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Key indicators

Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.001\text{ \AA}$
 R factor = 0.037
 wR factor = 0.109
Data-to-parameter ratio = 22.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrahydro-2,6,6-trimethyl-1,4-pyran-2,5-
dicarboxylic acid (cineolic acid)

In the title compound, $\text{C}_{10}\text{H}_{16}\text{O}_5$, the carboxylate group at the C-2 position is axial, but that at C-5 is equatorial. These carboxylate groups form hydrogen-bonded rings [average $\text{O}\cdots\text{O}'$ distance = $2.64(1)\text{ \AA}$] across the inversion centers at $(\frac{1}{2}, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, respectively, linking the molecules into stepped chains along the bc diagonal of the cell.

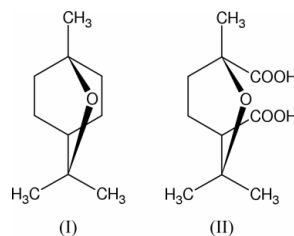
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Comment

Hydrogen bonding to give supramolecular arrays is a major factor in the design of the crystal structures of polycarboxylic acids and their salts with protonated cations (Jeffrey & Saenger, 1994). Network analysis of hydrogen bonding in these systems was introduced by Etter (1990) and extended by Bernstein *et al.* (1995). Structures of this type have been studied by many groups. Examples from this laboratory include di-, tri- and tetracarboxylates (Barnes & Paton, 1988; Barnes *et al.*, 1991, 1998; Barnes & Barnes, 1996). Oxidation of 1,8-epoxy-*p*-menthane, (1,8-cineol), (I), was reviewed by Simonsen (1931). The first product is racemic cineolic acid, (II) (Fig. 1). During this reaction, the configuration of the ring $\text{O1}\cdots\text{C6}$ changes from boat to chair as the bond between C8 and C11 is broken. The carboxylate group at C2 is still axial [$\text{C6}-\text{O1}-\text{C2}-\text{C8} = 76.17(7)^\circ$], but that at C5 takes the equatorial position [$\text{O1}-\text{C6}-\text{C5}-\text{C11} = -178.54(6)^\circ$]. The planes of the carboxylate groups C2/C8/O9/O10 and C5/C11/O12/O13 make angles of $89.00(3)$ and $57.23(3)^\circ$ to the ring plane O1/C3/C4/C6. The torsion angles $\text{O9}-\text{C8}-\text{C2}-\text{C3}$ and $\text{C6}-\text{C5}-\text{C11}-\text{O13}$ are $-16.61(9)$ and $-82.90(8)^\circ$, respectively. All bond lengths and angles have typical values.



The carboxylate groups form typical $R_2^2(8)$ intermolecular hydrogen-bonded rings across the centers of inversion at $(\frac{1}{2}, 0, 0)$ for C8 [$\text{O9}\cdots\text{O10}^i = 2.666(9)\text{ \AA}$] and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for C11 [$\text{O13}\cdots\text{O14}^{ii} = 2.623(9)\text{ \AA}$] [symmetry codes (i) $1-x, -y, -z$; (ii) $1-x, 1-y, 1-z$]. As a result of the (axial + equatorial) arrangement of the carboxylate groups the hydrogen-bonded chains (Fig. 2), which lie along the bc diagonal of the cell, form steps with the plane C2/C8/O9/O10, making an angle of $81.31(3)^\circ$ with C5/C11/O12/O13. The formation of hydrogen-bonded chains occurs commonly in dicarboxylic acids in which the acid groups are back to back across the

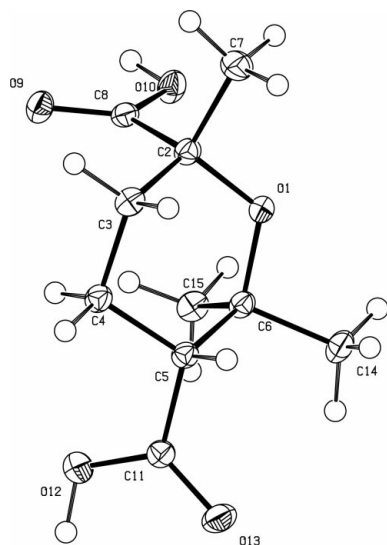


Figure 1
The structure of (II), showing ellipsoids at the 50% probability level.

