

- Nakanishi, K., Sasaki, S., Kiang, A. K., Goh, J., Kakisawa, H., Dhashi, M., Goto, M., Watanabe, J., Yokotani, H., Matsumura, C. & Togashi, M. (1965). *Chem. Pharm. Bull.* **13**, 882–890.
- Nardelli, M. (1983). *Acta Cryst.* **C39**, 1141–1142.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

*Acta Cryst.* (1998). **C54**, 1651–1653

### (±)-*cis*-10-Carboxymethyl-2-decalone: Catemeric Hydrogen Bonding in an $\epsilon$ -Keto Acid

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

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

(Received 26 March 1998; accepted 27 May 1998)

#### Abstract

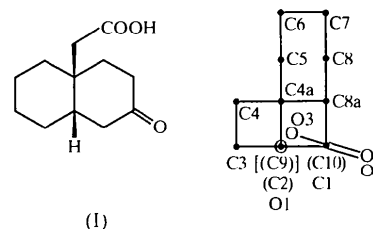
The crystal structure of the title compound, (±)-*cis*-2-oxoperhydronaphthalene-4a-acetic acid, C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>, involves hydrogen-bonding catemers. Hydrogen bonds progress from the carboxyl group of one molecule to the ketone group of a translationally related neighbor [O...O 2.715 (3) Å]. Eight parallel hydrogen-bonding chains proceed in the *a* direction through the chosen cell. Two C=O...H—C close contacts were found, involving the acid carbonyl group.

#### Comment

Our continuing interest in the crystal structures of keto carboxylic acids lies in the elucidation of their hydrogen-bonding behavior, which is more elaborate than in unadorned acids. Most often, the ketone fails to participate in the hydrogen bonding, giving typical carboxyl dimers, but less commonly, intermolecular carboxyl-to-ketone hydrogen bonds occur, yielding a catemer. A third, rare arrangement has an internal hydrogen bond, and instances are known of acid-to-ketone dimerization and acid-to-acid catemerization, while several cases are known of hydrates with more complex hydrogen-bonding patterns. We have previously referenced and discussed numerous examples of these hydrogen-bonding modes (Thompson *et al.*, 1992, 1998; Coté *et al.*, 1996; Lalancette *et al.*, 1998). To denote the handed-

ness of the intrachain units, we have further categorized such catemers as either hetero- or homochiral, and the latter grouping contains subcategories for screw-related and translational types. Most of the previously reported keto-acid catemers have screw-related components, but a sizable minority are translational. In addition to these necessarily homochiral catemer types, a small minority display a glide relationship between adjacent members and are thus heterochiral (Thompson *et al.*, 1998).

The title compound, (I), is an  $\epsilon$ -keto acid, a category that includes dimers and at least one instance each of an internal hydrogen bond and a carboxyl-to-ketone catemer [refcodes KENROK (Abell *et al.*, 1990) and FAXWOQ (Vanderhoff *et al.*, 1986), respectively; Cambridge Structural Database, 1998]. Compound (I) was of interest to us as a one-carbon homolog of a dimerically hydrogen-bonded keto acid whose structure and hydrogen-bonding behavior we had previously reported (Lalancette *et al.*, 1991). Our experience has led us often to anticipate similar hydrogen-bonding behavior among structurally similar compounds, especially in certain small cyclic or polycyclic systems with specific skeletal features, including some present in (I). We report here that (I), rather than dimerizing, forms carboxyl-to-ketone catemers.



The asymmetric unit of (I) with its numbering is shown in Fig. 1. The decalone system crystallizes in the 'non-steroidal' conformation, in which the angular substituent is axial to the ketone ring, as has been found in some similar angularly substituted decalone acids [refcodes VILZIZ (Lalancette *et al.*, 1991) and OCBDCX (Chadwick & Dunitz, 1979); Cambridge Structural Database, 1998]. The only options available for full rotation in (I) involve bonds C4a—C9 and C9—C10. The former adopts a staggered arrangement, with C9—C10 *anti* to C4—C4a, while the carboxyl is rotated about C9—C10 so that it lies in a plane close to that of the ketone [dihedral angle C1/C2/C3/O1 *versus* C9/C10/O2/O3 is 16.7 (1)°], with the carboxyl C=O aimed toward the ketone. The result is a linear-opposed arrangement of ketone O=C and carboxyl C—O or O—H, of the sort that often allows the formation of translational catemers (Lalancette *et al.*, 1997; Brunskill *et al.*, 1997). This spatial arrangement is shown formally in the 'octant-rule' depiction of the conformation (Moffitt *et al.*, 1961), alongside the usual schematic structure for (I). An alignment normal to *c*,

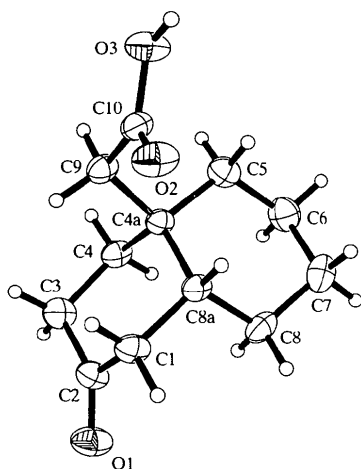


Fig. 1. The asymmetric unit of (I), with the atomic numbering scheme. Ellipsoids are set at the 30% probability level.

but rotated by 20.5° from the *a* direction, provides exactly such a view of the asymmetric unit.

