

Crystal structures of ethyl 3-azido-2,3-dideoxy-D-arabino-hexopyranoside anomers

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Abstract—The structures of the title α (**1**) and β (**2**) anomers of ethyl 3-azido-2,3-dideoxy-D-arabino-exopyranoside ($C_8H_{15}N_3O_4$) are reported. The single-crystal structures of $C_8H_{15}N_3O_4$ were determined by X-ray crystallography at 293 K. It has been found that both title compounds crystallize in the orthorhombic space group. In both cases, the unit cell contains four asymmetric molecules. From intensity measurements, it has been shown that each of these molecules adopts a 4C_1 chair conformation. The packing arrangement in the unit cell displays a stratified structure. Moreover, medium strength O–H...O hydrogen bonds in both crystal lattices can be observed.

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1. Introduction

Carbohydrates are biomolecules that are extensively found in nature.¹ In polyketide macrolides and nonribosomal peptides, unusual sugars such as aminodeoxy sugars are often present. These are essential for biological activity and are considered as the third most important group of biomolecules after proteins and nucleic acids. Oligosaccharides on the surfaces of eukaryotic cells mediate many fundamental cellular processes, including embryogenesis, tissue differentiation, inflammation, and metastasis. Cell-surface carbohydrates also function as receptors for bacteria, viruses, and toxins.^{2–4} Prokaryotic cells produce a variety of O-linked glycoconjugates with potent antitumor or anti-biotic activity.⁵

The multiple oxygen donor atoms in sugar molecules, together with the fact that metal cations co-exist

in biological fluids, suggest that coordination between saccharides and metal ions may occur in living organisms, and that such reactions may have some particular biological relevance.^{6–8} A number of studies have shown that such interactions have fundamental importance in many biochemical processes, such as the transfer and storage of metal ions,⁹ the action of metal-containing pharmaceuticals, toxic-metal metabolism,¹⁰ and Ca(II)-mediated carbohydrate–protein binding.¹¹

The present paper is a continuation of the studies on the synthesis and the crystal structure determination of 3-azido-3-deoxy derivatives of sugars, which are precursors of amino sugars.¹² In our previous studies, we synthesized and determined the structure of 3-amino-3-deoxy derivatives of sugars.^{13,14} Those compounds complexed with chromium(III) ions have been found to be biologically active and have consequently been tested as reagents in the uptake reactions of CO_2 and SO_2 .¹⁵ Our recent investigations have shown that complexes of Cr(III) with aminodeoxy sugars have fundamental importance as NO_2 radical scavengers.¹⁶

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2. Results and discussion

Two anomeric ethyl 3-azido-2,3-dideoxy-D-*arabino*-hexopyranosides, having the formula $C_8H_{15}N_3O_4$, have been carefully investigated. Both crystals are orthorhombic (Table 1). In both cases the unit cell contains four molecules. From intensity measurements it has been shown that each of these molecules adopts a 4C_1 chair conformation. Although the absolute structure could not be determined reliably by the Flack method, the correct enantiomorph was chosen based on the known chirality of centers in the substrate sugar.

Structures showing the atom numbering scheme and molecular packing in the crystal are illustrated in Figures 1 and 2, respectively. Details of the data collection and refinement for both anomers are presented in Table 1. The selection of the crystal's important geometric parameters is given in Table 2 (bond lengths and angles) and Table 3 (torsion angles). The hydrogen-bond distances and angles are included in Table 4.

2.1. Ethyl 3-azido-2,3-dideoxy- α -D-*arabino*-hexopyranoside (1)

The D-*arabino* ring system of compound **1** has a chair conformation (Fig. 1a), with the alternating positive and negative values of torsion angles, their absolute values being between $52.5(3)^\circ$ and $59.3(3)^\circ$. The valence geometry is typical, the C–C bond distances varying between 1.492(4) and 1.528(4) Å, while the ring C–O distances are O1–C1 1.415(3) and O1–C5 1.433(3) Å (Table 2). The position of the axially bound ethoxy group at C1 is described with the O1–C1–O2–C7 torsion angle being $61.1(3)^\circ$. The ethoxy group has an *anti* conformation, the C1–O2–C7–C8 torsion angle being $171.4(2)^\circ$. The azide group, occupying the equatorial position at C3, is almost linear, the N1–N2–N3 angle being $170.1(5)^\circ$ (Table 2). The N1–N2 and N2–N3 distances of 1.232(5) and 1.117(4) Å, respectively, reflect the differences in the bond order for that group. The hydroxymethyl group reveals the *gauche* conformation, with the C4–C5–C6–O4 torsion angle being $52.5(3)^\circ$.

