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(+)-Camphoracetic acid: catemeric hydrogen bonding in a γ-keto acid

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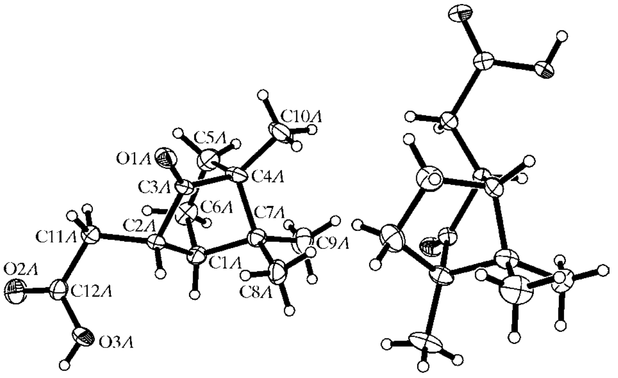
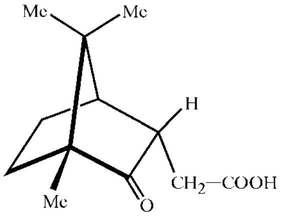


Figure 1
A view of the asymmetric unit of (I), with the atom-numbering scheme shown for molecule (I*A*); the second molecule in the asymmetric unit, (I*B*), is numbered in a similar manner. Displacement ellipsoids are set at the 20% probability level and H atoms are shown as small spheres of arbitrary radii.

The title compound, (1*R*)-4,7,7-trimethyl-3-oxobicyclo[2.2.1]-heptane-2-*endo*-acetic acid, $C_{12}H_{18}O_3$, like its lower homolog, forms carboxyl-to-ketone hydrogen-bonding catemers ($Z' = 2$) [O···O = 2.729 (5) and 2.707 (5) Å, and O—H···O = 165 and 170°] with screw-related components. The two molecules of the asymmetric unit differ slightly in conformation and produce two counter-aligned hydrogen-bonding chains, both aligned with the *b* axis. Close intermolecular C—H···O═C contacts exist for the ketone group of one molecule and for both the ketone and carboxyl functions in the other.

Comment

Simple crystalline carboxylic acids typically aggregate as hydrogen-bonding dimers, a pattern that often changes when other hydrogen-bonding functionalities are present. In our X-ray study of the five known hydrogen-bonding motifs for keto acids, we have found that carboxyl pairing is inhibited whenever centrosymmetry is thwarted (Lalancette & Thompson, 2003) or molecular flexibility is severely curtailed (Lalancette, Brunskill & Thompson, 1999; Barcon *et al.*, 2002). Hence, our attention has often centered on single enantiomers and on cyclic systems. The title compound, (I), incorporates both these restraints, and the observed hydrogen bonding involves carboxyl-to-ketone chains (catemers).



(I)

The category of γ-keto acids to which (I) belongs is rich in hydrogen-bonding types, embracing dimers, internal hydrogen bonds, and catemers of the screw, translational and glide types. In the lower homolog of (I), namely camphorcarboxylic acid (Lalancette *et al.*, 1991), both the enantiomeric and racemic forms exhibit the catemeric hydrogen-bonding arrangement. The relationship of camphorcarboxylic acid to (I) is of interest because we have found racemic cases in which homologation by a single CH_2 unit suffices to shift the hydrogen-bonding pattern from catemer to dimer (Lalancette, Brunskill & Thompson, 1999; Barcon *et al.*, 2002). This is believed to reflect the expanded repertoire of centrosymmetric dimerization patterns of low energy that results from greater molecular flexibility. However, in non-racemates, this flexibility is typically overridden by the unavailability of centrosymmetric modes (Coté *et al.*, 1997; Lalancette, Thompson & Brunskill, 1999).

Fig. 1 presents a view of the asymmetric unit of (I) with the atom-numbering scheme. Compound (I) is skeletally rigid except for rotation about the C2—C11 and C11—C12 bonds, and the two molecules differ almost solely in slight rotations about these two bonds. Both molecules adopt a C2—C11-staggered conformation, with the carboxyl aimed away from the ketone. In molecule (I*A*), the C3*A*—C2*A*—C11*A*—C12*A* torsion angle is −167.6 (4)°, while in (I*B*) this angle is −171.9 (4)°. The carboxyl group is rotated so that the O3—C12—C11—C2 torsion angles are 23.7 (7) and 21.3 (7)° in (I*A*) and (I*B*), respectively. The resulting dihedral angle between the carboxyl and ketone planes (O2—C12—O3 *versus* C2—C3—C4—O1) is 80.1 (2)° in the case of (I*A*) and 75.9 (2)° for (I*B*).

