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Isopropyl 6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-7-{[(*S*)-1-phenylethyl]amino}-L-*glycero*-α-D-*galacto*-octopyranuronate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.047
wR factor = 0.125
Data-to-parameter ratio = 11.6

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

The stereochemistry of the new chiral centre C7 in the title galactosyl α-aminoester diastereomer product, $C_{25}H_{37}NO_7$, has been established as *S*. The pyranose ring has a twist-boat conformation due to the presence of the two isopropylidene ketal moieties. The molecule contains no intramolecular hydrogen bond.

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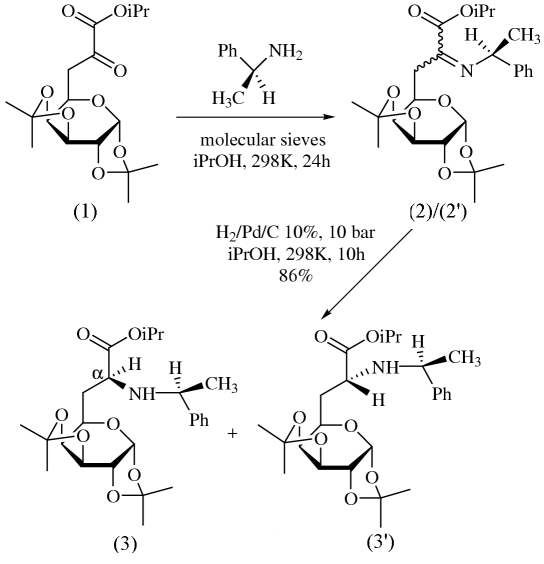
Comment

We have previously described a route to a new class of galactosyl α-amino acids which could be used in peptide chemistry (Coutrot *et al.*, 1998). The aim is to propose new glycopeptides with a conformational restraint on the peptide backbone and with an improved stability towards endopeptidases that could lead to a better ligand selectivity with various receptors (Graf von Roedern *et al.*, 1996, and references therein). The synthesis of the N- and C-protected galactosyl-α-amino acid (3) is based on the reductive amination of the galactosyl-α-ketoester (1) previously described (Coutrot, Grison, Tabyaoui *et al.*, 1998). The addition of (*S*)-α-methylbenzylamine to α-ketoester (1) yielded the non-isolated intermediate imine (2) which was immediately subjected to hydrogenation and led to (3)/(3′) (49/51) with a very high yield. The two diastereomers thus obtained, (3) and (3′), could be easily separated by selective precipitation in diethyl ether. Pure compound (3) was obtained as a white powder from this solvent and was further crystallized from chloroform, whereas evaporating the diethyl ether layer yielded (3′) as an oil. The crystallographic structure of (3) was investigated with the aim of determining the configuration of the generated Cα atom.



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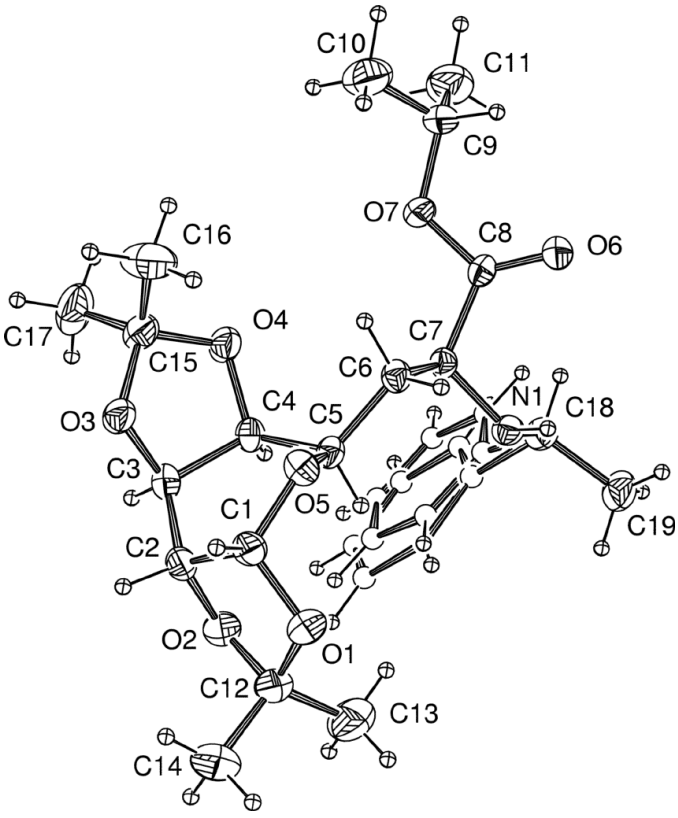

Figure 1
The molecular structure of (3) showing 50% probability displacement ellipsoids. The disordered phenyl ring is shown without numbering and with both components.

The structure of (3) is shown in Fig. 1. The configuration of C7 was deduced from the stereochemistry of the galactopyranose and from the (*S*)-α-methylbenzylamine moiety and appeared to be *S*, which corresponds to L in amino acid nomenclature. No intramolecular hydrogen bond was noted. The structure of the pyranose is not flexible, as a result of the presence of the isopropylidene ketal groups, and is locked in a twist-boat conformation (Cone & Hough, 1965). Dihedral angles of the ring are given in Table 1. The position of the lateral glucidic chain is defined by the following dihedral angle: C5—C6—C7—N1 −74.8 (4)°.

Experimental

See *Comment* for synthetic details.

Crystal data

$C_{25}H_{37}NO_7$
M_r = 463.56
Orthorhombic, $P2_12_12_1$
a = 9.809 (1) Å
b = 13.978 (5) Å
c = 18.730 (2) Å
V = 2568.1 (10) Å^3
Z = 4
D_x = 1.199 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 7.5–12.0°
μ = 0.09 mm^{-1}
T = 293 (2) K
Block, colourless
0.25 × 0.15 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
3143 measured reflections
3143 independent reflections
1782 reflections with $I > 2\sigma(I)$
θ_{max} = 27.0°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.125
S = 1.01
3143 reflections
270 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.5544P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.014
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.009 (1)

Table 1
Selected torsion angles (°).

C5—O5—C1—C2	−42.1 (4)	O3—C3—C4—O4	−26.6 (4)
O1—C1—C2—O2	−18.2 (4)	C2—C3—C4—C5	−22.8 (5)
O5—C1—C2—C3	−14.4 (5)	C1—O5—C5—C4	66.1 (4)
O2—C2—C3—O3	176.5 (3)	C3—C4—C5—O5	−30.3 (4)
C1—C2—C3—C4	46.4 (5)	O4—C4—C5—C6	−33.2 (4)

During the refinement calculations, the phenyl ring appeared with large displacement parameters. Anisotropic refinement showed elongated ellipsoids. This behaviour may be due to a tilt around the C18—C19 axis or a disorder between two positions. This was investigated and it was found there is a statistical disorder [55:45 (1)%] between two possible sites, with a tilt angle of 17.0°. It was necessary to use geometrical constraints. For the non-disordered part of the molecule, many H atoms were found with a difference Fourier map, in particular the amine H atom, the coordinates of which were refined, the other H atoms being set in riding mode. The data set contained no Friedel pairs, and the absolute configuration was assumed from the synthesis.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *PROCESS* in *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1998); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL*97.

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