Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(S)-(+)-Homoterpenyl Methyl Ketone

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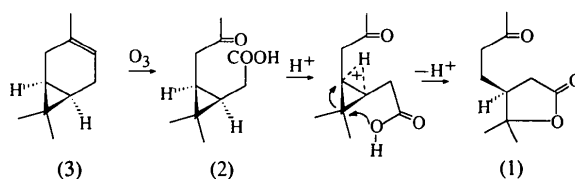
Abstract

In (+)-5,5-dimethyl-4-(3-oxobutyl)tetrahydrofuran-2-one, $C_{10}H_{16}O_3$, the absolute configuration at the chiral C atom is *S*. The five-membered ring adopts a deformed envelope conformation with the asymmetric C atom in the flap position. The oxobutyl group is planar.

Comment

Molecules containing γ-lactone subunits are useful compounds displaying interesting properties with regard to flavour and fragrance or their use in pharmaceutical chemistry. They also constitute an important class of synthetic intermediates for access to a variety of heterocyclic compounds (Giordano *et al.*, 1992; Matsuki *et al.*, 1994). Homoterpenyl methyl ketone (1) has been employed for the stereoselective synthesis of racemic

β-vetivone (Bozzato, Bachmann & Pesaro, 1974). Recently, lactone (1) was reported to be an intermediate in the synthesis of methyl-*trans*-chrysanthemate (Zhu-Jin, Ren-Rong & Yu-Gui, 1987). Optically active lactone (1) can be prepared from natural (+)- or (−)-α-pinene (Arcus & Bennett, 1955; Zhu-Jin *et al.*, 1987). Optical rotations of homoterpenyl methyl ketone (1) (in CHCl₃) are reported to be $[\alpha]_D = +58.6°$ ($c = 5.27$) (Arcus & Bennett, 1955), −58.6° ($c = 55$) (MacRae, Alberts, Carman & Shaw, 1979) and −57.73° ($c = 17$) (Zhu-Jin *et al.*, 1987). However, no pure enantiomers of α-pinene are commercially available and therefore homoterpenyl methyl ketone (1) obtained by the method described by Arcus & Bennett (1955) and Zhu-Jin *et al.* (1987) is racemized. The laevo-rotary enantiomer can be produced in another way by microbial oxidation of 1,8-cineole (MacRae *et al.*, 1979).

In the course of our investigation, we observed that when (−)-*cis*-3-acetonyl-2,2-dimethylcyclopropylacetic acid (2), obtained from (+)-car-3-ene (3) (Naves & Grampoloff, 1961), was treated with 85% orthophosphoric acid at 368 K, it resulted in the formation of (+)-lactone (1) in a yield of over 60%. After purification and crystallization, the molecular structure of (+)-lactone (1) was determined (Fig. 1) using data collected at room temperature. The absolute configuration at the chiral atom C3 was established to be *S*. The five-membered ring adopts a deformed envelope conformation with the C3 atom in the flap position. The oxobutyl group (C5, C6, C7, C8, O3) is planar, and the C5—C6 bond is antiperiplanar with respect to C7—C8 [torsion angle C5—C6—C7—C8 = 179.8 (2)°]. Fig. 2 presents a view of the crystal packing in (+)-lactone (1) showing the inter- and intramolecular hydrogen-bond contacts shorter then 2.65 Å (Table 3).
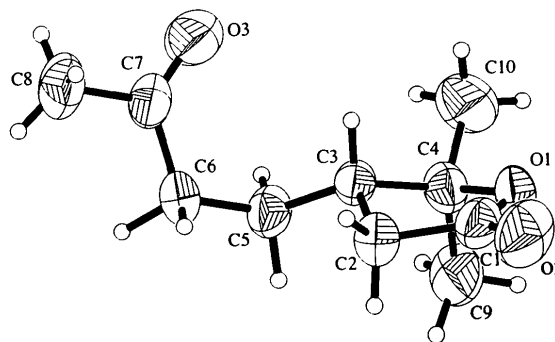

Fig. 1. Molecular structure of (+)-lactone (1) showing 50% probability displacement ellipsoids.
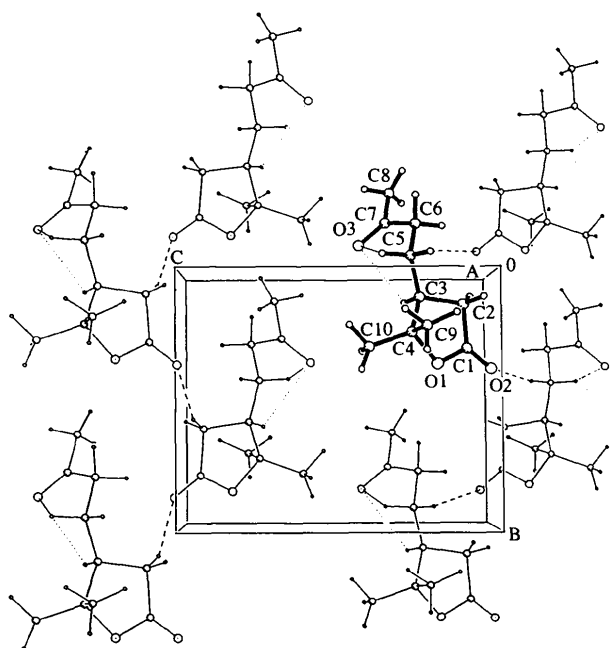
Fig. 2. Packing diagram of (+)-lactone (1) showing inter- and intra-molecular hydrogen contacts shorter then 2.65 Å (the a axis is behind the plane of the drawing).

