C4—C3—C10*B*	117 (1)	C12*A*—C13*A*—C14*A*	122 (4)
C2—C3—C10*A*	123 (2)	C15*A*—C14*A*—C13*A*	121 (4)
C4—C3—C10*A*	113 (1)	C14*A*—C15*A*—C16*A*	114 (4)
C9—C4—C3	112 (1)	C17*A*—C16*A*—C15*A*	125 (4)
C8—C4—C3	113 (2)	C16*A*—C17*A*—C12*A*	123 (4)
C9—C4—C5	110 (1)	C5—C6*B*—C1	109 (2)
C8—C4—C5	106 (2)	C11*B*—C10*B*—C3	115 (1)
C3—C4—C5	114 (1)	C10*B*—C11*B*—C12*B*	111 (2)
C6*B*—C5—C4	114 (1)	C17*B*—C12*B*—C13*B*	113 (3)
C4—C5—C6*A*	112 (2)	C17*B*—C12*B*—C11*B*	120 (3)
C1—C6*A*—C5	109 (3)	C13*B*—C12*B*—C11*B*	123 (3)
O3*A*—C7—C2	110 (2)	C14*B*—C13*B*—C12*B*	126 (4)
O3*B*—C7—C2	128 (2)	C15*B*—C14*B*—C13*B*	113 (4)
O2*A*—C8—O1*A*	125 (3)	C14*B*—C15*B*—C16*B*	119 (4)
O2*A*—C8—C4	121 (3)	C17*B*—C16*B*—C15*B*	123 (4)
O1*A*—C8—C4	114 (3)	C12*B*—C17*B*—C16*B*	122 (4)
O2*B*—C9—O1*B*	122 (2)		

C1—C2—C3—C4	−3 (2)
C3—C4—C5—C6*A*	34 (3)
C4—C5—C6*A*—C1	−61 (3)
C5—C6*A*—C1—C2	55 (3)
C6*A*—C1—C2—C3	−24 (3)
C2—C3—C10*A*—C11*A*	−80 (3)
C3—C10*A*—C11*A*—C12*A*	179 (3)
C2—C3—C4—C5	−2 (2)
C3—C4—C5—C6*B*	−27 (2)
C4—C5—C6*B*—C1	58 (2)
C5—C6*B*—C1—C2	−60 (2)
C6*B*—C1—C2—C3	34 (2)
C2—C3—C10*B*—C11*B*	82 (2)
C4—C3—C10*B*—C11*B*	−112 (2)
C3—C10*B*—C11*B*—C12*B*	165 (2)

All calculations were performed using a VAX3400 computer at the Computer Center, Indian Association for the Cultivation of Science.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(1-Hydroxy-4,4-dimethyl-2-oxobutyl)-4-methoxy-1-naphtholactone

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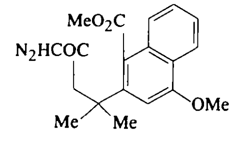
Abstract

The crystal structure of the tricyclic keto lactone, $C_{18}H_{18}O_4$, has been determined by X-ray diffraction. The eight-membered heterocyclic ring in the molecule displays a distorted boat conformation in contrast to the boat–chair conformation more favoured in various oxygen-containing eight-membered ring systems.

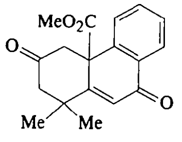
Comment

Medium-sized-ring lactone compounds (having a ring containing 8–11 atoms), which are among the ever-growing number of natural products (Rousseau, 1995), are becoming increasingly important. Several eight-membered-ring lactones having marine-plant origin have been isolated recently and characterized (Proksa, Uhrin, Adamcova & Fuska, 1992; Fang *et al.*, 1993; Brown, 1994). A systematic knowledge of the crystal structures and the effect of substituents on the conformation of the lactone rings is seen to play a vital rôle in the development of efficient methods for the synthesis of compounds possessing this framework. A tricyclic enedione (2) was obtained as the major product (60% yield) during an acid-induced intramolecular cyclization of the diazomethyl ketone (1) leading to the stereocontrolled synthesis of the angularly ester-substituted *trans*-octahydrophenanthrene ring systems related to diterpenes

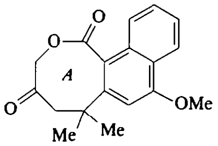
(Das, Saha & Mukherjee, 1995). A minor product (16% yield) isolated from the cyclization reaction as a crystalline compound (m.p. 446–447 K) was identified from spectroscopic data as a tricyclic keto lactone (3) incorporating an eight-membered oxygen-containing ring. Single crystal X-ray analysis of (3) was undertaken to confirm the structure, especially the conformation of the oxygen-containing heterocycle, and to build up a hierarchy for such systems.



