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5-Amino-5-deoxy-2-*C*-hydroxymethyl-2,3-*O*-isopropylidene-D-talono-1,5-lactam

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.034
Data-to-parameter ratio = 7.1

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

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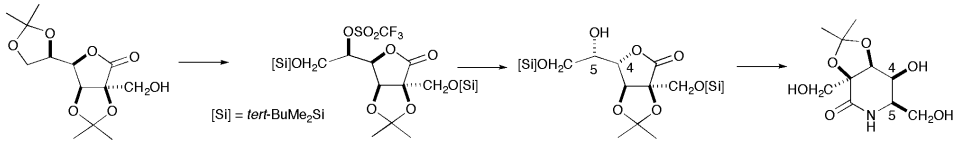
The title compound, $C_{10}H_{17}NO_6$, was prepared by carrying out three S_N2 displacements on a branched sugar derivative, one of which was not planned. Its crystal structure was determined to confirm the identity and stereochemistry of the product.

Comment

Even though the value of carbohydrate building blocks to provide access to enantiomerically pure synthetic materials is well recognized, there are no easily available branched sugar intermediates (Bols, 1996). The Kiliani reaction on cheap ketoses, although hitherto hardly explored, produces protected branched carbohydrates easily. Such materials are likely to have many uses, but initially we are studying the easy preparation of branched sugar mimetics in which the ring oxygen of the sugar is replaced by nitrogen (Winchester & Fleet, 1992; Asano *et al.*, 2000). The biological properties of branched alkaloids are promising (Ichikawa & Igarashi, 1995, Ichikawa *et al.*, 1998), but the difficulties in the synthesis of such compounds have hindered a substantive investigation of these properties. The branched diacetonide (I) was readily prepared from D-fructose and was readily transformed into the trifluoromethanesulfonate (2). It was anticipated that treatment of (2) with an oxygen nucleophile would result in a single inversion of configuration at C5. However, the major product isolated, (3) had undergone inversion of configuration at both C4 and C5. The alcohol (3) was elaborated by standard reactions to the title lactam (4), the structure of which is hereby firmly established by X-ray crystallographic analysis. The configuration at C4 of the lactam (4) unequivocally demonstrates that an unexpected double inversion took place in the transformation of (2) to (3).



(1) (2) (3) (4)

The NH and OH groups all form clearly defined intermolecular hydrogen bonds, linking bilayers of molecules running parallel to the crystallographic *ab* plane.

Experimental

The lactam (4) was prepared from the diacetonide (1) derived from fructose (Hotchliss et al., 2004). The title material was crystallized from methanol to yield colourless plates.

Crystal data

$C_{10}H_{17}NO_6$
M_r = 247.25
Monoclinic, $P2_1$
a = 6.1266 (2) Å
b = 6.7254 (2) Å
c = 13.8419 (5) Å
β = 99.6456 (14)°
V = 562.28 (3) Å^3
Z = 2
D_x = 1.460 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5291 reflections
θ = 5–28°
μ = 0.12 mm^{-1}
T = 150 K
Plate, colourless
0.38 × 0.38 × 0.14 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.96, T_{max} = 0.98
5291 measured reflections
1372 independent reflections
1211 reflections with $I > 3\sigma(I)$
R_{int} = 0.030
θ_{max} = 27.4°
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 17$

Refinement

Refinement on F
R = 0.028
wR = 0.034
S = 1.10
1211 reflections
170 parameters
H atoms treated by a mixture of independent and constrained refinement
Weighting scheme: see text
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O6^{i}	0.94 (3)	1.96 (3)	2.8510 (19)	156 (3)
O2—H2···O1^{ii}	0.86 (3)	1.89 (3)	2.7408 (17)	169 (3)
O5—H3···O2^{iii}	0.91 (4)	1.86 (4)	2.7338 (18)	161 (3)
O6—H4···O5^{iv}	0.93 (3)	1.75 (3)	2.6610 (18)	167 (3)

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

The weighting scheme used a Chebychev polynomial (Watkin, 1994, Prince, 1982): $w = \{1 - [(F_o - F_c)/6\sigma(F)]^2\}^2/[1.14T_0(x) + 0.561T_1(x) + 0.916T_2(x)]$, where $x = F_c/F_{max}$.

