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Levulinic acid

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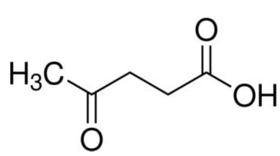
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.040; wR factor = 0.114; data-to-parameter ratio = 13.2.

The title compound (systematic name: 4-oxopentanoic acid), $C_5H_8O_3$, is close to planar (r.m.s. deviation = 0.0762 Å). In the crystal, the molecules interact *via* O—H···O hydrogen bonds in which the hydroxy O atoms act as donors and the ketone O atoms in adjacent molecules as acceptors, forming $C(7)$ chains along [20$\bar{1}$].

Related literature

For uses of levulinic acid, see: Timokhin *et al.* (1999). For density functional and Møller–Plesset perturbation theory calculations for levulinic acid, see: Reichert *et al.* (2010); Kim *et al.* (2011). For typical bond lengths and angles, see: Allen *et al.* (1987); Borthwick (1980). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); Etter *et al.* (1990). For background to the study, see: Flakus & Hachuła (2008); Flakus & Stachowska (2006).



Experimental

Crystal data

$C_5H_8O_3$
M_r = 116.11
Monoclinic, $P2_1/c$
a = 4.8761 (2) Å
b = 12.1025 (4) Å
c = 9.8220 (3) Å
β = 99.112 (3)°
V = 572.31 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.44 × 0.21 × 0.16 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire3 detector
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.585, T_{max} = 1.000
7178 measured reflections
1013 independent reflections
902 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.114
S = 1.06
1013 reflections
77 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{i}	0.83 (2)	1.87 (2)	2.6977 (13)	176 (2)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2114).

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supplementary materials

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Levulinic acid

Barbara Hachuła, Anna Polasz, Marzena Dzida, Maria Nowak and Joachim Kusz

1. Comment

Levulinic acid [systematic name: 4-oxopentanoic acid], (I), is a biogenic product of hexose acid hydrolysis at elevated temperatures that can be obtained from renewable resources. This functionalized carbon structure is widely used as chemical intermediate in the manufacture of fuel extenders, biodegradable polymers, herbicides, antibiotics, flavours and useful 5-carbon compounds (Timokhin *et al.*, 1999; Reichert *et al.*, 2010). Levulinic acid was investigated in a continuation of our studies of the IR spectra of hydrogen bonding in carboxylic acid derivatives (Flakus & Stachowska, 2006; Flakus & Hachuła, 2008). In order to study interactions occurring *via* hydrogen bonds and molecular packing in this compound, we have now determined the structure of (I) using diffraction data collected at 100 K.

The molecule of (I) is nearly planar (r.m.s. deviation of fitted all non-hydrogen atoms is equal to 0.0762 Å). The C—O (1.3373 (17) Å) and C=O (1.2044 (17) Å) bond distances differ slightly from the mean values given by Allen *et al.* (1987) for a variety of carboxylic acid groups (C—O 1.308 Å and C=O 1.214 Å). The bond-angle values at the central C atom in the carboxylic acid group of (I) (O2—C1—C2 124.51 (13) °; O1—C1—C2 112.48 (12)°) agree well with the mean values specified by Borthwick (1980) for a typical carboxylic acid group (O2—C1—C2 123 (2)°; O1—C1—C2 112 (2)°).

The monoclinic structure of (I) is composed of molecular sheets stacked along [101] direction. Atom O1 of the carboxylic group acts as a hydrogen-bond donor *via* H1 to carbonyl atom O3 belonging to the acetyl group of adjacent molecule. This interaction generates hydrogen-bonded chain with a graph-set motif of *C*(7) (Etter *et al.*, 1990; Bernstein *et al.*, 1995).

2. Experimental

Levulinic acid was purchased from Aldrich-Sigma. Crystals of title compound, suitable for X-ray diffraction, were selected directly from purchased sample.

3. Refinement

The H atoms were introduced in geometrically idealized positions and allowed for with an appropriate riding model with C—H distances of 0.99 Å (CH_2) and U_{iso}(H) values set at 1.2U_{eq}(C) or 0.98 Å (CH_3) and with U_{iso}(H) values set at 1.5U_{eq}(C). The H atom which takes part in hydrogen bonding was located in a difference Fourier map and was refined with U_{iso}(H) value set at 1.5U_{eq}(O).

Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

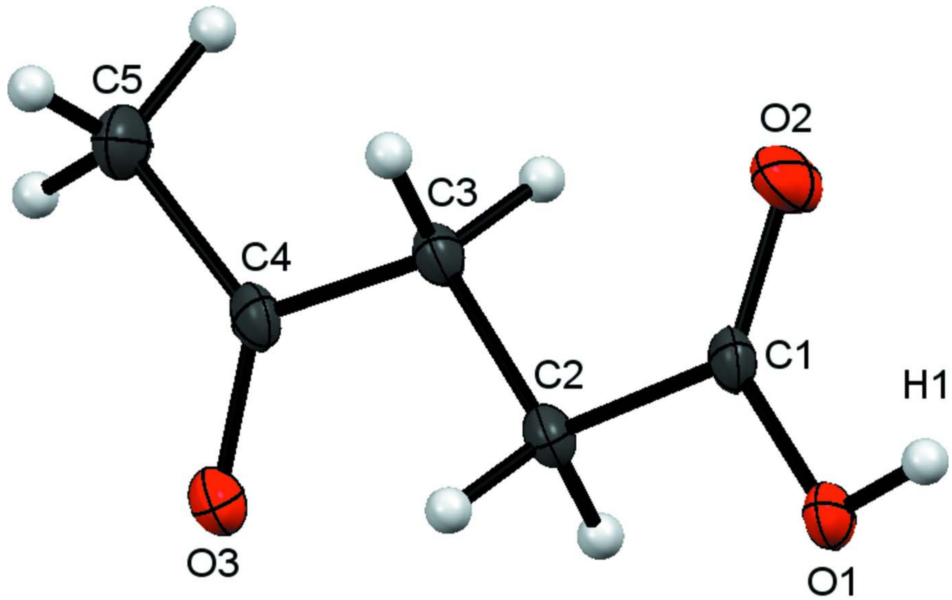

Figure 1

The asymmetric unit of (I), with the atom-numbering scheme, showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radius.

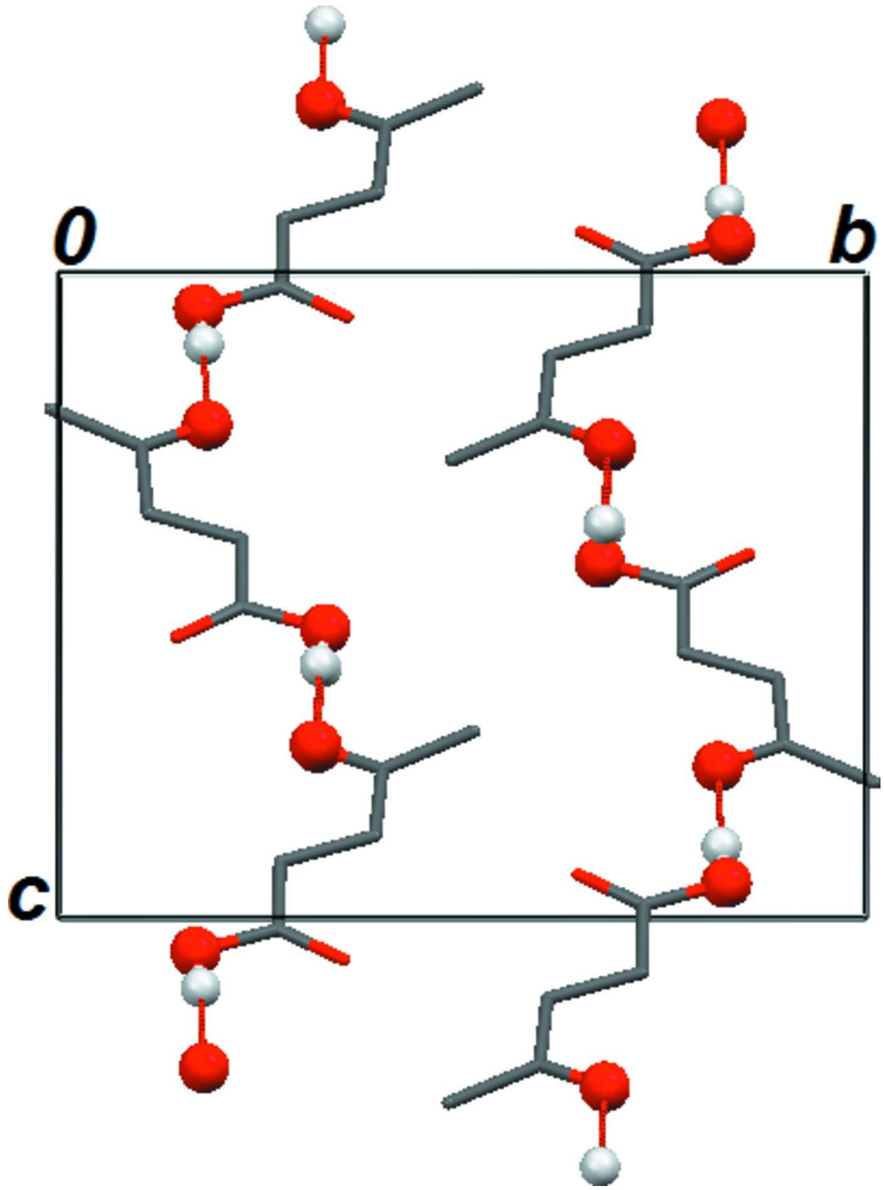

Figure 2

Part of the crystal structure of (I), viewed along the *a* axis, showing the *C*(7) chains. The red lines indicate the hydrogen-bonding interactions. For the sake of clarity, all H atoms bonded to C atoms were omitted.

