Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(2*S*,4a*R*,8a*S*)-6-Oxoperhydronaphthalene-2-acetic acid: 'conglomerate' crystallization and catemeric hydrogen bonding in a bicyclic *η*-keto acid

Marisa DeVita Dufort, Janish Desai, Roger A. Lalancette* and Hugh W. Thompson

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA
Correspondence e-mail: rogerlal@andromeda.rutgers.edu

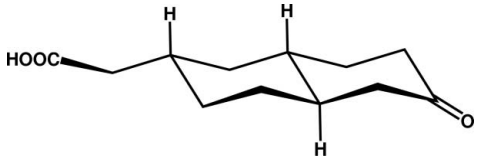
Received 28 March 2007; accepted 19 April 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.091; data-to-parameter ratio = 11.7.

The title compound, $C_{12}H_{18}O_3$, produces crystals of a single enantiomer from a racemic solution; these associate in the solid state in a translational acid-to-ketone catemeric mode [O···O = 2.7087 (15) Å and O—H···O = 175 (2)°], producing two screw-related hydrogen-bonded chains. The ring-fusion and side-chain stereochemistry arise during the synthesis from a 4-substituted cyclohexanone.

Related literature

For related literature describing enantiomeric segregation upon crystallization, see: Chen *et al.* (2000); Tsao *et al.* (2002); for the synthesis, see: Stork *et al.* (1963).



Experimental

Crystal data

$C_{12}H_{18}O_3$
M_r = 210.26
Monoclinic, $P2_1$
a = 9.7431 (2) Å
b = 6.0189 (2) Å
c = 9.8090 (2) Å
β = 105.4620 (10)°
V = 554.41 (2) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.72 mm^{-1}
T = 100 (2) K
0.43 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.746, T_{max} = 0.931
4000 measured reflections
1632 independent reflections
1623 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.091
S = 1.05
1632 reflections
140 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), 549 Friedel pairs
Flack parameter: 0.1 (2)

Table 1
Selected geometric parameters (Å, °).

O2—C10	1.202 (2)	O3—C10	1.336 (2)
O2—C10—C9	124.78 (14)	O3—C10—C9	112.65 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3*C*···O1^{i}	0.88 (3)	1.83 (3)	2.7087 (15)	175 (2)

Symmetry code: (i) $x-1, y-1, z$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2004); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank Professor Jonathan L. Vennerstrom of the University of Nebraska Medical Center for a generous gift of methyl cyclohexanone-4-acetate, and are grateful for financial support from NSF-CRIF grant #0443538. JD and HWT also thank the Rutgers University Undergraduate Research Fellows Program for support, and Professor Gree Loober Spoog for helpful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2124).

References

Bruker (2005). *SAINT* (Version 7.23a) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2006). *APEX2*. Version 2.0-2. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, C.-D., Brunskill, A. P. J., Hall, S. S., Lalancette, R. A. & Thompson, H. W. (2000). *Acta Cryst.* C**56**, 1148–1151.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Sheldrick, G. M. (2001). *SADABS*. Version 2. University of Göttingen, Germany.
Sheldrick, G. M. (2004). *SHELXTL*. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
Stork, G., Brizzolara, A., Landesman, H., Szmuszkovicz, J. & Terrell, R. (1963). *J. Am. Chem. Soc.* **85**, 207–222.
Tsao, J. F., Thompson, H. W. & Lalancette, R. A. (2002). *Struct. Chem.* **13**, 455–458.

 doi:10.1107/S1600536807019666

supplementary materials

Acta Cryst. (2007). E**63**, o2753 [**doi:10.1107/S1600536807019666**]

(2*S*,4a*R*,8a*S*)-6-Oxoperhydronaphthalene-2-acetic acid: `conglomerate' crystallization and catemeric hydrogen bonding in a bicyclic η-keto acid

M. D. Dufort, J. Desai, R. A. Lalancette and H. W. Thompson

Comment

In the hydrogen bonding of simple ketocarboxylic acids, single enantiomers and conformational constraints provide biases toward catemer formation, apparently due to reduced repertoires of low-energy dimers conformations. In this context we report the H-bonding arrangement for compound (I).