Table 1. Crystal data and structure refinement for **1** and **2**

	$C_8H_{15}N_3O_4$ (1)	$C_8H_{15}N_3O_4$ (2)
Empirical formula	$C_8H_{15}N_3O_4$ (1)	$C_8H_{15}N_3O_4$ (2)
Formula weight	217.230	217.230
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	5.6450(2)	5.836(1)
b (Å)	13.538(1)	11.383(2)
c (Å)	14.427(1)	17.628(4)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
V (Å ³)	1102.5(2)	1170.9(4)
Z	4	4
D_{calcd} (Mg m ^{−3})	1.309	1.232
Absorption coefficient (mm ^{−1})	0.105	0.099
$F(000)$	464	464
Crystal size (mm)	$0.43 \times 0.12 \times 0.12$	$0.76 \times 0.2 \times 0.17$
Crystal color	Colorless	Colorless
Habit	Needle	Needle
θ Range for data collection	2.82–31.33	2.92–31.32
Index ranges	$-7 \leq h \leq 8,$ $-19 \leq k \leq 18,$ $-18 \leq l \leq 21$	$-7 \leq h \leq 8,$ $-16 \leq k \leq 16,$ $-25 \leq l \leq 24$
Reflections collected	10,556	11,640
Independent reflections	3373 [$R_{\text{int}} = 0.0632$]	3594 [$R_{\text{int}} = 0.0901$]
Completeness of data (%)	95.1	95.2
Refinement method	Full-matrix least-squares on F^2	
Decay (%)	None	None
Data/restraints/parameters	3373/0/139	3594/0/139
Goodness-of-fit on F^2	1.006	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0646, wR_2 = 0.1115$	$R_1 = 0.0688, wR_2 = 0.1621$
Final R indices [all data]	$R_1 = 0.1789, wR_2 = 0.1476$	$R_1 = 0.1536, wR_2 = 0.2092$
Absolute structure parameter	2(2)	−2(2)
Largest difference in peak and hole (e Å ^{−3})	0.161 and −0.136	0.282 and −0.251

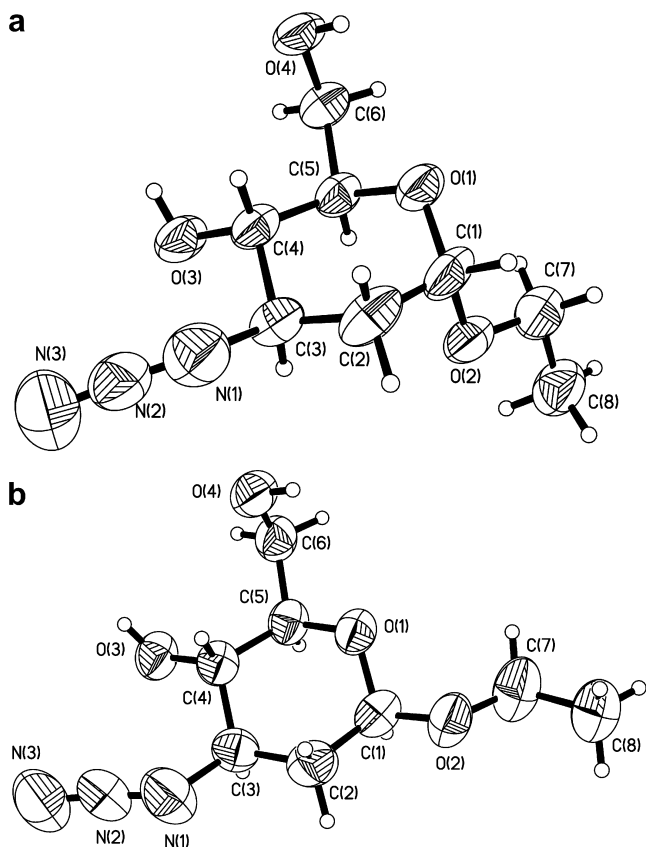


Figure 1. Structure (ORTEP drawing) and atomic numbering for **1** (a) and **2** (b). Thermal ellipsoids are drawn at 50% probability.

