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Methyl 3-amino-3-*N*,4-*O*-carbonyl-2,3,6-trideoxy-α-L-*lyxo*-hexopyranoside

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.003 Å
R factor = 0.035
wR factor = 0.079
Data-to-parameter ratio = 9.4

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

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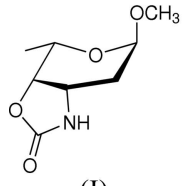
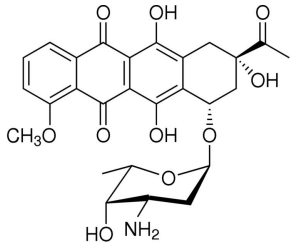
The structure of the title compound, $C_8H_{13}NO_4$, shows the oxazolidone ring to be essentially planar, which forces the pyranoside ring into a ^2S_O skew-boat conformation. The CH_3 and OCH_3 groups both adopt pseudo-equatorial orientations.

Comment

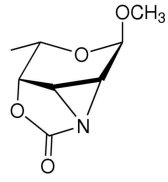
The title compound, (I), is an intermediate in a novel route (Mendlik *et al.*, 2006) for the preparation of glycosides of daunosamine, a sugar residue present in a number of natural products, *e.g.* the anticancer agent daunorubicin (II) (Arcamone & Cassinelli, 1998). Compound (I) was obtained in excellent yield (95%) upon treatment of a solution of the aziridine-containing methyl glycoside (III) in ethyl acetate with hydrogen and palladium on carbon. The presence of the oxazolidone ring in (I) altered the conformation of the pyranose ring from the usual $^4C_1$ chair conformer, thus complicating the unequivocal determination of its structure by NMR spectroscopy. Fortunately, (I) could be crystallized and the X-ray structure analysis confirmed the expected structure (Fig. 1).



(I)



(II)



(III)

The solid-state structure of (I) shows the oxazolidone ring to be nearly planar [N—C3—C4—O3 = 6.3 (2)°; atoms O3, O4, N, C3, C4, and C8 are at most 0.0481 (14) Å out of the least-squares plane]. The pyranose ring is thus forced into an unusual ^2S_O skew-boat conformation. As defined by Berces *et al.* (2001), the polar coordinates for the pyranoside ring in (I) are d = 1.13, φ = 259°, θ = 81°. In this pyranose ring conformation, the methyl group attached to C5 adopts the most sterically favourable pseudo-equatorial position. The OCH_3 group attached to the anomeric centre (C1) is also in the pseudo-equatorial orientation. The placement of the methoxy group pseudo-equatorially is not only favoured for steric reasons, but this orientation also allows the molecule to be stabilized by the *endo*-anomeric effect (Lemieux & Koto, 1974). The orientation about the C1—O2 bond is the one favoured by the *exo*-anomeric effect (Lemieux & Koto, 1974), *i.e.* O2 is *anti* to C2 and *gauche* to the pyranose ring O atom.

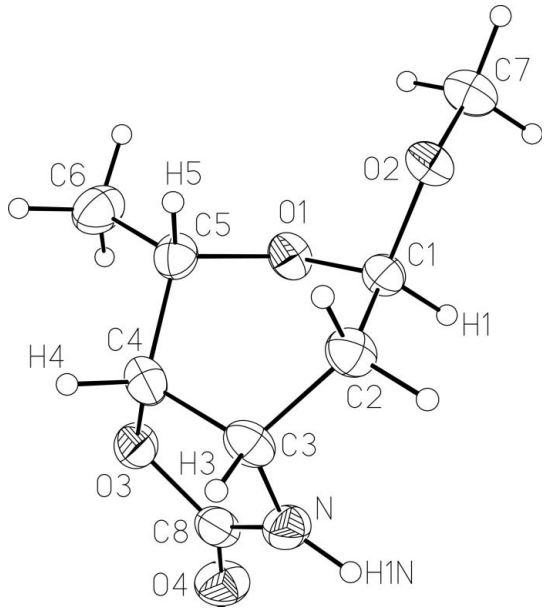


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level.

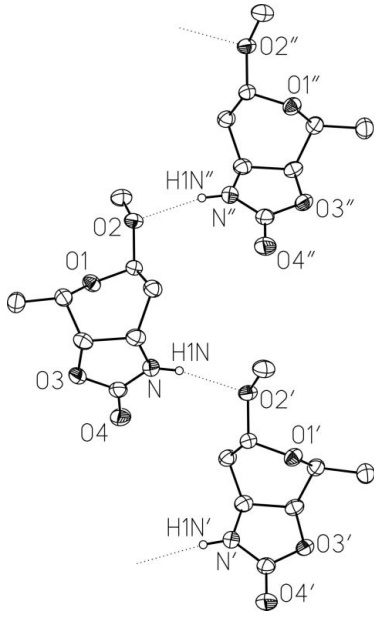


Figure 2
Molecules are connected by N—H···O hydrogen bonds (dotted lines), creating a chain parallel to the *b* axis along the 2_1 screw operation ($-x, \frac{1}{2}+y, \frac{1}{2}-z$).