Fig. 1 shows the asymmetric unit, whose bicyclic portion is rigid, with conformational options only in the side-chain. The C2—C9 staggering requires that C10 have a *gauche* interaction with an equatorial hydrogen either at C1 or C3. Such *gauche* arrangements are less serious here than in systems where all centers are tetrahedral, because the carboxyl's sp^2 hybridization diminishes the steric repulsions involved. The observed C2—C9 conformation has torsional angle C3—C2—C9—C10 = 53.37 (18)°. Within the asymmetric unit, any energy advantage for this arrangement appears so slight that the choice is likely dictated by packing considerations. The remaining available rotation yields a C2—C9—C10—O3 torsional angle of 59.9 (2)°.

Because compound (I) is not dimeric, the averaging mechanisms responsible for disordering of carboxyl bond lengths and angles in dimers cannot operate. Hence, in (I) these values (Table 1) resemble those in highly ordered carboxyls.

Fig. 2 shows the packing of the cell, with extra molecules included to illustrate the H-bonding scheme (Table 2). Although bulk (I) was racemic (see Experimental), both molecules in the cell are of identical handedness, as reflected in the space group ($P2_1$), and the two H-bonding chains passing through the cell are screw-related. Such enantiomeric segregation in the crystallization of either racemates or conformational enantiomers, known as "conglomerate" crystallization, is uncommon but constitutes a few percent of known simple keto-acid cases (Chen *et al.*, 2000; Tsao *et al.*, 2002). In the H bonding, each carboxylic acid is linked to the ketone of a molecule translationally related in both the a & b directions, so that the chains advance at an angle to the cell axes. Such translational catemers frequently arise in molecules capable of "linear-anti" arrangements of acid and ketone.

We characterize the geometry of H bonding to carbonyls using a combination of the H···O=C angle and the H···O=C—C torsional angle. These describe the approach of the H atom to the O in terms of its deviation from, respectively, C=O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). In (I) these angles are 121.6 (9) & 0.3 (8)°.

No intermolecular close contacts were found within the 2.6-Å range we standardly survey for such C—H···O packing interactions.

Experimental

Compound (I) has not previously been reported. It was prepared by an enamine version of the Robinson annulation (Stork *et al.*, 1963), which converted the methyl ester of cyclohexanone-4-acetic acid (see Acknowledgments) to methyl 6-octalone-

2-acetate; this ester was then saponified and gave (I) upon reduction with Li in liquid NH_3. The C2—C8a stereochemistry arises during the enamine synthesis, with the C4a stereochemistry being established in the subsequent reduction. Crystals suitable for X-ray were obtained from acetone, mp 395 K..

The solid-state (KBr) infrared spectrum of (I) has C=O absorptions at 1732 & 1676 cm^{-1}, with peak separation typical of the shifts seen in catemers, due, respectively, to removal of H bonding from the acid C=O and addition of H bonding to the ketone. In $CHCl_3$ solution, where dimers predominate, these bands coalesce to a single peak at 1708 cm^{-1}.

Refinement

Since the absolute configuration indicated by the Flack parameter agrees with what is known from the synthesis the Friedel pairs were not merged. All H atoms for (I) were found in electron density difference maps. The O—H was allowed to refine positionally with $U_{iso}(H) = 1.5U_{eq}(O)$. The methylene and methine Hs were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C—H distances of 0.99 and 1.00 Å, respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

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

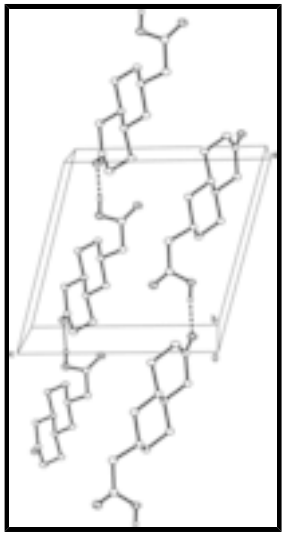


Fig. 2. A partial packing diagram with extracellular molecules, illustrating the two translational acid-to-ketone H-bonding chains. All carbon-bound H atoms are removed for clarity. Displacement ellipsoids are set at the 30% probability level.