Relevant dihedral angles are indicative of an almost perfect 4C_1 conformation for the six-membered pyranoside ring (O1–C1–C2–C3–C4–C5). The packing arrangements are shown in Figure 2a.

The IR spectrum of **1** shows a broad –OH stretching absorption band around 3400 cm^{-1} and the aliphatic C–H stretching between 2984 and 2875 cm^{-1} . A peak at 1081 cm^{-1} represents the –C–O stretching of the primary alcoholic group –CH₂–OH. An extensive network of hydrogen bonds involving two hydroxyl groups was confirmed by X-ray diffraction. Two hydroxyl groups are donors and acceptors in the H bonds (Fig. 3a), the O3–H3B···O4 [$x + 1/2, -y - 1/2, -z + 1$] and O4–H4B···O3 [$x - 1, y, z$] (Table 4).

2.2. Ethyl 3-azido-2,3-dideoxy-β-D-arabino-hexopyranoside (**2**)

The packing arrangements are shown in Figure 2b. The D-arabino ring system of this anomer (**2**) has a 4C_1 chair conformation, with the alternating positive and negative values of torsion angles, their absolute values varying between $51.0(4)^\circ$ and $61.8(3)^\circ$. The valence geometry is typical, the C–C bond distances varying between $1.492(5)$ and $1.518(4)\text{ Å}$, and the ring C–O distances are $1.424(3)$ and $1.432(4)\text{ Å}$ for O1–C5 and O1–C1, respectively (Table 2). The ethoxy group at C1 is bound in the equatorial position. It has a *gauche-anti* conformation, the C1–O2–C7–C8 torsion angle being

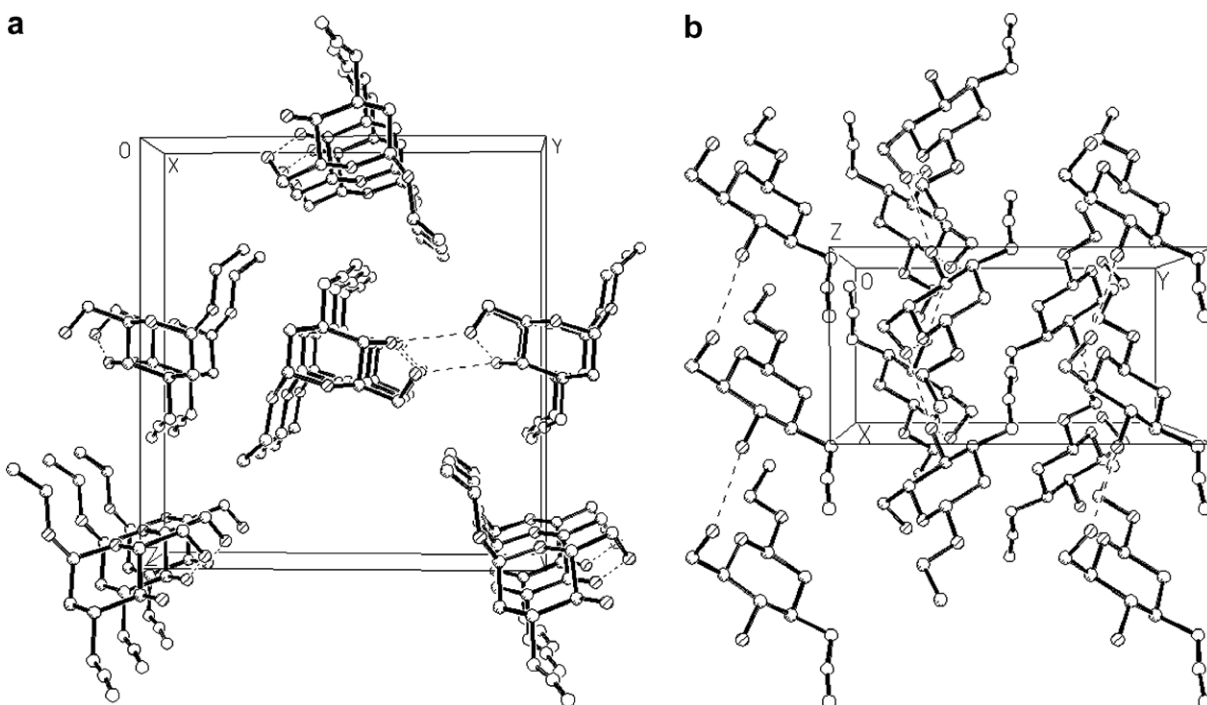


Figure 2. Molecular packing of **1** (a) and **2** (b), viewed along (1) the *x*- and (2) the *z*-axes.

