Thompson, H. W., Brunskill, A. P. J. & Lalancette, R. A. (1998). Acta Cryst. C54, 829–831.

Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). Acta Cryst. C48, 66–70.

Thompson, H. W. & McPherson, E. (1977). J. Org. Chem. 42, 3350–3353.

Thompson, H. W. & Shah, N. V. (1983). J. Org. Chem. 48, 1325–1328.

Winkler, J. D., Hey, J. P. & Williard, P. G. (1986). J. Am. Chem. Soc. 108, 6425–6427.

Santonic acid: catemeric hydrogen bonding in a γ,ε-diketo carboxylic acid

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Abstract

The title compound, (−)-2,3,3a,4,5,6,7,7a-octahydro-α,3a,5-trimethyl-6,8-dioxo-1,4-methano-1H-indene-1-acetic acid ($C_{15}H_{20}O_4$), exists in the solid state as a catemer, with the hydrogen bonding following a 2_1 screw axis from the carboxyl to the ε-ketone of a neighboring molecule [O···O = 2.752 (3) Å]. Two parallel counterdirectional screw-related single-strand helices pass through the cell in the a direction. Four intermolecular C=O···H—C close contacts were found, involving all three carbonyl groups.

Comment

Options for varying the standard pattern of dimeric hydrogen bonding that dominates functionally unadorned acids in the solid state may be created by attaching a ketone function. Frequently, such a ketone fails to participate, resulting in typical carboxyl dimers (Coté et al., 1996), but intermolecular carboxyl-to-ketone hydrogen bonds may also occur, yielding a catemer (Brunskill et al., 1997). A third, rare arrangement has an internal hydrogen bond (Thompson et al., 1996), and four instances are known of acid-to-ketone dimerization (Kosela et al., 1995), plus three of carboxyl catemerization (Lalancette, et al., 1998). Several cases also exist of hydrates with more complex hydrogen-bonding patterns (Lalancette et al., 1997, 1998).

Our continuing interest in this hydrogen-bonding behavior lies partly in defining the molecular characteristics that promote formation of the various hydrogen-bonding patterns. Among the factors that appear to discourage dimerization are (a) systems that restrict the conformations available and (b) the presence of a single enantiomer. An additional factor which ought obviously to favor carboxyl-to-ketone hydrogen-bonding patterns is (c), the presence of multiple ketone receptors for the hydrogen bond. We report here that the title compound, (I), embodying all these features, adopts the carboxyl-to-ketone catemeric hydrogen-bonding mode in the solid state. Compound (I), derived from a sesquiterpene isolate of Artemisia, is a tricyclic γ,ε-diketo acid. The category of ε-keto acids includes instances of both acid dimers and acid-to-ketone catemers, while that of γ-keto acids embraces internal hydrogen bonds as well.
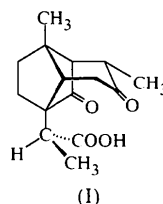

(I)

Fig. 1 shows the asymmetric unit of (I) with the atom-numbering scheme. The chirality about C9 is independent of the remainder of the molecule and has the S configuration. The rigidity of the tricyclic framework, plus the preference for a chair conformation in the flexible ring containing the ε-ketone, leave conformationally significant rotations possible only about C1—C9 and C9—C10. Of these, the conformation about the former is staggered, with the carboxyl and ketone anti to one another [C8—C1—C9—C10 = 169.0 (3)°]. The carboxyl is oriented so that the C1—C9—C10—O3 torsion angle is 76.4 (4)°, aligning the C=O double bond approximately parallel with the C1—C2 bond.
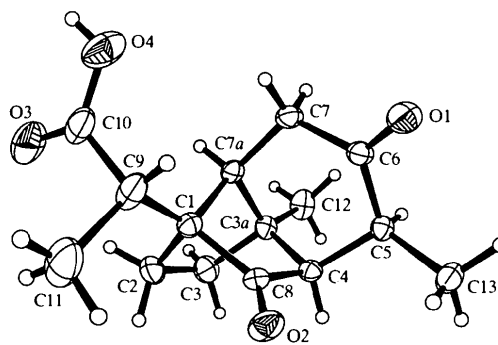

Fig. 1. The asymmetric unit of (I) with its numbering. Ellipsoids are set at the 20% probability level.

