

wR value has the C(7) equatorial substituent in β position, as in all sesquiterpene lactones of authenticated stereochemistry (Fischer, Olivier & Fischer, 1979). Further refinement was carried out on a data set with Bijvoet pairs not averaged and with dispersion effects considered for O and C atoms.

Programs used for (I) and (II) were *PRARA* (Jaskólski, 1982), *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986), *ORTEP* (Johnson, 1965), *PARST* (Nardelli, 1983) and *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreetti, 1986).

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55085 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1003]

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Structure of 2-(4-Methylphenyl)-1H-indene-1,3(2H)-dione

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Abstract

The structure determination of the title compound was undertaken in order to obtain more structural information about the derivatives of 1,3-indenedione and the effects of different substituents in different positions on the conformation of these compounds. The least-squares plane through the atoms of the six-membered ring fused to the five-membered ring and the least-squares plane through the atoms of the tolyl ring form a dihedral angle of $81.31(7)^\circ$. The atoms bound to the linking atom C(1') in the five-membered ring nearly form a tetrahedron (maximum deviation from the ideal angle 8.3°). The bond distances and angles are in the normal range. The length of the C—C bond between the ring systems is $1.514(3)$ Å and the tolyl C—C_{methyl} bond length is $1.513(3)$ Å.

Comment

By the removal of one proton from the methine group, the title compound may be easily transformed into the corresponding carbanion which is of great interest as an intermediate species in some chemical reactions. This compound also shows hypolipidemic activity in mice. 2-(4-Methylphenyl)-1H-indene-1,3(2H)-dione reduced both serum cholesterol and triglycerides after some days of administration (Murthy, Wyrick & Hall, 1985).

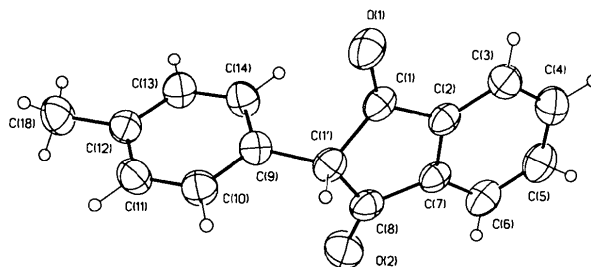


Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

Experimental

Crystal data



M_r = 236.27

Monoclinic

P2₁

a = 8.465 (2) Å

b = 6.062 (1) Å

c = 11.901 (2) Å

β = 95.78 (1)°

V = 607.6 (2) Å³

Z = 2

D_x = 1.291 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 20 reflections

θ = 8.0–13.0°

μ = 0.08 mm⁻¹

T = 293 (1) K

0.70 × 0.40 × 0.22 mm

Colourless

Data collection

Nicolet R3m/V diffractometer

θ/2θ scans

Absorption correction: none

2314 measured reflections

1194 independent reflections

1167 observed reflections

[F > 4.0σ(F)]

R_{int} = 0.022

θ_{max} = 22.5°

h = -10 → 10

k = -7 → 2

l = -13 → 13

6 standard reflections

frequency: 150 min

intensity variation: 0%

Refinement

Refinement on F

Final R = 0.033

wR = 0.043

S = 1.08

1167 reflections

164 parameters

Only H-atom U's refined

Calculated weights

w = 1/[σ²(F) + 0.0015F²]

(Δ/σ)_{max} = 0.007

Δρ_{max} = 0.24 e Å⁻³

Δρ_{min} = -0.26 e Å⁻³

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Nicolet R3m/V software, release 4.11. Cell refinement: Nicolet R3m/V software. Data reduction: Nicolet R3m/V software. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXTL-Plus*, *SHELX76* (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983), *EUCLID* (Spek, 1982), *MISSYM* (Le Page, 1987).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