Table 2. Selected bond lengths (Å) and valence angles (°)

	1	2
<i>Bond length</i>		
O(1)–C(1)	1.415(3)	1.432(4)
O(1)–C(5)	1.433(3)	1.424(3)
C(1)–O(2)	1.395(3)	1.387(4)
C(1)–C(2)	1.492(4)	1.492(5)
O(2)–C(7)	1.435(4)	1.417(4)
C(7)–C(8)	1.489(4)	1.476(5)
C(2)–C(3)	1.513(4)	1.509(5)
C(3)–N(1)	1.488(4)	1.484(4)
C(3)–C(4)	1.518(4)	1.517(4)
N(1)–N(2)	1.232(5)	1.204(5)
N(2)–N(3)	1.117(4)	1.140(5)
C(4)–O(3)	1.418(3)	1.418(3)
C(4)–C(5)	1.528(4)	1.518(4)
C(5)–C(6)	1.502(3)	1.495(4)
C(6)–O(4)	1.415(3)	1.403(4)
<i>Valence angle</i>		
C(1)–O(1)–C(5)	114.2(2)	111.9(2)
O(1)–C(1)–C(2)	111.3(2)	111.4(2)
C(1)–C(2)–C(3)	112.1(2)	110.7(3)
C(2)–C(3)–C(4)	109.8(2)	111.0(2)
C(3)–C(4)–C(5)	109.8(2)	109.6(2)
O(1)–C(5)–C(4)	109.9(2)	109.8(2)
O(2)–C(1)–O(1)	113.0(2)	107.8(2)
O(2)–C(1)–C(2)	107.4(2)	109.8(3)
C(1)–O(2)–C(7)	113.8(2)	115.0(3)
O(2)–C(7)–C(8)	108.3(3)	109.7(4)
N(1)–C(3)–C(2)	105.9(3)	106.8(3)
N(1)–C(3)–C(4)	111.3(2)	112.3(3)
O(3)–C(4)–C(3)	108.5(2)	109.3(2)
O(3)–C(4)–C(5)	110.3(2)	109.6(2)
O(1)–C(5)–C(6)	106.0(2)	107.8(2)
C(6)–C(5)–C(4)	113.0(2)	112.8(2)
O(4)–C(6)–C(5)	113.3(3)	112.7(3)
N(2)–N(1)–C(3)	117.1(3)	117.4(3)
N(3)–N(2)–N(1)	170.1(5)	171.8(4)

Table 3. Selected torsion angles (°)

Layer	1	2
C(5)–O(1)–C(1)–O(2)	63.3(3)	178.0(2)
C(5)–O(1)–C(1)–C(2)	–57.6(3)	–61.5(3)
O(1)–C(1)–O(2)–C(7)	61.1(3)	–70.4(3)
C(2)–C(1)–O(2)–C(7)	–175.7(2)	168.1(3)
C(1)–O(2)–C(7)–C(8)	171.4(2)	–170.5(3)
O(2)–C(1)–C(2)–C(3)	–70.7(3)	174.3(2)
O(1)–C(1)–C(2)–C(3)	53.5(3)	55.0(4)
C(1)–C(2)–C(3)–N(1)	–172.9(3)	–173.7(3)
C(1)–C(2)–C(3)–C(4)	–52.5(3)	–51.0(4)
C(2)–C(3)–N(1)–N(2)	–167.2(3)	–176.6(3)
C(4)–C(3)–N(1)–N(2)	73.4(4)	61.4(4)
C(3)–N(1)–N(2)–N(3)	167(2)	179(1)
N(1)–C(3)–C(4)–O(3)	–68.7(3)	–68.1(3)
C(2)–C(3)–C(4)–O(3)	174.3(2)	172.4(3)
N(1)–C(3)–C(4)–C(5)	170.6(3)	171.4(3)
C(2)–C(3)–C(4)–C(5)	53.6(3)	51.9(3)
C(1)–O(1)–C(5)–C(6)	–178.3(2)	–175.0(2)
C(1)–O(1)–C(5)–C(4)	59.3(3)	61.8(3)
O(3)–C(4)–C(5)–O(1)	–176.0(2)	–177.0(2)
C(3)–C(4)–C(5)–O(1)	–56.4(3)	–56.7(3)
O(3)–C(4)–C(5)–C(6)	65.8(3)	62.8(3)
C(3)–C(4)–C(5)–C(6)	–174.6(2)	–176.9(2)
O(1)–C(5)–C(6)–O(4)	–67.9(3)	–65.0(3)
C(4)–C(5)–C(6)–O(4)	52.5(3)	56.3(3)