Friedel pairs of reflections were merged prior to use in refinement. The absolute configuration of the compound was assumed on the basis of that of the optically pure starting material. The NH and OH H atoms were located in a difference Fourier map and their coordinates and isotropic displacement parameters were subsequently refined. All other H atoms were positioned geometrically (C—H = 1.00 Å), with isotropic displacement parameters set equal to $1.2U_{eq}$ of the parent atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS* (Shape Software, 2002); software used to prepare material for publication: *CRYSTALS*.

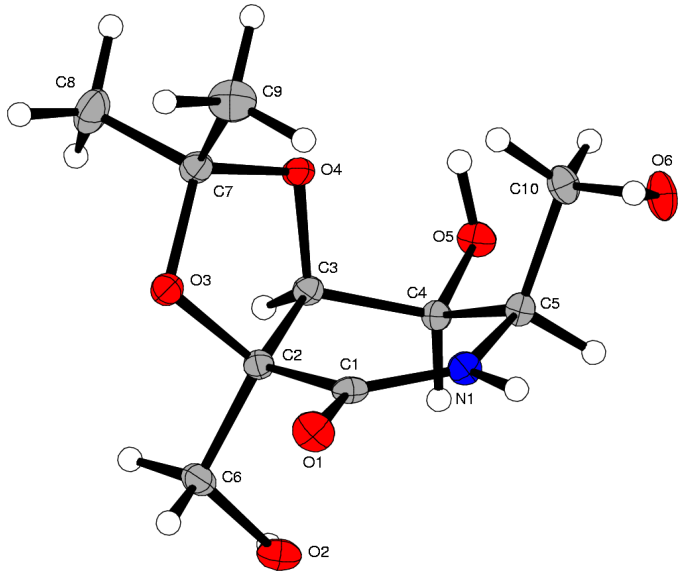


Figure 1
View of the title molecule, showing displacement ellipsoids at the 40% probability level. H atoms are shown as spheres of arbitrary radius.

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$V = 562.28$ (3) Å^3
$Z = 2$
$F(000) = 264$
$D_x = 1.460$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5291 reflections
$\theta = 5$–28°
$\mu = 0.12$ mm^{-1}
$T = 150$ K
Plate, colourless
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Data collection

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1372 independent reflections
1211 reflections with $I > 3.00u(I)$
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$\theta_{max} = 27.4°$, $\theta_{min} = 5.1°$
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 17$

Refinement

Refinement on F
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.034$
$S = 1.10$
1211 reflections
170 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)]$ where A_i are the Chebychev coefficients listed below and x = F /Fmax Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta$F$/6*sigma$F$)^2]^2 A_i are: 1.14 0.561 0.916
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.1580 (2)	0.3518 (2)	0.37174 (11)	0.0176