Averaging of C—O bond lengths and C—C—O angles by disorder, which is 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 C—O bond lengths are 1.205 (3) and 1.321 (3) Å, with angles of 124.5 (3) and 114.2 (2)°. Our survey of 28 catemeric keto-acid structures gives average values of 1.20 (1) and 1.32 (1) Å, and 124.5 (10) and 112.8 (14)° 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 packing arrangement for (I) is shown in Fig. 2. Carboxyl-to-ketone catemers having an O...O distance of 2.715 (3) Å are formed by hydrogen bonds that progress among molecules translationally related in the *a* direction, and each molecule in the cell participates in a separate chain. These eight parallel chains are centrosymmetrically arrayed around  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , and represent all the permutations of handedness, chain direction and up-down orientation of the asymmetric unit. Due to the translational nature of the catemer, the dihedral angle between the carboxyl and ketone planes in adjacent hydrogen-bonded molecules is the same as that between the carboxyl and ketone within a molecule [16.7 (1)°].

Two C=O...H—C close contacts are found to the acid carbonyl (O2), both involving the same neighboring molecule, related by a *b* glide perpendicular to *a*. The participating H atoms are H4B (2.66 Å) and H9B (2.69 Å), and the contacts may 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 C=O absorptions at 1721 cm<sup>-1</sup> for the carboxyl, and at 1687

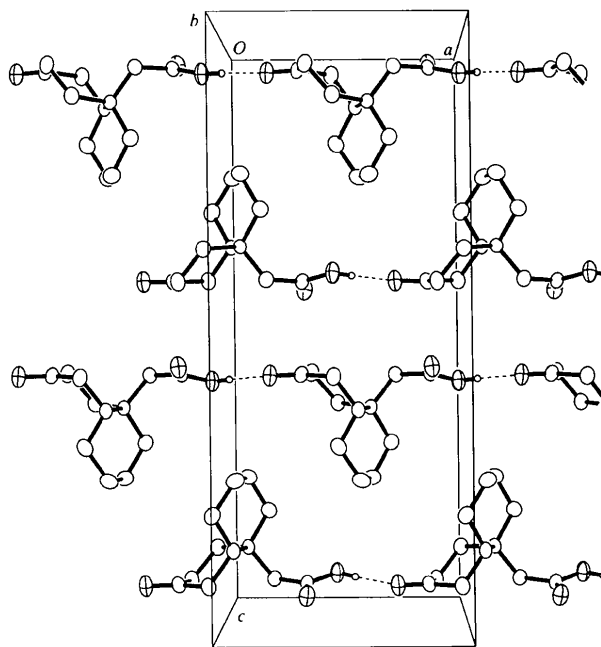


Fig. 2. A partial packing diagram for (I), with extracellular molecules, illustrating the counterdirectional pairs of parallel hydrogen-bonding chains. For clarity, all carbon-bound H atoms have been omitted and only four of the eight chains centrosymmetrically related around  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  are shown. Ellipsoids are set at the 30% probability level.

and 1680 cm<sup>-1</sup> for the ketone. These positions conform to the shifts seen typically in catemers, due to removal of hydrogen bonding from carboxyl C=O and addition of hydrogen bonding to the ketone (Coté *et al.*, 1997). In CHCl<sub>3</sub> solution, all these absorptions coalesce to a single broader peak centered at 1709 cm<sup>-1</sup>, consistent with a dimerically hydrogen-bonded carboxyl group.

## Experimental

Ethoxycarbonylmethylcyclohexanone (Stork *et al.*, 1963) was subjected to Robinson annelation and the purified product was hydrogenated under basic conditions, as described by Gula & Spencer (1980). Saponification provided (I) (m.p. 401 K), which was purified and finally crystallized from 50% ethanol (after seeding with small crystals grown from 10% ethanol).

### Crystal data

C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 210.26  
 Orthorhombic  
*Pbca*  
*a* = 9.182 (2) Å  
*b* = 10.917 (2) Å  
*c* = 21.955 (4) Å  
*V* = 2200.8 (7) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.269 Mg m<sup>-3</sup>  
*D<sub>m</sub>* = 1.269 (1) Mg m<sup>-3</sup>  
*D<sub>m</sub>* measured by flotation in CCl<sub>4</sub>/*p*-xylene

Mo Kα radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 27 reflections  
 $\theta$  = 3.45–15.02°  
 $\mu$  = 0.090 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Parallelepiped  
 0.76 × 0.40 × 0.20 mm  
 Colorless