Table 4. Hydrogen bonds with $H \cdots A < r(A) + 2.000 \text{ Å}$ and $\langle DHA \rangle 110^\circ$

Isomer	D–H \cdots A	$d(D-H)$	$d(H \cdots A)$	$\angle(DHA)$	$d(D \cdots A)$
1	O3–H3B \cdots O4 ⁱ	0.820	1.908	167.24	2.714
	O4–H4B \cdots O3 ⁱⁱ	0.820	2.056	149.01	2.791
2	O3–H3B \cdots O4 ⁱⁱⁱ	0.820	1.842	167.82	2.649
	O4–H4B \cdots O3 ^{iv}	0.820	1.955	151.54	2.704

Symmetry codes: (i) $x + 1/2, -y - 1/2, -z + 1$; (ii) $x - 1, y, z$; (iii) $x + 1/2, -y + 3/2, -z$; (iv) $x - 1, y, z$.

–170.5(3)°. Its orientation relative to the *arabinose* ring system is described by the O1–C1–O2–C7 torsion angle of –70.4(3)°. The azide group is bound to C3 in the equatorial position. It is almost linear, the N1–N2–N3 angle being 171.8(4)°. The N1–N2 and N2–N3 distances are 1.204(5) and 1.140(5) Å, respectively, which reflects the differences in the bond orders for these groups. This difference for **2** is smaller than that reported for **1**. The orientation of the azide group is defined with the C2–C3–N1–N2 torsion angle of –176.6(3)°. Nine atoms in molecule studied, N3–N2–N1–C3–C2–C1–O2–C7–C8, are almost coplanar (Fig. 1b). The torsion angles between these atoms are about 170° (antiperiplanar conformation). The hydroxymethyl group reveals the *gauche* conformation, with the C4–C5–C6–O4 torsion angle being 56.3(3)°. Structure **2** contains chains of molecules oriented along the crystallographic *x*-axis, and interacting via the O3–H3B \cdots O4 [$x + 1/2, -y + 3/2, -z$] and O4–H4B \cdots O3 [$x - 1, y, z$] hydrogen bonds involving both hydroxyl groups of the molecule (Fig. 3b, Table 4). The IR spectrum of **2** shows the same

absorption bands as its anomer, which is also indicative of the presence of intermolecular hydrogen bonds.

3. Experimental

3.1. Materials

Compounds **1** and **2** were prepared by a modification of published procedures.¹² The appropriate 3-azido-2,3-dideoxyhexopyranoses were converted to their respective ethyl glycosides by reaction of EtOH (instead of MeOH) with the 1-*O*-methanesulfonyl derivatives.¹²

3.1.1. Physicochemical and spectral data for ethyl 3-azido-2,3-dideoxy- α -D-arabino-hexopyranoside (1). Mp 73–75 °C; $[\alpha]_D^{20} +153$ (c 0.8, MeOH), R_f 0.3 (1:2 *n*-heptane–ethyl acetate); IR, ν [cm^{–1}]: 3422.4 (ν broad, intermolecular H bonds –OH), 2984 and 2903.1 (ν sharp; C–H), 2875.0 (ν sharp; –O–CH₂–), 2097.8 (ν_{as} sharp; –N \equiv N– in –N₃), 1356.4 (ν_{sym} sharp; –N \equiv N– in –N₃),

