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Methyl 2,3-amino-3-*N*,4-*O*-carbonyl-2,3-*N*-*cyclo*-2,3,6-trideoxy-α-L-allopyranoside

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Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.090
Data-to-parameter ratio = 8.8

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

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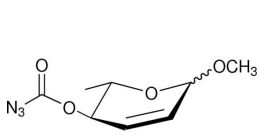
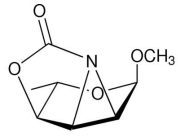
In the title molecule, $C_8H_{11}NO_4$, the pyranoside ring adopts a flattened E_5 conformation in which five of the six ring atoms are coplanar, and the sixth atom is displaced from this plane. The structure of this molecule differs little from that of the diastereomer in which the stereochemistry at the anomeric centre is inverted.

Comment

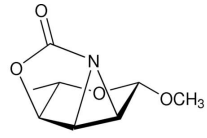
Photolysis of a solution of acylazide (I) in dichloromethane with light of wavelength 254 nm led to the formation of compound (II) together with its β-isomer (III). The latter two compounds are important intermediates in a recently developed method (Mendlik, Tao *et al.*, 2006) for the synthesis of ristosamine glycosides. Ristosamine (IV) is an aminosugar that is a constituent of many natural products, including the ristomycin antibiotics (Crowley *et al.*, 2004). Unambiguous differentiation between (II) and its isomer (III) by NMR spectroscopy was not possible; however, both were crystalline and X-ray crystallography was used to prove their structures. The structure of (III) is reported in the preceeding paper (Mendlik, Coleman *et al.*, 2006).



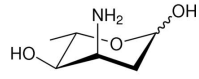
(I)



(II)



(III)



(IV)

The structure of (II) is shown in Fig. 1. As was observed in (III) (Mendlik, Coleman, *et al.*, 2006), the pyranoside ring is flattened away from the normal chair conformation by the fusion of the aziridine and oxazolidinone rings, such that the six-membered ring adopts an E_5 conformation [C5 is displaced by 0.642 (3) Å below the plane formed by atoms C1, C2, C3, C4 and O1]. The polar coordinates for this pyranoside conformation are d = 1.08, Φ = 73° and θ = 150° (Berces *et al.*, 2001). The bond lengths, angles and torsion angles in (II) are not substantially different than those in (III), indicating that the orientation of the methoxy group at C1 exerts little influence over the structure of the molecule. This would be expected, given the highly rigid tricyclic ring system.

Experimental

Methyl 4-*O*-azidocarbonyl-2,3,6-trideoxy-α/β-L-*erythro*-hex-2-enopyranoside, (I) (Mendlik, Tao *et al.*, 2006) (1.496 g, 7.02 mmol), was dissolved in CH_2Cl_2 (702 ml, 0.01 *M*). In 150 ml portions, the reaction mixture was exposed to 254 nm light at room temperature in a quartz

vessel for 1 h. The reaction mixtures were combined, concentrated, and the brown residue was purified by column chromatography (6 × 12 cm silica, 0.9 l of 2:1 hexane/EtOAc followed by 1.5 l 1:2 hexane/EtOAc) to afford (II) (788 mg, 61%) and (III) (394 mg, 30%) as white solids. Compound (II) was recrystallized from EtOAc (m.p. 366–368 K). Data for (II): R_F 0.25 (1:1 hexane/EtOAc); $[\alpha]_D^{23}$ +139.7 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.00 (*s*, 1H, C1—H), 4.72 (*dd*, 1H, *J* = 2.1, 6.3 Hz, C4—H), 3.94 (*dq*, 1H, *J* = 2.1, 7.2 Hz, C5—H), 3.52 (*s*, 3H, OCH_3), 3.51–3.48 (*m*, 1H, C3—H), 2.91 (*d*, 1H, *J* = 4.8 Hz, C2—H), 1.37 (*d*, 3H, *J* = 7.2 Hz, C6—H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 163.1 (C═O), 92.6 (C-1), 73.0 (C-4), 66.8 (C-5), 55.9 (OCH_3), 42.2 (C-2), 37.9 (C-3), 15.7 (C-6); HRMS (ESI) *m*/*z* calculated for $C_8H_{11}NO_4$ + Na: 208.0580, found: 208.0571.

Crystal data

$C_8H_{11}NO_4$	Z = 4
M_r = 185.18	D_x = 1.430 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 6.3749 (5) Å	μ = 0.12 mm^{-1}
b = 9.9173 (7) Å	T = 193 (2) K
c = 13.6010 (10) Å	Block, colourless
V = 859.88 (11) Å^3	0.61 × 0.25 × 0.14 mm

Data collection

Bruker PLATFORM/SMART 1000 CCD area-detector diffractometer	6587 measured reflections 1042 independent reflections 1000 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.027
Absorption correction: integration (*SHELXTL*; Sheldrick, 1997*a*) T_{min} = 0.947, T_{max} = 0.984	θ_{max} = 26.4°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.1002P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.032	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.090	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
S = 1.09	$\Delta\rho_{min}$ = −0.15 e Å^{-3}
1042 reflections	
118 parameters	
H-atom parameters constrained	

H atoms were placed in idealized positions (according to the sp^2 or sp^3 geometries of their parent C atoms), and then refined using a riding model with fixed C—H distances (0.98 and 1.00 Å) and with isotropic displacement parameters 1.2 times U_{eq} of the parent atoms. In the absence of significant anomalous dispersion effects, Friedel pairs were merged before the final cycles of least-squares refinement. The absolute configuration of the title molecule was assigned on the basis of the established stereochemistry of the precursor compound.

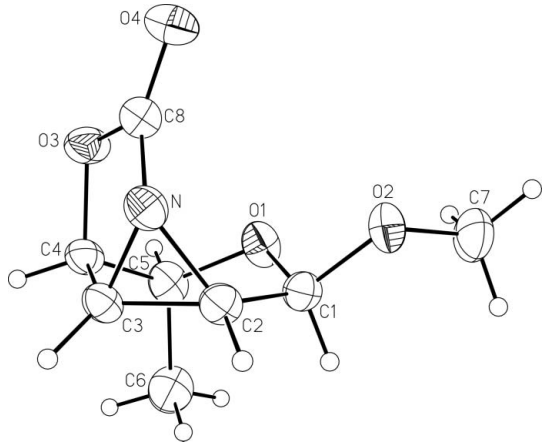


Figure 1
Perspective view of the molecular structure of (I), showing the atom-labelling scheme. Non-H atoms are represented by displacement ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary radii..

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*); molecular graphics: *SHELXTL* (Sheldrick, 1997*a*); software used to prepare material for publication: *SHELXTL*.

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