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## Structure of ( $\pm$ )-(1*R*\*,6*S*\*)-1-Benzylloxy-8,11,11-trimethyl-6-phenylthiobicyclo[5.3.1]undec-7-en-3-one

BY V. M. LYNCH, J. R. FISHPAUGH, S. F. MARTIN AND B. E. DAVIS

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA

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**Abstract.**  $C_{27}H_{32}O_2S$ ,  $M_r = 420.61$ , monoclinic,  $P2_1/c$ ,  $a = 8.4756$  (13),  $b = 14.710$  (2),  $c = 18.425$  (3) Å,  $\beta = 99.575$  (13)°,  $V = 2265.2$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.23$  g cm<sup>-3</sup>,  $\mu = 1.5567$  cm<sup>-1</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $F(000) = 904$ ,  $T = 298$  K,  $R = 0.0630$  for 2942 reflections [ $F_o \geq 6\sigma(F_o)$ ]. The cyclooctane portion of the [5.3.1] ring system assumes the boat-chair conformation while the cyclohexene portion has the boat conformation. As has been observed in other [5.3.1]undecene systems, ring strain appears to cause a distortion of the geometry of the bridgehead alkene. The bond length C7—C8 [1.343 (5) Å] is long for an isolated C—C double bond. The  $C_{sp^2}$ — $C_{sp^3}$  bond lengths at C7 are asymmetric with C7—C6 being 1.498 (5) Å while C7—C11 is 1.535 (5) Å. The maximum deviation from ideality for the torsion angles around the double bond is 16.2 (4)° (absolute value). This twist in the alkene group is reflected in the non-planarity of the group [max. deviation 0.193 (6) Å for C9] and in the dihedral angle between the nearly planar portions (C6, C7, C8, C11 and C7, C8, C9, C15), which is 9.4 (2)°.

**Experimental.** The bicyclo[5.3.1]undecene (1), which possesses the key structural subunit that is present in the taxane diterpenes (Martin, White & Wagner, 1982), was obtained by an anionic oxy-Cope rearrangement of a suitably substituted bicyclo[2.2.2]octane (Martin, White, Wagner, Guinn,

Tanaka, Assercq, Gluchowski, Austin & Dantanarayana, 1990). The data crystal was a colorless block that was cut from a larger crystal and had approximate dimensions 0.37 × 0.42 × 0.47 mm. Crystals were obtained by slow evaporation from ether. The data were collected at room temperature using graphite-monochromatized Mo  $K\alpha$  radiation on a Picker diffractometer that was automated by the Krisel Control Corporation. Lattice parameters were obtained from least-squares refinement of 20 reflections with  $27.6 < 2\theta < 32.3$ °. Data were collected using the  $\omega$ -scan technique (13 322 reflections, 6601 unique,  $R_{int} = 0.0325$ ), with a  $2\theta$  range 4.0–60°, over a  $1^\circ\omega$  scan at  $6^\circ\text{min}^{-1}$  ( $h = -11 \rightarrow 11$ ,  $k = -20 \rightarrow 20$ ,  $l = 0 \rightarrow 25$ ). Three reflections (004, 060, 200) were remeasured every two hours to monitor instrument and crystal stability (maximum correction on  $I$  was < 1%; Henslee & Davis, 1975). The data were also corrected for Lp effects and secondary extinction but not for absorption. The secondary-extinction correction is of the form  $F_{corr} = F_c \{1 - [2.64(2) \times 10^{-7}(F_c)^2/\sin\theta]\}$ . The data reduction is

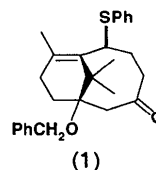


Table 1. Fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for the non-H atoms of (1)

