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19-(*p*-Bromophenyl)-12-methoxypodocarpa-8,11,13-trien-19-one,* C₂₄H₂₇BrO₂

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Abstract. $M_r = 427.386$, monoclinic, $P2_1$, $a = 7.830$ (1), $b = 19.049$ (5), $c = 7.361$ (1) Å, $\beta = 104.34$ (1)°, $V = 1063.7$ Å³, $Z = 2$, $D_m = 1.32$, $D_x = 1.33$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 18.82$ mm⁻¹, $F(000) = 444$, room temperature. Final $R = 0.0451$ for 1660 observed [$I > 2\sigma(I)$] reflections. The structure of the diterpene shows ring *A* in a chair and ring *B* in a half-chair conformation. The aromatic ring, *C*, has a methoxy substituent at C(12). The carbonyl oxygen of the 4 β -axial aryl carbonyl substituent is twisted out of the plane of the adjacent phenyl ring as suggested by chemical and spectroscopic data.

Introduction. Podocarpic acid (12-hydroxypodocarpa-8,11,13-trien-19-oic acid) provides a convenient source of chiral starting material for the synthesis of complex molecules (Spencer, Smith, Storm & Villarica, 1971; Bennett, Cambie, Franich & Fullerton, 1969). Attempts to functionalize podocarpic acid derivatives at the C(10) methyl group by photolysis of attached aryl ketone groups were unsuccessful, which was attributed to steric hindrance to π -electron delocalization between the aryl and carbonyl moieties (Smith, 1983). The structure of the title compound was determined to investigate this possibility.

Experimental. Crystals grown from ethanol as colourless plates, dimensions 0.48 × 0.60 × 0.28 mm. Density by flotation in aqueous KI. Preliminary precession photography (Cu $K\alpha$) indicated monoclinic space groups $P2_1$ or $P2_1/m$. The non-centrosymmetric alternative was preferred for the chiral molecule and this choice was confirmed by the success of the refinement. Nicolet $P\bar{3}$ diffractometer, Mo $K\alpha$ radiation (graphite monochromator), cell dimensions determined by least squares from settings of 24 strong reflections in the range $27 < 2\theta < 29^\circ$. Range of hkl : 10, 24, ± 10 , $2\theta_{\text{max}} = 52^\circ$; max. intensity variation of 7% in standard reflections 0,10,0, 013 and 320; intensities corrected for Lorentz and polarization effects, and empirical absorption corrections applied using *SHELXTL* (Sheldrick, 1980), transmission factors 0.355–0.427. Of 2174 unique reflections ($R_{\text{int}} = 0.0095$) 1660 were considered observed with $I > 2\sigma(I)$. Structure determined by Patterson and Fourier methods, and refined by full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, using *SHELX76* (Sheldrick, 1976). All non-hydrogen atoms assigned anisotropic thermal parameters with scattering factors from *SHELX76*. H atoms included in calculated positions (C–H = 1.08 Å) with fixed isotropic temperature factors. $w = [\sigma^2(F) + 0.0019F^2]^{-1}$. Final $R = 0.0451$, $wR = 0.0522$ for the 1660 observed reflections (the opposite enantiomorph refined to $R = 0.0531$, $wR = 0.0653$, so that the results presented here correspond to the correct absolute configuration). $(\Delta/\sigma)_{\text{max}} = 0.521$ (U_{12} for Br). The final difference map showed a maximum peak of 0.37 e Å⁻³ (0.95 Å from Br), remaining peaks < 0.20 e Å⁻³.

* IUPAC name: *p*-bromophenyl 1,2,3,4,4a,9,10,10a-octahydro-6-methoxy-1,4a-dimethyl-1-phenanthryl ketone.

