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(±)-3-Oxo-1,2,3,9,10,10a-hexahydro-phenanthrene-10a-carboxylic acid: catemeric hydrogen bonding in a δ-keto acid

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Abstract

The crystal structure of the title compound ($C_{15}H_{14}O_3$) involves hydrogen-bonding catemers, with hydrogen bonds progressing from the carboxyl group of each mol-ecule to the ketone group of a screw-related neigh-bor [O···O = 2.604 (3) Å]. This creates two parallel centrosymmetrically related single-strand hydrogen-bonding helices proceeding in the *b* direction through the chosen cell. Two intermolecular C=O···H—C close contacts were found, one involving the acid (2.39 Å) and one, the ketone (2.58 Å). A close contact was also found between a methylene C—H and the center of the aromatic π-cloud in a centrosymmetrically related mol-ecule.

Comment

Our continuing interest in the crystal structures of keto carboxylic acids lies in elucidating and predicting their hydrogen-bonding behavior. Beyond the acid-to-acid dimer and catemer modes characteristic of unadorned acids, keto acids display an additional three hydrogen-bonding patterns of the carboxyl-to-ketone type. Over 40 instances are now known of acid-to-ketone cate-mers, while internal hydrogen bonds and acid-to-ketone dimers are much rarer. The intra-chain units in keto-acid catemers may be categorized as homochiral (transla-tionally or screw-related) or heterochiral (glide-related), and for such catemers overall, the order of preva-lence observed thus far is: screw > translation > glide. Several cases are also known of hydrates with more complex hydrogen-bonding patterns. We have previ-ously referenced and discussed numerous examples of these hydrogen-bonding modes (Thompson *et al.*, 1992, 1998; Coté *et al.*, 1996; Lalancette *et al.*, 1998).

Compound (I) belongs to the category of δ-keto acids, which embraces examples of standard acid dimers (Lalancette *et al.*, 1997) and internal hydrogen bonds (Abell *et al.*, 1991), as well as both anhydrous (Coté *et al.*, 1997) and hydrated (Winkler *et al.*, 1986) acid-to-ketone catemers. Compound (I) was of interest to us as a benzo-annelated version of a carboxyoctalone whose structure and catemeric hydrogen-bonding be-havior we had described previously (Lalancette *et al.*, 1991). Experience has led us often to anticipate similar hydrogen-bonding behavior among structurally similar compounds, and we report here that, like its simpler analog, (I) forms carboxyl-to-ketone catemers in which the intra-chain units are screw-related.
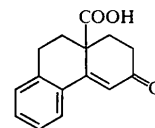
(I)

The asymmetric unit for (I), with its numbering, is shown in Fig. 1. The only skeletal option available for full rotation in (I) involves the C10A—C11 bond,

which is turned so that the plane of the carboxyl group lies close to the C4A—C10A—C11 plane, with the C=O aimed toward the ketone [torsion angle C4A—C10A—C11—O2 = 33.4 (4)°]. Within an asymmetric unit, the dihedral angle between the ketone (C2, C3, C4 and O1) and carboxyl (C11, O2 and O3) groups is 76.7 (2)°, while this angle is 96.2° in the non-benzo analog (Lalancette *et al.*, 1991). As is characteristic of catemers, the carboxyl group is fully ordered, with bond lengths of 1.207 (3) and 1.315 (3) Å for C=O and C—O, respectively.
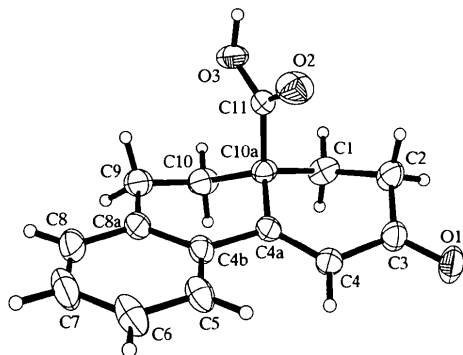

Fig. 1. The asymmetric unit of (I), with the atomic numbering. Ellipsoids are set at the 30% probability level.

