

Compounds (3) and (4)*Crystal data*2C₄₃H₃₄N₂O₇·2CH₂Cl₂ $M_r = 1551.36$

Monoclinic

P2₁ $a = 7.9574 (1) \text{ \AA}$ $b = 19.4192 (3) \text{ \AA}$ $c = 24.2174 (4) \text{ \AA}$ $\beta = 91.406 (2)^\circ$ $V = 3741.09 (10) \text{ \AA}^3$ $Z = 2$ $D_x = 1.377 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71069 \text{ \AA}$

Cell parameters from 420 reflections

 $\theta = 2.52\text{--}25.35^\circ$ $\mu = 0.23 \text{ mm}^{-1}$ $T = 200 (1) \text{ K}$

Flat needle

 $0.45 \times 0.15 \times 0.05 \text{ mm}$

Dark red

Data collection

Rigaku R-AXIS IIC area detector diffractometer

 φ oscillation scans

Absorption correction: none

29 922 measured reflections

7001 independent reflections

6613 reflections with

 $F > 2\sigma(F^2)$ $R_{\text{int}} = 0.036$ $\theta_{\text{max}} = 25.35^\circ$ $h = -9 \rightarrow 9$ $k = -23 \rightarrow 23$ $l = -29 \rightarrow 29$ Intensity decay: $\sim 5\%$

(estimated from frame-to-frame scaling)

*Refinement*Refinement on F^2 $R(F) = 0.062$ $wR(F^2) = 0.161$ $S = 1.07$

7001 reflections

999 parameters

H atoms constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0814P)^2 + 3.1440P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.019$ $\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.66 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

For both compounds, data collection: *BIOTEX* (Molecular Structure Corporation, 1995); data reduction: *BIOTEX*; program(s) used to solve structures: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1438). Services for accessing these data are described at the back of the journal.

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4-O-Benzyl-2,3-O-isopropylidene- α -L-rhamnopyranose

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Abstract

It is shown that the title compound, C₁₆H₂₂O₅, has the α -anomeric configuration, a fact of interest for its use as an intermediate in oligosaccharide synthesis. One plausible intermolecular hydrogen-bond chain is found in the direction of the *b* axis.

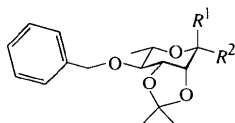
Table 1. Selected torsion angles ($^\circ$) in (3) and (4)

	(3)	(4)
C10—C18—C32—C33	−65.1 (4)	68.4 (4)
C17—C18—C32—C33	−172.8 (3)	176.6 (3)
C19—C18—C32—C33	59.3 (4)	−56.0 (4)
C10—C18—C32—C40	112.5 (4)	−109.3 (4)
C17—C18—C32—C40	4.8 (5)	−1.1 (4)
C19—C18—C32—C40	−123.1 (4)	126.4 (4)
C32—C40—N42—C43	−128.4 (4)	123.4 (4)
C39—C40—N42—C43	61.3 (5)	−65.5 (5)
C24—C25—O28—C29	−2.8 (6)	−179.0 (4)
C26—C25—O28—C29	175.7 (4)	0.9 (6)
C46—C47—O51—C52	15.9 (6)	177.9 (4)
C48—C47—O51—C52	−164.7 (4)	−1.2 (6)

The least-squares refinement of compound (2) included isotropic refinement of all H atoms. The mean C—H bond distance was 1.00 Å, with a range of 0.95–1.07 Å. The mean standard uncertainty on C—H bond distances was 0.004 Å. In the least-squares refinement of compounds (3) and (4), the H atoms were treated using a riding model in which the coordinate shifts of the atom to which the H atom was attached were applied to the idealized H-atom bond lengths. In addition, for methyl H atoms the torsion angle was refined. Thus, there were 999 refined parameters [one scale factor + (nine parameters \times 110 anisotropic atoms) + eight torsion angles].

Comment

The title compound, (I), has been used as an intermediate in the synthesis of site-specific deuterium-



- (I) $R^1 = \text{OH}, R^2 = \text{H}$
 (II) $R^1 = \text{H}, R^2 = \text{OMe}$

substituted α -L-Rhap-(1 \rightarrow 2)- α -L-Rhap-OMe (Söderman *et al.*, 1998) (Rhap = rhamnopyranosyl). In the synthetic procedure, an intermediate with a β -configuration was needed, (II), and this was synthesized from (I) by treatment with sodium hydride as a base and methyl iodide as the alkylating agent. Under the experimental conditions employed, a change of anomeric configuration occurs. Therefore, it would be of interest to prove that the starting configuration was an α -anomer. The basic reaction conditions used lead to a rapid equilibrium between the α - and the β -anomeric forms of 4-*O*-benzyl-2,3-*O*-isopropylidene-L-rhamnopyranose. The β -form subsequently reacts much faster, since the product is obtained in >90% yield. Here, we present the crystal structure of (I).