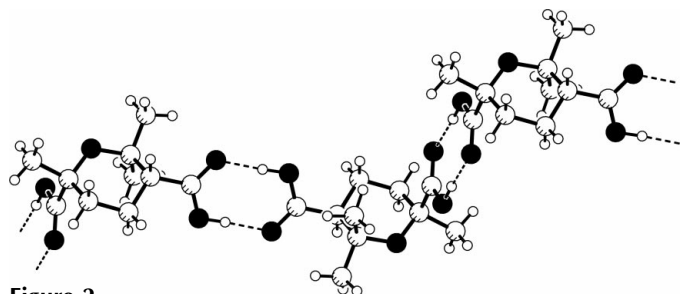


Figure 2
Hydrogen-bonded chain in (II).

molecule. In (II), the effect is a staircase in the *a* direction, unlike the alternate up and down molecules in the chains of camphoric acid (Barnes *et al.*, 1991), the zigzag chains in *trans*-cyclohexane-1,4-dicarboxylic acid (Luger *et al.*, 1972) or the flat chains in fumaric acid (Brown, 1966; Bednowitz & Post, 1966).

The structure of (II) was also determined from data collected at 296 K. There were no structural differences [$a = 6.5441$ (9), $b = 6.6087$ (7), $c = 13.9443$ (15) Å, $\alpha = 87.317$ (9), $\beta = 88.879$ (10), $\gamma = 64.321$ (10)°; $R1$ 0.041 for 2140 reflections with $I > 2\sigma(I)$].

Experimental

1,8-Cineol (10 ml) was oxidized with KMnO_4 as reported by Wallach & Gildermeister (1888). The cineolic acid was recrystallized from water.

Crystal data

$\text{C}_{10}\text{H}_{16}\text{O}_5$
 $M_r = 216.23$
Triclinic, $P\bar{1}$
 $a = 6.4737$ (3) Å
 $b = 6.5302$ (3) Å
 $c = 13.8836$ (6) Å
 $\alpha = 86.935$ (3)°
 $\beta = 88.987$ (3)°
 $\gamma = 64.078$ (3)°
 $V = 527.11$ (4) Å³

$Z = 2$
 $D_x = 1.362$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 5956 reflections
 $\theta = 2.9$ – 33.7 °
 $\mu = 0.11$ mm⁻¹
 $T = 100$ (2) K
Block, colorless
 $0.46 \times 0.32 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 φ and ω scans
Absorption correction: none
6332 measured reflections
3260 independent reflections

3044 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$
 $\theta_{\text{max}} = 31.0$ °
 $h = -9 \rightarrow 9$
 $k = -9 \rightarrow 9$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.109$
 $S = 1.11$
3260 reflections
145 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0704P)^2 + 0.0601P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.017$
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C2—C8	1.5374 (10)	C8—O10	1.3186 (9)
C5—C11	1.5066 (9)	C11—O13	1.2491 (9)
C8—O9	1.2231 (9)	C11—O12	1.2943 (9)
O9—C8—O10	123.46 (6)	O13—C11—O12	122.79 (7)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O10—H10A \cdots O9 ⁱ	0.922 (13)	1.745 (13)	2.6656 (8)	177.3 (12)
O12—H12A \cdots O13 ⁱⁱ	0.945 (13)	1.680 (13)	2.6234 (8)	177.1 (12)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, 1 - y, 1 - z$.

H atoms attached to C atoms were placed in calculated positions and allowed to ride during the refinement. Isotropic displacement parameters were constrained to be $1.3U_{\text{eq}}$ of the parent C atom. H atoms of the carboxylate groups were located from a difference synthesis. The positional and isotropic displacement parameters of these H atoms were allowed to refine.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON*, *Spek* (1999); software used to prepare material for publication: *SHELXL97*.

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