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(±)-*exo*-2-Hydroxy-5-oxo-4,8-dioxatricyclo-[4.2.1.0^{3,7}]nonane-9-*exo*-carboxylic acid

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.096
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 14 June 2006
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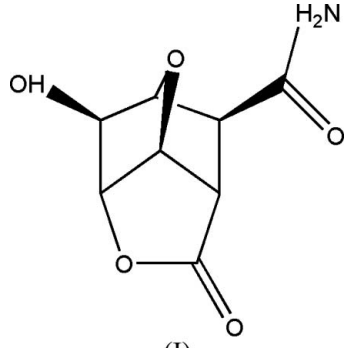
The title compound, $C_8H_9NO_5$, was prepared as a by-product in synthetic efforts to prepare a carbasugar analogue of a putative intermediate, *viz*. (±)-6-hydroxymethyl-7-oxabicyclo[2.2.1]hept-2-*exo*-3-*endo*-diol, in the uridine diphosphate–galactopyranose mutase-catalysed reaction. The structure shows extensive hydrogen bonding involving N—H···O and O—H···O as well as C—H···O interactions.

Comment

The title compound, (I), was prepared as a by-product in synthetic efforts to prepare a carbasugar analogue of a putative intermediate, *viz*. (±)-6-hydroxymethyl-7-oxabicyclo-[2.2.1]hept-2-*exo*-3-*endo*-diol in the uridine diphosphate–galactopyranose mutase-catalysed reaction, and was synthesized from racemic *exo*-5,6-epoxy-7-oxabicyclo[2.2.1]heptan-*trans*-2,3-dicarboxylic acid dimethyl ester (Sadeghi-Khomami *et al.*, 2005) through treatment with concentrated ammonia solution (30% *w*/*v*).



(I)

The molecular structure of (I) is shown in Fig. 1. There is extensive hydrogen bonding in the structure (see Table 1). N—H···O interactions form a ribbon structure (Fig. 2), which lies parallel to the *ac* plane and propagates along the *c*-axis direction. These ribbons can be considered to be linked by O—H···O interactions, forming a two-dimensional layer parallel to the *bc* plane (Fig. 3). In addition, there are C—H···O interactions in the structure (Table 1) which conform to the geometric conditions for the weak hydrogen bonds given by Desiraju & Steiner (1999).

Experimental

Formation of the title compound occurred *via* hydrolysis of the *endo*-methyl carboxylate, followed by a 5-*exo*-Tet lactonization on to the *exo*-epoxide. Concurrently, the *exo*-methyl carboxylate is hydrolysed

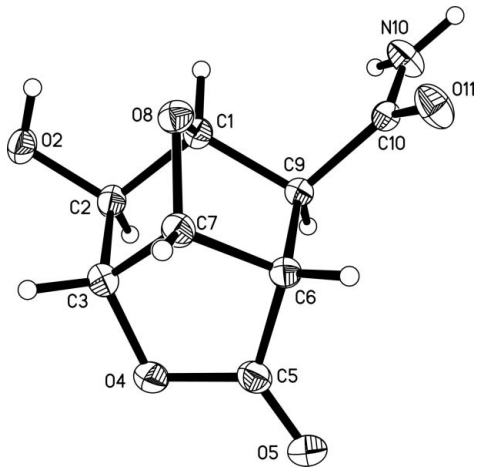


Figure 1
View showing the molecular structure and atom-labelling scheme of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

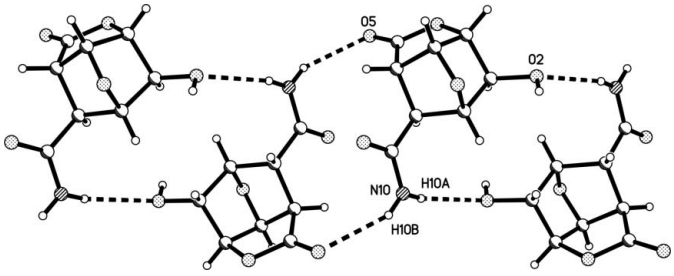


Figure 2
View showing N—H···O hydrogen-bonding interactions (dashed lines), leading to a ribbon structure parallel to the *ac* plane and propagating parallel to the *c* axis.

