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

Jeroen van Ameijde,[a] Andrew R. Cowley,[b]* George W. J. Fleet,[a] Robert J. Nash,[c] Michela Iezzi Simone[a] and Raquel Soengas[a]

[a]Department of Organic Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, England, [b]Chemical Crystallography Laboratory, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, England, and [c]Molecular Nature Ltd, Insitute of Grassland and Environmental Research, Aberystwyth SY23 3EB, Wales

Correspondence e-mail:
andrew.cowley@chem.ox.ac.uk

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.

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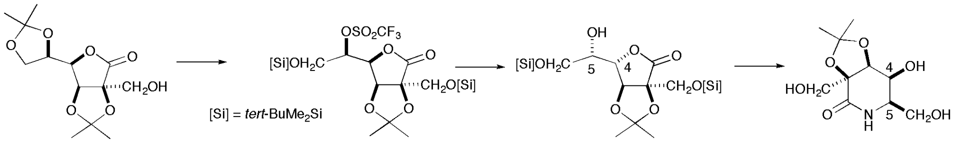
Key indicators

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.

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
$\beta = 99.6456$ (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
$\theta = 5$–28°
$\mu = 0.12$ 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 $I > 3\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 27.4$°
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 17$

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$^{\rm i}$	0.94 (3)	1.96 (3)	2.8510 (19)	156 (3)
O2—H2···O1$^{\rm ii}$	0.86 (3)	1.89 (3)	2.7408 (17)	169 (3)
O5—H3···O2$^{\rm iii}$	0.91 (4)	1.86 (4)	2.7338 (18)	161 (3)
O6—H4···O5$^{\rm iv}$	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 1.2$U_{\rm eq}$ 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*.

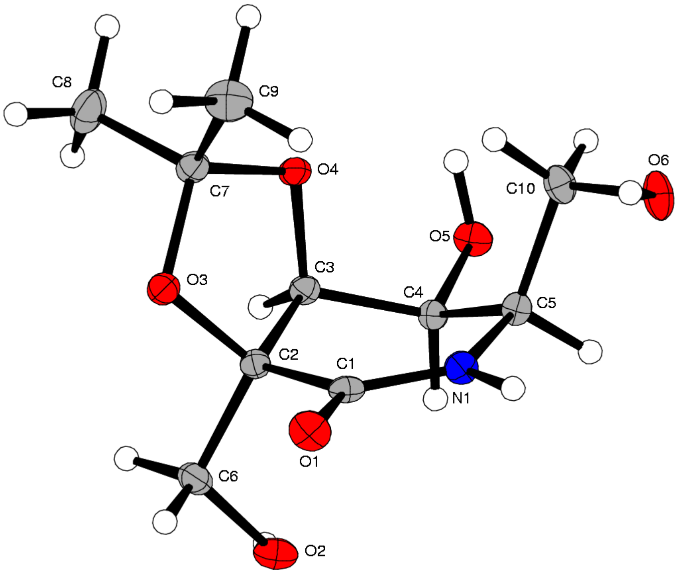


Figure 1
View of the title molecule, showing displacement ellipsoids at the 40% probability level. H atoms are shown as spheres of arbitrary radius.

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