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## Key indicators

Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(C-C) = 0.003$  Å  
 $R$  factor = 0.052  
 $wR$  factor = 0.139  
Data-to-parameter ratio = 13.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**(1R\*,4aR\*,8aS\*)-2-Oxoperhydronaphthalene-  
1-acetic acid: formation of heterogeneous  
carboxyl dimers in a bicyclic  $\gamma$ -keto acid**

The asymmetric unit chosen for the title racemate,  $C_{12}H_{18}O_3$ , contains two nearly identical molecules of opposite handedness, differing only slightly in the rotation of their side-chains and joined by pseudo-centrosymmetric  $O-H\cdots O$  hydrogen bonding [ $O\cdots O = 2.647(2)$  and  $2.622(2)$  Å;  $O-H\cdots O = 173$  and  $173^\circ$ ]. Three close intermolecular  $C-H\cdots O$  contacts exist.

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## Comment

Our study of hydrogen-bonding modes in crystalline keto-carboxylic acids includes a variety of examples based on the naphthalene skeleton. Many of these are accessible as enones *via* annulation reactions of cyclohexanones, and subsequent alkene reduction may then provide additional isoskeletal keto acids. The title racemate, (I), is the reduction product of an unsaturated keto acid whose hydrate structure we have previously reported (Lalancette *et al.*, 2002).

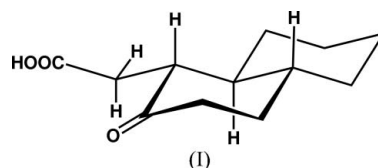
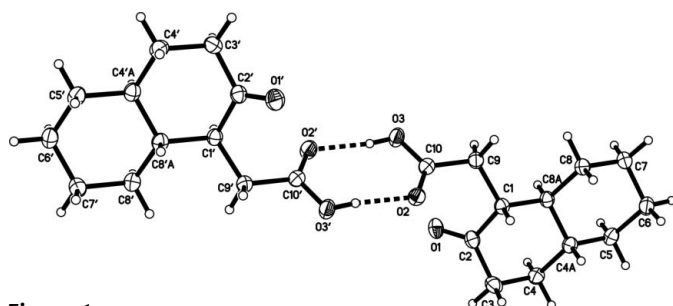


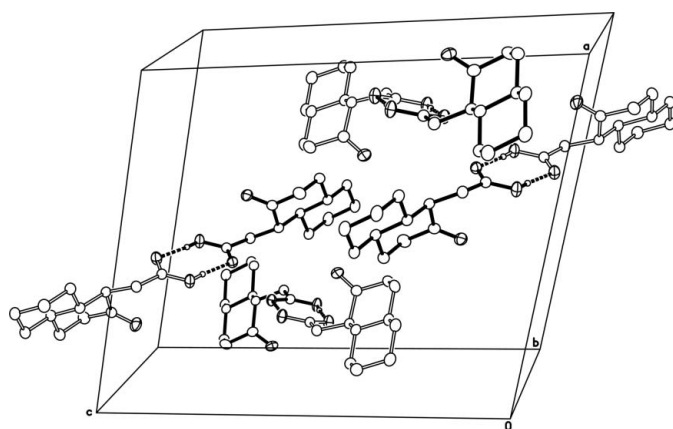
Fig. 1 shows the chosen asymmetric unit, consisting of two very similar molecules of opposite handedness, designated (I) and (I'). The *trans* bicyclic portion of (I) is rigid and all significant conformational differences are produced by small rotations within the side-chain, in which the substituents on C1 and C9 are staggered so as to minimize steric interactions with C10. Direct comparison of (I) and (I') by overlaying versions stripped of the carboxyl group and all H atoms finds an r.m.s. deviation of 0.013 (11) Å; when C10 is included, this number rises to 0.04 (3) Å. Torsion angle  $C8A-C1-C9-C10$  is  $169.51(16)^\circ$  in (I), while for (I') this angle is  $-174.81(16)^\circ$  and the carboxyl group is turned so that torsion angle  $O2-C10-C9-C1$  is  $38.6(3)^\circ$  in (I) and  $-29.4(3)^\circ$  in (I'). The net result is a dihedral angle for the ketone ( $O1-C1-C2-C3$ ) *versus* the carboxyl ( $O2-O3-C10-C9$ ) of  $71.54(8)^\circ$  in (I) and  $70.36(8)^\circ$  in (I').