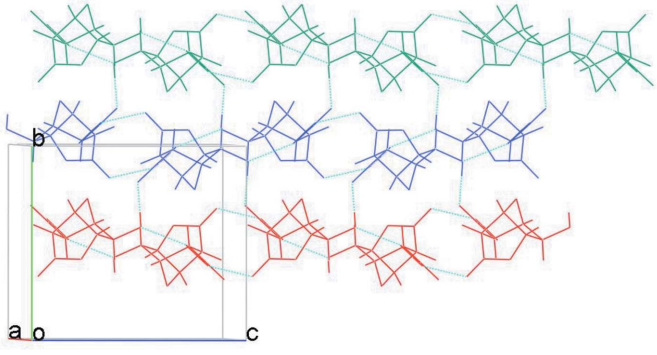
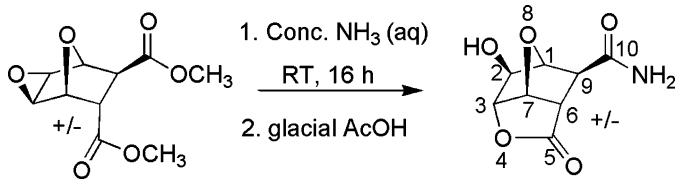


Figure 3
View showing linkage of the N—H···O ribbons (each shown as a single colour) by O—H···O interactions (dashed lines), forming a sheet in the *bc* plane.

and, somewhat surprisingly, forms the carboxamide rather than the expected ammonium salt of the carboxylic acid. The resulting solution was neutralized to pH 7.0 after 16 h at room temperature by dropwise addition of glacial acetic acid and the solvent removed by lyophilization (see scheme). This procedure gave the amide-lactone product (R_F = 0.5, 2-propanol/MeOH 2:1), which crystallized from methanol as colourless blocks. The IR spectrum of the title compound clearly revealed carbonyl bands for the lactone (1780 cm^{-1}) and carboxamide functional groups (1670 cm^{-1}).



Crystal data

$C_8H_9NO_5$
M_r = 199.16
Monoclinic, $P2_1/c$
a = 8.3843 (6) Å
b = 9.1844 (6) Å
c = 10.1638 (7) Å
β = 97.525 (1)°
V = 775.92 (9) Å^3
Z = 4
D_x = 1.705 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 150 (2) K
Block, colourless
0.67 × 0.49 × 0.31 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω scans
Absorption correction: none
6671 measured reflections
1744 independent reflections
1665 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.096
S = 1.03
1744 reflections
140 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.3811P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.025 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N10—H10A···O2^{i}	0.84 (2)	2.30 (2)	3.0871 (15)	156.1 (17)
N10—H10B···O5^{ii}	0.88 (2)	2.39 (2)	3.1743 (15)	149.8 (16)
O2—H2···O11^{iii}	0.84 (2)	2.06 (2)	2.8841 (13)	167 (2)
C2—H2A···O11^{iv}	1.00	2.55	3.4779 (15)	154
C1—H1A···O11^{iii}	1.00	2.38	2.9723 (14)	117
C7—H7A···O4^{v}	1.00	2.43	3.2000 (14)	133
C7—H7A···O5^{vi}	1.00	2.60	3.2862 (15)	126

Symmetry codes: (i) $-x+1, -y+2, -z+2$; (ii) $-x+1, -y+2, -z+1$; (iii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (vi) $-x, -y+2, -z+1$.

All H atoms could be located in a difference Fourier map. However, the H atoms bound to carbon were subsequently placed in idealized positions and included as part of a riding model, with C—H = 1.00 Å and U_{iso}(H) = 1.2U_{eq}(C). Positional and U_{iso} parameters were refined for H atoms bound to nitrogen and oxygen.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* and *SHELXTL* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4.1; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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supporting information

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$F(000)$ = 416
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ω scans
6671 measured reflections
1744 independent reflections
1665 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.5°, θ_{min} = 2.5°
h = −10→10
k = −11→11
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.096
S = 1.03
1744 reflections
140 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.3811P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.025 (4)