C1	0.1315 (2)	0.2536 (3)	0.28694 (12)	0.0160
C2	0.3054 (3)	0.2808 (2)	0.21935 (13)	0.0154
C3	0.4612 (2)	0.4553 (3)	0.24723 (10)	0.0153
C4	0.5232 (2)	0.4908 (2)	0.35601 (11)	0.0151
C5	0.3214 (2)	0.5061 (3)	0.40842 (11)	0.0161
O1	−0.0245 (2)	0.1385 (2)	0.26071 (10)	0.0239
C6	0.4241 (3)	0.0847 (3)	0.20754 (13)	0.0206
O2	0.5652 (2)	0.0291 (2)	0.29613 (10)	0.0215
O3	0.1949 (2)	0.3367 (2)	0.12375 (9)	0.0211
O4	0.3350 (2)	0.6200 (2)	0.20346 (9)	0.0182
C7	0.1964 (3)	0.5502 (3)	0.11614 (12)	0.0183
C8	0.2954 (3)	0.6069 (3)	0.02649 (14)	0.0292
C9	−0.0325 (3)	0.6348 (3)	0.11512 (15)	0.0303
O5	0.66148 (19)	0.66075 (19)	0.37549 (9)	0.0196
C10	0.2106 (3)	0.7109 (3)	0.40523 (12)	0.0203
O6	0.0666 (2)	0.7158 (2)	0.47624 (9)	0.0245
H1	0.050 (5)	0.324 (5)	0.411 (2)	0.042 (8)*
H2	0.699 (6)	0.064 (6)	0.293 (2)	0.054 (9)*
H3	0.604 (6)	0.768 (6)	0.340 (2)	0.052 (9)*
H4	−0.075 (5)	0.680 (5)	0.4463 (19)	0.038 (7)*
H31	0.6060	0.4317	0.2249	0.0186*
H41	0.6082	0.3709	0.3835	0.0179*
H51	0.3818	0.4842	0.4793	0.0194*
H61	0.5153	0.0999	0.1545	0.0252*
H62	0.3111	−0.0220	0.1891	0.0252*
H81	0.2976	0.7550	0.0203	0.0355*
H82	0.4501	0.5545	0.0336	0.0355*
H83	0.2039	0.5485	−0.0334	0.0355*
H91	−0.0270	0.7829	0.1098	0.0358*
H92	−0.0858	0.5974	0.1771	0.0358*
H93	−0.1361	0.5800	0.0578	0.0358*
H101	0.3263	0.8163	0.4205	0.0247*
H102	0.1232	0.7347	0.3385	0.0247*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0164 (7)	0.0179 (7)	0.0198 (6)	−0.0030 (5)	0.0066 (5)	0.0004 (6)
C1	0.0130 (7)	0.0138 (7)	0.0217 (8)	0.0014 (6)	0.0043 (5)	0.0041 (6)
C2	0.0166 (7)	0.0140 (7)	0.0159 (8)	−0.0015 (6)	0.0038 (6)	0.0003 (6)
C3	0.0151 (6)	0.0147 (7)	0.0167 (7)	−0.0016 (6)	0.0045 (5)	0.0009 (6)
C4	0.0140 (7)	0.0152 (8)	0.0155 (7)	−0.0008 (5)	0.0011 (5)	−0.0004 (6)
C5	0.0147 (7)	0.0186 (7)	0.0152 (7)	−0.0019 (6)	0.0026 (5)	−0.0004 (6)
O1	0.0182 (6)	0.0233 (6)	0.0307 (6)	−0.0075 (5)	0.0056 (4)	−0.0016 (6)
C6	0.0246 (8)	0.0146 (8)	0.0237 (9)	0.0000 (6)	0.0076 (6)	−0.0018 (6)
O2	0.0155 (6)	0.0166 (6)	0.0326 (7)	−0.0008 (5)	0.0047 (5)	0.0034 (5)
O3	0.0300 (7)	0.0156 (6)	0.0166 (6)	−0.0047 (5)	0.0004 (5)	−0.0006 (5)
O4	0.0234 (6)	0.0134 (5)	0.0162 (6)	−0.0013 (4)	−0.0010 (4)	0.0009 (4)

C7	0.0208 (8)	0.0164 (8)	0.0170 (8)	−0.0048 (6)	0.0011 (6)	0.0010 (6)
C8	0.0362 (10)	0.0332 (11)	0.0192 (8)	−0.0112 (9)	0.0076 (7)	0.0018 (7)
C9	0.0208 (9)	0.0315 (10)	0.0371 (10)	0.0010 (8)	0.0004 (7)	0.0023 (9)
O5	0.0141 (5)	0.0185 (6)	0.0248 (6)	−0.0042 (5)	−0.0007 (4)	−0.0012 (5)
C10	0.0178 (7)	0.0227 (8)	0.0213 (8)	−0.0004 (6)	0.0063 (6)	−0.0046 (7)
O6	0.0161 (5)	0.0370 (7)	0.0215 (6)	−0.0008 (5)	0.0060 (4)	−0.0103 (6)