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

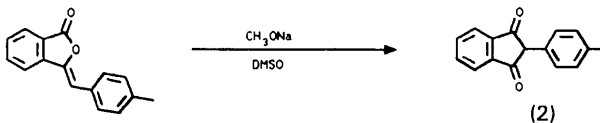
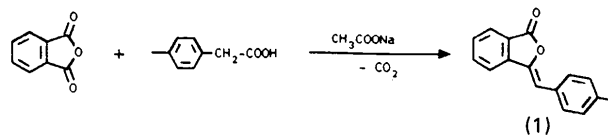
	x	y	z	U _{eq}
O(1)	0.0334 (2)	0.2469	0.4118 (1)	0.0559
O(2)	-0.2921 (2)	0.7678 (5)	0.2052 (2)	0.0721
C(1)	-0.0806 (2)	0.3560 (5)	0.3733 (2)	0.0398
C(1')	-0.0728 (2)	0.5801 (5)	0.3163 (2)	0.0419
C(2)	-0.2496 (2)	0.2950 (5)	0.3752 (2)	0.0390
C(3)	-0.3153 (3)	0.1126 (6)	0.4233 (2)	0.0489
C(4)	-0.4784 (3)	0.0873 (6)	0.4074 (2)	0.0555
C(5)	-0.5738 (3)	0.2420 (6)	0.3460 (2)	0.0550
C(6)	-0.5099 (2)	0.4238 (6)	0.2991 (2)	0.0509
C(7)	-0.3451 (2)	0.4479 (5)	0.3137 (2)	0.0394
C(8)	-0.2452 (2)	0.6211 (5)	0.2694 (2)	0.0452
C(9)	0.0440 (2)	0.6082 (5)	0.2290 (2)	0.0396
C(10)	0.1281 (2)	0.8031 (6)	0.2248 (2)	0.0490
C(11)	0.2264 (3)	0.8391 (5)	0.1401 (2)	0.0513
C(12)	0.2438 (2)	0.6806 (5)	0.0578 (2)	0.0436

C(13)	0.1591 (2)	0.4870 (5)	0.0623 (2)	0.0470
C(14)	0.0605 (2)	0.4496 (5)	0.1475 (2)	0.0462
C(18)	0.3545 (3)	0.7217 (6)	-0.0322 (2)	0.0594

Table 2. Geometric parameters (Å, °)

O(1)—C(1)	1.220 (3)	C(5)—C(6)	1.371 (5)
O(2)—C(8)	1.212 (4)	C(6)—C(7)	1.396 (3)
C(1)—C(1')	1.523 (4)	C(7)—C(8)	1.479 (4)
C(1)—C(2)	1.480 (3)	C(9)—C(10)	1.383 (4)
C(1')—C(8)	1.530 (3)	C(9)—C(14)	1.382 (4)
C(1')—C(9)	1.514 (3)	C(10)—C(11)	1.387 (3)
C(2)—C(3)	1.387 (4)	C(11)—C(12)	1.391 (4)
C(2)—C(7)	1.389 (4)	C(12)—C(13)	1.379 (4)
C(3)—C(4)	1.383 (3)	C(12)—C(18)	1.513 (3)
C(4)—C(5)	1.395 (4)	C(13)—C(14)	1.396 (3)
O(1)—C(1)—C(2)	126.0 (2)	C(2)—C(7)—C(8)	109.8 (2)
O(1)—C(1)—C(1')	125.6 (2)	C(1')—C(8)—C(7)	108.3 (2)
C(1')—C(1)—C(2)	108.4 (2)	O(2)—C(8)—C(7)	125.7 (2)
C(1)—C(1')—C(9)	117.8 (2)	O(2)—C(8)—C(1')	126.1 (2)
C(1)—C(1')—C(8)	103.0 (2)	C(1')—C(9)—C(14)	121.5 (2)
C(8)—C(1')—C(9)	113.3 (2)	C(1')—C(9)—C(10)	119.7 (2)
C(1)—C(2)—C(7)	109.7 (2)	C(10)—C(9)—C(14)	118.7 (2)
C(1)—C(2)—C(3)	129.4 (2)	C(9)—C(10)—C(11)	120.6 (3)
C(3)—C(2)—C(7)	120.9 (2)	C(10)—C(11)—C(12)	121.1 (3)
C(2)—C(3)—C(4)	117.9 (3)	C(11)—C(12)—C(18)	120.1 (3)
C(3)—C(4)—C(5)	120.9 (3)	C(11)—C(12)—C(13)	117.9 (2)
C(4)—C(5)—C(6)	121.5 (2)	C(13)—C(12)—C(18)	121.9 (2)
C(5)—C(6)—C(7)	117.6 (2)	C(12)—C(13)—C(14)	121.2 (2)
C(2)—C(7)—C(6)	121.2 (2)	C(9)—C(14)—C(13)	120.5 (3)
C(6)—C(7)—C(8)	129.0 (2)		

Phthalic anhydride and 4-methylphenylacetic acid reacted in the presence of dry CH₃COONa to give 3-(4-methylbenzylidene)phthalide (1) which was rearranged in DMSO solution in the presence of dry CH₃ONa (Bowden & Chelel-Amiran, 1986) to give the title compound (2). The final product was purified by multifold recrystallization from anhydrous ethanol (m.p. 416.5–417.5 K). The IR spectrum of the title compound shows bands at 1746, 1705 cm⁻¹ in the carbonyl stretching region with Raman bands at 1745, 1708 cm⁻¹. The C—H stretching vibration for the methine group is at 2883 cm⁻¹ in both the IR and the Raman spectra.



