Table 2. *Hydrogen bonding parameters (Å, °)*

D—H···*A*	*D*···*A*	H···*A*	*D*—H···*A*
Mo *Kα* data			
N1—H1*A*···O1	2.8243 (16)	1.98	152
N1—H1*B*···O1^{iii}	2.7493 (14)	1.83	176
O3—H31—O2	2.8268 (15)	1.95 (2)	164 (2)
O3—H32—O2^{iv}	2.7669 (15)	1.87 (2)	178 (2)
Synchrotron data			
N1—H1*A*···O1	2.8255 (12)	1.98	152
N1—H1*B*···O1^{iii}	2.7450 (11)	1.82	176
O3—H31—O2	2.8233 (12)	1.98 (2)	163 (2)
O3—H32—O2^{iv}	2.7605 (12)	1.89 (2)	178 (2)

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

Compound (1) crystallized in the monoclinic system; space group $P2_1/n$ from the systematic absences. H atoms bonded to C and N were treated as riding, with C—H = 0.99 and N—H = 0.92 Å. The two water H atoms were located from a difference map and then allowed to refine, subject to the restraints that they should both have the same O—H distance refined as a free variable, and a common isotropic displacement parameter, also refined as a free variable.

Data collection: *KappaCCD Server Software* (Nonius, 1997) for the Mo *Kα* data; *SMART* (Siemens, 1996) for the synchrotron data. Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997) for the Mo *Kα* data; *SMART* for the synchrotron data. Data reduction: *DENZO-SMN* for the Mo *Kα* data; *SAINT* (Siemens, 1996) for the synchrotron data. For both compounds, program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

One data set was collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada. The other data set was collected at the CLRC synchrotron radiation facility, Daresbury. We acknowledge the provision of time on DARTS, the UK national synchrotron radiation service at the CLRC Daresbury Laboratory, through funding by the EPSRC.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1317). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Coupar, P. I., Ferguson, G. & Glidewell, C. (1996). *Acta Cryst.* C**52**, 3052–3055.
Ferguson, G. (1999). *PRPKAPPA. A WordPerfect-5.1 Macro to Formulate and Polish CIF Format Files.* University of Guelph, Canada.
Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 129–138.
Glidewell, C., Ferguson, G., Gregson, R. M. & Campana, C. F. (1999). *Acta Cryst.* B**55**. In the press.
Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (1999). *Acta Cryst.* B**55**. In the press.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Karle, I. L., Ranganathan, D. & Haridas, V. (1996). *J. Am. Chem. Soc.* **118**, 7128–7133.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1999). *PLATON. Molecular Geometry and Graphics Program*. Version of January 1999. University of Utrecht, The Netherlands.

Acta Cryst. (1999). C**55**, 1899–1902

(+)-*trans*-Pinononic acid: hydrogen-bonding patterns in a non-racemic *δ*-keto acid

ALAN BARCON, ANDREW P. J. BRUNSKILL, HUGH W. THOMPSON AND ROGER A. LALANCETTE*

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA.
E-mail: lalancette@hades.rutgers.edu

(Received 14 July 1999; accepted 28 July 1999)

Abstract

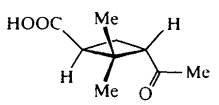
The title keto acid, (+)-*trans*-3-acetyl-2,2-dimethylcyclobutanecarboxylic acid, $C_9H_{14}O_3$, derived from (−)-verbenone, aggregates in the solid as helical acid-to-ketone hydrogen-bonding chains extending in the *b*-cell direction [O···O = 2.711 (3) Å]. Each of the carboxyl-O atoms has a close C—H contact to a separate neighboring molecule. Comparisons are drawn with the corresponding (−)-*cis*-epimer, as well as with the homologous (+)- and (±)-*cis*-pinonic acids.