Special details

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.39752 (13)	0.90298 (12)	0.83551 (11)	0.0162 (2)
H1A	0.5033	0.8833	0.8904	0.019*
O2	0.27189 (11)	0.91959 (10)	1.03823 (8)	0.0221 (2)
H2	0.329 (3)	0.843 (2)	1.040 (2)	0.046 (6)*
C2	0.27728 (14)	0.98325 (13)	0.91116 (11)	0.0184 (3)
H2A	0.3023	1.0896	0.9187	0.022*
C3	0.11901 (14)	0.95537 (14)	0.81764 (12)	0.0203 (3)
H3A	0.0316	0.9169	0.8661	0.024*
O4	0.06852 (11)	1.08301 (10)	0.73785 (9)	0.0251 (2)
O5	0.10540 (11)	1.17205 (10)	0.53941 (9)	0.0272 (2)
C5	0.13596 (14)	1.08018 (13)	0.62312 (12)	0.0205 (3)
C6	0.24340 (13)	0.94895 (13)	0.62351 (11)	0.0171 (3)
H6A	0.2473	0.9071	0.5332	0.020*
C7	0.17366 (13)	0.84289 (13)	0.71936 (11)	0.0185 (3)
H7A	0.0875	0.7762	0.6771	0.022*
O8	0.30882 (10)	0.77254 (9)	0.79295 (8)	0.0184 (2)
C9	0.41311 (13)	0.97821 (12)	0.70168 (11)	0.0155 (2)
H9A	0.4365	1.0846	0.7126	0.019*
C10	0.54303 (13)	0.89808 (12)	0.63801 (11)	0.0163 (2)
N10	0.69432 (13)	0.92649 (13)	0.68952 (12)	0.0243 (3)
H10A	0.715 (2)	0.989 (2)	0.7503 (19)	0.038 (5)*
O11	0.50958 (10)	0.80859 (11)	0.54905 (9)	0.0258 (2)
H10B	0.769 (2)	0.881 (2)	0.6526 (18)	0.035 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0159 (5)	0.0172 (5)	0.0153 (5)	−0.0015 (4)	0.0017 (4)	0.0003 (4)
O2	0.0267 (5)	0.0245 (5)	0.0161 (4)	0.0012 (3)	0.0063 (3)	0.0021 (3)
C2	0.0200 (6)	0.0192 (5)	0.0165 (5)	−0.0004 (4)	0.0043 (4)	0.0008 (4)
C3	0.0176 (5)	0.0241 (6)	0.0197 (5)	0.0018 (4)	0.0046 (4)	0.0022 (4)
O4	0.0242 (5)	0.0295 (5)	0.0224 (5)	0.0107 (4)	0.0055 (3)	0.0031 (3)
O5	0.0257 (5)	0.0292 (5)	0.0263 (5)	0.0087 (4)	0.0020 (4)	0.0065 (4)
C5	0.0163 (5)	0.0243 (6)	0.0208 (6)	0.0022 (4)	0.0016 (4)	−0.0009 (4)
C6	0.0156 (5)	0.0192 (5)	0.0163 (5)	0.0009 (4)	0.0013 (4)	0.0005 (4)
C7	0.0153 (5)	0.0209 (6)	0.0191 (5)	−0.0011 (4)	0.0019 (4)	0.0006 (4)

O8	0.0186 (4)	0.0161 (4)	0.0203 (4)	−0.0009 (3)	0.0012 (3)	0.0010 (3)
C9	0.0147 (5)	0.0164 (5)	0.0153 (5)	0.0008 (4)	0.0021 (4)	0.0004 (4)
C10	0.0170 (5)	0.0160 (5)	0.0162 (5)	0.0002 (4)	0.0037 (4)	0.0025 (4)
N10	0.0159 (5)	0.0285 (6)	0.0287 (6)	0.0011 (4)	0.0030 (4)	−0.0103 (4)
O11	0.0199 (4)	0.0308 (5)	0.0270 (5)	−0.0007 (4)	0.0044 (3)	−0.0123 (4)

Geometric parameters (Å, º)