As car-3-ene with the specific rotation value of +17.2 (2)° is considered to be the pure (1*S*,6*R*)-enantiomer (Misra, Soman & Dev, 1988), we conclude that the formation of (+)-homoterpenyl methyl ketone (1) occurs with retention of the configuration at C3 and that the product is homochiral.

In addition, the enantiopurity of lactone (1) was determined to be 100% by chiral phase GLC (β-cyclodextrin column, isothermal, 423 K); the compound showed no detectable evidence for the presence of (−)-enantiomer by comparison with its GLC racemized mixture.

Experimental

2 g of keto acid (2) {$[\alpha]_D = -18.2°$ ($c = 1$, $CHCl_3$)} obtained from car-3-ene (3) (Naves & Grampoloff, 1961) {$[\alpha]_D^{20} = +17.17°$ (neat)} was dissolved in 8 ml of 85% H_3PO_4 and kept at 368 K for 5 min. It was then poured into water, made alkaline with Na_2CO_3, extracted with $CHCl_3$ and vacuum distilled to give 1.35g of (1) (purity 92%, GC): b.p. 415–418 K/40 Pa, ^1H NMR (80 MHz, $CHCl_3$, TMS) $\delta = 2.58$–2.31 (br. m, 4H), 2.16 (s, 3H), 1.45 (s, 3H), 1.27 (s, 3H). The product (1) was purified by crystallization from hexane/ethyl acetate (3:2) to give crystals, purity >99.9% (GLC), m.p. 319 K, $[\alpha]_D^{20} = +60.7 (1)°$ ($c = 1$, $CHCl_3$).

Crystal data

$C_{10}H_{16}O_3$
$M_r = 184.24$
Monoclinic
$P2_1$
$a = 6.124 (2)$ Å
$b = 8.407 (3)$ Å
$c = 10.277 (3)$ Å
$\beta = 90.00 (3)°$
$V = 529.1 (3)$ Å^3
$Z = 2$
$D_x = 1.156$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 15.94$–29.39°
$\mu = 0.654$ mm^{-1}
$T = 291$ K
Plate
0.35 × 0.35 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical, ψ scan (North, Phillips & Mathews, 1968; Frenz, 1986)
$T_{min} = 0.9273$, $T_{max} = 0.9992$
4271 measured reflections
2135 independent reflections

1772 observed reflections
$[F > 8\sigma(F)]$
$R_{int} = 0.034$
$\theta_{max} = 75°$
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$
3 standard reflections frequency: 60 min intensity decay: 17.3%

Refinement

Refinement on F
$R = 0.0420$
$wR = 0.0487$
$S = 1.3698$
1772 reflections
175 parameters
All H-atom parameters refined, except H81, H82 and H83 where only H-atom U's refined
$w = 1/[\sigma^2(F) + 0.0003F^2]$
$(\Delta/\sigma)_{max} = 0.0007$

$\Delta\rho_{max} = 0.284$ e Å^{-3}
$\Delta\rho_{min} = -0.290$ e Å^{-3}
Extinction correction: SHELXTL/PC (Sheldrick, 1991)
Extinction coefficient: 0.011 (2)
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
O1	0.6254 (2)	0.3556	0.1678 (1)	0.0652 (3)
O2	0.8230 (3)	0.3737 (3)	−0.0119 (2)	0.0900 (4)
O3	0.9316 (4)	−0.1377 (3)	0.4164 (2)	0.1021 (5)
C1	0.7367 (3)	0.2919 (3)	0.0689 (2)	0.0584 (3)
C2	0.7334 (3)	0.1127 (2)	0.0794 (2)	0.0545 (3)
C3	0.6756 (2)	0.0859 (2)	0.2213 (1)	0.0451 (3)
C4	0.5326 (3)	0.2307 (3)	0.2524 (2)	0.0551 (3)
C5	0.5732 (3)	−0.0748 (2)	0.2528 (2)	0.0559 (4)
C6	0.7265 (3)	−0.2140 (2)	0.2315 (2)	0.0619 (4)
C7	0.9094 (3)	−0.2291 (2)	0.3279 (2)	0.0613 (4)
C8	1.0620 (4)	−0.3669 (3)	0.3082 (3)	0.0844 (6)
C9	0.2941 (3)	0.2116 (3)	0.2125 (3)	0.0764 (5)
C10	0.5543 (5)	0.2891 (4)	0.3906 (2)	0.0883 (6)

Table 2. *Selected geometric parameters* ($\AA$, °)