(1)



(2)



(3)

An *ORTEP*II (Johnson, 1976) view of the molecule with atom-labelling and ring-numbering schemes is given in Fig 1. The structure consists of discrete molecules with a methoxynaphthalene moiety fused to a substituted oxa-cyclooctene ring (*A*) with methyl groups at C17 and C18 in axial and equatorial positions, respectively. The eight-membered ring *A* adopts a distorted boat conformation, as shown by the ring torsion angles (Table 2). The two halves of ring *A*, C12,C13,C14,O3 and C15,C1,C10,C11, are planar with maximum deviations of 0.010 (1) Å for C13 and 0.018 (1) Å for C1 from the respective least-squares planes, and are inclined to each other at 67.39 (9)°. A basal plane can be defined by C1, C10, C13 and C14 [maximum displacement 0.080 (1) Å for C1]; the remaining four endocyclic atoms, C11, C12, O3 and C15, are displaced in the same direction from the basal plane by 0.835 (3), 1.236 (3), 0.998 (3) and 1.195 (3) Å, respectively. The dihedral angle between the basal plane of the eight-membered ring and the planar naphthalene moiety is 56.26 (6)°. There is a marked deviation between the geometry observed for the oxygen-containing eight-membered ring and that of the corresponding boat–chair conformation (Petasis & Patane, 1992) which the most favoured in eight-membered heterocycles. This is due to strong ring torsional constraints (Moore & Anet, 1984) such as the endocyclic double bond (C1═C10) and various ring substituents (═O at C13, C15 and CH_3 groups at C11). The Cremer & Pople (1975) puckering parameters for the eight-membered ring are: q_2 = 1.542 (2), q_3 = 0.091 (2), q_4 = −0.104 (2), Q = 1.548 (2) Å, θ_2 = 86.6 (1) θ_3 = 138.9 (7)°, φ_2 = 123.2 (1), φ_3 = −80.2 (10)°. Bond lengths and angles are comparable to the values reported for related lactone structures containing an eight-membered ring (Tapiolas, Roman, Fenical, Stout & Clardy, 1991; Pirrung, Steeman, Hiemstra & Speckamp, 1992).

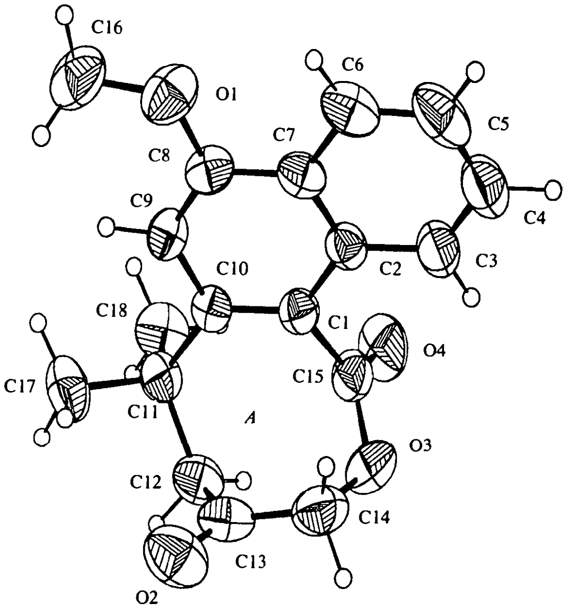


Fig. 1. *ORTEP*II (Johnson, 1976) view (50% probability level) of the molecule showing the atom-labelling and ring-numbering schemes.

Experimental

Single crystals were obtained by recrystallization from petroleum ether (boiling range 333–353 K).

Crystal data

$C_{18}H_{18}O_4$
M_r = 298.32
Monoclinic
$P2_1/n$
a = 11.3530 (10) Å
b = 9.5860 (10) Å
c = 14.0950 (10) Å
β = 97.360 (10)°
V = 1521.3 (2) Å^3
Z = 4
D_x = 1.302 Mg m^{-3}
D_m = 1.31 Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 8–16°
μ = 0.092 mm^{-1}
T = 293 (2) K
Prismatic
0.7 × 0.5 × 0.3 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta-\omega$ scans
Absorption correction: none
2669 measured reflections
2669 independent reflections
2114 observed reflections [$I > 2\sigma(I)$]