	x	y	z	U
C1	1.0645 (4)	0.2115 (2)	0.0834 (2)	0.0369 (13)
C2	1.0846 (5)	0.3083 (3)	0.1169 (2)	0.046 (2)
C3	0.9402 (5)	0.3485 (2)	0.1452 (2)	0.051 (2)
C4	0.9426 (7)	0.3553 (3)	0.2280 (3)	0.061 (2)
C5	1.0168 (6)	0.2787 (3)	0.2782 (2)	0.057 (2)
C6	0.9274 (5)	0.1882 (2)	0.2599 (2)	0.0410 (14)
C7	0.9134 (4)	0.1652 (2)	0.1799 (2)	0.0339 (12)
C8	0.7735 (4)	0.1801 (2)	0.1353 (2)	0.0459 (14)
C9	0.7608 (5)	0.1823 (4)	0.0524 (2)	0.062 (2)
C10	0.9156 (5)	0.2022 (3)	0.0230 (2)	0.048 (2)
C11	1.0572 (4)	0.1387 (2)	0.1435 (2)	0.0329 (12)
C12	1.0274 (7)	0.0438 (3)	0.1088 (3)	0.056 (2)
C13	1.2181 (5)	0.1310 (4)	0.1942 (3)	0.050 (2)
O14	0.8330 (3)	0.3829 (2)	0.1037 (2)	0.0669 (12)
C15	0.6162 (5)	0.2061 (4)	0.1582 (3)	0.070 (2)
S16	1.01150 (12)	0.09982 (7)	0.32662 (5)	0.0498 (4)
C17	0.8350 (4)	0.0537 (2)	0.3515 (2)	0.0410 (14)
C18	0.8211 (5)	0.0478 (2)	0.4248 (2)	0.050 (2)
C19	0.6875 (6)	0.0088 (3)	0.4460 (3)	0.068 (2)
C20	0.5645 (6)	-0.0232 (3)	0.3941 (3)	0.073 (2)
C21	0.5772 (5)	-0.0171 (3)	0.3208 (3)	0.072 (2)
C22	0.7136 (5)	0.0210 (3)	0.2996 (2)	0.058 (2)
O23	1.2040 (3)	0.1903 (2)	0.05082 (13)	0.0435 (9)
C24	1.2383 (5)	0.2508 (3)	-0.0053 (2)	0.058 (2)
C25	1.3484 (4)	0.2040 (3)	-0.0501 (2)	0.0460 (15)
C26	1.3637 (5)	0.1124 (3)	-0.0545 (2)	0.059 (2)
C27	1.4671 (6)	0.0765 (4)	-0.0969 (3)	0.087 (2)
C28	1.5555 (7)	0.1296 (5)	-0.1350 (3)	0.098 (3)
C29	1.5396 (6)	0.2201 (5)	-0.1319 (3)	0.090 (3)
C30	1.4370 (5)	0.2603 (4)	-0.0895 (2)	0.067 (2)

For anisotropic atoms, the  $U$  value is  $U_{\text{eq}}$ , calculated as  $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ , where  $A_{ij}$  is the dot product of the  $i$ th and  $j$ th direct-space unit-cell vectors.

described in Riley & Davis (1976). Reflections having  $F_o < 6\sigma(F_o)$  were considered unobserved (3659 reflections). Structure solved by the heavy-atom method and refined by full-matrix least squares (Sheldrick, 1976). The non-H atoms were refined with anisotropic thermal parameters. The H atoms were obtained from a  $\Delta F$  map. However, the H atoms for the methyl C, C15, the methylene C, C24, and the phenyl ring H atoms did not refine well and were idealized. The remaining H atoms were refined and all H atoms had refined isotropic thermal parameters. In all, a total of 355 parameters were refined. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized, where  $w = 1/[\sigma(F_o)]^2$  and  $\sigma(F_o) = 0.5kI^{-1/2} \times \{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$ . The intensity  $I$  is given by  $(I_{\text{peak}} - I_{\text{background}}) \times (\text{scan rate})$ ; 0.02 is a factor to downweight intense reflections and to account for instrument instability and  $k$  is the correction due to Lp effects and decay.  $\sigma(I)$  was estimated from counting statistics;  $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times (\text{scan rate})]$ . The final  $R = 0.0630$  for 2942 reflections,  $wR = 0.0531$  ( $R_{\text{all}} = 0.156$ ,  $wR_{\text{all}} = 0.0624$ ) and goodness of fit = 2.596. The maximum  $|\Delta/\sigma| < 0.1$  in the final refinement cycle and the minimum and maximum peaks in the final  $\Delta F$  map were  $-0.35$  and  $0.53 \text{ e \AA}^{-3}$ , respectively. Scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with anomalous-dispersion corrections from

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the non-H atoms of (1)

1	2	3	1—2	1—2—3
C2	C1	C10	1.550 (5)	113.1 (3)
C2	C1	C11		111.4 (3)
C10	C1	C11	1.544 (5)	109.2 (3)
C10	C1	O23		107.9 (3)
C11	C1	O23	1.549 (5)	106.3 (3)
O23	C1	C2	1.446 (4)	108.7 (3)
C3	C2	C1	1.527 (6)	116.7 (3)
C4	C3	O14	1.526 (6)	119.6 (4)
C4	C3	C2		119.2 (4)
O14	C3	C2	1.198 (5)	120.8 (4)
C5	C4	C3	1.526 (6)	119.6 (4)
C6	C5	C4	1.542 (6)	111.5 (4)
C7	C6	S16	1.498 (5)	117.0 (2)
C7	C6	C5		111.5 (3)
S16	C6	C5	1.849 (4)	109.9 (2)
C8	C7	C11	1.343 (5)	117.3 (3)
C8	C7	C6		118.8 (3)
C11	C7	C6	1.535 (5)	123.2 (3)
C9	C8	C15	1.514 (6)	111.0 (3)
C9	C8	C7		121.9 (4)
C15	C8	C7	1.513 (6)	126.9 (4)
C10	C9	C8	1.529 (6)	116.1 (3)
C1	C10	C9		114.1 (3)
C12	C11	C13	1.539 (6)	104.8 (3)
C12	C11	C1		110.7 (3)
C12	C11	C7		108.9 (3)
C13	C11	C1	1.523 (5)	110.6 (3)
C13	C11	C7		116.5 (3)
C1	C11	C7		105.4 (3)
C17	S16	C6	1.770 (4)	101.1 (2)
C18	C17	C22	1.379 (6)	119.0 (4)
C18	C17	S16		119.5 (3)
C22	C17	S16	1.370 (5)	121.6 (3)
C19	C18	C17	1.382 (7)	120.7 (4)
C20	C19	C18	1.374 (6)	120.6 (4)
C21	C20	C19	1.375 (8)	119.1 (5)
C22	C21	C20	1.398 (6)	120.2 (4)
C17	C22	C21		120.4 (4)
C24	O23	C1	1.430 (5)	116.4 (3)
C25	C24	O23	1.510 (6)	109.3 (3)
C26	C25	C30	1.357 (6)	119.4 (4)
C26	C25	C24		124.0 (4)
C30	C25	C24	1.399 (6)	116.6 (4)
C27	C26	C25	1.373 (7)	119.5 (4)
C28	C27	C26	1.357 (8)	122.2 (5)
C29	C28	C27	1.340 (10)	118.8 (6)
C30	C29	C28	1.393 (7)	121.5 (5)
C25	C30	C29		118.6 (5)