Comment

Carboxylic acids and ketones are similar in basicity and sufficiently competitive as hydrogen-bond acceptors that keto acids display several hydrogen-bonding modes beyond those characteristic of functionally unelaborated acids. Our continuing interest in the crystal structures of keto carboxylic acids lies in mapping the molecular characteristics that control their five known hydrogen-bonding modes. The commonest of these is

acid dimerization without ketone involvement (Thompson *et al.*, 1992), but carboxyl-to-ketone chains (catemers) constitute a sizable minority of cases (Brunskill *et al.*, 1997). The remaining types, *i.e.* intramolecular hydrogen bonds (Thompson *et al.*, 1996), acid-to-acid catemers (Lalancette *et al.*, 1998) and carboxyl-to-ketone dimers (Kosela *et al.*, 1995), are all comparatively rare. Several cases also exist of hydrates with more complex hydrogen-bonding patterns (Lalancette *et al.*, 1990, 1997, 1998). We have previously referenced numerous examples and discussed factors that appear to govern the choice of hydrogen-bonding mode (Brunskill *et al.*, 1999; Lalancette, Brunskill & Thompson, 1999).

Our study has included several keto acids derived from the pinane skeleton and containing its *gem*-dimethylated cyclobutane ring (Vanderhoff *et al.*, 1986; Coté *et al.*, 1997; Lalancette, Thompson & Brunskill, 1999). All of these display catemeric acid-to-ketone hydrogen bonding, suggesting an inherent bias toward this mode. The title compound, (+)-*trans*-3-acetyl-2,2-dimethylcyclobutanecarboxylic acid, (I), similarly derived, was synthesized by way of its *cis*-epimer, (II) (Coté *et al.*, 1997). Compound (I) belongs to the category of δ-keto acids, embracing examples of dimeric and internal hydrogen bonds, as well as both anhydrous and hydrated catemers. We report here that (I) also adopts the catemeric hydrogen-bonding mode.



(I)

A view of the asymmetric unit of (I) with its numbering is shown in Fig. 1. The cyclobutane ring, as is typical, is not flat but flexed as though folded from C2 to C4, with a dihedral angle of 160.9 (2)°, compared to an angle of 154.5 (3)° in the *cis*-epimer, (II). This angle was found to be 150.2 (1)° in the homologous (±)-*cis*-pinonic acid (Vanderhoff *et al.*, 1986) and 150.2 (2)° in (+)-*cis*-pinonic acid (Lalancette, Thompson & Brunskill, 1999). In the *cis*-1,3-disubstituted compounds cited, the flexure diminishes ipso-facial interactions by projecting the 1- and 3-substituents more 'equatorially'. However, for *trans* substitution, the theoretically preferred direction of flex may be less obvious, and *ab initio* (HF/STO-3G) molecular modeling (Wavefunction, 1995) found no enthalpy difference between these two conformational alternatives in (I). Fig. 1 shows that the actual ring-flex in (I) extends the carboxyl group 'equatorially' and the acetyl group 'axially', a result presumably dictated by the crystal packing. The lessening of eclipsing interactions between carboxyl and methyl achieved [C9—C1—C2—C5 = −24.7 (3)°] comes at the expense of an increase of eclipsing between acetyl and methyl [C7—C3—C2—C6 = 11.2 (3)°]. In (II), the analogous angles are C9—C1—C2—C5 = −27.1 (3)° and C7—C3—C2—C5 = 27.9 (3)°. The acetyl group is turned so that its carbonyl lies across its face of the ring, with a C4—C3—C7—O1 torsion angle of −19.8 (3)°. On the opposite ring face, the carboxyl group adopts a similar conformation, but its carbonyl lies almost in the plane defined by C4—C1—C9, with a C4—C1—C9—O2 torsion angle of −5.3 (4)°.