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Table 1. Final positional and equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | x | y | z | $U_{eq}(\text{\AA}^2)$ |
|-------|------------|-------------|------------|------------------------|
| Br | 0.1567 (1) | -0.2500 | 0.9115 (1) | 0.091 |
| C(1) | 0.061 (1) | 0.1864 (4) | 0.706 (1) | 0.075 |
| C(2) | 0.004 (1) | 0.1089 (4) | 0.688 (1) | 0.076 |
| C(3) | 0.0201 (8) | 0.0792 (4) | 0.501 (1) | 0.064 |
| C(4) | 0.2083 (9) | 0.0835 (4) | 0.4731 (8) | 0.058 |
| C(5) | 0.2678 (9) | 0.1619 (4) | 0.4999 (9) | 0.057 |
| C(6) | 0.445 (1) | 0.1802 (5) | 0.458 (1) | 0.074 |
| C(7) | 0.442 (1) | 0.2575 (5) | 0.405 (1) | 0.083 |
| C(8) | 0.3732 (9) | 0.3037 (4) | 0.5408 (9) | 0.058 |
| C(9) | 0.2836 (8) | 0.2764 (3) | 0.6690 (9) | 0.055 |
| C(10) | 0.2506 (8) | 0.1977 (4) | 0.6865 (9) | 0.051 |
| C(11) | 0.2283 (9) | 0.3241 (3) | 0.7905 (9) | 0.053 |
| C(12) | 0.2516 (9) | 0.3951 (4) | 0.7766 (8) | 0.053 |
| C(13) | 0.3338 (8) | 0.4227 (4) | 0.644 (1) | 0.060 |
| C(14) | 0.3938 (9) | 0.3766 (4) | 0.530 (1) | 0.065 |
| C(18) | 0.203 (1) | 0.0596 (5) | 0.270 (1) | 0.089 |
| C(19) | 0.3371 (8) | 0.0328 (4) | 0.6011 (8) | 0.054 |
| C(20) | 0.382 (1) | 0.1692 (4) | 0.8630 (9) | 0.069 |
| C(21) | 0.2797 (8) | -0.0343 (4) | 0.6739 (9) | 0.054 |
| C(22) | 0.3670 (8) | -0.0551 (4) | 0.8544 (9) | 0.059 |
| C(23) | 0.3292 (8) | -0.1178 (4) | 0.926 (1) | 0.066 |
| C(24) | 0.2066 (8) | -0.1612 (4) | 0.817 (1) | 0.060 |
| C(25) | 0.1192 (9) | -0.1443 (4) | 0.6352 (9) | 0.065 |
| C(26) | 0.1585 (9) | -0.0799 (4) | 0.5673 (9) | 0.059 |
| C(27) | 0.137 (1) | 0.4224 (5) | 1.036 (1) | 0.091 |
| O(1) | 0.4953 (6) | 0.0451 (3) | 0.6351 (8) | 0.080 |
| O(2) | 0.1997 (7) | 0.4446 (3) | 0.8857 (7) | 0.073 |

Discussion. Atomic positional parameters are listed in Table 1* with bond distances and angles in Table 2. The overall molecular geometry is illustrated in Fig. 1. Ring *A* adopts the usual chair conformation with the aryl ketone function in the 4 β -axial position. The conformation of ring *B* is best described as a half-chair, with C(5) displaced by 0.732 (7) Å from the C(6), C(7), C(9), C(10) plane; in contrast C(8) is displaced by only 0.096 (7) Å in the opposite direction. Previous structural determinations of podocarp derivatives have shown a variation in the conformation of ring *B* from almost pure boat (Clark & Waters, 1970; Cutfield, Waters & Clark, 1974) to chair (Beecham, Cambie, Hayward & Poppleton, 1979) which has been attributed to changes in the substituents on ring *B* (Mondal & Guha, 1978). The aromatic ring *C* of the diterpene is planar with the methoxy substituent at C(12) displaced from the β face of the molecule.

The carbonyl oxygen, O(1), is twisted out of the plane of the C(21)–C(26) aromatic ring such that the perpendicular displacement of O(1) from the ring plane is 0.891 (5) Å and the dihedral angle between the planes defined by O(1), C(19), C(21), and C(19), C(21), C(22) is 41.0°. This confirms the previous conclusions (Smith, 1983), based on UV and ¹³C NMR

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, mean-plane and torsion-angle data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42092 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

evidence, that it is possible to induce steric hindrance to π -electron delocalization in aryl ketones without the introduction of bulky *ortho* substituents on the phenyl ring.