The partial averaging of C—O bond lengths and C—C—O angles by disorder often found in acids is seen only in the dimeric hydrogen-bonding mode, the geometry of which allows transposition of the two carboxyl O atoms. As in other catemers, no significant averaging is observed for the carboxyl groups of (I*A*) and (I*B*). The bond lengths for (I*A*) are 1.190 (6) and 1.304 (6) Å, with angles of 124.4 (5) and 113.0 (5)°, while for (I*B*) these lengths are 1.171 (5) and 1.326 (6) Å, with angles of 123.7 (5) and 111.7 (5)°. Our own survey of 56 non-dimeric keto acid structures gives average values of 1.200 (10) and 1.32 (2) Å, and 124.5 (14) and 112.7 (17)° for these lengths and angles, in accord with typical

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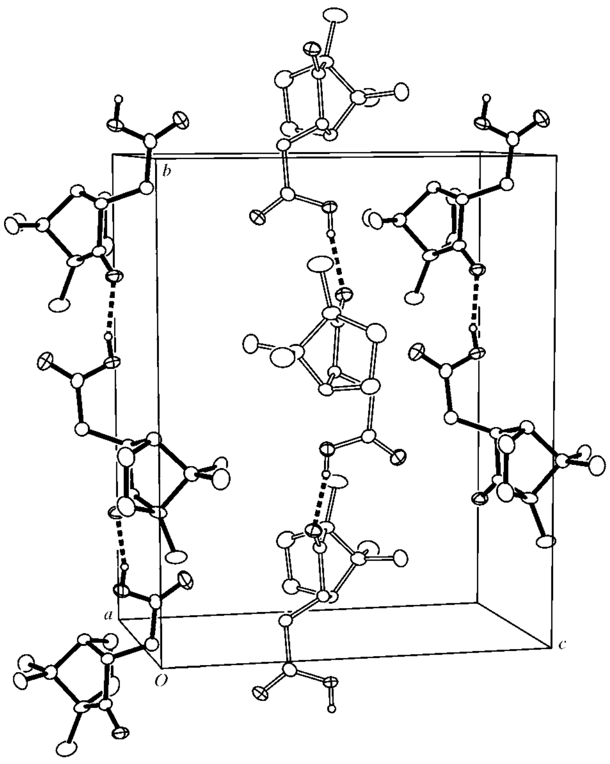

Figure 2
A packing diagram for (I), with extracellular molecules, showing the two counterdirectional acid-to-ketone catemers. Heavy bonds denote molecule (I*A*) and open bonds are used for molecule (I*B*). For clarity, all C-bound H atoms have been omitted. Displacement ellipsoids are set at the 20% probability level.

values of 1.21 and 1.31 Å, and 123 and 112° cited for highly ordered dimeric carboxyls (Borthwick, 1980). The three methyl groups present are fully ordered in both (I*A*) and (I*B*) and staggered relative to the substituents at their points of attachment.

Fig. 2 shows a packing diagram for the cell of (I). Each molecule in the asymmetric unit aggregates with its own type to generate the two single-strand hydrogen-bonding catemers illustrated by the inclusion of extracellular molecules. Both of these independent counterdirectional chains follow screw axes parallel to *b*.

We characterize the geometry of hydrogen bonding to carbonyls using a combination of the H···O═C angle and the H···O═C—C torsion angle. These describe the approach of the H atom to the O in terms of its deviation from, respectively, C═O axiality (ideal 120°) and planarity with the carbonyl (ideal 0°). For (I*A*), these angles are H···O═C = 136.0° and H···O═C—C = −14.9°. For the (I*B*) catemers, the corresponding values are 133.2 and −23.6°, respectively.

Three close C—H···O═C contacts exist for the ketone and carboxyl functions. The ketone group in (I*A*) has a contact to atom H5*B* in a translationally related neighbor (2.58 Å), and the ketone group in (I*B*) has a corresponding translational contact to atom H5*C* of 2.63 Å. The carboxyl carbonyl group (C═O2*B*) has a 2.64 Å contact to atom H6*A* in a screw-related neighbor. These distances all lie within the 2.7 Å range we normally employ for non-bonded H···O packing interactions (Steiner, 1997). Using compiled data for a large number of C—H···O contacts, Steiner & Desiraju (1998) find significant statistical directionality even as far out as 3.0 Å, and conclude that these are legitimately viewed as 'weak hydrogen bonds', with a greater contribution to packing forces than simple van der Waals attractions.

