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Structure of Helioscopinolide A, $C_{20}H_{28}O_3$, a Novel Diterpene

By S. Ohba, M. Ito, Y. Saito, Y. Shizuri, S. Kosemura and S. Yamamura

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, *Kohoku-ku, Yokohama* 223, *Japan*

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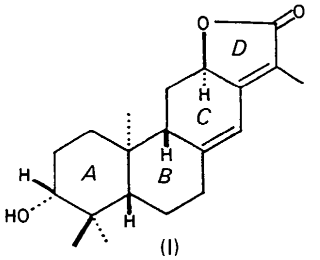
Abstract. $M_r = 316\cdot4$, monoclinic, $P2_1$, $a = 8\cdot222\,(1)$, $b = 15\cdot645\,(3)$, $c = 7\cdot385\,(1)$ Å, $\beta = 115\cdot84\,(1)°$, $V = 855\cdot0\,(2)$ Å^3, $Z = 2$, $D_x = 1\cdot23$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 0\cdot075$ mm^{-1}, $F(000) = 344$, $T = 297\,(2)$ K. Final $R = 0\cdot045$ for 1397 observed reflections. This diterpene has an $\alpha\beta$-unsaturated five-membered ring lactone with a conjugated double bond at the β-position and an OH group on the A ring.

Introduction. Helioscopinolide A (I) is a new toxic substance isolated from the plant *Euphorbia helioscopia* L. (Shizuri, Kosemura, Yamamura, Ohba, Ito & Saito, 1983). The crystal-structure analysis of this compound has been undertaken to determine its stereostructure.



(I)

Experimental. Hexagonal prisms grown along **c**, recrystallization from ethanol solutions; crystal dimensions 0·2 × 0·2 × 0·35 mm, Rigaku AFC-5 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$, Laue group $2/m$. Cell parameters refined by least-squares methods on basis of 25 2θ values ($30 < 2\theta < 39°$). Intensity measurement performed to $2\theta = 55°$ (h −10–9, k 0–20, l 0–9), θ–2θ scan technique, scan speed 2° min^{-1}(θ). Mean ratio of structure factors of three standard reflections $0\cdot997 \leq \sum(|F_o|/|F_o|_{\rm initial})/3 \leq 1\cdot008$. Space group $P2_1$ determined from extinction rule ($0k0$, k odd), established by 10 reflections showing a weak exception with $3\sigma(|F_o|) < |F_o| < 1\cdot6$. 2200 reflections measured, 433 weak reflections classified as unobserved [$|F_o| \leq 3\sigma(|F_o|)$], 277 zero and 1490 observed reflections; after averaging equivalent reflections 1397 unique ones used for structure determination. Corrections for Lorentz, polarization, not for absorption. Structure solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); all positions of non-H atoms determined from E map and refined by block-diagonal least squares with anisotropic thermal parameters using *UNICS* III computation program system (Sakurai & Kobayashi, 1979); all H atoms found from a difference density map and refined with isotropic thermal parameters. $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0\cdot015|F_o|)^2$; final $R = 0\cdot045$, $wR = 0\cdot039$, $S = 1\cdot5$. All shifts on final cycle of refinement $< 1\cdot1\sigma$. No peaks higher than 0·15 e Å^{-3} observed in final difference map. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

The absolute configuration of the molecule was assigned as shown in Fig. 1 according to the octant rule for the sign of the Cotton effect exhibited by saturated ketones (Moffitt, Woodward, Moscowitz, Klyne & Djerassi, 1961). 3-Oxotetrahydrohelioscopinolide A was derived from helioscopinolide A in two steps [(1) pyridinium chlorochromate in CH_2Cl_2, (2) H_2/10% Pd–C in CH_3COOH]. Its CD spectra showed a positive Cotton effect ($\Delta\varepsilon = +17\cdot5$) at 300 nm in MeOH.