(2*S*,4a*R*,8a*S*)-6-Oxoperhydronaphthalene-2-acetic acid

Crystal data

$C_{12}H_{18}O_3$	$F_{000} = 228$
$M_r = 210.26$	$D_x = 1.260$ Mg m^{-3}
Monoclinic, $P2_1$	Cu $K\alpha$ radiation $\lambda = 1.54178$ Å
Hall symbol: P 2yb	Cell parameters from 4000 reflections

a = 9.7431 (2) Å	θ = 5.7–68.1º
b = 6.0189 (2) Å	μ = 0.72 mm^{-1}
c = 9.8090 (2) Å	T = 100 (2) K
β = 105.4620 (10)º	Parallelepiped, colourless
V = 554.41 (2) Å^3	0.43 × 0.12 × 0.10 mm
Z = 2	

Data collection

Bruker SMART CCD APEXII area-detector diffractometer	1632 independent reflections
Radiation source: fine-focus sealed tube	1623 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.035
T = 100(2) K	θ_{max} = 68.1º
φ and ω scans	θ_{min} = 5.7º
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	h = −11→11
T_{min} = 0.746, T_{max} = 0.931	k = −5→6
4000 measured reflections	l = −11→11

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.032	$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.0892P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.091	$(\Delta/\sigma)_{max} < 0.001$
S = 1.05	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
1632 reflections	$\Delta\rho_{min}$ = −0.17 e Å^{-3}
140 parameters	Extinction coefficient: ?
1 restraint	Absolute structure: Flack (1983), 549 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.1 (2)
Secondary atom site location: difference Fourier map	

Special details

Experimental. 'crystal mounted on cryoloop using Paratone-N'

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-

factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.05589 (12)	1.1793 (3)	0.14309 (12)	0.0317 (3)
C1	0.76888 (14)	0.5088 (3)	0.34338 (15)	0.0204 (3)
H1A	0.7845	0.5864	0.4352	0.025*
H1B	0.8149	0.3612	0.3619	0.025*
O2	0.30780 (11)	0.3959 (3)	0.40647 (12)	0.0327 (3)
C2	0.60841 (15)	0.4767 (3)	0.27935 (15)	0.0199 (3)
H2A	0.5938	0.3817	0.1930	0.024*
O3	0.34362 (11)	0.2108 (3)	0.22233 (11)	0.0288 (3)
H3C	0.250 (3)	0.202 (5)	0.202 (2)	0.043*
C3	0.53495 (14)	0.7004 (3)	0.23610 (15)	0.0214 (4)
H3A	0.5389	0.7892	0.3220	0.026*
H3B	0.4335	0.6746	0.1868	0.026*
C4A	0.76422 (14)	0.8641 (3)	0.20743 (14)	0.0198 (3)
H4AA	0.7748	0.9525	0.2959	0.024*
C4	0.60514 (14)	0.8316 (3)	0.13876 (15)	0.0209 (3)
H4A	0.5919	0.7509	0.0482	0.025*
H4B	0.5585	0.9785	0.1178	0.025*
C5	0.83379 (15)	0.9960 (3)	0.10946 (15)	0.0222 (4)
H5A	0.8071	0.9265	0.0146	0.027*
H5B	0.7949	1.1489	0.0995	0.027*
C6	0.99427 (15)	1.0086 (3)	0.16033 (15)	0.0235 (4)
C7	1.07203 (15)	0.8034 (3)	0.22431 (17)	0.0273 (4)
H7A	1.1693	0.8448	0.2796	0.033*
H7B	1.0811	0.7024	0.1475	0.033*
C8	0.99776 (15)	0.6795 (3)	0.32098 (16)	0.0243 (4)
H8A	1.0451	0.5343	0.3478	0.029*
H8B	1.0070	0.7666	0.4086	0.029*
C8A	0.84004 (15)	0.6416 (3)	0.24823 (15)	0.0200 (3)
H8AA	0.8326	0.5543	0.1598	0.024*
C9	0.54735 (14)	0.3545 (3)	0.38752 (15)	0.0224 (4)
H9A	0.5921	0.2059	0.4053	0.027*
H9B	0.5736	0.4377	0.4778	0.027*
C10	0.38814 (16)	0.3265 (3)	0.34231 (16)	0.0223 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0234 (5)	0.0324 (8)	0.0381 (6)	−0.0101 (5)	0.0063 (4)	0.0033 (5)
C1	0.0167 (6)	0.0177 (9)	0.0254 (7)	0.0014 (6)	0.0028 (5)	0.0024 (6)
O2	0.0225 (5)	0.0410 (9)	0.0360 (6)	0.0032 (5)	0.0099 (4)	−0.0018 (6)
C2	0.0168 (6)	0.0188 (9)	0.0235 (7)	−0.0007 (6)	0.0041 (5)	0.0002 (6)
O3	0.0199 (5)	0.0330 (7)	0.0332 (6)	−0.0067 (5)	0.0065 (4)	−0.0030 (5)

