

structure: *PATSEE* in *SHELXS97* (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*). Molecular graphics: *SHELXL97*. Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1199). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). **C55**, 1680–1682

## (+)-3-Oxoandrosta-1,4-diene-17 $\beta$ -carboxylic acid: catemeric hydrogen bonding in a steroidal keto acid

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(Received 14 April 1999; accepted 3 June 1999)

## Abstract

The title keto acid, C<sub>20</sub>H<sub>26</sub>O<sub>3</sub>, forms translational carboxyl–ketone hydrogen-bonding catemers [O $\cdots$ O = 2.665 (3) Å]. The cell contains two molecules screw-related in **b**, with opposite end-to-end orientation, yielding two parallel, counterdirectional screw-related hydrogen-bonding chains. Intermolecular C—H $\cdots$ O=C close contacts to the carboxyl group were found, involving three different neighboring molecules.

## Comment

Our interest in the crystal structures of keto carboxylic acids centers on the molecular characteristics that control their five known solid-state hydrogen-bonding patterns. In achiral and racemic keto acids, the most common motif is acid dimerization, in which the ketone is not involved (Thompson *et al.*, 1991; Coté *et al.*, 1995). However in nonracemates with significant conformational restrictions (*e.g.* polycyclics), the prevalence of acid-to-ketone catemers rises dramatically (Brunskill *et al.*, 1999). We have consequently sought keto acids with terpenoid origins as subject materials, and now report the crystal structure and hydrogen-bonding behavior of the title steroid, (I).

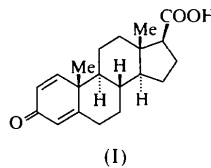


Fig. 1 shows the asymmetric unit with its steroid numbering. The only significant conformational option is rotation of the carboxyl group, which is turned so that the C16—C17 bond lies near the carboxyl plane, with the C=O turned toward C16 [C16—C17—C20—O2 =  $-14.2(5)^\circ$ ]. In the 1,2-dihydro analog of this compound, (II), whose structure we have previously reported (Brunskill *et al.*, 1997), this angle was  $-10.3(4)^\circ$ . The two

angular methyls are staggered relative to the C atoms to which they are attached, C10 and C13. The unsaturated ring is remarkably planar; none of its six C atoms deviates from the average plane by more than 0.013 Å. Within the molecule, the dihedral angle between the carboxyl (C17,C20,O2,O3) and ketone planes (C2,C3,C4,O1) is 11.7 (2)°, contrasted with 27.6 (2)° for (II).

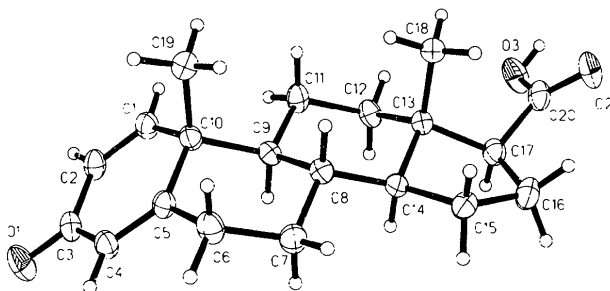


Fig. 1. Compound (I) with its steroidal numbering. Ellipsoids are set at the 30% probability level.

Complete or partial averaging of C—O bond lengths and C—C—O angles by disorder is frequent in carboxyl dimers (Leiserowitz, 1976). However, acids involved in catemeric hydrogen bonding have geometry that precludes any of the usual disordering processes, and are highly ordered. In (I) these lengths are 1.202 (4) and 1.331 (4) Å (for C=O and C—O, respectively), with angles of 125.4 (3) and 112.1 (3)° (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 124.5 (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).

Fig. 2 illustrates the packing of (I) in the cell, with extracellular molecules included to illustrate the two hydrogen-bonding chains created by acid-to-ketone hydrogen bonding [ $O \cdots O = 2.665 (3) \text{ \AA}$ ,  $O—H \cdots O$  angle = 163°]. The two units in the cell are screw-related in **b**, and lie with their long axes parallel, but with opposite end-to-end orientation. In spite of a relatively slight change in molecular shape this is markedly different from the case of (II), whose molecules are aligned in a nonparallel fashion in the crystal. Because the catemers in both (I) and (II) are translational, the intermolecular dihedral angle between the ketone and carboxyl planes for each hydrogen bond is the same as the corresponding intramolecular dihedral angle. The angular approach of a carboxyl hydrogen to the hydrogen-bonding lone pair of a ketone is often found to depart significantly from ideality. We characterize this by the  $C=O \cdots H$  angle and the  $C—C=O \cdots H$  torsion angle, which 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°). In (I) these angles are found to be 134 and -6.3° (132 and -7.6°, upon normalization of the O—H distance to an ideal 'neutron-determined' distance of 1.08 Å).

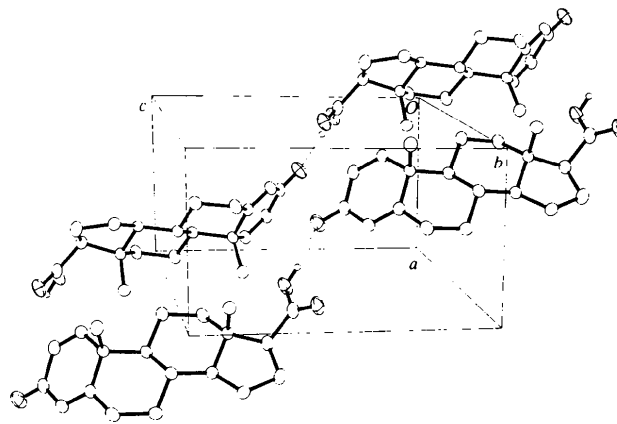


Fig. 2. A packing diagram illustrating one screw-related counterdirectional pair of parallel translational catemers passing through the cell. All non-carboxyl H atoms have been removed for clarity. Ellipsoids are set at the 30% probability level.