The methoxy O atom is an acceptor of a proton from the oxazolidone NH group of an adjacent molecule (Fig. 2), generating a hydrogen-bonded helix running parallel to the *b* axis.

Experimental

Methyl 2,3-diamino-3-*N*-,4-*O*-carbonyl-2,3-*N*-*cyclo*-2,3,6-trideoxy-α-L-talopyranoside, (III) (460 mg, 2.48 mmol), and 10% palladium on carbon (400 mg, 0.62 mmol Pd) were dissolved in EtOAc (20 ml). The reaction vessel was charged with a balloon of H_2 gas and the reaction mixture was stirred at room temperature for 3 h, when it was filtered through Celite. The filtrate was concentrated and the residue was filtered through silica gel (1 × 3 cm, 5:1 chloroform/methanol) to afford (I) as white crystalline plates (440 mg, 95%). The solid was recrystallized from 3:1 EtOAc–hexane (m.p. 390–393 K). R_F 0.49 (6:1, chloroform/methanol); $[\alpha]_D^{23}$ −47.1 (*c* 0.4, $CHCl_3$); IR: 2936, 2253, 1757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.87 (*s*, 1H, NH), 4.84 (*app. t*, 1H, *J* = 6.0 Hz, C1—H), 4.46 (*dd*, 1H, *J* = 1.7, 8.8 Hz, C4—H), 4.19 (*app. dt*, 1H, *J* = 4.3, 8.8 Hz, C3—H), 3.99 (*dq*, 1H, *J* = 1.7, 6.6 Hz, C5—H), 2.08 (*app. dt*, 1H, *J* = 4.9, 15.0 Hz, C2—Hb), 1.75 (*ddd*, 1H, *J* = 4.3, 6.0, 15.0 Hz, C2—Hα), 1.31 (*d*, 3H, *J* = 6.6 Hz C6—H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (C═O), 96.8 (C-1), 76.2 (C-4), 63.3 (C-5), 54.8 (OCH_3), 47.8 (C-3), 30.0 (C-2), 15.6 (C-6); HRMS (ESI) *m*/*z* calculated for $[C_8H_{13}NO_4]Na^+$: 210.0742, found: 210.0736.

Crystal data

$C_8H_{13}NO_4$	$Z = 4$
$M_r = 187.19$	$D_x = 1.375$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 5.2411$ (8) Å	$\mu = 0.11$ mm^{-1}
$b = 10.2928$ (16) Å	$T = 193$ (2) K
$c = 16.760$ (3) Å	Rod, colourless
$V = 904.1$ (2) $Å^3$	0.59 × 0.12 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area detector/PLATFORM diffractometer	6168 measured reflections 1114 independent reflections 940 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.052$
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	$\theta_{max} = 26.4°$
$T_{min} = 0.739$, $T_{max} = 0.989$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.1378P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.079$	$\Delta\rho_{max} = 0.15$ e $Å^{-3}$
$S = 1.04$	$\Delta\rho_{min} = -0.18$ e $Å^{-3}$
1114 reflections	
118 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.410 (3)	N—C3	1.454 (3)
O1—C5	1.435 (3)	N—C8	1.335 (3)
O2—C1	1.424 (2)	C1—C2	1.518 (3)
O2—C7	1.425 (3)	C2—C3	1.522 (3)
O3—C4	1.447 (3)	C3—C4	1.545 (3)
O3—C8	1.366 (3)	C4—C5	1.508 (3)
O4—C8	1.212 (3)	C5—C6	1.508 (3)
C1—O1—C5	114.36 (16)	C2—C3—C4	112.03 (19)
C1—O2—C7	112.79 (17)	O3—C4—C3	105.32 (17)
C4—O3—C8	110.17 (17)	O3—C4—C5	109.24 (18)
C3—N—C8	113.8 (2)	C3—C4—C5	111.81 (18)
O1—C1—O2	110.95 (18)	O1—C5—C4	108.35 (18)
O1—C1—C2	113.31 (18)	O1—C5—C6	108.11 (19)
O2—C1—C2	105.41 (17)	C4—C5—C6	113.75 (19)
C1—C2—C3	112.93 (19)	O3—C8—N	109.4 (2)
N—C3—C2	113.69 (19)	O4—C8—N	129.3 (2)
N—C3—C4	100.78 (18)	O3—C8—O4	121.3 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N—H1N···O2^{i}	0.88	2.18	2.976 (3)	150

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

In the absence of significant anomalous dispersion effects, Freidel pairs were merged. The assignment of the absolute stereochemistry is based on the known stereochemistries of the optically pure precursor compounds. H atoms were placed in idealized positions (N—H = 0.88 Å and C—H = 0.98–1.00 Å) and these were assigned isotropic displacement parameters 1.2 times U_{eq} of their parent C atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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