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

| | | | |
|-------------------|-----------|-------------------|-----------|
| C(1)–C(2) | 1.54 (1) | C(25)–C(26) | 1.39 (1) |
| C(1)–C(10) | 1.544 (9) | C(5)–C(6) | 1.530 (9) |
| C(2)–C(3) | 1.52 (1) | C(5)–C(10) | 1.570 (9) |
| C(3)–C(4) | 1.540 (9) | C(6)–C(7) | 1.52 (1) |
| C(4)–C(18) | 1.55 (1) | C(7)–C(8) | 1.52 (1) |
| C(4)–C(19) | 1.54 (1) | C(8)–C(9) | 1.407 (9) |
| C(4)–C(5) | 1.563 (9) | C(8)–C(14) | 1.40 (1) |
| C(19)–O(1) | 1.225 (7) | C(9)–C(10) | 1.53 (1) |
| C(19)–C(21) | 1.50 (1) | C(9)–C(11) | 1.416 (9) |
| C(21)–C(22) | 1.393 (9) | C(10)–C(20) | 1.54 (1) |
| C(21)–C(26) | 1.379 (9) | C(11)–C(12) | 1.373 (9) |
| C(22)–C(23) | 1.37 (1) | C(12)–O(2) | 1.363 (9) |
| C(23)–C(24) | 1.37 (1) | C(12)–C(13) | 1.40 (1) |
| C(24)–C(25) | 1.38 (1) | O(2)–C(27) | 1.39 (1) |
| C(24)–Br | 1.905 (7) | C(13)–C(14) | 1.37 (1) |
| C(2)–C(1)–C(10) | 112.9 (6) | C(4)–C(5)–C(10) | 116.0 (5) |
| C(1)–C(2)–C(3) | 110.3 (6) | C(6)–C(5)–C(10) | 110.7 (5) |
| C(2)–C(3)–C(4) | 113.4 (5) | C(5)–C(6)–C(7) | 108.4 (6) |
| C(3)–C(4)–C(18) | 108.2 (6) | C(6)–C(7)–C(8) | 112.1 (6) |
| C(3)–C(4)–C(19) | 112.9 (6) | C(7)–C(8)–C(9) | 122.7 (6) |
| C(3)–C(4)–C(5) | 107.4 (5) | C(7)–C(8)–C(14) | 118.1 (7) |
| C(18)–C(4)–C(19) | 105.3 (6) | C(9)–C(8)–C(14) | 119.2 (7) |
| C(18)–C(4)–C(5) | 109.8 (6) | C(8)–C(9)–C(10) | 122.7 (6) |
| C(19)–C(4)–C(5) | 113.1 (5) | C(8)–C(9)–C(11) | 117.9 (6) |
| C(4)–C(19)–O(1) | 118.8 (6) | C(10)–C(9)–C(11) | 119.3 (5) |
| C(4)–C(19)–C(21) | 123.1 (5) | C(1)–C(10)–C(5) | 108.2 (5) |
| O(1)–C(19)–C(21) | 117.9 (6) | C(1)–C(10)–C(9) | 109.3 (6) |
| C(19)–C(21)–C(22) | 117.7 (6) | C(1)–C(10)–C(20) | 109.3 (6) |
| C(19)–C(21)–C(26) | 124.0 (6) | C(5)–C(10)–C(9) | 107.4 (5) |
| C(22)–C(21)–C(26) | 118.0 (6) | C(5)–C(10)–C(20) | 113.6 (6) |
| C(21)–C(22)–C(23) | 121.0 (6) | C(9)–C(10)–C(20) | 108.9 (6) |
| C(22)–C(23)–C(24) | 119.4 (6) | C(9)–C(11)–C(12) | 121.2 (6) |
| C(23)–C(24)–C(25) | 122.2 (7) | C(11)–C(12)–O(2) | 125.0 (6) |
| C(23)–C(24)–Br | 120.1 (5) | C(11)–C(12)–C(13) | 121.0 (7) |
| C(25)–C(24)–Br | 117.6 (5) | O(2)–C(12)–C(13) | 114.0 (6) |
| C(24)–C(25)–C(26) | 117.0 (7) | C(12)–O(2)–C(27) | 118.5 (6) |
| C(21)–C(26)–C(25) | 122.3 (6) | C(12)–C(13)–C(14) | 118.1 (7) |
| C(4)–C(5)–C(6) | 116.7 (6) | C(8)–C(14)–C(13) | 122.5 (7) |