The packing arrangement is shown in Fig. 2. Carboxyl-to-ketone catemers are formed by hydrogen bonds that progress among molecules screw-related in the *b* direction, generating two parallel centrosymmetrically related single-strand helical chains for each cell, and a typical 'herring-bone' arrangement. The O···O distance for the hydrogen bonding is 2.604 (3) Å, and the O—H···O angle is 167 (1)°. For the ketone and carboxyl groups involved in each intermolecular hydrogen bond, the C2/C3/C4/O1 *versus* C11'/O2'/O3' dihedral angle is 62.2 (3)° (primed atoms at $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$). This may be compared with a value of 39.3° for the corresponding angle in the non-benzo analog (Lalancette *et al.*, 1991). The resulting packing arrangement is such that the acid proton approaches the putative lone pairs on the sp^2 ketone O atom slightly out-of-plane. This geometry can be designated by a combination of the H3···O1'—C3' angle [120 (1)°] and the H3···O1'—C3'—C4' torsion angle [−6.6 (7)°]. These angles describe the approach of the acid H atom to the ketone O atom in terms of its deviation from C=O axiality (ideal = 120°) and from planarity with the ketone (ideal = 0°). For the non-benzo analog, these angles are 125 and 14.3°, with an O···O distance of 2.652 (4) Å and an O—H···O angle of 168°. The better geometry for (I) may account for the shorter O···O distance for its hydrogen bond [2.604 (3) Å].
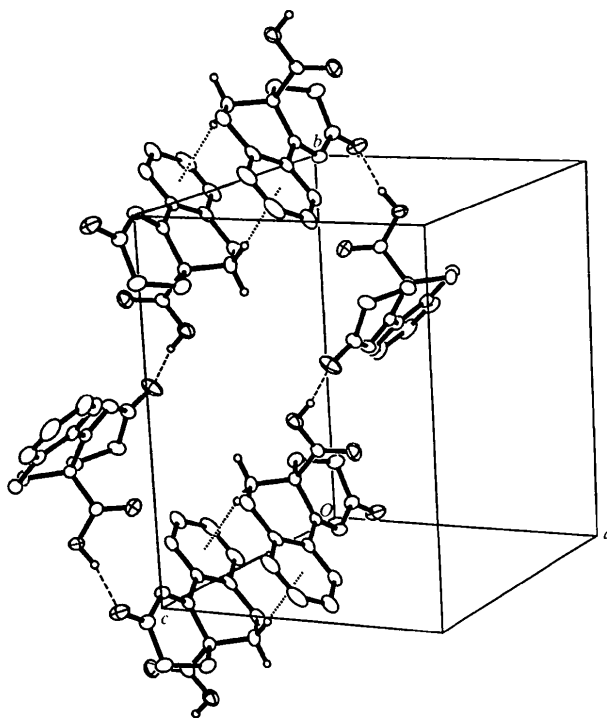

Fig. 2. A packing diagram for (I), with extracellular molecules, illustrating the two parallel counterdirectional single-strand hydrogen-bonding helices passing through the cell in the *b* direction. Ellipsoids are set at the 20% probability level. All non-carboxyl H atoms (except for the methylene H atom making a close contact with the aromatic π-cloud in a centrosymmetrically related molecule) have been excluded for clarity.

Two intermolecular C=O···H—C close contacts were found in the packing. One of these (2.39 Å) involves the acid carbonyl (O2) and the H2A atom of an enantiomeric molecule. The second (2.58 Å) involves the ketone (O1) and an aromatic proton (H8A) of a molecule translationally related in *c*. A reciprocal close contact was also found between a methylene hydrogen (H10B) and the center of the aromatic π-cloud in a centrosymmetrically related molecule. This kind of close contact has been described many times (Steiner *et al.*, 1995; Jeffrey, 1997) and has been shown to be very important in determining molecular-packing arrangements. The present instance is among the shortest of such reported interactions, which typically lie between 2.50 and 2.85 Å. The distance from H10B to the centroid of the aromatic ring is 2.66 Å (2.55 Å upon C—H distance normalization to the neutron-determined distance of 1.08 Å). The C—H···π angle involved (to the centroid of the aromatic ring) is 176°, but H10B is not precisely centered over the ring; the six H···C distances involved are 2.93, 2.79, 2.89, 3.08, 3.17 and 3.14 Å (H10B to C4B, C5, C6, C7, C8 and C8A, respectively). All of the above contacts probably represent polar attractions contributing materially to the packing forces

(Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

The solid-state (KBr) IR spectrum of (I) has complex $C{=}O$ absorptions centering around 1708 (COOH) and 1619 cm^{-1} (ketone). The latter position conforms to the shifts seen typically in catemers, due to addition of hydrogen bonding to a ketone (Coté *et al.*, 1997). In CHCl$_3$ solution, the absorptions are at 1720 and 1660 cm^{-1}, consistent with a dimerically hydrogen-bonded carboxyl and a normal ketone, respectively.

