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# X-ray investigations of bicyclic α-methylene-δ-valerolactones. III.[1] *trans*-(4a*R*,8a*R*)-4a-Methoxy-3-methyleneperhydrochromen-2-one

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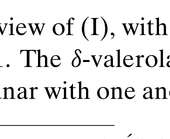
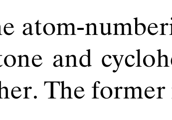
The title compound, $C_{11}H_{16}O_3$, adopts a conformation in which the δ-valerolactone and cyclohexane rings are almost coplanar with one another. The β-methoxy substituent occupies an axial position with respect to the cyclohexane ring. The δ-valerolactone moiety adopts a half-chair arrangement, while the cyclohexane ring exists in a chair conformation.

## Comment

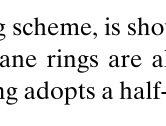
The title compound, (I), represents a novel group of optically active α-methylene-δ-valerolactones synthesized in a highly stereoselective Michael reaction (Krawczyk & Śliwiński, 2003). Recently, we have reported the crystal structures of two compounds in the series, *i.e.* the ethyl 3-methylene-2-oxohexahydrochromene-4a-carboxylate, (II) (Krawczyk, Śliwiński, Wolf & Bodalski, 2004), and 4a-methyl-3-methyleneperhydrochromen-2-one, (III) (Krawczyk, Śliwiński & Wolf, 2004). A search of the Cambridge Structural Database (CSD, Version 5.26, November 2004 update; Allen, 2002) shows that the system in which the δ-valerolactone ring is condensed with the cyclohexene moiety along the individual $C_\delta-C_\gamma$ single bond [as in (I)–(III)] is unique among crystal structures examined to date.



(I)



(II)



(III)

A view of (I), with the atom-numbering scheme, is shown in Fig. 1. The δ-valerolactone and cyclohexane rings are almost coplanar with one another. The former ring adopts a half-chair conformation, with atoms O1, C1, C2, C3 and C5 almost coplanar and atom C6 situated at the flap. The main ring pseudosymmetry element is a mirror plane passing through endocyclic atoms C6 and C11. The three lowest ring asymmetry parameters (Griffin *et al.*, 1984) are $C_S(\text{C6}) = 1.7\ (1)$, $C_2(\text{C5}-\text{C6}) = 25.3\ (2)^\circ$ and $C_2(\text{C1}-\text{C6}) = 28.8\ (2)^\circ$. The cyclohexane ring exists in a chair conformation. The 4a-methoxy substituent and 8a-H atom occupy axial positions with respect to the cyclohexane ring. The molecule has two chiral centres at C1 and C6. Their absolute configurations are consistent with the reaction mechanism and are both *R*.

The bond lengths in (I) (Table 1) are close to those observed in the similar compounds (II) and (III). In particular, both exocyclic double bonds [$\text{O3}{=}\text{C2} = 1.2105\ (19)$ Å and $\text{C3}{=}\text{C4} = 1.316\ (2)$ Å] are shorter than similar bonds observed in the O=C—C=C moiety (1.222 and 1.340 Å, respectively; Allen *et al.*, 1992). These bonds are separated by

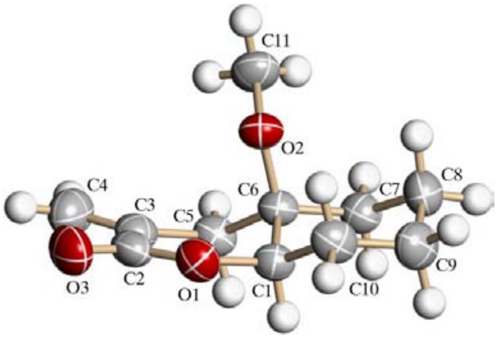


**Figure 1**
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

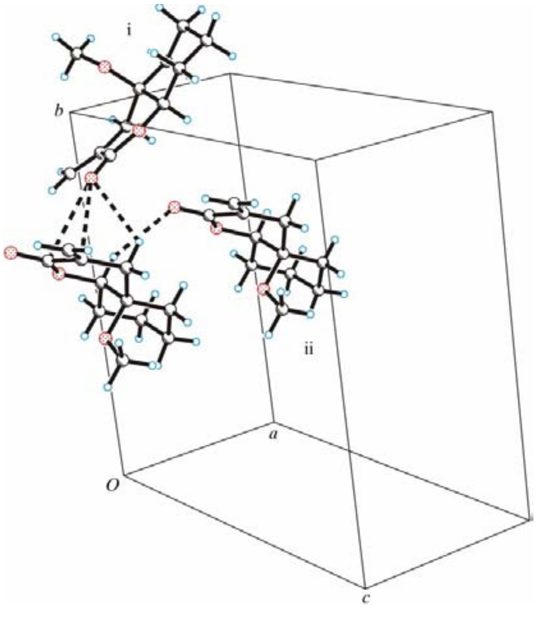


**Figure 2**
The intermolecular interactions (dashed lines) involving the carbonyl O3 atoms. [Symmetry codes: (i) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (ii) $1+x, y, z$.]

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[1] Part II: Krawczyk, Śliwiński & Wolf (2004).

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a relatively long C2—C3 bond [1.495 (2) Å; standard value 1.465 Å] and are not strictly coplanar, as shown by a non-zero value for the O3═C2—C3 ═C4 torsion angle [4.6 (2)°].