The crystal structure of (I) shows the anticipated α -anomeric configuration. One intermolecular hydrogen bond is formed, O1—HO1 \cdots O2(1 - x, -1/2 + y, 2 - z), and this connects a chain of molecules in the *b* axis direction at *z* = 0. The rest of the packing of the crystal can be described as hydrophobic interactions between the benzyl substituents centred at *z* = 0.5 and hydrophobic interactions between methyl groups and benzyl rings.

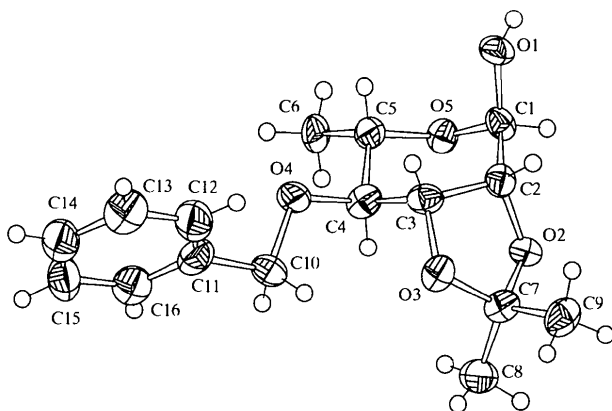


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as circles of an arbitrary radius.

The hexapyranose ring is somewhat distorted from a regular 1C_4 -chair conformation, with Cremer & Pople (1975) puckering parameters $q_2 = 0.185(7)$, $q_3 = -0.522(7)$ Å, $\varphi_2 = 130(2)^\circ$, $Q = 0.554(7)$ Å and $\theta = 160.5(7)^\circ$. The five-membered ring has an envelope conformation on C2, with puckering parameters $q_2 = 0.362(7)$ Å and $\varphi_2 = 33.2(11)^\circ$.

Experimental

The synthesis of (I) from allyl 4-*O*-benzyl-2,3-*O*-isopropylidene- α -L-rhamnopyranoside by isomerization of the allyl group followed by hydrolysis of the prop-1-enyl glycoside has been described previously by Söderman *et al.* (1998). The monosaccharide was crystallized from *n*-hexanol at ambient temperature.

Crystal data

$C_{16}H_{22}O_5$
 $M_r = 294.34$
 Monoclinic
 $P2_1$
 $a = 8.626(2)$ Å
 $b = 6.5402(12)$ Å
 $c = 14.524(4)$ Å
 $\beta = 100.21(3)^\circ$
 $V = 806.4(3)$ Å³
 $Z = 2$
 $D_x = 1.212$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 126 reflections
 $\theta = 2.5$ – 26.0°
 $\mu = 0.089$ mm⁻¹
 $T = 293(2)$ K
 Prism
 0.15 \times 0.10 \times 0.06 mm
 Colourless

Data collection

Stoe IPDS diffractometer
 Area-detector scans
 Absorption correction: none
 6320 measured reflections
 1724 independent reflections
 548 reflections with
 $I > 2\sigma(I)$

$R_{int} = 0.261$
 $\theta_{max} = 26.13^\circ$
 $h = -10 \rightarrow 10$
 $k = -8 \rightarrow 7$
 $l = -18 \rightarrow 17$
 Intensity decay: <1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.081$
 $S = 0.715$
 1724 reflections
 194 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.214$ e Å⁻³
 $\Delta\rho_{min} = -0.213$ e Å⁻³
 Extinction correction:
 SHELXL97 (Sheldrick, 1997)
 Extinction coefficient:
 0.093(6)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected torsion angles ($^\circ$)

O5—C1—C2—C3	-41.6(9)	C3—C4—C5—O5	61.6(8)
C1—C2—C3—C4	37.1(10)	C2—C1—O5—C5	57.7(8)
C2—C3—C4—C5	-47.3(9)	C4—C5—O5—C1	-69.1(8)

Table 2. Hydrogen-bonding geometry (Å, $^\circ$)

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
O1—HO1 \cdots O2 ⁱ	0.82	2.05	2.805(7)	154

Symmetry code: (i) 1 - x, y - 1/2, 2 - z.

The low fraction of significant reflections is connected with the quality of the crystals. The large number of weak reflections gives a large contribution to the internal R value; the internal R value calculated from reflections with $I \geq 2\sigma(I)$ is 0.0485. The low value of S indicates a slightly 'overfitted' model, but we think this fact is also connected with the large number of weak reflections and thus can be neglected. All non-H atoms were refined with anisotropic displacement parameters using a 'rigid-bond' restraint to U_{ij} of two bonded atoms (Rollett, 1970), implemented as the *DELU* instruction in *SHELXL97* (Sheldrick, 1997). The reflection data were merged before refinement. The absolute configuration of the molecule is set by the absolute configuration of the reactant, as it cannot be deduced with certainty from the present diffraction data.

Data collection: *EXPOSE* (Stoe, 1997a). Cell refinement: *CELL* (Stoe, 1997b). Data reduction: *INTEGRATE* (Stoe, 1997c). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *PLATON98* (Spek, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1535). Services for accessing these data are described at the back of the journal.

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