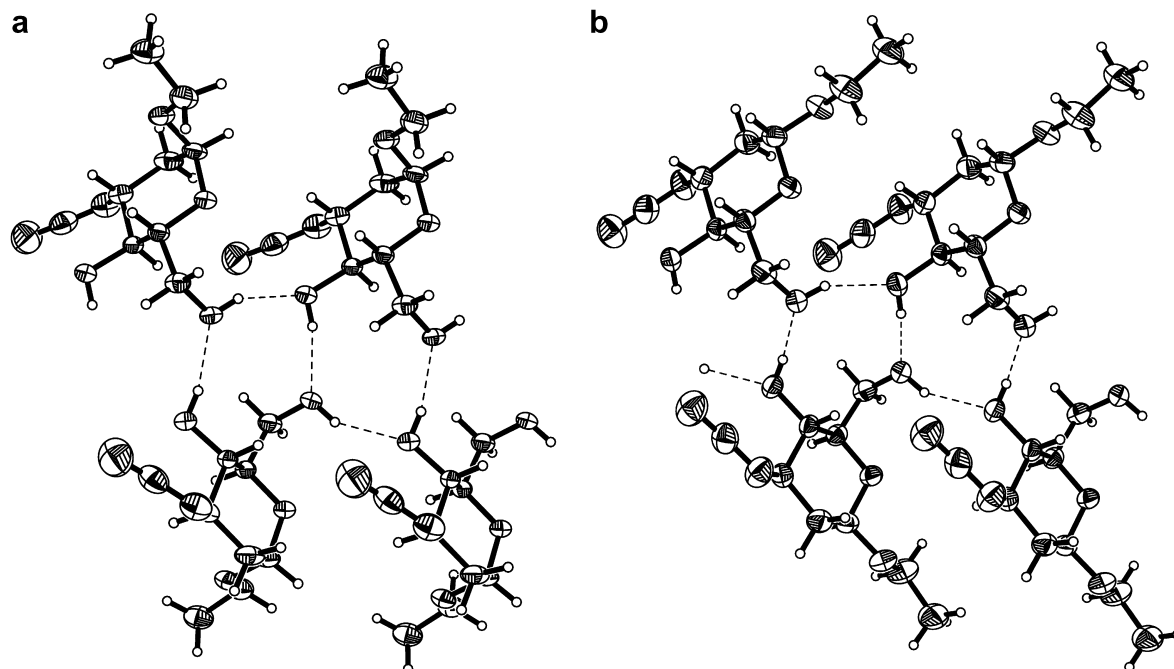


Figure 3. Projection of the packed crystal in the structure of **1** (a) and **2** (b). The dashed lines represent hydrogen bonds.

1081.1 (ν sharp; C–O in $-\text{CH}_2\text{--OH}$), 1057.8 (ν sharp; C–O–C); ^1H NMR, δ [ppm]: 4.898 (d, 1H, $J_{1,2a}$ 2.93 Hz, $J_{1,2e}$ 0.98 Hz, H-1), 3.8 (dd, 1H, J_{gem} 11.96 Hz, $J_{6B,5}$ 2.44 Hz, H-6B), 3.755 (m, 1H, J_{gem} = 11.71 Hz, $J_{-\text{CH}_2\text{--CH}_3}$ 6.84 Hz, H-7A), 3.704 (dd, 1H, $J_{6A,5}$ 5.37 Hz, H-6A), 3.581 (m, 1H, $J_{5,4}$ 10.15 Hz, H-5), 3.46 (m, 1H, H-7B), 3.364 (t, 1H, $J_{4,3}$ 9.28 Hz, H-4), 3.732 (m, 1H, $J_{3,2a}$ 12.7 Hz, $J_{3,2e}$ 3.91 Hz, H-3), 2.045 (dd, 1H, J_{gem} 13.9 Hz, H-2e), 1.59 (td, 1H, H-2a), 1.223 (t, 3H, H-8); ^{13}C NMR, δ [ppm]: 97.411 (C-1), 74.004 (C-5), 71.679 (C-4), 63.617 (C-7), 62.476 (C-3), 61.899 (C-6), 36.264 (C-2), 15.328 (C-8). FDMS: m/z 217 ($[\text{M}^+]$). Anal. Calcd for $\text{C}_8\text{H}_{15}\text{N}_3\text{O}_4$ (217.23): C, 44.23; H, 6.96; N, 19.34. Found: C, 44.22; H, 7.03; N, 19.05.