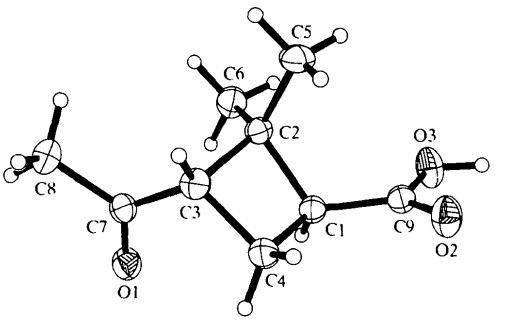


Fig. 1. A view of the asymmetric unit of (I) with the atomic numbering scheme. Ellipsoids are set at the 20% probability level.

The geometry of catemers cannot support the averaging mechanisms responsible for the disordering of C—O bond lengths and C—C—O angles often observed in dimerically hydrogen-bonded acids (Leiserowitz, 1976). Thus, in (I), these bond lengths are 1.203 (3) and 1.323 (3) Å, with angles of 125.8 (2) and 112.4 (2)°. Our own survey of 56 keto acid structures which are not acid dimers gives average values of 1.20 (1) and 1.32 (2) Å, and 124.5 (14) and 112.7 (17)° for these lengths and angles, in accord with typical values of 1.21 and 1.31 Å, and 123 and 112° cited for highly ordered dimeric carboxyls (Borthwick, 1980). The methyls show no detectable disorder.

The packing of the cell (Z = 2), with an extracellular molecule, to show the carboxyl-to-ketone hydrogen bonds connecting screw-related molecules and yielding a single-strand hydrogen-bonding chain passing through the cell in the *b* direction, is illustrated in Fig. 2. The pitch of the molecules within the hydrogen-bonding helix, as we have defined this term previously (Coté *et al.*, 1997), is 52.5°, nearly the same as that for the homologous but epimeric *cis*-pinonic acids [51.2° for the racemate and 50.0° for the (+)-enantiomer], but is significantly less prolated than for (−)-*cis*-pinononic acid, (II) (31.5°). A close contact to a separate neighboring molecule was found for each of the carboxyl-O atoms: for O2, 2.68 Å to H8*B* of a molecule translated in **c**; for O3, 2.69 Å to H3*A* of a neighbor translated in **a**. These presumably represent polar attractions contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

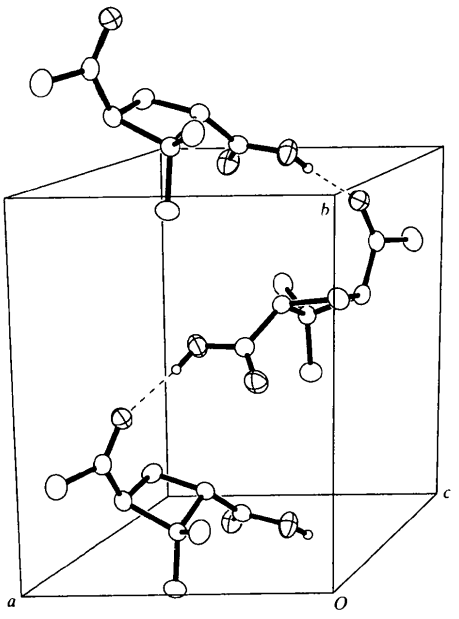


Fig. 2. A packing diagram for (I), with an extracellular molecule, showing the single-strand catemer in the cell, created by acid-to-ketone hydrogen bonds proceeding along a chain of molecules screw-related in **b**. Ellipsoids are set at the 20% probability level.

The observed cell volume for (I) is greater than that for (II) by 3.5%, corresponding, within experimental error, to the observed difference in densities for (I) *versus* (II) (1.176 *versus* 1.217 g cm^{-3}, respectively). The diminished efficiency of packing for (I) is also evident in its lower 'percent filled space' (67.8%), which differs by 3.7% from the value found for (II) (70.3%). As a measure of this packing efficiency, we utilize the 'packing coefficient' (Kitaigorodsky, 1973) calculated as 'percent filled space' using the *PLATON* program (Spek, 1998). For this calculation, C—H and O—H distances are neutron normalized to 1.08 and 1.02 Å, respectively. We have calculated packing coefficient values for 144 keto acids, which fall into the range 65.1–75.4% and depend on such factors as shape, chirality, rigidity *etc.*