θ_{max} = 24.92°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 100 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0466$
$wR(F^2) = 0.1273$
$S = 1.038$
2669 reflections
271 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 0.1869P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.214$
$\Delta\rho_{\text{max}} = 0.223$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.199$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.11053 (13)	0.1567 (2)	0.81573 (10)	0.0395 (4)
C2	0.01857 (13)	0.0552 (2)	0.81507 (11)	0.0411 (4)
C3	−0.0895 (2)	0.0650 (2)	0.75226 (14)	0.0555 (5)
C4	−0.1768 (2)	−0.0311 (3)	0.7541 (2)	0.0677 (6)
C5	−0.1617 (2)	−0.1426 (3)	0.8182 (2)	0.0711 (6)
C6	−0.0589 (2)	−0.1576 (2)	0.87928 (14)	0.0575 (5)
C7	0.03367 (13)	−0.0594 (2)	0.87900 (11)	0.0430 (4)
C8	0.14371 (14)	−0.0716 (2)	0.93861 (11)	0.0446 (4)
C9	0.22975 (14)	0.0273 (2)	0.93801 (11)	0.0436 (4)
C10	0.21414 (13)	0.1467 (2)	0.87842 (10)	0.0384 (4)
C11	0.31398 (14)	0.2559 (2)	0.88365 (11)	0.0457 (4)
C12	0.2643 (2)	0.4060 (2)	0.8689 (2)	0.0566 (5)
C13	0.1581 (2)	0.4277 (2)	0.92131 (15)	0.0596 (5)
C14	0.0346 (2)	0.4148 (2)	0.8671 (2)	0.0671 (6)
C15	0.0867 (2)	0.2684 (2)	0.74184 (12)	0.0505 (4)
C16	0.2652 (2)	−0.2143 (3)	1.0494 (2)	0.0711 (6)
C17	0.3922 (2)	0.2523 (3)	0.9813 (2)	0.0687 (6)
C18	0.3928 (2)	0.2233 (3)	0.8058 (2)	0.0635 (5)
O1	0.15382 (12)	−0.18795 (14)	0.99422 (10)	0.0651 (4)
O2	0.16670 (14)	0.4510 (2)	1.00634 (11)	0.0829 (5)
O3	0.03371 (12)	0.38682 (14)	0.76707 (10)	0.0681 (4)
O4	0.10405 (14)	0.2549 (2)	0.66025 (9)	0.0732 (4)

Table 2. *Selected geometric parameters* (Å, °)

C1—C10	1.381 (2)	C9—C10	1.417 (2)
C1—C2	1.426 (2)	C10—C11	1.538 (2)
C1—C15	1.494 (2)	C11—C18	1.535 (2)
C2—C7	1.417 (2)	C11—C17	1.540 (3)
C2—C3	1.421 (2)	C11—C12	1.549 (3)
C3—C4	1.357 (3)	C12—C13	1.507 (3)
C4—C5	1.395 (3)	C13—O2	1.211 (2)
C5—C6	1.366 (3)	C13—C14	1.514 (3)
C6—C7	1.412 (2)	C14—O3	1.434 (3)
C7—C8	1.418 (2)	C15—O4	1.198 (2)
C8—O1	1.359 (2)	C15—O3	1.354 (2)
C8—C9	1.362 (2)	C16—O1	1.419 (3)
C10—C1—C2	121.29 (14)	C1—C10—C11	123.05 (13)
C10—C1—C15	123.99 (14)	C9—C10—C11	119.08 (13)
C2—C1—C15	114.68 (14)	C18—C11—C10	108.70 (14)
C7—C2—C3	118.2 (2)	C18—C11—C17	108.2 (2)
C7—C2—C1	119.72 (14)	C10—C11—C17	111.39 (14)
C3—C2—C1	122.1 (2)	C18—C11—C12	109.2 (2)
C4—C3—C2	121.2 (2)	C10—C11—C12	111.86 (13)
C3—C4—C5	120.2 (2)	C17—C11—C12	107.4 (2)
C6—C5—C4	120.9 (2)	C13—C12—C11	111.30 (15)
C5—C6—C7	120.3 (2)	O2—C13—C12	122.8 (2)
C6—C7—C2	119.3 (2)	O2—C13—C14	117.8 (2)
C6—C7—C8	122.9 (2)	C12—C13—C14	119.3 (2)
C2—C7—C8	117.82 (14)	O3—C14—C13	113.6 (2)
O1—C8—C9	124.5 (2)	O4—C15—O3	118.4 (2)
O1—C8—C7	114.37 (14)	O4—C15—C1	123.7 (2)
C9—C8—C7	121.10 (14)	O3—C15—C1	117.69 (14)
C8—C9—C10	122.03 (15)	C8—O1—C16	117.7 (2)
C1—C10—C9	117.83 (14)	C15—O3—C14	117.92 (14)
C15—C1—C10—C11	4.3 (2)	C12—C13—C14—O3	−2.1 (3)
C1—C10—C11—C12	37.3 (2)	C10—C1—C15—O3	−90.1 (2)
C10—C11—C12—C13	41.4 (2)	C1—C15—O3—C14	17.4 (2)
C11—C12—C13—C14	−97.9 (2)	C13—C14—O3—C15	60.3 (2)

The structure was solved by direct methods followed by Fourier synthesis and refined by anisotropic full-matrix least-squares methods on F^2 for all non-H atoms; H atoms were located from difference Fourier maps and refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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