Discussion. Final atomic parameters are presented in Table 1 and a perspective view of the molecule is shown in Fig. 1.*

The structure of helioscopinolide A is compatible with results of ^{1}H NMR and mass-spectra measurements. Helioscopinolides represented by helioscopinolide A have the same basic molecular structure as that of jolkinolides isolated from *Euphorbia jolkini* Boiss (Uemura & Hirata, 1974; Uemura, Katayama & Hirata, 1977). Both helioscopinolides and jolkinolides constitute a small group of novel diterpenes with an $\alpha\beta$-unsaturated five-membered ring lactone with a conjugated double bond at the β-position contributing to some physiological activities. The A and B rings are in a chair form with *trans* configuration at the ring junction. C(8), C(9), C(13) and C(14) in ring C are planar with a maximum deviation of 0·003 Å. The C(11)–C(12) bond axis twists with respect to this plane. C(11) and C(12) deviate from the plane by −0·22 (1) and 0·44 (1) Å respectively. Ring D adopts an envelope conformation. C(12) deviates by 0·12 (1) Å from the least-squares plane of C(13), C(15), C(16) and O(2). These four atoms are planar within 0·003 Å.

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* Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms, bond lengths involving H atoms and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38577 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional* ($\times 10^4$) *and equivalent isotropic thermal parameters* (*Hamilton*, 1959)

	x	y	z	B_{eq}(Å^2)
C(1)	7198 (4)	0	9252 (4)	3·3
C(2)	8509 (4)	−752 (2)	9827 (5)	3·8
C(3)	9148 (4)	−906 (2)	8222 (5)	3·9
C(4)	7579 (4)	−1143 (2)	6189 (5)	3·5
C(5)	6144 (4)	−416 (2)	5623 (4)	3·1
C(6)	4528 (4)	−550 (2)	3578 (4)	4·0
C(7)	3453 (4)	281 (2)	2852 (4)	4·1
C(8)	2934 (4)	627 (2)	4408 (4)	3·1
C(9)	4479 (4)	728 (2)	6500 (4)	2·9
C(10)	5508 (4)	−143 (2)	7254 (4)	2·8
C(11)	3937 (4)	1218 (2)	7973 (4)	3·5
C(12)	2014 (4)	1025 (2)	7602 (5)	3·7
C(13)	740 (4)	1178 (2)	5470 (4)	3·4
C(14)	1230 (4)	842 (2)	3968 (4)	3·4
C(15)	−641 (4)	1654 (2)	5368 (5)	3·9
C(16)	−251 (4)	1907 (2)	7416 (5)	4·5
C(17)	8334 (5)	−1156 (3)	4618 (5)	4·9
C(18)	6864 (5)	−2033 (2)	6271 (5)	4·8
C(19)	4250 (4)	−784 (2)	7571 (5)	3·6
C(20)	−2251 (4)	1975 (3)	3583 (5)	5·2
O(1)	10601 (3)	−1488 (2)	8835 (4)	6·0
O(2)	1364 (3)	1570 (2)	8731 (3)	5·0
O(3)	−1130 (3)	2352 (2)	8002 (4)	6·5

