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Methyl 2-Aza-2-deoxy-4,6-di-*O*-methyl-2-*N*-(*p*-nitrophenylamino)-β-D-*erythro*-hexopyranosid-3-ulose

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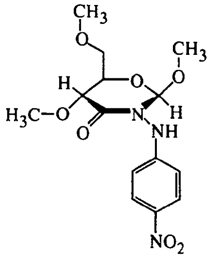
Abstract

All asymmetric C atoms of the title compound, $C_{14}H_{19}N_3O_7$, are in the *R* configuration. The azapyranose ring adopts a half-chair conformation with substituents in equatorial and quasi-equatorial positions. The molecular packing is fixed by hydrogen bonds involving the amino group and one of the methoxy substituents.

Comment

Six-membered sugar lactams can be obtained by oxidative ring enlargement of furanose *p*-nitrophenyl hydrazones (Tronchet, Tronchet, Rachidzadeh, Barbalat-Rey & Bernardinelli, 1988). The reaction proceeds generally regioselectively and the configuration of the existing asymmetric C atoms is preserved. These compounds are potential glycosidase inhibitors (Look, Fotsh & Wong, 1993). The title compound has been prepared (Tronchet, Tronchet, Barbalat-Rey & Bernardinelli, 1997) from methyl 2-deoxy-3,5-di-*O*-methyl-2-(*p*-nitrophenylhydrazono)-β-D-*erythro*-pentofuranoside which was oxidized (lead tetraacetate) to an epimeric mixture of azoacetates, which upon saponification of their ester function underwent a base-catalyzed ring enlargement. X-ray analysis was deemed necessary to assess the geometrical features of this new type of sugar analogue which has an anomeric center of the unusual orthoester type, particularly its solid-state conformation, and to confirm the configuration established by ^{1}H NMR. Despite numerous attempts at crystallization only very fine needle crystals could be obtained.



(I)

Since the configuration at the C3 atom is known (*R*) and preserved during the regioselective synthesis, the absolute configuration of the molecule is well determined as 2*R*,3*R*,4*R*. The minimum value of the asymmetry parameters (Nardelli, 1983) shows that the azapyranose ring adopts a half-chair conformation with a pseudo-twofold axis passing through the O1—C3 bond [ΔC_2(O1—C3) = 0.012 (5)]. The substituents at C2 and C4 are located in quasi-equatorial positions whereas the methoxymethyl group at C3 is equatorial. In the crystal the molecules are associated in chains along the *b* axis by hydrogen-bond interactions involving the amino group and the anomeric methoxy group at C4 [N2···O5(x, $y-1$, z) = 2.89 (1) Å; N2—H02···O5 = 138.2 (4)°].

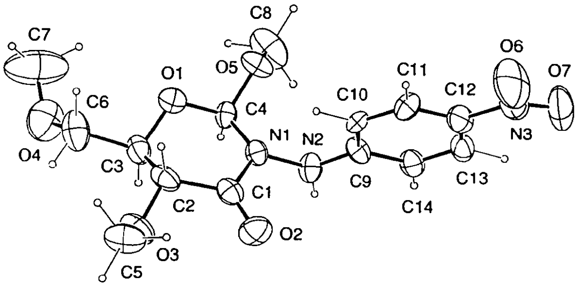


Fig. 1. View of the title compound with atomic labelling. Ellipsoids are represented at the 40% probability level.

Experimental

Crystals [m.p. 419.9–420.11 K, $[\alpha]_D^{21}$ +11.7 (*c*, 0.6, $CHCl_3$)] were grown at room temperature from ethyl ether/ethanol solution.

Crystal data

$C_{14}H_{19}N_3O_7$
$M_r = 341.3$
Monoclinic
$C2$
$a = 21.574 (1)$ Å
$b = 4.5576 (9)$ Å
$c = 17.039 (2)$ Å
$\beta = 104.238 (5)°$
$V = 1623.9 (4)$ Å^3
$Z = 4$
$D_x = 1.396$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 23 reflections
$\theta = 5.5–21.5°$
$\mu = 0.965$ mm^{-1}
$T = 293$ K
Fine needle elongated along **b**
0.27 × 0.07 × 0.025 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical by integration
$T_{\min} = 0.887$, $T_{\max} = 0.972$
2491 measured reflections
2403 independent reflections
1371 reflections with $F > 4\sigma(F)$

$R_{\rm int} = 0.032$
$\theta_{\max} = 54°$
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 4$
$l = 0 \rightarrow 17$
2 standard reflections frequency: 30 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.076$
$wR(F^2) = 0.074$
$S = 2.342$
1804 reflections
217 parameters
H atoms in calculated positions with $U_{\rm iso} = 0.05$
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{\max} = 0.09$

$\Delta\rho_{\max} = 0.326$ e Å^{-3}
$\Delta\rho_{\min} = -0.333$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute configuration: Flack *XABS* refined
Flack parameter = 0.5 (1.0)

Table 1. *Selected geometric parameters (Å, °)*

O1—C3	1.427 (14)	N1—C1	1.408 (14)
O1—C4	1.394 (14)	N1—C4	1.471 (14)
O2—C1	1.197 (15)	N2—C9	1.366 (14)
O3—C2	1.391 (16)	C1—C2	1.541 (18)
O5—C4	1.376 (16)	C2—C3	1.502 (16)
N1—N2	1.384 (13)	C3—C6	1.518 (19)
C3—O1—C4	111.4 (8)	N1—C1—C2	113.0 (10)
N2—N1—C1	117.1 (10)	C1—C2—C3	111.7 (9)
N2—N1—C4	112.6 (7)	O1—C3—C2	108.3 (10)
C1—N1—C4	124.8 (9)	O1—C4—N1	110.4 (8)
N1—N2—C9	120.7 (10)		
C4—O1—C3—C2	70.9 (11)	C4—N1—C1—C2	−16.3 (17)
C3—O1—C4—N1	−55.1 (12)	C1—N1—C4—O1	28.7 (17)
C5—O3—C2—C1	100.2 (12)	N1—N2—C9—C10	5.0 (17)
C7—O4—C6—C3	−104.3 (18)	N1—C1—C2—C3	28.6 (16)
C8—O5—C4—N1	127.7 (10)	C1—C2—C3—O1	−55.0 (14)
C1—N1—N2—C9	−89.7 (14)	C2—C3—C6—O4	−162.2 (13)

The coordinates of the H atoms have been calculated.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *Xtal LATCON* (Hall, Flack & Stewart, 1992). Data reduction: *Xtal REFCAL, LSABS* (Blanc, Schwarzenbach & Flack, 1991), *SORTRF*. Program(s) used to solve structure: *MULTAN*87 (Main *et al.*, 1987). Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *Xtal ORTEP*. Software used to prepare material for publication: *Xtal BONDLA, CIFIO*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1186). Services for accessing these data are described at the back of the journal.

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Refinement of Ibuprofen at 100 K by Single-Crystal Pulsed Neutron Diffraction

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Abstract

The structure of racemic ibuprofen [α-methyl-4-(2-methylpropyl)benzeneacetic acid], $C_{13}H_{18}O_2$, has been refined using single-crystal pulsed neutron diffraction data collected at 100 K. Accurate positional and

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