C3	0.0162 (6)	0.0208 (10)	0.0267 (7)	−0.0003 (6)	0.0050 (5)	0.0029 (7)
C4A	0.0177 (6)	0.0186 (9)	0.0227 (6)	−0.0014 (7)	0.0049 (5)	0.0002 (6)
C4	0.0173 (6)	0.0188 (9)	0.0254 (7)	0.0002 (6)	0.0034 (5)	0.0028 (6)
C5	0.0191 (7)	0.0219 (9)	0.0258 (7)	−0.0017 (6)	0.0063 (5)	0.0010 (6)
C6	0.0205 (7)	0.0274 (11)	0.0232 (7)	−0.0061 (7)	0.0071 (5)	−0.0008 (7)
C7	0.0158 (6)	0.0303 (11)	0.0357 (8)	−0.0032 (6)	0.0067 (6)	0.0000 (7)
C8	0.0157 (7)	0.0266 (10)	0.0289 (7)	−0.0003 (6)	0.0033 (5)	0.0033 (7)
C8A	0.0167 (6)	0.0181 (9)	0.0249 (7)	−0.0005 (6)	0.0049 (5)	−0.0014 (6)
C9	0.0198 (7)	0.0204 (9)	0.0265 (7)	0.0001 (6)	0.0051 (5)	0.0032 (7)
C10	0.0214 (7)	0.0191 (9)	0.0258 (7)	−0.0018 (6)	0.0053 (5)	0.0065 (6)

Geometric parameters (Å, °)

O1—C6	1.224 (2)	C4A—H4AA	1.0000
C1—C8A	1.528 (2)	C4—H4A	0.9900
C1—C2	1.5339 (18)	C4—H4B	0.9900
C1—H1A	0.9900	C5—C6	1.5111 (18)
C1—H1B	0.9900	C5—H5A	0.9900
O2—C10	1.202 (2)	C5—H5B	0.9900
C2—C3	1.531 (2)	C6—C7	1.497 (3)
C2—C9	1.535 (2)	C7—C8	1.531 (2)
C2—H2A	1.0000	C7—H7A	0.9900
O3—C10	1.336 (2)	C7—H7B	0.9900
O3—H3C	0.88 (3)	C8—C8A	1.5290 (18)
C3—C4	1.533 (2)	C8—H8A	0.9900
C3—H3A	0.9900	C8—H8B	0.9900
C3—H3B	0.9900	C8A—H8AA	1.0000
C4A—C4	1.5289 (18)	C9—C10	1.5049 (18)
C4A—C8A	1.531 (2)	C9—H9A	0.9900
C4A—C5	1.536 (2)	C9—H9B	0.9900
C8A—C1—C2	113.25 (11)	C6—C5—H5B	108.7
C8A—C1—H1A	108.9	C4A—C5—H5B	108.7
C2—C1—H1A	108.9	H5A—C5—H5B	107.6
C8A—C1—H1B	108.9	O1—C6—C7	122.58 (13)
C2—C1—H1B	108.9	O1—C6—C5	119.93 (16)
H1A—C1—H1B	107.7	C7—C6—C5	117.42 (15)
C3—C2—C1	110.65 (13)	C6—C7—C8	113.05 (12)
C3—C2—C9	111.97 (12)	C6—C7—H7A	109.0
C1—C2—C9	108.53 (11)	C8—C7—H7A	109.0
C3—C2—H2A	108.5	C6—C7—H7B	109.0
C1—C2—H2A	108.5	C8—C7—H7B	109.0
C9—C2—H2A	108.5	H7A—C7—H7B	107.8
C10—O3—H3C	107.6 (16)	C8A—C8—C7	111.45 (12)
C2—C3—C4	111.87 (12)	C8A—C8—H8A	109.3
C2—C3—H3A	109.2	C7—C8—H8A	109.3
C4—C3—H3A	109.2	C8A—C8—H8B	109.3
C2—C3—H3B	109.2	C7—C8—H8B	109.3
C4—C3—H3B	109.2	H8A—C8—H8B	108.0
H3A—C3—H3B	107.9	C1—C8A—C8	110.86 (11)