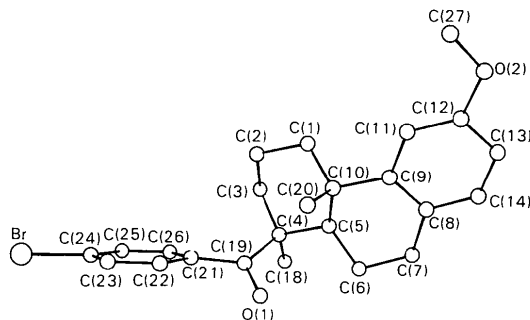


Fig. 1. Molecule with numbering scheme.

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2-Chloro-9-oxothioxanthenium-10-bis(methoxycarbonyl)methylide, C₁₈H₁₃ClO₅S

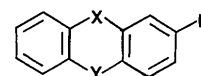
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Abstract. $M_r = 376.79$, triclinic, $P\bar{1}$, $a = 5.562$ (2), $b = 12.176$ (2), $c = 12.763$ (2) Å, $\alpha = 99.01$ (2), $\beta = 99.80$ (2), $\gamma = 78.35$ (2)°, $V = 827.8$ (3) Å³, $Z = 2$, $D_x = 1.511$, $D_m = 1.52$ Mg m⁻³ (by flotation), graphite-monochromatized Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.328$ mm⁻¹, $F(000) = 388$, $T = 298$ K, $R = 0.043$ and $wR = 0.042$ for 1720 observed reflections. The thioxanthone ring is nearly planar with a folding angle of 173.7 (2)°. The bis(methoxycarbonyl)methylide group is in a pseudoequatorial conformation with respect to the central ring of the thioxanthone ring system. Both of the ester groups have the *endo* conformation with one carbonyl O *anti* and the other *syn* to the nonbonding electron pair on S.

Introduction. The determination of the crystal structure of the title compound (I) is one of a series of thioxanthenium and 9-oxothioxanthenium ylides under study in this laboratory. It has been deduced from the NMR studies in solution that the sulfonium ylides derived from thioxanthene and thioxanthone have the same conformation as those of the corresponding sulfoxides (Tamura, Mukai & Ikeda, 1979; Ternay, Craig & O'Neal, 1980). The purpose of the present study is to determine the conformation of the sulfonium ylide in the solid state and to compare the conformation of the sulfonium ylide with that of the corresponding sulfoxides. Single crystals of the title compound were obtained through the courtesy of Dr A. L. Ternay Jr of the Department of Chemistry, University of Texas at Arlington.



| X | Y | R |
|-----------|---|----|
| (I) C=O | S ⁺ C ⁻ (CO ₂ CH ₃) ₂ | Cl |
| (II) C=O | S(O) | H |
| (III) C=O | S | Cl |
| (IV) C=O | S ⁺ C ⁻ (CO ₂ CH ₃) ₂ | H |
| (V) S | S ⁺ C ⁻ (CO ₂ C ₂ H ₅) ₂ | H |

Experimental. Single crystals are in the form of transparent colorless elongated prisms; unit-cell parameters by least-squares analysis of 15 reflections with 2θ values from 20 to 30° measured on the diffractometer; two molecules in a unit cell; $P\bar{1}$ confirmed from the structure analysis; Syntex $P2_1$ automatic diffractometer; crystal $0.39 \times 0.15 \times 0.06$ mm; $\theta/2\theta$ scanning mode; 2968 independent reflections; $2\theta < 50^\circ$; range of hkl : $0 \rightarrow 6$, $-13 \rightarrow 14$, $-15 \rightarrow 15$; 1720 observed, $I > 3\sigma(I)$; three standard reflections measured after every 50 reflections showed no significant variation in intensities; Lorentz-polarization corrections; no absorption or extinction corrections; structure solved by direct methods (*MULTAN78*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); refinement by full-matrix least squares using *SHELX76* (Sheldrick, 1976), anisotropic; H positions located in a difference Fourier synthesis, isotropic temperature factors for H atoms; 277 variables; $w = k/[\sigma(F)]^2$, with $\sigma(F)$ from counting statistics, $k = 1.508$ from least squares; $\sum w(|F_o| -$