In the crystal structure of (I), the exocyclic carbonyl O3 atoms are involved in two kinds of intermolecular interactions, namely with atoms C2 and C3 of the O═C—$C_\alpha$═$C_\beta$ moiety, and very weak C—H···O interactions (Steiner; 1997; Steiner & Desiraju, 1998) involving the axial atoms H11 and H51 of the $\delta$-valerolactone ring (Fig. 2). The respective interatomic distances are given in Tables 1 and 2.

The simultaneous intermolecular interactions of the carbonyl O atom with the carbonyl C atom and the $C_\alpha$ atom of the O═C—$C_\alpha$═$C_\beta$ unsaturated system are uncommon among crystal structures examined to date. Only eight structures for which both intermolecular C···O distances are shorter than the sum of the respective van der Waals radii (3.22 Å; Bondi, 1964) are reported in the CSD. The most prominent examples are cuenicin acetate (Sen Gupta *et al.*, 1986) and cordifene oxide (Steurer & Podlech, 2002).

Presumably, in (I), the intermolecular interactions follow from the prevailing electrostatic attraction of the negatively charged atom O3 (−0.64 e) with the positively charged carbonyl atom C2 (0.87 e). However, the origin of the second interaction, that between two negatively charged atoms O3 and C3 (−0.20 e), is unclear.

## Experimental

The synthesis of enantiomerically pure $\alpha$-methylene-$\delta$-valerolactone, (I), was based on a highly stereoselective Michael reaction of a chiral imine derived from (*R*)-1-phenylethylamine and 2-methoxycyclohexanone with dicyclohexylammonium 2-(diethoxyphosphoryl)-acrylate. Subsequent reduction of the carbonyl group in the adduct with $KBH_4$ was followed by lactonization of the resulting 2-(diethoxyphosphoryl)-5-hydroxyalkanoic acid. The final step in the synthesis pathway was the Horner–Wadsworth–Emmons olefination of the resulting $\alpha$-phosphono-$\delta$-valerolactone with formaldehyde. The enantiomeric purity of (I) as higher than 0.99 was confirmed by gas-chromatographic analysis on a chiral column. Details of the procedure have been described elsewhere (Krawczyk & Śliwiński, 2003; Krawczyk, Śliwiński, Wolf & Bodalski, 2004). Colourless crystals of (I) (m.p. 397 K) were grown in 4 d by slow evaporation from a 1:1 mixture of methanol and ethyl acetate.

*Crystal data*

$C_{11}H_{16}O_3$
$M_r = 196.24$
Orthorhombic, $P2_12_12_1$
$a = 6.1555$ (2) Å
$b = 12.3990$ (2) Å
$c = 13.3019$ (2) Å
$V = 1015.23$ (4) Å$^3$
$Z = 4$
$D_x = 1.284$ Mg m$^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 4441 reflections
$\theta = 3.3$–70.6°
$\mu = 0.75$ mm$^{-1}$
$T = 293$ (2) K
Prism, colourless
0.30 × 0.20 × 0.15 mm

*Data collection*

Bruker SMART APEX CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2003)
$T_{\min} = 0.795$, $T_{\max} = 0.895$
5162 measured reflections
1816 independent reflections
1793 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 70.7°$
$h = -5 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 15$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.080$
$S = 1.06$
1816 reflections
185 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.0969P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.16$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.14$ e Å$^{-3}$
Extinction correction: *SHELXTL* (Bruker, 2003)
Extinction coefficient: 0.0045 (7)
Absolute structure: Flack (1983), with 720 Friedel pairs
Flack parameter: 0.0 (2)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—C2 | 1.3374 (18) | C2—C3 | 1.495 (2) |
| O1—C1 | 1.4490 (17) | C3—C4 | 1.316 (2) |
| O3—C2 | 1.2105 (19) | | |
| C3···O3$^{i}$ | 3.035 (2) | C2···O3$^{i}$ | 3.025 (2) |
| C4—C3—C2 | 117.42 (16) | C2—C3—C5 | 118.11 (12) |
| C4—C3—C5 | 124.46 (16) | | |
| C2—O1—C1—C6 | 32.16 (16) | O1—C2—C3—C5 | 5.81 (18) |
| O1—C1—C6—C5 | −58.90 (14) | C2—C3—C5—C6 | −34.72 (16) |
| C1—O1—C2—C3 | −4.28 (18) | C3—C5—C6—C1 | 59.24 (15) |

Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z$.

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H11···O3$^{ii}$ | 0.99 (2) | 2.68 (2) | 3.605 (2) | 156 (1) |
| C5—H51···O3$^{i}$ | 1.00 (2) | 2.65 (2) | 3.278 (2) | 121 (1) |

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (ii) $x + 1, y, z$.

Methyl H atoms were placed in calculated positions (C—H = 0.96 Å) and allowed for as riding atoms. All other H atoms were located in a difference Fourier map calculated after three cycles of anisotropic refinement, and their positional and isotropic displacement parameters were allowed to refine freely [C—H = 0.94 (2)–1.04 (2) Å]. The refinement of the Flack (1983) parameter is in agreement with the assigned absolute configuration. An attempt to refine the inverted structure led to a Flack parameter of 1.0 (2). Atomic charges derived from electrostatic potentials were calculated using *GAUSSIAN03* (Frisch *et al.*, 2003) at the MP2/6–311++G(*d*,*p*) level for the X-ray determined coordinates. Grid points were selected according to the *CHELPG* procedure of Breneman & Wiberg (1990).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Atomic charges derived from electrostatic potentials were calculated in the ACK CYFRONET, Kraków, Poland; support through computational grant Nos. 030/1999 and 050/1999 is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1200). Services for accessing these data are described at the back of the journal.

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