3.1.2. Physicochemical and spectral data for ethyl 3-azido-2,3-dideoxy- β -D-arabino-hexopyranoside (2). Mp 57–60 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{20}$ -15 (c 1.0, MeOH), R_f 0.27 (1:2 *n*-heptane–ethyl acetate); IR, $\tilde{\nu}$ [cm^{-1}]: 3419.8 (ν broad, intermolecular H bonds OH), 2979.5 and 2923.7 (ν sharp; C–H), 2852.0 (ν sharp; $-\text{O--CH}_2-$), 2091.7 (ν_{as} , sharp, $-\text{N}_3$), 1616.1 (ν broad; H–O–H); 1377.6 (ν_{sym} sharp; $-\text{N}\equiv\text{N}-$ in $-\text{N}_3$), 1078 (ν sharp; C–O in $\text{CH}_2\text{--OH}$), 1078 (ν sharp; C–O–C); ^1H NMR, δ [ppm]: 4.605 (dd, 1H, $J_{1,2a}$ 9.77 Hz, $J_{1,2e}$ 1.95 Hz, H-1), 3.947 (m, 1H, J_{gem} = 11.71 Hz, $J_{-\text{CH}_2\text{--CH}_3}$ 6.84 Hz, H-7A), 3.859 (dd, 1H, J_{gem} 11.96 Hz, $J_{6B,5}$ 2.44 Hz, H-6B), 3.704 (dd, 1H, $J_{6A,5}$ 5.37 Hz, H-6A), 3.574 (m, 1H, H-7B), 3.496 (m, 1H, $J_{3,2a}$ 12.45 Hz, $J_{3,2e}$ 4.88 Hz, H-3), 3.317 (t, 1H, $J_{4,3}$ 9.27 Hz, H-4), 3.279 (dq, 1H, $J_{5,4}$ 9.27 Hz, H-5), 2.119 (dq, 1H, J_{gem} 12.7 Hz, H-2e), 1.422 (q, 1H, H-2a), 1.196 (t, 3H, H-8); ^{13}C NMR, δ [ppm]: 100.64

(C-1), 78.593 (C-5), 71.63 (C-4), 65.59 (C-7), 64.042 (C-3), 62.616 (C-6), 37.57 (C-2), 15.425 (C-8). FDMS: m/z 217 ($[\text{M}^+]$). Anal. Calcd for $\text{C}_8\text{H}_{15}\text{N}_3\text{O}_4$ (217.23): C, 44.23; H, 6.96; N, 19.34. Found: C, 44.07; H, 7.07; N, 18.96.

3.2. Physical measurements

The ^1H and ^{13}C NMR spectra were measured using a Varian Mercury 400-MHz spectrometer with CD_3OD using Me_4Si as the internal standard. Mass spectra were recorded on Varian Matt 711 spectrometer in the FD ionization mode. Infrared spectra were carried out in Nujol mulls using a Bruker IFS 66 spectrophotometer. The optical rotations were determined with a Hilgel–Watts polarimeter in a 1 dm tube at the sodium D line for solutions in MeOH at room temperature (rt). The melting points are uncorrected. Field desorption mass spectra (FDMS) were recorded using a Varian Matt 711 spectrometer. Elemental analyses were conducted using a Carlo Erba EA1108 elemental analyzer.

The diffraction data were collected with Oxford Sapphire CCD diffractometer, Mo $\text{K}\alpha$ radiation $\lambda = 0.71073$ Å at 293(2) K. The numerical absorption correction was applied with RED 171 software,¹⁷ the minimum and maximum transmission being 0.9564 and 0.9880 for **1** and 0.9288 and 0.9831 for **2**. The hydrogen atoms in the polar groups have been located from the electron density maps and subsequently refined with the riding model. The other H atoms positions were calculated from geometry and included in the refinement with the riding model approach. The structure was

refined with SHELX-97 package.¹⁸ The Flack parameter was 2(2) for **1** and –2(2) for **2**.¹⁹

4. Supplementary data

Full crystallographic details for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 627909 for ethyl 3-azido-2,3-dideoxy- α -D-arabino-hexopyranoside (**1**) and No. CCDC 627910 for ethyl 3-azido-2,3-dideoxy- β -D-arabino-hexopyranoside (**2**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 1223/336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

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