetate groups.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38182 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Examination of the fused six-membered rings shows that both are in the chair conformation. It is also apparent from Fig. 2 that the stereochemical relationship between the methoxy group and the ester is clearly *cis* and is thus the desired intermediate in the ajugarin (I) synthesis.

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Structure of 5*H*,8*H*-Dibenzo[*d,f*][1,2]oxathiocin 7,7-Dioxide, C₁₄H₁₂O₃S

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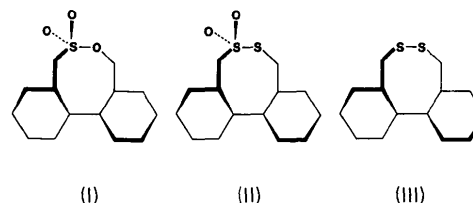
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Abstract. $M_r = 260.31$, monoclinic, $P2_1/c$, $a = 10.672$ (19), $b = 13.780$ (5), $c = 8.354$ (9) Å, $\beta = 99.47$ (10)°, $V = 1211.5$ Å³, $D_m = 1.43$, $D_x = 1.427$ Mg m⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.25$ mm⁻¹, $T = 293$ K. Final $R = 0.040$ for 1442 observed reflections. The structure consists of an eight-membered ring system incorporating a bridged diphenyl. The conformation of the eight-membered ring is 'pseudo-chair'. The two exocyclic S–O bond distances are equal to 1.420 (4) Å while the S–O bond within the eight-membered ring is 1.550 (2) Å. The two phenyl groups are at 63° from each other.

Introduction. The structure determination of the title compound, (I), is part of a project undertaken to establish the possible conformations of eight-membered rings which incorporate a bridged diphenyl unit as part of the cyclic structure. In a previous paper, Wahl, Bordner, Harpp & Gleason (1973) reported that in the dithiocin analog (II), the eight-membered ring adopts a 'pseudo-chair' conformation in the crystalline state. The same conformation was also found to be favored by the related disulfide (III) (Wahl, Bordner, Harpp & Gleason, 1972). However, a totally different ring conformation was observed in the case of the peroxide analog of (III) (Brown, Towns, Kovelan & Andrist, 1976).



Experimental. Preparation of the sultone (I) has been described elsewhere (Steliou, 1978); colorless tabular crystals (from benzene/hexane), D_m by flotation, $0.16 \times 0.45 \times 0.50$ mm, Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, intensity check every hour, orientation verified every 100 reflections, 2131 (hkl , hkl) with $2\theta \leq 50^\circ$, 1442 with $I \geq 1.90\sigma(I)$, 688 unobserved, Lp correction, no absorption correction, direct methods (*MULTAN*, Main, Woolfson, Lessinger, Germain & Declercq, 1978), anisotropic block-diagonal approximation, H (calculated) isotropic, final $R = 0.040$ (observed), $R = 0.072$ (all), $w = 1$, $R_w = 0.037$, final electron density fluctuations -0.34 to $+0.24$ e Å⁻³, maximum (shift/ σ) = 0.95, average (shift/ σ) = 0.15; scattering factors for S, O and C from Cromer & Mann (1968) and from Stewart, Davidson & Simpson (1965) for H, $F(000) = 464$, anomalous dispersion of S (real and imaginary) from Cromer & Liberman (1970); programs used in this work are modified versions of *NRC-2* (data