Geometric parameters (Å, º)

N1—C1	1.333 (2)	C6—H62	1.000
N1—C5	1.471 (2)	O2—H2	0.86 (3)
N1—H1	0.94 (3)	O3—C7	1.440 (2)
C1—C2	1.542 (2)	O4—C7	1.435 (2)
C1—O1	1.236 (2)	C7—C8	1.518 (2)
C2—C3	1.521 (2)	C7—C9	1.511 (2)
C2—C6	1.528 (2)	C8—H81	1.000
C2—O3	1.432 (2)	C8—H82	1.000
C3—C4	1.509 (2)	C8—H83	1.000
C3—O4	1.426 (2)	C9—H91	1.000
C3—H31	1.000	C9—H92	1.000
C4—C5	1.538 (2)	C9—H93	1.000
C4—O5	1.4215 (19)	O5—H3	0.91 (4)
C4—H41	1.000	C10—O6	1.427 (2)
C5—C10	1.533 (2)	C10—H101	1.000
C5—H51	1.000	C10—H102	1.000
C6—O2	1.427 (2)	O6—H4	0.93 (3)
C6—H61	1.000		

C1—N1—C5	128.95 (13)	C2—C6—H62	108.982
C1—N1—H1	114.5 (19)	O2—C6—H62	108.982
C5—N1—H1	116 (2)	H61—C6—H62	109.467
N1—C1—C2	118.74 (14)	C6—O2—H2	109 (2)
N1—C1—O1	122.89 (15)	C2—O3—C7	108.74 (13)
C2—C1—O1	118.36 (15)	C3—O4—C7	107.81 (13)
C1—C2—C3	113.93 (13)	O3—C7—O4	105.95 (14)
C1—C2—C6	110.60 (13)	O3—C7—C8	108.57 (16)
C3—C2—C6	113.79 (13)	O4—C7—C8	110.19 (14)
C1—C2—O3	108.93 (13)	O3—C7—C9	111.03 (15)
C3—C2—O3	102.22 (13)	O4—C7—C9	107.58 (15)
C6—C2—O3	106.70 (13)	C8—C7—C9	113.27 (16)
C2—C3—C4	114.70 (13)	C7—C8—H81	109.467
C2—C3—O4	102.65 (12)	C7—C8—H82	109.467
C4—C3—O4	109.21 (13)	H81—C8—H82	109.476
C2—C3—H31	110.567	C7—C8—H83	109.467
C4—C3—H31	104.177	H81—C8—H83	109.476
O4—C3—H31	115.933	H82—C8—H83	109.476
C3—C4—C5	113.15 (13)	C7—C9—H91	109.467
C3—C4—O5	111.05 (13)	C7—C9—H92	109.467

C5—C4—O5	110.94 (13)	H91—C9—H92	109.476
C3—C4—H41	106.285	C7—C9—H93	109.467
C5—C4—H41	106.403	H91—C9—H93	109.476
O5—C4—H41	108.711	H92—C9—H93	109.476
N1—C5—C4	110.13 (13)	C4—O5—H3	112 (2)
N1—C5—C10	110.58 (13)	C5—C10—O6	108.81 (14)
C4—C5—C10	115.68 (13)	C5—C10—H101	109.637
N1—C5—H51	110.696	O6—C10—H101	109.637
C4—C5—H51	104.970	C5—C10—H102	109.637
C10—C5—H51	104.465	O6—C10—H102	109.637
C2—C6—O2	111.42 (13)	H101—C10—H102	109.467
C2—C6—H61	108.982	C10—O6—H4	109.0 (16)
O2—C6—H61	108.982		

Hydrogen-bond geometry (Å, º)

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