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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.051
 wR factor = 0.167
Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

7-Hydroxy-2,2,7-trimethylperhydronaphthalene-1,5-dione

The title compound, $\text{C}_{13}\text{H}_{20}\text{O}_3$, crystallizes as a racemic mixture in which the two enantiomeric forms of the molecule are related by an inversion center. The crystal structure confirms the one proposed on the basis of spectroscopic data and provides the information required to assign the relative stereochemistry of the chiral centers of the molecule. The crystal packing is directed by intermolecular hydrogen bonds and short intramolecular $\text{C}-\text{H}\cdots\text{O}$ contacts.

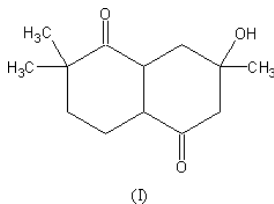
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Comment

Decalin ring systems represent a common structural motif of a large variety of active molecules (Fraga, 2001; Faulkner, 2002; Hanson, 2003). In particular, terpenoids and steroids display a wide range of biological activities. The preparation of this bicyclic unit with appropriate stereochemistry has attracted widespread attention in the field of medicinal and synthetic organic chemistry, not only in consideration of their abundance in nature, but also their usefulness as versatile synthetic building blocks. Consequently, numerous methodologies have been developed and continue to be explored for its synthesis (Varner & Grossman, 1999; Tokoroyama, 2000). Among them, annulations routes based on the combination of classical and modified carbonyl reactions have proved to be very useful strategies to access various carbocyclic frameworks.



Recently, in the course of our studies on the application of cyclocondensation reactions of acyclic triketones, a racemic mixture of the title compound, (I), was prepared (Mischne, 2003). The structure was elucidated on the basis of the analysis of its ^1H and ^{13}C NMR spectroscopic data, and a preliminary relative stereochemical assignment was made on the basis of $^1\text{H}-^1\text{H}$ J -coupling values (Mischne, 2003). However, due to the potential use of this compound as an intermediate in the synthesis of more complex natural product analog products, it was important to unambiguously confirm the proposed structure and the relative stereochemistry by single-crystal X-ray diffraction.

The compound crystallizes in the triclinic space group $P\bar{1}$ with an inversion center relating the two enantiomeric forms of the molecule. Fig. 1 shows one of these enantiomeric forms,

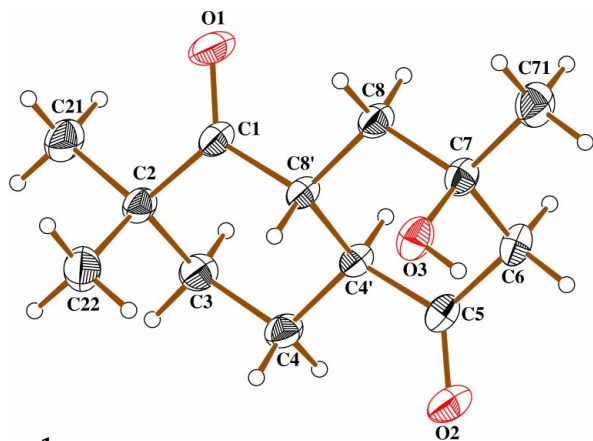


Figure 1
ORTEP drawing (Zsolnai & Pritzkow, 1995) of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

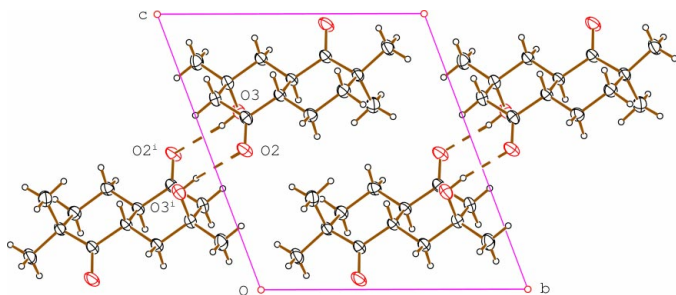


Figure 2
ORTEP packing diagram (Zsolnai & Pritzkow, 1995) projected on to the *bc* plane. Intermolecular hydrogen bonds are marked as dashed lines. [Symmetry code: (i) $2 - x, 2 - y, 1 - z$.]

consisting of two *trans*-fused cyclohexanone rings substituted by one hydroxyl and three methyl groups. All the geometric parameters (Table 1) are consistent with those reported for other *trans*-decalindione systems (Ariel & Trotter, 1984; Garcia *et al.*, 1991).

As in the case of the *trans*-decalin-1,5-dione structure, each cyclohexanone ring has an almost ideal chair conformation. The puckering parameters are $\theta = 0.66$ (19) $^\circ$ and $Q_T = 0.5615$ (19) Å for the C1–C8' ring and $\theta = 2.02$ (19) $^\circ$ and $Q_T = 0.5735$ (19) Å for the C4'–C8' ring (Cremer & Pople, 1975). The sp^2 hybridization of atoms C1 and C5 place the carbonyl O atoms (O1 and O3) coplanar with the C atoms of the rings in which they are located and bisect the Cremer and Pople normal planes. The respective angles with these planes are 53.29 (11) and 54.53 (11) $^\circ$. The hydroxyl and methyl (C22) groups on C7 and C2 adopt axial positions, the other two methyl substituent groups (C21 and C71) being in equatorial positions.