the work of Cromer & Liberman (1970). Scattering factors for the H atoms are from Stewart, Davidson & Simpson (1965). The linear absorption coefficient was calculated from values found in *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55). \* Positional and thermal parameters for the non-H atoms are listed in Table 1, while bond lengths and angles for the non-H atoms are listed in Table 2. The atom-labeling scheme is shown in Fig. 1. All figures were generated using *SHELXTL-Plus* (Sheldrick, 1987). The least-squares-planes program was supplied by Cordes (1983); other computer programs from reference 11 of Gadol & Davis (1982).

\* Tables of anisotropic thermal parameters, H-atom positional parameters, bond distances and angles involving the H atoms, torsion angles, least-squares planes, structure-factor amplitudes and a unit-cell packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53422 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

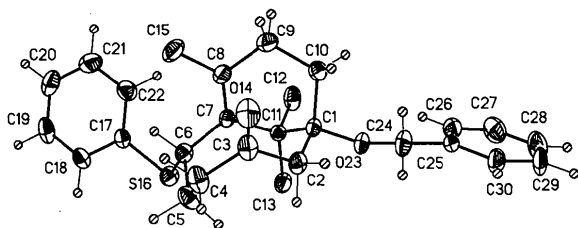


Fig. 1. View of (1) showing the atom-labeling scheme and illustrating the boat-chair conformation of the cyclooctane ring. The methyl H atoms were omitted for clarity. The non-H atoms are scaled to the 30% probability level while the H atoms are drawn to an arbitrary size.

**Related literature.** The structures of three molecules having the [5.3.1]undecene ring system showing similar distortions at the bridgehead alkene moiety have been reported (Lynch, Fishpaugh, Martin & Davis, 1990; Lynch, Tanaka, Fishpaugh, Martin & Davis, 1990; Lynch, Assercq, Martin & Davis, 1990).

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## Structure of Phomozin: Ester of Dimethylglyceric Acid and *O*-Orsellinic Acid. A New Phytotoxin from the Phytopathogenic Fungus *Phomopsis helianthi*

BY J.-P. DECLERCO

*Laboratoire de Chimie Physique et de Cristallographie, Université Catholique de Louvain,  
1 Place Louis Pasteur, 1348 Louvain-la-Neuve, Belgium*

A. KLAEBE

*Laboratoire Synthèse Structure et Réactivité des Molécules Phosphorées, URA CNRS 454,  
Université Paul Sabatier, 31062 Toulouse CEDEX, France*

AND M. ROSSIGNOL AND C. MAZARS

*Laboratoire de Physiologie Végétale, URA CNRS 241, Université Paul Sabatier, 31062 Toulouse CEDEX,  
France*

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**Abstract.** 2,3-Dimethyl-3-(*o*-orsellinoyl)lactic acid, C<sub>13</sub>H<sub>16</sub>O<sub>7</sub>·H<sub>2</sub>O, *M<sub>r</sub>* = 302.28, triclinic, *P*1, *a* = 6.465 (1), *b* = 6.801 (1), *c* = 16.951 (4) Å, *α* = 89.97 (2), *β* = 88.00 (2), *γ* = 76.54 (2)°, *V* = 724.4 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.39 g cm<sup>-3</sup>, *Cu Kα*, *λ* = 1.54178 Å, *μ* = 10.1 cm<sup>-1</sup>, *F*(000) = 320, *T* = 291 K, *R* = 0.040 for 3315 observed reflections. A new phytotoxin, phomozin, isolated from culture filtrates

of *Phomopsis helianthi* [Muntanola-Cvetkovic, Mihaljcevic & Petrov (1981). *Nova Hedwigia Z. Kryptogamenkd.* **34**, 417–435] was purified by high-pressure liquid chromatography using both liquid-solid and ion-pair liquid chromatographies. The two molecules have identical configurations. Intramolecular hydrogen bonds appear between O(15)⋯O(17) and O(18)⋯O(19).