The solid-state (KBr) IR spectrum of (I) displays C=O stretching absorptions consistent with known shifts produced when hydrogen bonding is removed from carboxyl C=O (1730 cm^{-1}) and added to a ketone (1686 cm^{-1}); these bands appear at 1731 and 1689 cm^{-1} in the *cis*-epimer (II). As with (II), these coalesce into a single peak in $CHCl_3$ solution, at 1704 cm^{-1}, with the usual carboxyl-dilution shoulder near 1740 cm^{-1}.

Experimental

The absolute stereochemistry and rotation of (I) have been established previously by its isolation and its relationship to (−)-*cis*-pinononic acid, (II), and to (−)-verbenone. Compound (I) was prepared by base-catalyzed stereochemical equilibration (Harispe *et al.*, 1964) of (II) synthesized as described previously (Coté *et al.*, 1997). Our attempt at titrative separation of the resulting oily 3:1 *cis–trans* equilibrium mixture, following the procedure outlined by Delépine & Harispe (1961), was unsuccessful, as judged by NMR. Since the pK_a values we have determined experimentally for (I) (*trans* = 4.38) and (II) (*cis* = 4.47) do not suggest any realistic basis for a separation based on acidity differences, this aspect of the report of Delépine & Harispe (1961) remains mysterious. In our hands, selective seeding of the 3:1 mixture with the high-melting *cis*-epimer (m.p. 404 K) eventually led to isolation of pure (I) from the oily residue (m.p. 348 K). The crystal used for data collection was obtained from Et_2O–cyclohexane.

Crystal data

$C_9H_{14}O_3$
M_r = 170.20
Monoclinic
$P2_1$
a = 7.3872 (9) Å
b = 9.6082 (13) Å
c = 7.4972 (14) Å
β = 115.444 (10)°
V = 480.52 (13) $Å^3$
Z = 2
D_x = 1.176 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 21 reflections
θ = 11.3–14.4°
μ = 0.087 mm^{-1}
T = 298 (2) K
Parallelepiped
0.58 × 0.52 × 0.32 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: numerical (Sheldrick, 1997)
T_{min} = 0.95, T_{max} = 0.97
1930 measured reflections
1698 independent reflections
787 reflections with $I > 2\sigma(I)$

R_{int} = 0.030
θ_{max} = 25°
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 8$
3 standard reflections every 97 reflections
intensity variation: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.090
S = 1.06
903 reflections
121 parameters
H atoms treated by a mixture of constrained and independent refinement

$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.0315P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.10 e $Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.216 (3)	O3—C9	1.323 (3)
O2—C9	1.203 (3)		
O2—C9—C1	125.8 (2)	O3—C9—C1	112.4 (2)

Table 2. *Hydrogen-bonding and C—H···O contact geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1^{i}	0.89 (4)	1.83 (4)	2.711 (3)	170 (3)
C8—H8*B*···O2^{ii}	0.96	2.68	3.64	175
C3—H3*A*···O3^{iii}	0.98	2.69	3.52	143

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

All H atoms were found in electron-density difference maps but were replaced in calculated positions and allowed to refine as riding models, except for the hydroxyl H3 atom whose coordinates and isotropic displacement parameter were allowed to refine individually. Isotropic displacement parameters for the methine, methylene and each of the three methyl-H-atom sets were refined as individual groups, yielding values of 0.064 (5), 0.081 (6), 0.083 (5), 0.097 (6) and 0.129 (9) Å^2, respectively.

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: GD1053). Services for accessing these data are described at the back of the journal.

References

Berkovitch-Yellin, Z. & Leiserowitz, L. (1982). *J. Am. Chem. Soc.* **104**, 4052–4064.

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

Brunskill, A. P. J., Thompson, H. W. & Lalancette, R. A. (1997). *Acta Cryst.* C**53**, 599–601.