Although centers of symmetry are present in the cell, none is involved in the hydrogen bonding, which pairs (I) and (I') in a stereochemically heterogeneous carboxyl dimer. The absence of any element of such symmetry in carboxyl dimers (Lalancette *et al.*, 1991, 1996; Lalancette & Thompson, 2003; Davison *et al.*, 2005) is much more commonly encountered in chiral non-racemates than in cases like (I) where centrosym-



**Figure 1**

The asymmetric unit for (I); because molecules (I) and (I') have slight conformational differences, their relationship is pseudo-centrosymmetric. Displacement ellipsoids are drawn at the 40% probability level. Dashed lines indicate hydrogen bonds.



**Figure 2**

A partial packing diagram, illustrating the centrosymmetric arrangement of the heterogeneous dimers of the asymmetric unit. Dashed lines indicate hydrogen bonds. For clarity, all carbon-bound H atoms have been removed and molecules of (I') are distinguished by the use of hollow bonds. Displacement ellipsoids are drawn at the 40% probability level.

metric pairing is possible (Gavezzotti & Filippini, 1994; Allen *et al.*, 1999; Sørensen & Larsen, 2003). The C—O bond lengths and C—C—O angles conform to values typical for highly ordered dimeric carboxyls (Borthwick, 1980) and no significant averaging by disorder is observed (Table 1).

Fig. 2 illustrates the packing of the cell, with the dimers of the asymmetric unit arrayed centrosymmetrically about  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . Three intermolecular C—H...O close approaches exist, all making contacts with disparate halves of asymmetric units in adjoining cells (Table 2). These distances all lie within the 2.7 Å range we standardly survey for non-bonded C—H...O packing interactions (Steiner, 1997).

## Experimental

Compound (I) was produced from the hydrate of the  $\beta'$ -carboxy- $\alpha,\beta$ -unsaturated ketone we have previously reported (Lalancette *et al.*, 2002) by reduction with Li in liquid  $\text{NH}_3$ , from which the *trans* stereochemistry observed in (I) is expected. Compound (I) was also isolated from atmospheric pressure hydrogenations of the same unsaturated keto acid over a 5% Pd/C catalyst in a variety of solvents. Recrystallization from  $\text{Et}_2\text{O}$ -hexane or EtOAc yielded material suitable for X-ray analysis (m.p. 391 K). The solid-state (KBr) IR

spectrum of (I) features a single broad peak at  $1704\text{ cm}^{-1}$  for both C=O functions in both molecules, typical of carboxyl-paired keto acids. In  $\text{CHCl}_3$  solution, this combined absorption is seen at  $1709\text{ cm}^{-1}$ .

## Crystal data

$\text{C}_{12}\text{H}_{18}\text{O}_3$   
 $M_r = 210.26$   
 Monoclinic,  $P2_1/n$   
 $a = 15.7329(6)\text{ \AA}$   
 $b = 7.8709(3)\text{ \AA}$   
 $c = 18.3530(7)\text{ \AA}$   
 $\beta = 105.155(2)^\circ$   
 $V = 2193.65(14)\text{ \AA}^3$

$Z = 8$   
 $D_x = 1.273\text{ Mg m}^{-3}$   
 Cu  $K\alpha$  radiation  
 $\mu = 0.73\text{ mm}^{-1}$   
 $T = 100(2)\text{ K}$   
 Block, colorless  
 $0.30 \times 0.23 \times 0.22\text{ mm}$

## Data collection

Bruker SMART CCD APEX-II  
 area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 2001)  
 $T_{\min} = 0.82$ ,  $T_{\max} = 0.86$

12997 measured reflections  
 3748 independent reflections  
 3266 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$   
 $\theta_{\max} = 67.6^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.139$   
 $S = 1.04$   
 3748 reflections  
 273 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 2.4583P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.38\text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.24\text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: none

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

O2—C10	1.237 (2)	O3—C10	1.303 (2)
O2'—C10'	1.231 (3)	O3'—C10'	1.303 (2)
O2—C10—C9	121.52 (17)	O2'—C10'—C9'	122.17 (17)
O3—C10—C9	114.88 (18)	O3'—C10'—C9'	113.95 (18)

**Table 2**

Hydrogen-bond and close contact geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O3—H3C...O2'	0.84	1.81	2.647 (2)	173
O3'—H3'C...O2	0.84	1.79	2.622 (2)	173
C8'—H8'A...O3 <sup>i</sup>	0.99	2.61	3.534 (2)	156
C1—H1A...O1 <sup>ii</sup>	1.00	2.51	3.398 (2)	147
C4A—H4C...O1 <sup>ii</sup>	1.00	2.62	3.489 (2)	145

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

All H atoms in (I) were found in electron-density difference maps. The O—H groups were constrained to idealized positions with distances fixed at 0.84 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The methylene and methine H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C—H = 0.99 and 1.00 Å, respectively, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 2000); cell refinement: SAINT-Plus (Bruker, 2000); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000); software used to prepare material for publication: SHELXTL.

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