C4—C4A—C8A	111.41 (13)	C1—C8A—C4A	110.58 (11)
C4—C4A—C5	110.80 (11)	C8—C8A—C4A	110.27 (13)
C8A—C4A—C5	110.67 (12)	C1—C8A—H8AA	108.3
C4—C4A—H4AA	107.9	C8—C8A—H8AA	108.3
C8A—C4A—H4AA	107.9	C4A—C8A—H8AA	108.3
C5—C4A—H4AA	107.9	C10—C9—C2	114.14 (12)
C4A—C4—C3	111.07 (11)	C10—C9—H9A	108.7
C4A—C4—H4A	109.4	C2—C9—H9A	108.7
C3—C4—H4A	109.4	C10—C9—H9B	108.7
C4A—C4—H4B	109.4	C2—C9—H9B	108.7
C3—C4—H4B	109.4	H9A—C9—H9B	107.6
H4A—C4—H4B	108.0	O2—C10—O3	122.56 (14)
C6—C5—C4A	114.19 (12)	O2—C10—C9	124.78 (14)
C6—C5—H5A	108.7	O3—C10—C9	112.65 (13)
C4A—C5—H5A	108.7		
C8A—C1—C2—C3	−53.30 (17)	C6—C7—C8—C8A	50.12 (19)
C8A—C1—C2—C9	−176.53 (13)	C2—C1—C8A—C8	176.78 (13)
C1—C2—C3—C4	53.51 (15)	C2—C1—C8A—C4A	54.16 (17)
C9—C2—C3—C4	174.73 (11)	C7—C8—C8A—C1	177.46 (13)
C8A—C4A—C4—C3	56.41 (16)	C7—C8—C8A—C4A	−59.74 (16)
C5—C4A—C4—C3	−179.91 (13)	C4—C4A—C8A—C1	−55.16 (15)
C2—C3—C4—C4A	−55.74 (17)	C5—C4A—C8A—C1	−178.92 (11)
C4—C4A—C5—C6	−172.05 (14)	C4—C4A—C8A—C8	−178.13 (11)
C8A—C4A—C5—C6	−47.94 (18)	C5—C4A—C8A—C8	58.12 (14)
C4A—C5—C6—O1	−142.83 (15)	C3—C2—C9—C10	53.37 (18)
C4A—C5—C6—C7	40.16 (19)	C1—C2—C9—C10	175.81 (14)
O1—C6—C7—C8	142.30 (15)	C2—C9—C10—O2	−121.22 (18)
C5—C6—C7—C8	−40.78 (18)	C2—C9—C10—O3	59.9 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3C···O1^{i}	0.88 (3)	1.83 (3)	2.7087 (15)	175 (2)

Symmetry codes: (i) *x*−1, *y*−1, *z*.

Fig. 1

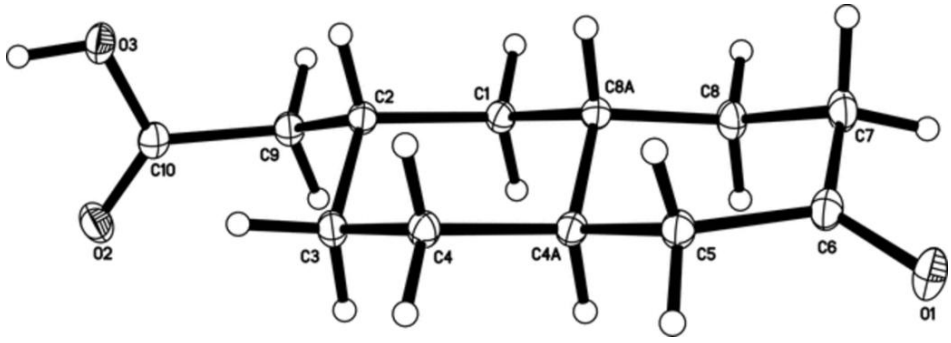


Fig. 2