4-Oxopentanoic acid

Crystal data

$C_5H_8O_3$
M_r = 116.11
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 4.8761 (2) Å
b = 12.1025 (4) Å
c = 9.8220 (3) Å
β = 99.112 (3)°
V = 572.31 (3) Å^3
Z = 4
F(000) = 248
D_x = 1.348 Mg m^{-3}
Melting point = 303–306 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6623 reflections
θ = 3.4–34.5°

μ = 0.11 mm^{-1}
T = 100 K

Polyhedron, colourless
0.44 × 0.21 × 0.16 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire3 detector
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.0328 pixels mm^{-1}
ω scan
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.585, T_{max} = 1.000

7178 measured reflections
1013 independent reflections
902 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.1°, θ_{min} = 3.4°
$h = -5 \rightarrow 4$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.114
S = 1.06
1013 reflections
77 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 0.128P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Special details

Experimental. CrysAlis RED (Oxford Diffraction, 2006). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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	0.4194 (2)	0.16988 (8)	1.05179 (10)	0.0186 (3)
O2	0.3930 (2)	0.35384 (9)	1.06449 (12)	0.0286 (4)
O3	1.0589 (2)	0.31839 (8)	0.73324 (10)	0.0197 (3)
C1	0.4836 (3)	0.27238 (11)	1.01688 (14)	0.0159 (4)
C2	0.6782 (3)	0.27359 (12)	0.91177 (14)	0.0164 (4)
H2A	0.5932	0.2323	0.8288	0.020*
H2B	0.8537	0.2361	0.9505	0.020*
C3	0.7411 (3)	0.39098 (12)	0.87113 (14)	0.0170 (4)
H3A	0.5641	0.4276	0.8328	0.020*
H3B	0.8221	0.4319	0.9552	0.020*
C4	0.9364 (3)	0.39950 (11)	0.76733 (13)	0.0163 (4)

C5	0.9722 (3)	0.51213 (13)	0.70857 (16)	0.0242 (4)
H5A	1.1394	0.5130	0.6648	0.036*
H5B	0.9909	0.5671	0.7827	0.036*
H5C	0.8097	0.5299	0.6398	0.036*
H1	0.311 (4)	0.1766 (16)	1.108 (2)	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0253 (6)	0.0186 (6)	0.0137 (5)	−0.0011 (4)	0.0093 (4)	0.0006 (4)
O2	0.0435 (7)	0.0204 (6)	0.0275 (7)	0.0010 (5)	0.0231 (5)	−0.0016 (5)
O3	0.0240 (6)	0.0218 (6)	0.0148 (5)	0.0025 (4)	0.0072 (4)	0.0001 (4)
C1	0.0200 (7)	0.0187 (7)	0.0088 (7)	−0.0002 (6)	0.0020 (5)	0.0003 (5)
C2	0.0202 (7)	0.0187 (8)	0.0112 (7)	0.0017 (5)	0.0050 (5)	−0.0009 (5)
C3	0.0218 (7)	0.0183 (8)	0.0118 (7)	−0.0002 (5)	0.0060 (6)	−0.0015 (5)
C4	0.0183 (7)	0.0207 (8)	0.0092 (7)	0.0000 (5)	0.0001 (5)	−0.0016 (6)
C5	0.0334 (8)	0.0224 (8)	0.0195 (8)	0.0008 (6)	0.0125 (6)	0.0036 (6)

Geometric parameters (Å, º)

O1—C1	1.3373 (17)	C3—C4	1.5050 (19)
O1—H1	0.83 (2)	C3—H3A	0.9900
O2—C1	1.2044 (17)	C3—H3B	0.9900
O3—C4	1.2231 (17)	C4—C5	1.501 (2)
C1—C2	1.5092 (19)	C5—H5A	0.9800
C2—C3	1.520 (2)	C5—H5B	0.9800
C2—H2A	0.9900	C5—H5C	0.9800
C2—H2B	0.9900		
C1—O1—H1	106.3 (14)	C4—C3—H3B	108.6
O2—C1—O1	123.01 (13)	C2—C3—H3B	108.6
O2—C1—C2	124.51 (13)	H3A—C3—H3B	107.6
O1—C1—C2	112.48 (12)	O3—C4—C5	122.14 (13)
C1—C2—C3	111.32 (12)	O3—C4—C3	121.30 (12)
C1—C2—H2A	109.4	C5—C4—C3	116.57 (12)
C3—C2—H2A	109.4	C4—C5—H5A	109.5
C1—C2—H2B	109.4	C4—C5—H5B	109.5
C3—C2—H2B	109.4	H5A—C5—H5B	109.5
H2A—C2—H2B	108.0	C4—C5—H5C	109.5
C4—C3—C2	114.68 (12)	H5A—C5—H5C	109.5
C4—C3—H3A	108.6	H5B—C5—H5C	109.5
C2—C3—H3A	108.6		
O2—C1—C2—C3	−1.2 (2)	C2—C3—C4—O3	−8.66 (18)
O1—C1—C2—C3	178.42 (10)	C2—C3—C4—C5	171.36 (11)
C1—C2—C3—C4	179.46 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{i}	0.83 (2)	1.87 (2)	2.6977 (13)	176 (2)

Symmetry code: (i) $x-1, -y+1/2, z+1/2$.