O1—C1	1.336 (2)	C3—C5	1.524 (2)
O1—C4	1.477 (2)	C4—C9	1.525 (3)
O2—C1	1.201 (2)	C4—C10	1.509 (3)
O3—C7	1.198 (3)	C5—C6	1.516 (3)
C1—C2	1.511 (3)	C6—C7	1.501 (3)
C2—C3	1.518 (2)	C7—C8	1.502 (3)
C3—C4	1.533 (3)		

C1—O1—C4	111.1 (1)	O1—C4—C10	106.8 (2)
O1—C1—O2	121.4 (2)	C3—C4—C9	114.0 (2)
O1—C1—C2	109.8 (2)	C3—C4—C10	113.9 (2)
O2—C1—C2	128.8 (2)	C9—C4—C10	111.8 (2)
C1—C2—C3	102.7 (1)	C3—C5—C6	113.5 (1)
C2—C3—C4	102.5 (1)	C5—C6—C7	115.6 (2)
C2—C3—C5	115.6 (1)	O3—C7—C6	122.1 (2)
C4—C3—C5	115.1 (1)	O3—C7—C8	121.8 (2)
O1—C4—C3	102.8 (1)	C6—C7—C8	116.1 (2)
O1—C4—C9	106.6 (2)		

O1—C1—C2—C3	−19.5 (2)	C1—C2—C3—C5	157.0 (1)
O1—C4—C3—C2	−31.8 (2)	C2—C1—O1—C4	−1.2 (2)
O1—C4—C3—C5	−158.1 (1)	C2—C3—C4—C9	83.1 (2)
O2—C1—O1—C4	179.2 (2)	C2—C3—C4—C10	−147.0 (2)
O2—C1—C2—C3	160.0 (2)	C2—C3—C5—C6	65.7 (2)
O3—C7—C6—C5	0.5 (3)	C3—C5—C6—C7	71.4 (2)
C1—O1—C4—C3	21.3 (2)	C4—C3—C5—C6	−175.1 (2)
C1—O1—C4—C9	−99.0 (2)	C5—C3—C4—C9	−43.2 (2)
C1—O1—C4—C10	141.4 (2)	C5—C3—C4—C10	86.8 (2)
C1—C2—C3—C4	31.0 (2)	C5—C6—C7—C8	179.8 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C2—H21$\cdots$O2^i	1.01 (1)	2.51 (2)	3.449 (3)	154 (1)
C3—H31$\cdots$O3	0.97 (1)	2.64 (2)	3.164 (3)	114 (1)
C5—H51$\cdots$O2^{ii}	1.02 (2)	2.49 (2)	3.493 (3)	167 (2)
C5—H52$\cdots$O3	0.99 (2)	2.60 (2)	2.815 (3)	92 (1)
C6—H61$\cdots$O2^i	1.00 (2)	2.80 (2)	3.640 (3)	142 (1)
C6—H62$\cdots$O1^{iii}	1.06 (2)	2.76 (2)	3.729 (2)	152 (2)
C9—H92$\cdots$O2^{ii}	1.04 (2)	2.73 (2)	3.583 (4)	139 (2)

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

Anisotropic displacement parameters were applied for all non-H atoms. H atoms were found in a difference Fourier map and refined isotropically, except H atoms attached to C8, which were set as riding and refined isotropically. The absolute structure was determined by the Rogers η-test (Rogers, 1981) (using *SHELXTL/PC*; Sheldrick, 1991). Results: $\eta = 1.1$ (3), $\eta_{inv} = -1.1$ (3).

Data collection and cell refinement: *CAD*-4 (Schagen, Straver, van Meurs & Williams, 1989; Frenz, 1986). Intensity data correction: *DECAY* (*SDP*; Frenz, 1986); correction factors: 1.00007 (min) and 1.09991 (max). Structure solution and refinement: *SHELXTL/PC* (Sheldrick, 1991). Molecular graphics: *SHELXTL/PC*; *CSU* (Vicković, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1217). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diethyl 2,5-Dihydroxyterephthalate at 200 K

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Abstract

The crystal structure of the title compound, $C_{12}H_{14}O_6$, has been determined by X-ray diffraction at 200 K. The ester molecules, which are connected by intermolecular O—H$\cdots$O hydrogen bonds, form infinite strings along the *b* axis. Within the molecules, both ester groups as well as the hydroxy H atoms are almost in the plane of the six-membered ring, thus allowing the formation of intramolecular O—H$\cdots$O hydrogen bonds. Each hydroxy H atom is therefore involved in a bifurcated inter/intramolecular hydrogen bond.

Comment

Halogenated terephthalic acid esters are well known for their conformational polymorphism (Byrn, Curtin & Paul, 1972; Yang, Richardson & Dunitz, 1985, 1989) due to the formation of different intra- and intermolecular hydrogen-bond patterns as well as the formation of halogen–oxygen contacts. Our investigations on diethyl 3,6-dibromo-2,5-dihydroxyterephthalate have established that this compound crystallizes in two different crystal forms which differ in their molecular conformation as well as in their hydrogen bonding and halogen–oxygen interactions (Näther, Nagel, Bock, Seitz & Havlas,