Brunskill, A. P. J., Thompson, H. W. & Lalancette, R. A. (1999). *Acta Cryst.* C**55**, 566–568.

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

Delépine, M. & Harispe, M. (1961). *C. R. Acad. Sci.* **252**, 637–639.

Harispe, M., Mea, D. & Horeau, M. (1964). *Bull. Soc. Chim. Fr.* pp. 1035–1037.

Jönsson, P.-G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.

Kitaigorodsky, A. I. (1973). *Molecular Crystals and Molecules*, pp. 24–37. New York: Academic Press.

Kosela, S., Yulizar, Y., Chairul, Tori, M. & Asakawa, Y. (1995). *Phytochemistry*, **38**, 691–694.

Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1997). *Acta Cryst.* C**53**, 1838–1842.

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

Lalancette, R. A., Thompson, H. W. & Brunskill, A. P. J. (1998). *Acta Cryst.* C**54**, 421–424.

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. (1990). *Acta Cryst.* C**46**, 1682–1686.

Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.

Sheldrick, G. M. (1997). *SHELXTL User's Manual.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

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

Spek, A. L. (1998). *PLATON98 for Windows.* University of Utrecht, The Netherlands.

Thompson, H. W., Lalancette, R. A. & Coté, M. L. (1996). *Acta Cryst.* C**52**, 2372–2376.

Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* C**48**, 66–70.

Vanderhoff, P. A., Thompson, H. W. & Lalancette, R. A. (1986). *Acta Cryst.* C**42**, 1766–1769.

Wavefunction (1995). *SPARTAN.* Version 4.0. Wavefunction Inc., 18401 Von Karman Ave., Irvine, CA 92715, USA.

Acta Cryst. (1999). C**55**, 1902–1905

(+)-3-Oxoglycyrrhetinic acid: catemeric hydrogen bonding in a non-racemic triterpenoid diketo acid

ANDREW P. J. BRUNSKILL, HUGH W. THOMPSON AND ROGER A. LALANCETTE*

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA.
E-mail: lalancette@hades.rutgers.edu

(Received 17 June 1999; accepted 26 July 1999)

Abstract

The crystal structure of the title compound, (+)-10,13-dioxo-2α,4aβ,6aα,6bβ,9,9,12aβ-heptamethyl-1,2,3,4,4a,-5,6,6a,6b,7,8,8aα,9,10,11,12,12a,12bα,13,14bβ-icosahydropicene-2β-carboxylic acid, $C_{30}H_{44}O_4$, involves carboxyl-to-ketone hydrogen-bonding catemers. Distorted hydrogen bonds progress from the carboxyl H atom of one molecule to the remote-ring ketone O atom of a screw-related neighbor [O···O = 2.975 (5) Å], yielding helical hydrogen-bonding chains which proceed in the *b* direction. Two C—H···O close contacts were found, connecting the unsaturated ketone (2.71 Å) and the acid carbonyl (2.55 Å) to separate screw-related neighbors.

Comment

The carbonyl basicities of carboxylic acids and ketones are sufficiently similar that the two may compete as hydrogen-bond acceptors. As a result, keto acids display several solid-state hydrogen-bonding modes beyond those seen in functionally unelaborated acids and occupy a cusp of behavioral territory where these patterns may be markedly changed by minor structural differences. Our continuing interest in the crystallography of keto acids lies in mapping the molecular characteristics that control the five known hydrogen-bonding modes. The most common of these is acid dimerization without ketone involvement (Lalancette *et al.*, 1996), but carboxyl-to-ketone chains (catemers) constitute a sizable minority of cases (Brunskill *et al.*, 1997). The remaining types, *i.e.* intramolecular hydrogen bonds (Thompson *et al.*, 1996), acid-to-acid catemers (Lalancette *et al.*, 1998) and carboxyl-to-ketone dimers (Kosela *et al.*, 1995), are