Averaging of carboxyl bond lengths and angles by disorder, although common in carboxyl dimers (Leiserowitz, 1976), is not observed in catemers, whose geometry cannot support the mechanisms underlying the averaging processes involved. In (I), these bond lengths are 1.205 (5) and 1.288 (5) Å for C=O and C—O, respectively, with angles of 124.0 (4) and 113.2 (4)° for C—C=O and C—C—O, respectively. 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 (1) and 113 (2)° 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).

Fig. 2 illustrates the packing which involves catemers whose hydrogen bonding follows the 2_1 screw axis along **a** (infinite chains with base vector 1, 0, 0), from the carboxyl to the ε-ketone of a neighboring molecule [O···O = 2.752 (3) Å]. Two parallel single-strand helices, which are themselves screw-related along **c**, pass counterdirectionally through the cell. The hydrogen-bonding pattern in (I) conforms to the commonest of the sub-types of acid-to-ketone catemer we have described, categorized by the symmetry between adjacent chain members. In order of decreasing prevalence, these symmetry relations are: screw, translation (collectively, 'homochiral') and glide ('heterochiral'). Several intermolecular C=O···H—C close contacts (Table 2) were found involving all three carbonyl groups. All these presumably represent polar attractions contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).
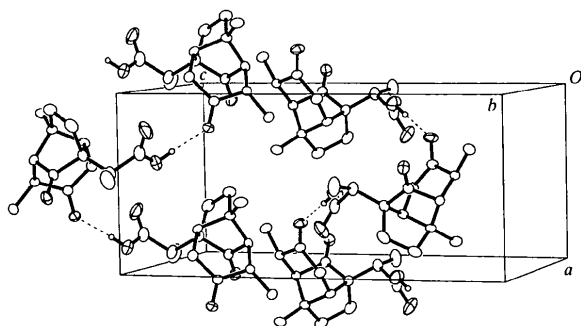

Fig. 2. A packing diagram for (I), with extracellular molecules, illustrating the two parallel counterdirectional screw-related single-strand hydrogen-bonding chains passing through the cell in the *a* direction. Ellipsoids are set at the 20% probability level. All non-carboxyl H atoms have been excluded for clarity.

The solid-state (KBr) infrared spectrum of (I) has absorptions at 1737 (strained γ-ketone) and 1729 cm^{-1} (carboxyl C=O), with a double peak at 1687 and 1681 cm^{-1} for the hydrogen-bonded ε-ketone. The shifts involved conform to those typically seen in catemers

which are due to the removal of hydrogen bonding from carboxyl C=O and addition of hydrogen bonding to ketone C=O (Coté *et al.*, 1997). The band for strained C=O is unchanged (1738 cm^{-1}) in CHCl$_3$ solution, while the remaining absorptions coalesce to a single broader peak at 1710 cm^{-1}.

Experimental

Commercial (−)-α-santonin of known absolute stereochemistry (Barton *et al.*, 1962; Nakazaki & Arakawa, 1962; Asher & Sim, 1965; Coggin & Sim, 1969) was obtained from Aldrich Chemical Co., Milwaukee, WI, USA, and subjected to the basic hydrolysis and rearrangement procedure described by Woodward *et al.* (1948), as modified by Hortmann & Daniel (1972).

Crystals of (I), m.p. 446 K, were obtained by slow evaporation from a 1:1 acetone/benzene solution. The crystal chosen, although large, was well within the focal spot of the normal focus tube.

Crystal data

$C_{15}H_{20}O_4$	Mo $K\alpha$ radiation
$M_r = 264.31$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 26
$P2_12_12_1$	reflections
$a = 7.791$ (1) Å	$\theta = 10.06–14.66°$
$b = 11.198$ (1) Å	$\mu = 0.085$ mm^{-1}
$c = 16.986$ (2) Å	$T = 293$ (2) K
$V = 1481.9$ (3) Å^3	Trapezoid
$Z = 4$	$0.75 \times 0.55 \times 0.40$ mm
$D_x = 1.185$ Mg m^{-3}	Colorless
$D_m = 1.184$ (2) Mg m^{-3}	
D_m measured by flotation in	
p-xylene/CCl$_4$	