Experimental

1-Tetralone was carbomethoxylated and then subjected to Robinson annelation as described by Thompson & McPherson (1977). Mild saponification, modeled on that described by Thompson & Shah (1983), provided (I), which was purified and finally crystallized from acetone/toluene to give the crystal used; (I) decomposes with melting and loss of CO_2, at temperature-dependent rates, above about 420 K.

Crystal data

$C_{15}H_{14}O_3$	Mo $K\alpha$ radiation
$M_r = 242.26$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 40
$P2_1/n$	reflections
$a = 9.305 (2)$ Å	$\theta = 2.53-14.82°$
$b = 12.780 (3)$ Å	$\mu = 0.092$ mm^{-1}
$c = 10.444 (3)$ Å	$T = 293 (2)$ K
$\beta = 101.79 (2)°$	Block
$V = 1215.8 (5)$ Å^3	$0.64 \times 0.40 \times 0.22$ mm
$Z = 4$	Pale yellow
$D_x = 1.324$ Mg m^{-3}	
$D_m = 1.32 (1)$ Mg m^{-3}	
D_m measured by flotation in	
CCl$_4$/p-xylene	

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.030$
$2\theta/\theta$ scans	$\theta_{max} = 26°$
Absorption correction:	$h = -11 \rightarrow 1$
face-indexed numerical	$k = -15 \rightarrow 1$
(Sheldrick, 1994)	$l = -12 \rightarrow 12$
$T_{min} = 0.964$, $T_{max} = 0.981$	3 standard reflections
3110 measured reflections	every 97 reflections
2393 independent reflections	intensity variation: $<1\%$
1304 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.059$	$\Delta\rho_{max} = 0.162$ e Å^{-3}
$wR(F^2) = 0.138$	$\Delta\rho_{min} = -0.162$ e Å^{-3}
$S = 1.04$	Extinction correction:
2392 reflections	*SHELXTL/PC*
167 parameters	Extinction coefficient:
H atoms: see below	refined to 0
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2$	Scattering factors from
$+ 0.5421P]$	*International Tables for*
where $P = (F_o^2 + 2F_c^2)/3$	*Crystallography* (Vol. C)

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

O1—C3	1.223 (3)	O3—C11	1.315 (3)
O2—C11	1.207 (3)		
O2—C11—C10A	123.1 (3)	O3—C11—C10A	113.7 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$O1'	0.90 (3)	1.72 (3)	2.604 (3)	167 (1)
C8—H8A$\cdots$O1"	0.93	2.58	3.319 (4)	137
C2—H2A$\cdots$O2'''	0.97	2.39	3.319 (4)	160
C10—H10B$\cdots\pi^v$	0.97	2.66	3.624	176

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

All non-carboxyl H atoms were found in electron-density difference maps, but were replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms. Displacement parameters for the aromatic and methylene H atoms were refined as two groups. The carboxyl H atom was found in an electron-density difference map, but was replaced in a calculated position and was allowed to pivot around the C—O bond; the O—H distance was also allowed to refine. The displacement parameter of the carboxyl H atom was fixed to be 0.08 Å^2.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS* (Siemens, 1996). Data reduction: *XSCANS* (Siemens, 1996). 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*.

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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-1*H*-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.
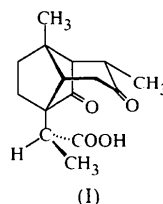

(I)

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.
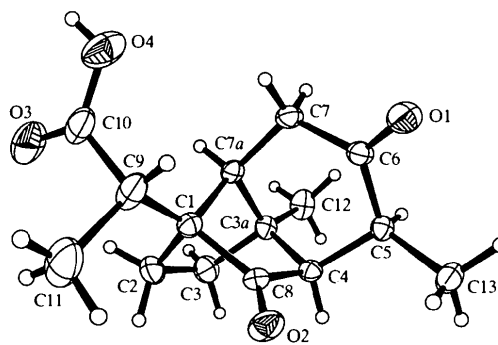

Fig. 1. The asymmetric unit of (I) with its numbering. Ellipsoids are set at the 20% probability level.