C1—O8	1.4460 (13)	C5—C6	1.5044 (16)
C1—C2	1.5344 (15)	C6—C7	1.5457 (16)
C1—C9	1.5464 (15)	C6—C9	1.5594 (15)
C1—H1A	1.0000	C6—H6A	1.0000
O2—C2	1.4238 (14)	C7—O8	1.4279 (14)
O2—H2	0.84 (2)	C7—H7A	1.0000
C2—C3	1.5491 (16)	C9—C10	1.5270 (15)
C2—H2A	1.0000	C9—H9A	1.0000
C3—O4	1.4565 (14)	C10—O11	1.2269 (14)
C3—C7	1.5476 (16)	C10—N10	1.3332 (15)
C3—H3A	1.0000	N10—H10A	0.84 (2)
O4—C5	1.3612 (15)	N10—H10B	0.88 (2)
O5—C5	1.2018 (15)		
O8—C1—C2	101.66 (9)	C5—C6—C9	111.68 (9)
O8—C1—C9	101.92 (8)	C7—C6—C9	100.53 (8)
C2—C1—C9	111.28 (9)	C5—C6—H6A	113.4
O8—C1—H1A	113.6	C7—C6—H6A	113.4
C2—C1—H1A	113.6	C9—C6—H6A	113.4
C9—C1—H1A	113.6	O8—C7—C6	105.99 (9)
C2—O2—H2	105.8 (14)	O8—C7—C3	104.22 (9)
O2—C2—C1	110.99 (9)	C6—C7—C3	98.89 (9)
O2—C2—C3	111.24 (9)	O8—C7—H7A	115.3
C1—C2—C3	100.33 (9)	C6—C7—H7A	115.3
O2—C2—H2A	111.3	C3—C7—H7A	115.3
C1—C2—H2A	111.3	C7—O8—C1	97.10 (8)
C3—C2—H2A	111.3	C10—C9—C1	107.73 (9)
O4—C3—C7	105.48 (9)	C10—C9—C6	110.79 (9)
O4—C3—C2	111.82 (10)	C1—C9—C6	101.22 (8)
C7—C3—C2	101.78 (9)	C10—C9—H9A	112.2
O4—C3—H3A	112.4	C1—C9—H9A	112.2
C7—C3—H3A	112.4	C6—C9—H9A	112.2
C2—C3—H3A	112.4	O11—C10—N10	122.30 (11)
C5—O4—C3	109.79 (9)	O11—C10—C9	121.89 (10)
O5—C5—O4	121.27 (11)	N10—C10—C9	115.73 (10)
O5—C5—C6	129.53 (11)	C10—N10—H10A	121.0 (13)
O4—C5—C6	109.20 (10)	C10—N10—H10B	115.9 (12)
C5—C6—C7	103.34 (9)	H10A—N10—H10B	122.9 (17)
O8—C1—C2—O2	76.24 (11)	O4—C3—C7—O8	142.70 (9)

C9—C1—C2—O2	−175.90 (9)	C2—C3—C7—O8	25.84 (11)
O8—C1—C2—C3	−41.43 (10)	O4—C3—C7—C6	33.59 (11)
C9—C1—C2—C3	66.43 (11)	C2—C3—C7—C6	−83.27 (10)
O2—C2—C3—O4	139.66 (10)	C6—C7—O8—C1	51.80 (10)
C1—C2—C3—O4	−102.85 (10)	C3—C7—O8—C1	−51.99 (10)
O2—C2—C3—C7	−108.18 (10)	C2—C1—O8—C7	58.46 (9)
C1—C2—C3—C7	9.31 (11)	C9—C1—O8—C7	−56.51 (9)
C7—C3—O4—C5	−20.84 (12)	O8—C1—C9—C10	−76.25 (10)
C2—C3—O4—C5	88.98 (11)	C2—C1—C9—C10	176.06 (9)
C3—O4—C5—O5	176.83 (11)	O8—C1—C9—C6	40.06 (10)
C3—O4—C5—C6	−2.27 (13)	C2—C1—C9—C6	−67.62 (11)
O5—C5—C6—C7	−154.72 (13)	C5—C6—C9—C10	−145.28 (10)
O4—C5—C6—C7	24.28 (12)	C7—C6—C9—C10	105.67 (10)
O5—C5—C6—C9	98.04 (15)	C5—C6—C9—C1	100.68 (10)
O4—C5—C6—C9	−82.96 (12)	C7—C6—C9—C1	−8.38 (10)
C5—C6—C7—O8	−141.71 (9)	C1—C9—C10—O11	100.73 (12)
C9—C6—C7—O8	−26.23 (11)	C6—C9—C10—O11	−9.14 (15)
C5—C6—C7—C3	−34.04 (11)	C1—C9—C10—N10	−76.22 (12)
C9—C6—C7—C3	81.44 (9)	C6—C9—C10—N10	173.92 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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