Data collection

Siemens *P*4 diffractometer	$R_{int} = 0.017$
$2\theta/\theta$ scans	$\theta_{max} = 26°$
Absorption correction:	$h = -9 \rightarrow 9$
face-indexed numerical	$k = 0 \rightarrow 13$
(Sheldrick, 1994)	$l = 0 \rightarrow 20$
$T_{min} = 0.951$, $T_{max} = 0.974$	3 standard reflections
3373 measured reflections	every 97 reflections
2908 independent reflections	intensity variation: $<1\%$
2174 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.21$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.053$	$\Delta\rho_{min} = -0.19$ e Å^{-3}
$wR(F^2) = 0.135$	Extinction correction:
$S = 1.08$	*SHELXTL/PC* (Sheldrick,
2907 reflections	1994)
179 parameters	Extinction coefficient:
H atoms: see below	0.015 (2)
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2$	Scattering factors from
$+ 0.3413P]$	*International Tables for*
where $P = (F_o^2 + 2F_c^2)/3$	*Crystallography* (Vol. C)
$(\Delta/\sigma)_{max} = 0.001$	

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

O1—C6	1.216 (3)	O3—C10	1.205 (5)
O2—C8	1.210 (3)	O4—C10	1.288 (5)
O3—C10—C9	124.0 (4)	O4—C10—C9	113.2 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1^i	0.91 (6)	1.84 (6)	2.752 (3)	175 (1)
C12—H12C···O1^{ii}	0.96	2.58	3.509 (4)	163
C5—H5A···O2^{iii}	0.98	2.45	3.280 (3)	141
C12—H12B···O2^{iii}	0.96	2.70	3.621 (4)	160
C4—H4A···O3^{iv}	0.98	2.47	3.298 (4)	142

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

All non-carboxyl H atoms were found in electron-density difference maps but replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms. Torsion angles for the methyl rotors were allowed to refine. Displacement parameters for the methine- and methylene-H atoms were refined as two groups and displacement parameters for the H atoms of each methyl group were fixed to be 150% of the isotropic displacement parameter of their associated C atom. The carboxyl-H atom was found in an electron-density difference map but was replaced in a calculated position and the O—H distance allowed to refine with its displacement parameter fixed to be 150% of the isotropic displacement parameter of its associated O atom.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS* (Siemens, 1996). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

References

Asher, J. D. M. & Sim, G. A. (1965). *J. Chem. Soc.* pp. 6041–6055.
Barton, D. H. R., Miki, T., Pinhey, J. T. & Wells, R. J. (1962). *Proc. Chem. Soc. London*, p. 112.
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.
Coggin, P. & Sim, G. A. (1969). *J. Chem. Soc. B*, pp. 237–242.
Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1997). *Acta Cryst.* C**53**, 102–106.
Coté, M. L., Thompson, H. W., Lalancette, R. A. & Williams, J. A. IV (1996). *Acta Cryst.* C**52**, 2612–2614.
Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hortmann, A. G. & Daniel, D. S. (1972). *J. Org. Chem.* **37**, 4446–4460.
Jönsson, P.-G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.
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., Thompson, H. W. & Brunskill, A. P. J. (1998). *Acta Cryst.* C**54**, 421–424.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Nakazaki, M. & Arakawa, H. (1962). *Proc. Chem. Soc. London*, p. 151.
Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *XSCANS. X-ray Single Crystal Analysis Software*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Thompson, H. W., Lalancette, R. A. & Coté, M. L. (1996). *Acta Cryst.* C**52**, 2372–2376.
Woodward, R. B., Brutschy, F. J. & Baer, H. (1948). *J. Am. Chem. Soc.* **70**, 4216–4221.

(±)-1-Indanone-2-acetic and -2-propionic acids: catemeric *versus* dimeric hydrogen bonding in homologous γ- and δ-keto acids

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Abstract

The crystal structure of (±)-2,3-dihydro-1-oxo-1*H*-indene-2-acetic acid ($C_{11}H_{10}O_3$) involves catemeric hydrogen bonds, which progress from the carboxyl H atom of one molecule to the ketone O atom of a neighbor screw-related in **b** [O···O = 2.709 (2) Å]. This yields centrosymmetrically related counterdirectional pairs of hydrogen-bonding chains following parallel helical axes. Four intermolecular C=O···H—C close contacts were found, involving both carbonyl groups. By contrast, the hydrogen bonding in (±)-3-(2,3-dihydro-1-oxo-1*H*-inden-2-yl)propionic acid ($C_{12}H_{12}O_3$) produces carboxyl dimers [O···O = 2.639 (2) Å], which also have a 2.62 Å C=O···H—C close contact involving the ketone carbonyl group and the *peri*-hydrogen on a centrosymmetrically related molecule. The difference in hydrogen-bonding behavior between the two molecules is discussed.

Comment

Our continuing interest in crystalline keto acids involves elucidation of factors controlling the one intra- and four