The molecule has three chiral centers, *viz.* C4', C7 and C8'. Since the compound was obtained and crystallized as a racemic mixture, only a relative assignment of the absolute configuration of these chiral centers can be made: an *S*(*R*) configuration for C7 and C8' and *R*(*S*) configuration for C4'.

The crystal packing is directed by a pair of intermolecular hydrogen bonds that link two inversion-related molecules, generating discrete dimeric units [O3–H3 \cdots O2ⁱ: O3–H3 =

0.82 Å, H3 \cdots O2 = 2.09 Å, O3–H3 \cdots O2 = 172 $^\circ$; symmetry code: (i) $2 - x, 2 - y, 1 - z$]. Another short intramolecular contact involving atom O3 (C8'–H8' \cdots O3: C8'–H8' = 0.98 Å, H8' \cdots O3 = 2.50 Å and C8'–H8' \cdots O3 = 101 $^\circ$) also influences the packing and stabilizes the conformation of the molecule.

Experimental

The title compound was synthesized *via* the sequential intramolecular Michael/aldol strategy, as described previously (Mischne, 2003). Suitable single crystals for X-ray diffraction were obtained by vapor diffusion (ethyl acetate/petroleum ether) at room temperature.

Crystal data

C₁₃H₂₀O₃
M_r = 224.29
 Triclinic, *P* $\bar{1}$
a = 6.0562 (13) Å
b = 9.827 (2) Å
c = 11.1075 (16) Å
 α = 109.289 (14) $^\circ$
 β = 102.766 (15) $^\circ$
 γ = 92.771 (19) $^\circ$
V = 603.2 (2) Å³

Z = 2
D_x = 1.235 Mg m^{−3}
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 35.0–47.5 $^\circ$
 μ = 0.09 mm^{−1}
T = 293 (2) K
 Block, colorless
 0.30 × 0.15 × 0.10 mm

Data collection

Rigaku AFC-7S diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan
 (MSC/AFC Diffractometer Control Software; Molecular Structure Corporation, 1993)
 T_{\min} = 0.965, T_{\max} = 0.991
 3565 measured reflections
 2768 independent reflections

1951 reflections with $I > 2\sigma(I)$
 R_{int} = 0.030
 θ_{max} = 27.5 $^\circ$
 h = $-7 \rightarrow 7$
 k = $-2 \rightarrow 12$
 l = $-14 \rightarrow 14$
 3 standard reflections
 every 150 reflections
 intensity decay: 2.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.051
 $wR(F^2)$ = 0.167
 S = 1.04
 2768 reflections
 149 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0851P)^2 + 0.1359P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.055 (11)

Table 1

Selected geometric parameters (Å, $^\circ$).

C1–O1	1.2115 (19)	C2–C22	1.533 (3)
C1–C8'	1.5222 (19)	C2–C3	1.540 (2)
C1–C2	1.528 (2)	C6–C5	1.500 (2)
C8–C8'	1.522 (2)	C6–C7	1.542 (2)
C8–C7	1.528 (2)	O2–C5	1.214 (2)
C4'–C4	1.514 (2)	C7–O3	1.429 (2)
C4'–C5	1.515 (2)	C7–C71	1.522 (2)
C4'–C8'	1.551 (2)	C4–C3	1.524 (2)
C2–C21	1.528 (2)		
O1–C1–C8'	121.32 (14)	C1–C2–C3	107.03 (13)
O1–C1–C2	122.12 (14)	C5–C6–C7	110.42 (13)
C8'–C1–C2	116.48 (12)	O3–C7–C71	109.78 (14)
C8'–C8–C7	111.47 (12)	C8–C7–C6	109.90 (13)
C4–C4'–C8'	112.03 (13)	C4'–C4–C3	110.79 (12)
C5–C4'–C8'	107.69 (12)	C4–C3–C2	113.71 (13)
C8–C8'–C1	112.79 (12)	O2–C5–C6	122.73 (14)
C1–C8'–C4'	108.38 (12)	O2–C5–C4'	122.31 (15)
C21–C2–C22	108.60 (15)	C6–C5–C4'	114.95 (13)

The H atoms were included in geometrically calculated positions, with fixed C–H distances of 0.97 Å for CH₂ groups and 0.96 Å for CH₃ groups, and with an O–H distance of 0.82 Å for the hydroxyl group. The $U_{\text{iso}}(\text{H})$ values for these H atoms were fixed at $1.2U_{\text{eq}}$ of the attached atom.

Data collection: (*MSC/AFC Diffractometer Control Software*; Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON* (Spek, 2003) and *enCIFer* (Allent *et al.*, 2004).

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