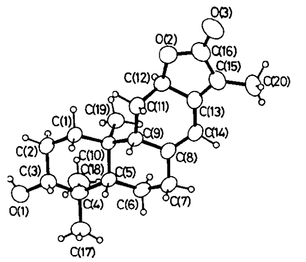

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the molecule with thermal ellipsoids scaled at 50% probability level. H atoms are represented by circles of radius 0·08 Å.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1·528 (4)	C(8)—C(14)	1·336 (5)
C(1)—C(10)	1·538 (3)	C(9)—C(10)	1·572 (4)
C(2)—C(3)	1·510 (6)	C(9)—C(11)	1·546 (5)
C(3)—C(4)	1·539 (4)	C(10)—C(19)	1·530 (5)
C(3)—O(1)	1·412 (4)	C(11)—C(12)	1·512 (5)
C(4)—C(5)	1·559 (4)	C(12)—C(13)	1·482 (4)
C(4)—C(17)	1·537 (6)	C(12)—O(2)	1·448 (5)
C(4)—C(18)	1·522 (5)	C(13)—C(14)	1·435 (5)
C(5)—C(6)	1·530 (3)	C(13)—C(15)	1·332 (5)
C(5)—C(10)	1·567 (5)	C(15)—C(16)	1·458 (5)
C(6)—C(7)	1·532 (5)	C(15)—C(20)	1·490 (4)
C(7)—C(8)	1·491 (5)	C(16)—O(2)	1·364 (4)
C(8)—C(9)	1·521 (3)	C(16)—O(3)	1·211 (5)
C(2)—C(1)—C(10)	112·8 (2)	C(1)—C(10)—C(5)	108·3 (3)
C(1)—C(2)—C(3)	110·5 (3)	C(1)—C(10)—C(9)	109·5 (2)
C(2)—C(3)—C(4)	111·9 (3)	C(1)—C(10)—C(19)	109·6 (2)
C(2)—C(3)—O(1)	112·8 (3)	C(5)—C(10)—C(9)	105·8 (2)
C(4)—C(3)—O(1)	112·9 (3)	C(5)—C(10)—C(19)	114·4 (3)
C(3)—C(4)—C(5)	107·5 (3)	C(9)—C(10)—C(19)	109·1 (3)
C(3)—C(4)—C(17)	107·3 (3)	C(9)—C(11)—C(12)	111·9 (3)
C(3)—C(4)—C(18)	110·9 (3)	C(11)—C(12)—C(13)	111·1 (3)
C(5)—C(4)—C(17)	108·3 (3)	C(11)—C(12)—O(2)	113·4 (3)
C(5)—C(4)—C(18)	114·7 (3)	C(13)—C(12)—O(2)	104·4 (2)
C(17)—C(4)—C(18)	107·9 (3)	C(12)—C(13)—C(14)	117·1 (3)
C(4)—C(5)—C(6)	113·3 (2)	C(12)—C(13)—C(15)	109·9 (3)
C(4)—C(5)—C(10)	117·4 (3)	C(14)—C(13)—C(15)	132·9 (3)
C(6)—C(5)—C(10)	111·0 (3)	C(8)—C(14)—C(13)	121·5 (3)
C(5)—C(6)—C(7)	110·5 (3)	C(13)—C(15)—C(16)	107·3 (3)
C(6)—C(7)—C(8)	110·8 (3)	C(13)—C(15)—C(20)	130·2 (3)
C(7)—C(8)—C(9)	115·3 (3)	C(16)—C(15)—C(20)	122·3 (3)
C(7)—C(8)—C(14)	121·7 (3)	C(15)—C(16)—O(2)	109·8 (3)
C(9)—C(8)—C(14)	123·0 (3)	C(15)—C(16)—O(3)	129·1 (3)
C(8)—C(9)—C(10)	110·6 (2)	O(2)—C(16)—O(3)	121·0 (3)
C(8)—C(9)—C(11)	113·4 (2)	C(12)—O(2)—C(16)	107·9 (2)
C(10)—C(9)—C(11)	117·1 (3)		

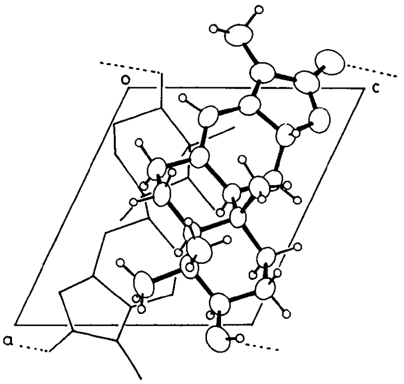

Fig. 2. A projection of the crystal structure along **b**. Hydrogen bonds are marked by broken lines.

