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2-*C*-Hydroxymethyl-2,3-*O*-isopropylidene-D-ribono-1,5-lactam

Christopher R. Newton,[a]* Iezzi Simone Michela,[b] George W. J. Fleet,[b] Yves Blériot[c] and David J. Watkin[a]

[a]Department of Chemical Crystallography, Chemistry Research Laboratory, Oxford OX1 3TA, England, [b]Department of Organic Chemistry, Chemistry Research Laboratory, Oxford OX1 3TA, England, and [c]Ecole Normale Supérieure, Département de Chimie, UMR 8642, 24 rue Lhomond, 75231 Paris Cedex 05, France

Correspondence e-mail:
christopher.newton@new.ox.ac.uk

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Key indicators

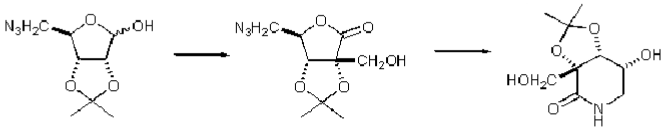
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.087
Data-to-parameter ratio = 9.7

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

The title compound, $C_9H_{14}NO_5$, was formed by catalytic hydrogenation of an azidolactone using Pd-black in 1,4-dioxane.

Comment

The replacement of the ring O atom of a carbohydrate by nitrogen gives a range of sugar mimics (Winchester & Fleet, 1992), many of which are natural products widely spread in plants (Asano *et al.*, 2000). Because of the multitude of potential biological activities, interest in understanding the structures in the search for transition-state analogues continues (Heck *et al.*, 2004). Almost all of the natural products and their synthetic analogues contain straight carbon chains; however, there are some very promising indications that carbohydrate mimics with hydroxymethyl branches (Ichikawa & Igarashi, 1995; Ichikawa *et al.*, 1998), as well as their deoxygenated equivalents (Lillelund *et al.*, 2003; Ostrowski *et al.*, 2003), will show significant inhibition of sugar-metabolizing enzymes. However, the chemistry of simple branched sugars as starting materials is little explored. The title compound, (3), is a powerful intermediate in which a stereochemical ambiguity arises from an aldol reaction; additionally, information about the conformation of both protected and unprotected lactams may help to understand the basis of their biological activity.



(1) (2) (3)

The azidolactol (1) was prepared from D-ribose and submitted to the key aldol branching step. Subsequent oxidation of the aldol product with bromine water gave the branched azidolactone (2). Hydrogenation of (2) resulted in initial reduction of the azide to the corresponding amine which underwent subsequent isomerization to the title lactam (3). The X-ray crystal structure of (3) removes any ambiguity about the course of the aldol condensation.

Experimental

2-*C*-Hydroxymethyl-2,3-*O*-isopropylidene-D-ribono-1,5-lactam was obtained on reduction of 5-azido-2,3-*O*-isopropylidene-D-hamamelono-1,4-lactone, (2), using Pd-black and hydrogen gas in 1,4-dioxane at low reaction concentration (2.5 mg ml^{-1}). A quantitative yield of the title compound was obtained. The title material was then recrystallized using solvent evaporation (methanol), appearing as colourless block crystals.

Crystal data

$C_9H_{14}NO_5$
$M_r = 216.21$
Orthorhombic, $P2_12_12_1$
$a = 7.3137$ (1) Å
$b = 10.6657$ (2) Å
$c = 12.6476$ (3) Å
$V = 986.59$ (3) Å^3
$Z = 4$
$D_x = 1.456$ Mg m^{-3}

Mo Kα radiation
Cell parameters from 1329 reflections
$\theta = 5$–27°
$\mu = 0.12$ mm^{-1}
$T = 150$ K
Block, colourless
0.20 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.976$, $T_{\max} = 0.988$
2272 measured reflections

1315 independent reflections
1195 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.01$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 0.98$
1315 reflections
136 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F^*) + (0.0403p)^2 + 0.549p]$ where $p = 0.333\max(F_o^2,0) + 0.667F_c^2$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

C1—C14	1.528 (3)	C4—N5	1.473 (3)
C1—O11	1.428 (2)	N5—C6	1.331 (3)
C1—C6	1.531 (3)	C6—O7	1.259 (3)
C1—C2	1.521 (3)	O9—C10	1.438 (2)
C2—O9	1.432 (2)	C10—C13	1.513 (3)
C2—C3	1.513 (3)	C10—C12	1.512 (3)
C3—O8	1.431 (2)	C10—O11	1.444 (2)
C3—C4	1.517 (3)	C14—O15	1.419 (3)
C14—C1—O11	107.00 (17)	C6—N5—C4	125.82 (18)
C14—C1—C6	110.38 (17)	O7—C6—N5	122.03 (19)
O11—C1—C6	107.11 (16)	O7—C6—C1	118.13 (18)
C14—C1—C2	114.23 (17)	N5—C6—C1	119.79 (18)
O11—C1—C2	103.03 (16)	C10—O9—C2	108.04 (15)
C6—C1—C2	114.30 (16)	C13—C10—C12	114.02 (19)
O9—C2—C3	110.70 (16)	C13—C10—O11	107.24 (16)
O9—C2—C1	102.89 (15)	C12—C10—O11	110.31 (17)
C3—C2—C1	111.33 (17)	C13—C10—O9	111.49 (18)
O8—C3—C4	109.83 (16)	C12—C10—O9	107.55 (17)
O8—C3—C2	111.11 (16)	O11—C10—O9	105.94 (16)
C4—C3—C2	109.97 (16)	C1—O11—C10	109.05 (14)
N5—C4—C3	110.11 (16)	O15—C14—C1	109.28 (17)

H atoms were placed geometrically after each cycle, at a distance of 1.0 Å; $U_{\rm iso}$ values were set to 1.2 times the $U_{\rm eq}$ value of the parent atom. The absolute configuration was assumed to be the same as that of the sugar and the Friedel pairs were merged in the final refinement.

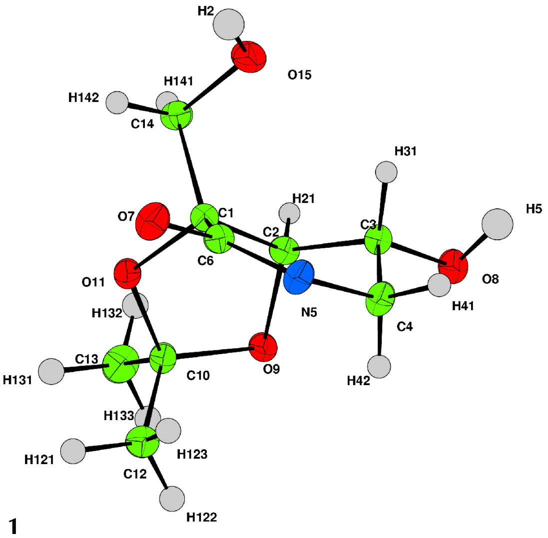


Figure 1
The molecular structure of (3), with 50% probability displacement ellipsoids.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; 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: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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