The solid-state (KBr) IR spectrum of (I) has broad C═O absorption with maxima at 1736 and 1711 cm^{-1}, essentially identical to those for camphorcarboxylic acid (Lalancette *et al.*, 1991). These peaks are consistent with hydrogen-bonding shifts due, respectively, to its removal from COOH and its addition to a strained ketone. In $CHCl_3$, where dimers predominate, the absorptions appear, presumably reversed, at 1738 and 1712 cm^{-1}.

Experimental

Compound (I) was prepared by Jones oxidation of (−)-(1*R*)-2-*endo*-3-*exo*-isoborneolacetic acid, purchased from the Aldrich Chemical Co., Milwaukee, Wisconsin, USA. Recrystallization from 1:1 cyclohexane–ethyl ether provided crystals of (I) suitable for X-ray analysis (m.p. 358 K). The positive rotation of the 1*R* enantiomer of (I) has been established (Rupe & Häfliger, 1940).

Crystal data

$C_{12}H_{18}O_3$
M_r = 210.26
Monoclinic, $P2_1$
a = 6.6423 (10) Å
b = 14.734 (3) Å
c = 11.817 (2) Å
β = 93.756 (13)°
V = 1154.0 (4) Å^3
Z = 4
D_x = 1.210 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 6.0–13.2°
μ = 0.09 mm^{-1}
T = 296 (2) K
Tablet, colorless
0.38 × 0.30 × 0.18 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{\min}$ = 0.972, $T_{\max}$ = 0.986
4574 measured reflections
2110 independent reflections
1161 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.077

$\theta_{\max}$ = 25.0°
$h = -7 \rightarrow 7$
$k = -17 \rightarrow 17$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections intensity variation: <2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.096
S = 0.99
2110 reflections
271 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.006P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\min}$ = −0.16 e Å^{-3}
Absolute structure: none

Table 1
Selected geometric parameters (Å, °).

O2*A*—C12*A*	1.190 (6)	O3*A*—C12*A*	1.304 (6)
O2*B*—C12*B*	1.171 (5)	O3*B*—C12*B*	1.326 (6)
O2*B*—C12*B*—C11*B*	123.7 (5)	O2*A*—C12*A*—C11*A*	124.4 (5)
O3*B*—C12*B*—C11*B*	111.7 (5)	O3*A*—C12*A*—C11*A*	113.0 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3A—H3A···O1$A^{\rm i}$	0.82	1.93	2.729 (5)	165
O3B—H3B···O1$A^{\rm ii}$	0.82	1.89	2.707 (5)	170

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

All H atoms for (I) were found in electron-density difference maps but were placed in calculated positions, with C—H distances of 0.97 Å for methylene, 0.98 Å for methine and 0.96 Å for methyl H atoms, and O—H distances of 0.82 Å for carboxyl H atoms, and allowed to refine as riding models on their respective C and O atoms, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O,C$_{\rm methyl}$) and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for the remainder.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1504). Services for accessing these data are described at the back of the journal.

References

Barcon, A., Brunskill, A. P. J., Lalancette, R. A. & Thompson, H. W. (2002). *Acta Cryst.* C**58**, o154–o156.

Borthwick, P. W. (1980). *Acta Cryst.* B**36**, 628–632.

Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1997). *Acta Cryst.* C**53**, 102–106.

Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1999). *Acta Cryst.* C**55**, 568–572.

Lalancette, R. A. & Thompson, H. W. (2003). *Acta Cryst.* C**59**, o274–o276.

Lalancette, R. A., Thompson, H. W. & Brunskill, A. P. J. (1999). *Acta Cryst.* C**55**, 1908–1911.

Lalancette, R. A., Vanderhoff, P. A. & Thompson, H. W. (1991). *Acta Cryst.* C**47**, 132–136.

Rupe, H. & Häfliger, F. (1940). *Helv. Chim. Acta*, **23**, 53–90.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Steiner, T. (1997). *J. Chem. Soc. Chem. Commun.* pp. 727–734.

Steiner, T. & Desiraju, G. R. (1998). *J. Chem. Soc. Chem. Commun.* pp. 891–892.