Intermolecular  $C—H \cdots O=C$  close contacts less than 2.7 Å to the carboxyl group (O2) were found, involving three separate neighboring molecules: 2.62 Å to H2A (screw-related in **b**), 2.63 Å to H4A (translationally related in **a** and **c**), and 2.47 Å to H19B (translationally related in **c**). Such contacts presumably represent polar attractions contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

The KBr infrared spectrum of (I) displays absorptions at 1726  $\text{cm}^{-1}$  (C=O of the acid group) and at 1654 (ketone C=O), with an alkene absorption at 1603  $\text{cm}^{-1}$ . In  $\text{CHCl}_3$  solution, where dimers predominate, the peaks for (I) appear, normally, at 1705 and 1660  $\text{cm}^{-1}$ , with a peak for C=C at 1620  $\text{cm}^{-1}$  and a typical carboxyl-dilution shoulder at *ca* 1730  $\text{cm}^{-1}$ .

## Experimental

Remarkably, although the methyl ester of (I) has been reported several times (Djerassi & Scholz, 1947; Jones & Cole, 1952; Jones *et al.*, 1955; Sallmann & Tamm, 1956), the keto acid itself was first reported only in 1997 (Fagart *et al.*, 1997). For our material, (+)-21-hydroxy-3,20-dioxo-pregna-1,4-diene, of known absolute configuration, was purchased from Steraloids Inc., Newport, RI, USA, and subjected to cleavage by sodium periodate in aqueous dioxane. The crystals of (I) employed were obtained from methyl acetate by evaporation (m.p. 554 K). The crystal chosen had one long dimension, but was suitable for use with a normal-focus X-ray tube.

**Crystal data**

C<sub>20</sub>H<sub>26</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 314.41  
 Monoclinic  
*P*2<sub>1</sub>  
*a* = 6.597 (1) Å  
*b* = 11.468 (1) Å  
*c* = 11.103 (1) Å  
 $\beta$  = 91.90 (1)°  
*V* = 839.5 (2) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.244 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

**Data collection**

Siemens *P4* diffractometer  
 2 $\theta$ / $\theta$  scans  
 Absorption correction:  
 numerical (Sheldrick;  
 1997)  
*T<sub>min</sub>* = 0.960, *T<sub>max</sub>* = 0.992  
 3366 measured reflections  
 2951 independent reflections  
 2007 reflections with  
*I* > 2 $\sigma$ (*I*)

**Refinement**

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.050  
*wR*(*F*<sup>2</sup>) = 0.099  
*S* = 1.02  
 2951 reflections  
 215 parameters  
 H atoms constrained  
*w* = 1/[ $\sigma^2(F_o^2) + (0.0301P)^2$ ]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 30  
 reflections  
 $\theta$  = 3.57–14.40°  
 $\mu$  = 0.082 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Rectangular plate  
 0.58 × 0.46 × 0.10 mm  
 Colorless

*R<sub>int</sub>* = 0.038  
 $\theta_{\max}$  = 25°  
*h* = -7 → 7  
*k* = -13 → 13  
*l* = -1 → 13  
 3 standard reflections  
 every 97 reflections  
 intensity variation: <2%

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\max}$  = 0.12 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.13 e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C3	1.239 (3)	O3—C20	1.331 (4)
O2—C20	1.202 (4)		
O2—C20—C17	125.4 (3)	O3—C20—C17	112.1 (3)
C16—C17—C20—O2	-14.2 (5)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O1 <sup>i</sup>	0.82	1.87	2.665 (3)	163
C2—H2A...O2 <sup>ii</sup>	0.93	2.62	3.495 (4)	157
C4—H4A...O2 <sup>iii</sup>	0.93	2.63	3.476 (4)	151
C19—H19B...O2 <sup>iv</sup>	0.96	2.47	3.351 (4)	152

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

There were 1395 Friedel pairs in the refinement, but because there were no significant anomalous scatterers, the analysis was not able to confirm the known absolute configuration.

Data collection: XSCANS (Siemens, 1996). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997*a*). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997*b*). Molecular graphics: SHELXL97. Software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1554). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1999). **C55**, 1682–1685

**2-Chloro-6-hydroxypyridinium chloride hydrate**

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(Received 26 May 1999; accepted 14 June 1999)

**Abstract**

The title compound, C<sub>5</sub>H<sub>5</sub>ClNO<sup>+</sup>·Cl<sup>-</sup>·H<sub>2</sub>O, shows typical features of pyridinium cations (*i.e.* wider angles at nitrogen and narrower angles at C-2 and C-6 than in unprotonated pyridines). Short C—Cl and C—O bonds may indicate mesomeric stabilization of the positive charge at the N atom. The extended structure involves classical hydrogen bonds of forms N—H...Cl<sup>-</sup>, O<sub>hydroxy</sub>—H...O<sub>water</sub> and O<sub>water</sub>—H...Cl<sup>-</sup>.