**Data collection**

Siemens P4 diffractometer  $R_{\text{int}} = 0.060$   
 $2\theta/\theta$  scans  $\theta_{\text{max}} = 25.05^\circ$   
 Absorption correction:  $h = -10 \rightarrow 1$   
 face-indexed numerical  $k = -13 \rightarrow 1$   
 (Sheldrick, 1994)  $l = -26 \rightarrow 26$   
 $T_{\text{min}} = 0.961$ ,  $T_{\text{max}} = 0.983$  3 standard reflections  
 4800 measured reflections every 97 reflections  
 1943 independent reflections intensity decay: 1.84%  
 999 reflections with  
 $I > 2\sigma(I)$

**Refinement**

Refinement on  $F^2$   $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   $\Delta\rho_{\text{max}} = 0.182 \text{ e } \text{\AA}^{-3}$   
 $wR(F^2) = 0.135$   $\Delta\rho_{\text{min}} = -0.132 \text{ e } \text{\AA}^{-3}$   
 $S = 1.001$  Extinction correction: none  
 1942 reflections Scattering factors from  
 147 parameters *International Tables for*  
 H atoms: see below *Crystallography* (Vol. C)  
 $w = 1/[\sigma^2(F_o^2) + (0.055P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C2	1.214 (3)	O3—C10	1.321 (3)
O2—C10	1.205 (3)		
O2—C10—C9	124.5 (3)	O3—C10—C9	114.2 (2)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O1 <sup>i</sup>	0.94 (3)	1.78 (3)	2.715 (3)	174 (1)
C4—H4B...O2 <sup>ii</sup>	0.97	2.66	3.566 (3)	155
C9—H9B...O2 <sup>ii</sup>	0.97	2.69	3.537 (3)	146

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

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 methylene H-atom pairs were allowed to refine independently, as was the single methine H 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 and displacement parameter allowed to refine.

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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1471). Services for accessing these data are described at the back of the journal.

**References**

- Abell, A. D., Morris, K. B. & McKee, V. (1990). *Aust. J. Chem.* **43**, 765–771.  
 Berkovitch-Yellin, Z. & Leiserowitz, L. (1982). *J. Am. Chem. Soc.* **104**, 4052–4064.  
 Borthwick, P. W. (1980). *Acta Cryst.* **B36**, 628–632.

- Brunskill, A. P. J., Lalancette, R. A. & Thompson, H. W. (1997). *Acta Cryst.* **C53**, 903–906.  
 Cambridge Structural Database (1998). Version 5.15. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.  
 Chadwick, D. J. & Dunitz, J. D. (1979). *J. Chem. Soc. Perkin Trans.* **2**, pp. 276–284.  
 Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1996). *Acta Cryst.* **C52**, 684–687.  
 Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1997). *Acta Cryst.* **C53**, 102–106.  
 Fait, J. (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Gula, M. J. & Spencer, T. A. (1980). *J. Org. Chem.* **45**, 805–809.  
 Jönsson, P.-G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.  
 Lalancette, R. A., Thompson, H. W. & Brunskill, A. P. J. (1998). *Acta Cryst.* **C54**, 421–424.  
 Lalancette, R. A., Thompson, H. W. & Coté, M. L. (1997). *Acta Cryst.* **C53**, 901–903.  
 Lalancette, R. A., Thompson, H. W. & Vanderhoff, P. A. (1991). *Acta Cryst.* **C47**, 986–990.  
 Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.  
 Moffitt, W., Woodward, R. B., Moscovitz, A., Klyne, W. & Djerassi, C. (1961). *J. Am. Chem. Soc.* **83**, 4013–4018.  
 Sheldrick, G. M. (1994). *SHELXTL/PC User's Manual*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Siemens (1996). *XSCANS User's Manual*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Stork, G., Brizzolara, A., Landesman, H., Szmuszkovicz, J. & Terrell, R. (1963). *J. Am. Chem. Soc.* **85**, 207–222.  
 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.  
 Vanderhoff, P. A., Thompson, H. W. & Lalancette, R. A. (1986). *Acta Cryst.* **C42**, 1766–1769.

*Acta Cryst.* (1998). **C54**, 1653–1659

### **Amaryllidaceae Alkaloids: (+)-Tazettine, (+)-3-O-Demethylcriwelline and (+)-3-Epimacronine at 173 K**

ANTHONY LINDEN,<sup>a</sup> GÜLNUR AKINERİ,<sup>b</sup> SEDA NOYAN,<sup>b</sup> TEKANT GÖZLER<sup>b</sup> AND MANFRED HESSE<sup>a</sup>

<sup>a</sup>Institut of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland, and <sup>b</sup>Faculty of Pharmacy, Ege University, Bornova 35100, Izmir, Turkey. E-mail: alinden@oci.unizh.ch

(Received 13 March 1998; accepted 15 May 1998)

**Abstract**

The Amaryllidaceae alkaloids (+)-tazettine [(+)-(3*S*,4*aS*,6*aS*,13*bS*)-3-methoxy-5-methyl-3,4,4*a*,5,6,6*a*-hexahydro-8*H*,11*H*-[1,3]dioxolo[6,7][2]benzopyrano[3,4-*c*]indol-