Bond lengths and bond angles are listed in Table 2. The bond lengths of C(7)—C(8), C(12)—C(13), C(13)—C(14) and C(15)—C(16) are 1·491 (5), 1·482 (4), 1·435 (5) and 1·458 (5) Å, respectively. The mean bond length for the other C—C single bond in the rings is 1·538 (5) Å. The shorter bond lengths may be due to the conjugate double bonds of C(7)—C(8)=C(14)—C(13)=C(15)—C(16)=O(3). The torsion angles of C(8)—C(14)—C(13)—C(15) and C(13)—C(15)—C(16)—O(3) are 157·3 (4) and 178·6 (4)° respectively. The intramolecular distance between the two methyl C atoms C(18) and C(19), which are axial with respect to the *A* ring, is 3·340 (6) Å. It is a little shorter than the sum of van der Waals radii of C atoms, 3·40 Å (Bondi, 1964). The weak steric repulsion between C(18) and C(19) is reflected in slightly larger angles of C(5)—C(10)—C(19), 114·4 (3)° and C(5)—C(4)—C(18), 114·7 (3)° than the normal tetrahedral angle. The mean value of the other C—C—C angles involving C(18) and C(19) is 109·4 (3)°.

The molecular packing is illustrated in Fig. 2. There is a hydrogen bond from the OH group to the carbonyl O(3) atom. The O(3)···O(1^{i}), O(3)···H(O1^{i}) and O(1)—H(O1) distances are 2·838 (4), 2·01 (4) and 0·87 (4) Å, respectively, where the superscript refers to the atom at $1-x, y-\frac{1}{2}, 2-z$.

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Ring asymmetry parameters from out-of-plane atomic displacements.

By M. Nardelli, *Istituto di Chimica Generale e Inorganica della Università, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Via M. D'Azeglio* 85, *Parma, Italy*

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Abstract

Formulae are given for calculating ring asymmetry parameters and e.s.d.'s from the out-of-plane displacements of the atoms of a ring.

The *asymmetry parameters* have been proposed by Duax, Weeks & Rohrer (1976) to give a quantitative evaluation of how a ring of any size deviates from ideal symmetry and to help in describing its conformation. These parameters are calculated as r.m.s.'s of the sums of mirror-related torsion angles (ΔC_S) or r.m.s.'s of the differences of twofold-axis-related torsion angles (ΔC_2).

Similar parameters, but directly connected with Cremer & Pople's (1975) total *puckering amplitude*, can be defined using the perpendicular displacements of the atoms from the mean plane through them. These parameters, which could be called *displacement asymmetry parameters*, are defined, together with their e.s.d.'s, by the following equations, where n is the number of the atoms of the ring, r_i is the perpendicular displacement of atom i from the mean plane and R_i is its distance from the center of the ring (the nomenclature is that proposed by Duax *et al.*).

Writing

$$\sin \varphi_i = r_i/R_i$$

where φ_i is the angle the vector $\mathbf{R}_i$ forms with the mean plane through the ring,

$$A_i = \sin\varphi_i - \sin\varphi_i'$$

$$B_i = \sin\varphi_i + \sin\varphi_i'$$

$$C_i = \frac{1}{R_i^2}\left\{\sigma^2(r_i) + \left[\frac{\sin\varphi_i}{R_i}\,\sigma(R_i)\right]^2\right\}$$

$$D = \sin^2\varphi_a\left\{\left[\frac{\sigma(r_a)}{R_a}\right]^2 + \left[\frac{\sin\varphi_a}{R_a}\,\sigma(R_a)\right]^2\right\}$$

$$S_1 = \sum_{i=1}^{m} A_i^2, \qquad S_2 = \sum_{i=1}^{m} B_i^2$$

$$S_3 = \sum_{i=1}^{m} A_i^2(C_i + C_i'),\ S_4 = \sum_{i=1}^{m} B_i^2(C_i + C_i'),$$

all the possible cases are as follows.

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