The lattice parameters were determined from a symmetry-constrained least-squares fit. Refinement was based on full-matrix least-squares methods with H atoms in calculated positions (C—H 0.96 Å) except for the H atom at C(1') (1.07 Å) which was taken from a difference Fourier map. For the H atom at C(1'), the coordinates were kept fixed and an isotropic temperature factor refined whereas for the remaining H atoms one common temperature factor was refined. The y coordinate of O(1) was fixed and the absolute configuration of the crystal was not determined.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, together with a packing diagram, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55171 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1009]

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Methyl 1,2,4,5,6,10b-Hexahydro-8,9-methylenedioxy-2-oxobenzo[d]cyclopenta[b]azepine-4-carboxylate

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Abstract

The title compound contains the tetracyclic *A-B-C-E* ring system of *cephalotaxus* alkaloids. Unexpectedly, the five-membered-ring plane is twisted 67.2° from the aromatic ring plane and, like *cephalotaxine*, the seven-membered ring is oriented in a boat form with the nitrogen at the prow.

Comment

The title compound was synthesized as a key intermediate in studies of the total synthesis of the antileukemic agents harringtonine and homoharringtonine (Powell, Weisleder & Smith, 1972), the natural esters of *cephalotaxine*. Structures of the related alkaloid (Arora, Bates, Grady, Ger-

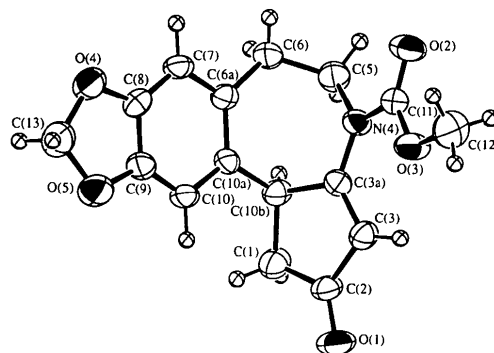


Fig. 1. Molecular configuration and atom-numbering scheme with thermal ellipsoids at the 50% probability level. H atoms are shown as unlabeled isotropic spheres with B values of 1.0 \AA^2 .

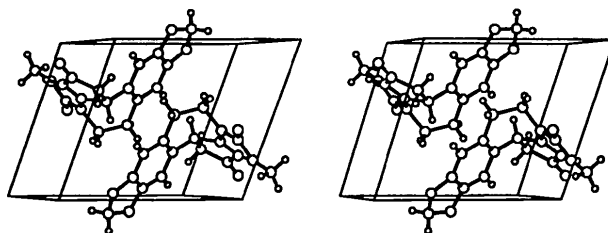
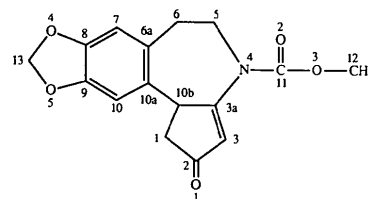


Fig. 2. Stereoscopic illustration of the molecular packing. The origin is at the lower-left-back corner, a is vertical, c is horizontal and b is out of the plane of the paper.

main, Declercq & Powell, 1976), its *p*-bromobenzoate (Arora, Bates, Grady & Powell, 1974) and its methiodide (Abraham, Rosenstein & McGandy, 1969) have been reported. The present study firmly establishes the structure of the synthetic compound and identifies the boat conformation of the seven-membered ring, a salient feature of the *cephalotaxus* alkaloids.

The title compound (1) was synthesized from the cyclization of methyl *N*-[2-(2-iodo-4,5-methylenedioxyphenyl)ethyl]-*N*-(3-oxo-1-cyclopentyl)carbamate [palladium acetate (catalytic amount), tri-*o*-tolylphosphine and triethylamine in acetonitrile (Hong, 1991)] followed by regioselective dehydrogenation [benzeneselenenyl chloride in ethyl acetate (Sharpless, Lauer & Teranishi, 1973)] and oxidation (hydrogen peroxide in tetrahydrofuran). M.p. 451–453 K (recrystallized from ether-hexane).



Experimental

Crystal data

$C_{16}H_{15}NO_5$
 $M_r = 301.30$

$D_x = 1.481 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation