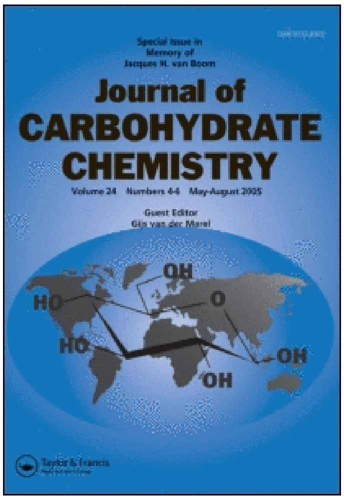

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Crystal Structures of Methyl (Methyl 3-azido-2,3-dideoxy-β-L-*lyxo*- and -β-D-*arabino*-hexopyranosid)uronates

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Crystal Structures of Methyl (Methyl 3-azido-2,3-dideoxy-β-L-*lyxo*- and -β-D-*arabino*-hexopyranosid)uronates

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Single-crystal x-ray diffraction data for methyl (methyl 3-azido-2,3-dideoxy-β-L-*lyxo*- and β-D-*arabino*-hexopyranosid)uronates are presented. Three independent molecules in the asymmetric part of the unit cell of the β-D-*arabino* stereoisomer were found. These differ slightly in the geometry of the groups bound to the pyranose rings. Conformations and the geometry parameters of all the molecules as well as the planarity of the carbomethoxy group, the linearity of the azido group, and the orientation of the aglycone in the crystal lattice are discussed. Influence of the hybridization, resonance, and crystal packing on the geometry parameters is shown.

Keywords Sugar amino acid; Geometry parameters; Conformation; Hybridization; Resonance; *Exo*-anomeric effect.

INTRODUCTION

Sugar amino acids (SAAs) are carbohydrates bearing both an amino group and a carboxyl group. Syntheses and applications of SAAs have recently been widely reviewed.[1–5] Applications of SAAs, especially as the polyfunctional scaffolds or isosters, requires the sugar ring to be rigid with a well-defined spatial orientation. X-ray crystallography is still the best method for characterizing the atomic structure of new compounds. It provides geometric parameters needed for visualization of a conformational space of the molecule. An agreement of the crystallographic and NMR data allows a conclusion on the geometry of sugar ring in a solution to be made.[6,7]

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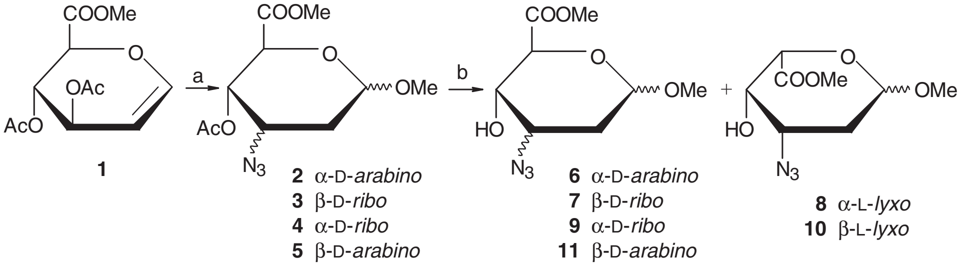
Previously we reported on the synthesis of methyl 3-amino-2,3-dideoxyhexopyranosiduronic acids, new sugar amino acids, and their diglycotides.[8] It began with the addition of hydrazoic acid to the α,β-unsaturated aldehyde derived from methyl 3,4-di-*O*-acetyl-2,6-anhydro-5-deoxy-D-*lyxo*-hex-5-enopyranonate (commercial name—methyl 3,4-di-*O*-acetyl-D-glucuronal) (**1**) followed by methyl glycosylation. The methyl (methyl 4-*O*-acetyl-3-azido-2,3-dideoxy-α/β-D-*arabino*- and -α/β-D-*ribo*-hexopyranosid)uronates (**2–5**) obtained were then *O*-deacetylated to yield the corresponding methyl (methyl 3-azido-2,3-dideoxyhexopyranosid)uronates (**6–11**). As reported, under the basic conditions of the *O*-deacetylation reaction, small amounts of the D-*ribo* substrates (**3** and **4**) altered their configuration at the C-5 carbon atom (α relative to the 5-carbomethoxy group). In this way the unexpected products **8** and **10** were obtained. Specifically, it was only the D-*ribo* compounds that epimerized in the basic environment of the reaction; the configuration of the D-*arabino* compounds remained unchanged. This happened because the D-*ribo* structures are conformationally less stable (${}^4C_1 \rightleftharpoons {}^1C_4$ conformational equilibrium) than the D-*arabino* structures (${}^4C_1$ form). C-5 epimerization of **3** and **4** provided the conformationally stable products **8** and **10** (${}^1C_4$ form). Possible C-5 epimerization of **2** and **5** did not occur because this would have led from the conformationally stable D-*arabino* structure to the conformationally unstable L-*xylo*[9,10] structure. This is an example of how conformation may influence the chemical properties of sugars.



a: 1. $HgSO_4$, H_2SO_4, H_2O, dioxane; 2. NaN_3, CH_3COOH; 3. MsCl, MeOH, s-collidine; **b:** MeONa / MeOH

The structure of *O*-deacetylation products **6–11** were established by NMR spectroscopy.[8] This paper reports on single-crystal x-ray diffraction data for methyl (methyl 3-azido-2,3-dideoxy-β-L-*lyxo*- (**10**) and β-D-*arabino*-hexopyranosid)uronates (**11**), which were recently obtained in their crystal forms. Presented data complete the discussion on the configuration and conformation of the previously reported sugar amino acids. These also demonstrate how hybridization, resonance, and crystal packing affect the geometry parameters of presented molecules. The application of SAAs as polyfunctional scaffolds or isosters requires the pyranose ring to be rigid with a well-defined spatial orientation. The presentation of the crystal structures of **10** and **11** provides concrete geometric parameters, which are useful in the study of the SAA geometry.

RESULTS AND DISCUSSION

The Crystal Structure of 10

The crystal structure of **10** undoubtedly corroborates our earlier statements that this compound is the β-L-*lyxo* stereoisomer of methyl (methyl 3-azido-2,3-dideoxyhexopyranosid)uronate. In the crystal **10** adopts the $^1C_4$ conformation[11,12] (Fig. 1) with ring puckering parameters[13,14] Q = 0.563(3) Å, $\theta = 175.2(3)^\circ$, and $\varphi = 176(4)^\circ$. This conformation is the same as established for **10** in methanol solution on the basis of NMR data.[8] This finding also confirms the geometry of the 3-amino analog of **10** (**10a**), which was previously established on the basis of NMR data only.[8] Recorded for **10** and **10a,** $J_{H,H}$ coupling constants are indicative for the same configuration and conformation of 3-azido and 3-amino analogs (Table 1).

X-ray analysis of **10** revealed that the 5-COOCH$_3$ group is almost planar in the region of the C5, C10, O3, O4, and C11 atoms (Fig. 1). This is demonstrated by the C5-C10-O3-C11 torsion angle of 178.1° as well as the O4-C10-O3-C11 torsion angle of –1.4° (Table 4). This planarity is due to the resonance that causes the O3 oxygen lone pair of electrons to delocalize onto the O4 carbonyl oxygen atom. Such delocalization stabilizes the compound and increases the O3-C10 rotational barrier. On the other hand, this resonance requires the O3

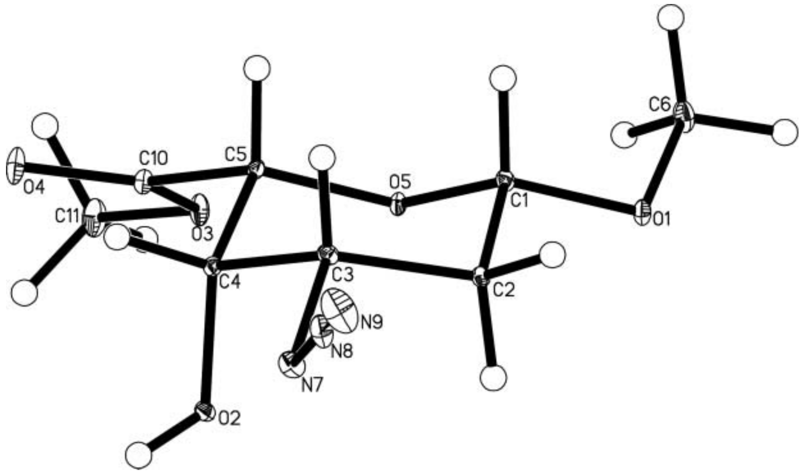
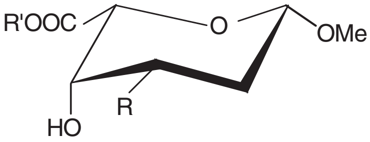
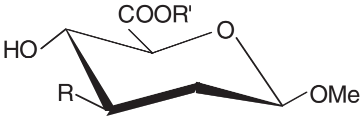


Figure 1: Structure of **10** showing 25% probability displacements for ellipsoids. The hydrogen atoms are shown as small spheres of arbitrary radius.

Table 1: The ^{1}H-^{1}H coupling constants (Hz) for **10**, **10a**, **11**, **11a**, and **11b**

Comp.	Structure	$J_{1,2a}$	$J_{1,2e}$	$J_{2a,2e}$	$J_{2a,3}$	$J_{2e,3}$	$J_{3,4}$	$J_{4,5}$
								
	β-L-lyxo							
10[a,c,e]	$R = N_3$, $R' = Me$	6.84		—	8.79		2.93	< 1
10a[a,d]	$R = NH_2$, $R' = Me$	9.6	2.0	12.8	12.4	4.4	3.2	1.2
								
	β-D-arabino							
11[a,c]	$R = N_3$, $R' = Me$	9.28	1.95	12.70	12.21	4.40	*n.d.*	9.28
11a[a,c]	$R = NH_2$, $R' = Me$	9.28	1.96	12.70	12.21	4.40	9.77	9.27
11b[b,d]	$R = NH_2$, $R' = H$	9.2	2.0	12.4	12.4	4.8	9.6	9.6

n.d., not determined.

[a] CD_3OD.

[b] D_2O.

[c] 500 MHz.

[d] 400 MHz.

[e] The H-2 protons are chemically and magnetically equivalent.

oxygen atom to be sp^2 hybridized. Indeed, the C10-O3-C11 valence angle of 115.3° (Table 4) is suited to a hybridization intermediate between sp^2 and sp^3.

The carbonyl O4 oxygen atom in the crystal lattice of **10** is oriented opposite to the O5 ring oxygen atom with the O5-C5-C10-O4 torsion angle of 175.4° (Table 4). Such an orientation is in agreement with findings, according to which repulsion of the carbonyl oxygen and ring oxygen lone pairs of electrons strongly determine the rotational preferences of the carboxyl group in the glucuronic acid.[15]

As required by the respective resonance structures, the azido group is almost linear with the C3-N7-N8-N9 torsion angle of 159° and the N7-N8-N9 valence angle of 172.7° (Table 4). These data are indicative of the sp hybridization of the N8 nitrogen atom. The hybridization of the N7 nitrogen atom seems to be between sp^3 and sp^2, which is manifested by the C3-N7-N8 valence angle of 115.4° (Table 4).

The nearly antiperiplanar orientation of the methyl C6 carbon atom to the C2 carbon atom, resulting from the rotation around the C1-O1 bond, with the C2-C1-O1-C6 torsion angle of –173.9° (Table 4) is typical of glycosides and is due to the *exo*-anomeric effect.

Both C–H···O close contacts and O–H···O intermolecular hydrogen bonds are observed in the crystal structure of **10** (Table 5).

The Crystal Structure of 11

X-ray analysis shows that there are three independent molecules in the asymmetric part of the unit cell of the methyl (methyl 3-azido-2,3-dideoxy-β-D-*arabino*-hexopyranosid)uronate (**11**). All these molecules adopt the $^4C_1$ conformation[11, 12] (Fig. 2) with ring puckering parameters[13,14] $Q = 0.572(3)$ Å, $\theta = 5.1(3)°$, and $\varphi = 335(3)°$ for ring A; $Q = 0.587(3)$ Å, $\theta = 4.6(3)°$, and $\varphi = 1(4)°$ for ring B; and $Q = 0.583(3)$ Å, $\theta = 3.9(3)°$, and $\varphi = 14(4)°$ for ring C. This conformation is the same as established for **11** in methanol solution on the basis of NMR spectra.[8] This finding also confirms the geometry of the 3-amino analog of **11** (**11a**) and geometry of SAA **11b**, which were previously established on the basis of NMR data only.[8] Recorded for **11**, **11a**, and **11b**, $J_{H,H}$ coupling constants are indicative for the same configuration and conformation of all these analogs (Table 1).

Although there are three molecules in the asymmetric part of the unit cell of **11**, the geometry of these molecules does not differ substantially. In particular, the geometry parameters of the pyranose rings are almost the same in these three molecules (Fig. 3). Small differences are found in the geometry of the groups bound to the pyranose rings. As far as the respective bond lengths—hard geometry parameters—are concerned, the biggest difference is found for the C3-N7 bond lengths, which range from 1.468 Å to 1.493 Å (Table 4). The difference of 0.025 Å is small enough for all measured C3-N7

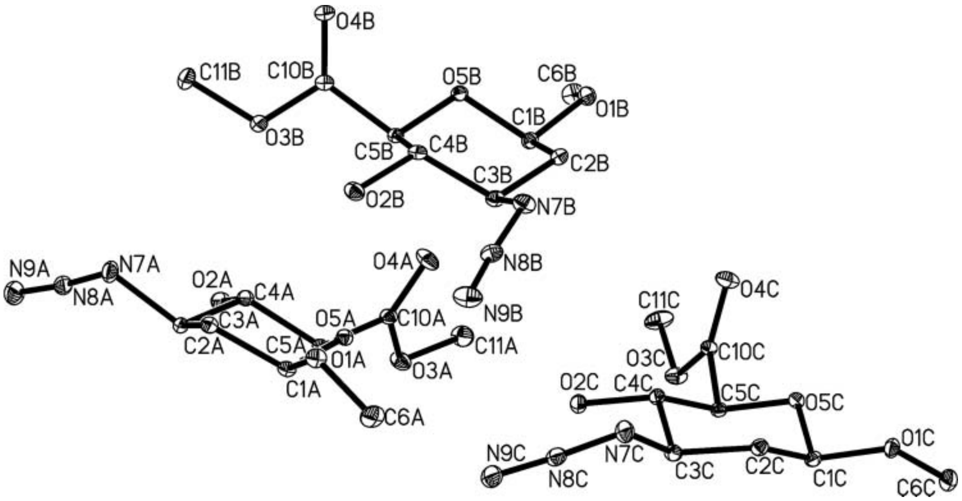


Figure 2: Structures of three molecules of **11** showing 25% probability displacements for ellipsoids. The hydrogen atoms have been omitted for clarity.

bond lengths to be classified as single bonds. The three molecules of **11** likewise do not differ significantly in their valence angles. The largest difference is found for the C4-C5-C10 valence angles, which range from 110.0° to 112.1°. Such a difference is small and yet still indicative of the sp^3 hybridization of the C5 carbon atom. The biggest differences in the geometry of the three molecules of **11** refer to the torsion angle, the softest geometry parameter. However, these differences are still small and they do not disturb the $^4C_1$ conformation of the rigid pyranose ring, because they refer not to the pyranose ring but to the ring substituents (Fig. 3).

The 5-$COOCH_3$ group in all molecules of **11** is planar in the region of the C5, C10, O3, O4, and C11 atoms, as is the 5-$COOCH_3$ group in **10**. This is

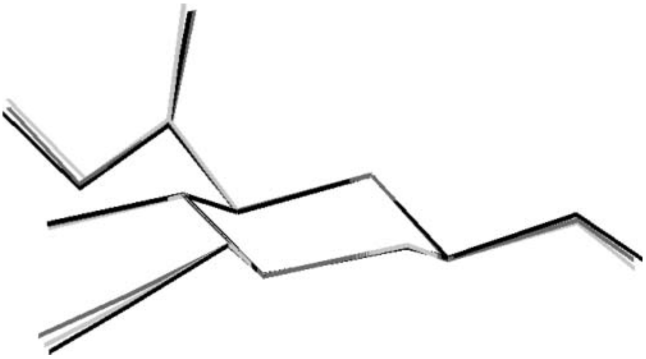


Figure 3: Overlapping of the A (black), B (gray), and C (light gray) molecules of **11**.

demonstrated by the C5-C10-O3-C11 torsion angles of –177.3°, –179.0°, and –175.6° in molecules A, B, and C, respectively, as well as the O4-C10-O3-C11 torsion angles of 2.1°, 0.0°, and 3.3° in molecules A, B, and C, respectively (Table 4). This planar group rotates around the C5-C10 bond, and the torsion angles related to this rotation seem to be relatively flexible. They differ by 6.6° (the C4-C5-C10-O3 torsion angle), 6.7° (the C4-C5-C10-O4 and O5-C5-C10-O3 torsion angles), and 6.8° (the O5-C5-C10-O4 torsion angle). Typically, the azido group is linear with C3-N7-N8-N9 torsion angles of 171°, 176°, and 179° in molecules A, B, and C, respectively, and with N7-N8-N9 valence angles of 173.6°, 172.2°, and 173.0° in molecules A, B, and C, respectively. These data are indicative of the sp hybridization of the N8 nitrogen atom, as in the case of **10**. The hybridization of the N7 nitrogen atom seems to be between sp^3 and sp^2, which is manifested by the C3-N7-N8 valence angles of 115.6°, 115.6°, and 115.1° in molecules A, B, and C, respectively, and which is in agreement with the resonance structures of the azido group. Rotation around the C3-N7 bond also slightly differentiates the geometries of the molecules in **11**. The C4-C3-N7-N8 torsion angles of molecules A, B, and C differ by 4.5°. With regard to the aglycone, it is clear that the rotation around the C1-O1 bond also contributes to the geometric diversity of **11**. The measured difference in the C2-C1-O1-C6 torsion angles of molecules A, B, and C is 6.6°, whereas in the O5-C1-O1-C6 torsion angles it is 5.8°.

The observed differences in the geometries of the three molecules of **11** emerge from the properties of the crystal lattice of **11**. There is only one molecule in the asymmetric part of the unit cell of **10**, which is a stereoisomer of **11**, and in the 4-*O*-acetyl derivative of **11**.[16] It is probably the advantageous crystal packing that gives rise to the slight changes in the geometry of **11**, which results in three molecules being in the asymmetric part of the unit cell.

In contrast to compound **10**, the carbonyl O4 oxygen atom in all molecules of **11** is not oriented opposite to the O5 ring oxygen atom—this is demonstrated by the O5-C5-C10-O4 torsion angles of –40.6°, –39.3°, and –46.1° in molecules A, B, and C, respectively (Table 4). In **11**, the O3 oxygen atom seems to be repulsed more strongly than the O4 oxygen atom by the O5 ring oxygen atom, because the respective O5-C5-C10-O3 torsion angles are 140.0°, 141.7°, and 135.0° in molecules A, B, and C. These results may indicate that the considerable repulsion between the carbonyl O4 oxygen atom and the ring O5 oxygen atom lone pairs is not as significant as theoretical calculations suggest.[15]

Typically, the methyl C6 carbon atom in all the molecules of **11** is oriented nearly antiperiplanarly to the C2 carbon with the C2-C1-O1-C6 torsion angles of 159.1°, 165.7°, and 162.7° in molecules A, B, and C, respectively (Table 4); this is due to the *exo*-anomeric effect.

Both C–H$\cdots$O close contacts and O–H$\cdots$O intermolecular hydrogen bonds are present in the crystal structure of **11** (Table 6).

Table 2: Crystal data and structure refinement for **10** and **11**

	10	**11**
Empirical formula	$C_8H_{13}N_3O_5$	$C_8H_{13}N_3O_5$
Formula weight	231.21	231.21
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit cell dimensions		
a (Å)	4.5430(6)	11.0505(10)
b (Å)	12.5027(18)	12.7980(8)
c (Å)	19.764(4)	12.7647(10)
α (°)	90	90
β (°)	90	106.948(9)
γ (°)	90	90
V (Å^3)	1122.6(3)	1726.8(2)
Z	4	6
D_{calcd} (mg/m^{-3})	1.368	1.334
Absorption coefficient (mm^{-1})	0.115	0.112
F(000)	488	732
Crystal size (mm)	0.35 × 0.25 × 0.12	0.30 × 0.15 × 0.10
Θ Range for data collection (°)	3.26–24.98	3.18–25.00
Limiting indices	$-5 \leq h \leq 5, -14 \leq k \leq 14, -3 \leq l \leq 23$	$-13 \leq h \leq 11, -15 \leq k \leq 14, -15 \leq l \leq 15$
Reflections collected/unique	21854/1193 (R_{int} = 0.1412)	12891/3162 (R_{int} = 0.0464)
Completeness 2Θ = 50.00° (%)	99.7	99.2
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1193/0/162	3162/1/462
Goodness of fit on F^2	0.771	0.806
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0369$	$R_1 = 0.0300$
	$wR_2 = 0.0735$	$wR_2 = 0.0575$
R indices (all data)	$R_1 = 0.0834$	$R_1 = 0.0675$
	$wR_2 = 0.0794$	$wR_2 = 0.0624$
Largest diff. peak and hole (e Å^{-3})	0.106 and –0.143	0.092 and –0.109

Table 3: Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **10** and **11**

10					**11**				
Atom	*x*	*y*	*z*	*U(eq)*^{a}	*Atom*	*x*	*y*	*z*	*U(eq)*^{a}
C-1	7087(9)	9462(2)	1915(2)	49(1)	C-1A	3491(3)	8793(2)	4228(2)	55(1)
					C-1B	−24(3)	5441(2)	3301(2)	55(1)
					C-1C	−1535(3)	7165(3)	8817(3)	54(1)
O-1	8586(6)	10377(2)	1683(1)	59(1)	O-1A	3867(2)	8194(2)	5182(2)	71(1)
					O-1B	−1138(2)	4903(2)	2784(2)	63(1)
					O-1C	−2302(2)	6642(2)	9337(2)	64(1)
C-2	7792(9)	9285(3)	2646(2)	47(1)	C-2A	391(3)	8591(2)	3567(2)	59(1)
					C-2B	417(3)	5132(2)	4492(2)	56(1)
					C-2C	−170(3)	6888(2)	9361(2)	58(1)
O-2	10276(5)	7080(2)	2454(1)	56(1)	O-2A	2083(2)	9325(2)	859(2)	69(1)
					O-2B	3819(2)	5878(2)	4868(2)	72(1)
					O-2C	893(2)	7624(2)	6905(2)	66(1)
C-3	6427(10)	8248(3)	2891(2)	50(1)	C-3A	3929(3)	9099(2)	2460(3)	56(1)
					C-3B	1686(3)	5631(2)	5041(2)	58(1)
					C-3C	657(3)	7391(2)	8735(2)	57(1)
O-3	9011(7)	7007(2)	717(1)	71(1)	O-3A	−343(2)	9453(2)	1743(2)	73(1)
					O-3B	3572(2)	6134(2)	2331(2)	75(1)
					O-3C	−1946(2)	7723(2)	5193(2)	70(1)
C-4	7198(8)	7315(3)	2424(2)	46(1)	C-4A	2562(3)	8812(2)	1890(2)	52(1)
					C-4B	2625(3)	5385(2)	4408(2)	56(1)
					C-4C	192(3)	7114(2)	7529(2)	52(1)
O-4	6444(7)	5830(2)	1318(1)	93(1)	O-4A	75(2)	7794(2)	2159(2)	91(1)
					O-4B	2956(3)	4489(2)	2192(3)	112(1)
					O-4C	−1888(3)	6065(2)	5672(2)	84(1)
C-5	6517(9)	7633(3)	1699(2)	46(1)	C-5A	1769(3)	9034(2)	2661(2)	48(1)
					C-5B	2059(3)	5679(2)	3202(2)	51(1)
					C-5C	−1229(3)	7357(2)	7074(2)	49(1)
O-5	8024(5)	8586(2)	1509(1)	49(1)	O-5A	2248(2)	8460(1)	3652(2)	52(1)
					O-5B	893(2)	5129(1)	2769(2)	52(1)
					O-5C	−1904(2)	6817(1)	7702(2)	51(1)
C-6	7841(12)	10687(3)	1009(2)	82(2)	C-6A	3402(5)	8561(3)	6048(3)	103(2)
					C-6B	−1793(4)	5335(3)	1722(3)	81(1)
					C-6C	−3556(4)	7079(3)	9100(3)	87(1)
N-7	7479(8)	7960(3)	3574(2)	74(1)	N-7A	4783(3)	8740(3)	1816(3)	80(1)
					N-7B	2120(3)	5196(2)	6152(2)	79(1)
					N-7C	1951(3)	6985(3)	9237(3)	80(1)
N-8	6006(12)	8295(3)	4037(2)	90(1)	N-8A	4861(3)	9322(3)	1083(3)	79(1)
					N-8B	2937(3)	5700(2)	6810(3)	73(1)
					N-8C	2807(4)	7533(3)	9103(2)	78(1)
N-9	4737(15)	8530(4)	4517(2)	156(3)	N-9A	5024(4)	9808(3)	389(3)	110(1)
					N-9B	3682(4)	6086(3)	7504(3)	107(1)
					N-9C	3684(4)	7967(3)	9041(3)	113(1)
C-10	7318(9)	6721(3)	1227(2)	57(1)	C-10A	424(3)	8674(2)	2173(2)	55(1)
					C-10B	2888(3)	5346(3)	2519(3)	63(1)
					C-10C	−1723(3)	6964(2)	5925(3)	52(1)
C-11	9745(13)	6153(3)	242(2)	101(2)	C-11A	−1649(4	9197(3)	1205(3)	92(1)
					C-11B	4425(5)	5904(4)	1696(5)	97(1)
					C-11C	−2336(4)	7425(3)	4057(3)	98(1)
H-1	4961	9566	1862	58	H-1A	3490	9537	4411	66
					H-1B	−166	6197	3230	66

(Continued on next page)

Table 3: Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **10** and **11** (*Continued*)

10					**11**				
Atom	*x*	*y*	*z*	*U(eq)*^{a}	*Atom*	*x*	*y*	*z*	*U(eq)*^{a}
					H-1C	−1690(30)	7940(30)	8830(20)	64
H-2A	7130(70)	9850(20)	2944(14)	57	H-2A	4471	7844	3478	71
					H-2D	492	4378	4553	67
					H-2G	−65	6136	9371	69
H-2B	10010(80)	9300(20)	2718(14)	57	H-2B	5220	8864	3954	71
					H-2E	−198	5357	4854	67
					H-2H	82	7136	10112	69
H-2C	10350(90)	6490(30)	2778(17)	84	H-2C	2130(40)	9980(30)	940(30)	104
					H-2F	3740(40)	6580(30)	4830(30)	108
					H-2I	810(30)	8350(30)	7010(30)	99
H-3	4240(80)	8310(30)	2897(15)	60	H-3A	3998	9860	2548	67
					H-3B	1585	6390	5080	70
					H-3C	652	8152	8822	69
H-4	6053	6681	2550	56	H-4A	2530	8058	1752	62
					H-4B	2766	4629	4445	68
					H-4C	301	6360	7463	62
H-5	4410(80)	7720(20)	1655(14)	56	H-5A	1760(30)	9810(20)	2850(20)	57
					H-5B	1911	6434	3132	61
					H-5C	−1374	8111	7097	59
H-6A	8662	11379	915	123	H-6A	3833	8206	6714	154
					H-6D	−2580	4973	1426	121
					H-6G	−4015	6726	9528	131
H-6B	5739	10717	964	123	H-6B	2511	8425	5870	154
					H-6E	−1278	5254	1238	121
					H-6H	−3990	6993	8336	131
H-6C	8621	10174	695	123	H-6C	3550	9299	6141	154
					H-6F	−1955	6064	1798	121
					H-6I	−3497	7810	9280	131
H-11A	11031	6428	−102	152	H-11A	−2067	9792	800	138
					H-11D	4910(50)	6550(40)	1620(40)	145
					H-11G	−2571	8037	3609	147
H-11B	7974	5888	36	152	H-11B	−2061	9008	1744	138
					H-11E	3850(50)	5630(40)	940(40)	145
					H-11H	−3047	6961	3923	147
H-11C	10711	5582	479	152	H-11C	−1689	8622	714	138
					H-11F	4870(50)	5350(40)	1950(40)	145
					H-11I	−1649	7078	3881	147

$^a U_{eq}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4: Selected geometry parameters for methyl (methyl 3-azido-2,3-dideoxy-β-L-*lyxo*- (**10**) and β-D-*arabino*-hexopyranosid)uronates (**11**)

10		**11**		
Bond length	*(Å)*	*Bond length*	*(Å)*	*Difference*[a] *(Å)*
C-3—N-7	1.476(4)	C-3A—N-7A	1.493(5)	0.025
		C-3B—N-7B	1.468(4)	
		C-3C—N-7C	1.481(4)	
Valence angles	*(°)*	*Valence angles*	*(°)*	*Difference*[a] *(°)*
C-3—N-7—N-8	115.4(3)	C-3A—N-7A—N-8A	115.6(3)	0.5
		C-3B—N-7B—N-8B	115.6(3)	
		C-3C—N-7C—N-8C	115.1(3)	
C-4—C-5—C-10	109.7(3)	C-4A—C-5A—C-10A	111.1(2)	2.1
		C-4B—C-5B—C-10B	112.1(3)	
		C-4C—C-5C—C-10C	110.0(2)	
N-7—N-8—N-9	172.7(5)	N-7A—N-8A—N-9A	173.6(4)	1.4
		N-7B—N-8B—N-9B	172.2(4)	
		N-7C—N-8C—N-7C	173.0(4)	
C-10—O-3—C-11	115.3(3)	C-10A—O-3A—C-11A	117.3(3)	0.6
		C-10B—O-3B—C-11B	116.7(3)	
		C-10C—O-3C—C-11C	117.3(2)	
Torsion angles	*(°)*	*Torsion angles*	*(°)*	*Difference*[a] *(°)*
C-2—C-1—O-1—C-6	−173.9(3)	C-2A—C-1A—O-1A—C-6A	159.1(3)	6.6
		C-2B—C-1B—O-1B—C-6B	165.7(3)	
		C-2C—C-1C—O-1C—C-6C	162.7(3)	
C-3—N-7—N-8—N-9	159(4)	C-3A—N-7A—N-8A—N-9A	171(3)	—
		C-3B—N-7B—N-8B—N-9B	176(3)	
		C-3C—N-7C—N-8C—N-9C	179(3)	
C-4—C-5—C-10—O-3	−128.7(3)	C-4A—C-5A—C-10A—O-3A	−100.4(3)	6.6
		C-4B—C-5B—C-10B—O-3B	−99.6(3)	
		C-4C—C-5C—C-10C—O-3C	−106.2(3)	
C-4—C-5—C-10—O-4	51.8(5)	C-4A—C-5A—C-10A—O-4A	78.9(4)	6.7
		C-4B—C-5B—C-10B—O-4B	79.3(4)	
		C-4C—C-5C—C-10C—O-4C	72.6(4)	
C-4—C-3—N-7—N-8	−146.9(4)	C-4A—C-3A—N-7A—N-8A	83.6(4)	4.5
		C-4B—C-3B—N-7B—N-8B	79.1(4)	
		C-4C—C-3C—N-7C—N-8C	82.4(4)	
O-4—C-10—O-3—C11	−1.4(6)	O-4A—C-10A—O-3A—C11A	2.1(5)	3.3
		O-4B—C-10B—O-3B—C11B	0.0(5)	
		O-4C—C-10C—O-3C—C11C	3.3(5)	
C-5—C-10—O-3—C11	178.1(4)	C-5A—C-10A—O-3A—C11A	−177.3(3)	3.4
		C-5B—C-10B—O-3B—C11B	−179.0(3)	
		C-5C—C-10C—O-3C—C11C	−175.6(3)	
O-5—C-5—C-10—O-3	−5.1(4)	O-5A—C-5A—C-10A—O-3A	140.0(2)	6.7
		O-5B—C-5B—C-10B—O-3B	141.7(2)	
		O-5C—C-5C—C-10C—O-3C	135.0(2)	
O-5—C-5—C-10—O-4	175.4(4)	O-5A—C-5A—C-10A—O-4A	−40.6(4)	6.8
		O-5B—C-5B—C-10B—O-4B	−39.3(4)	
		O-5C—C-5C—C-10C—O-4C	−46.1(4)	
O-5—C-1—O-1—C-6	65.1(4)	O-5A—C-1A—O-1A—C-6A	−81.5(3)	5.8
		O-5B—C-1B—O-1B—C-6B	−75.7(3)	
		O-5C—C-1C—O-1C—C-6C	−78.3(3)	

[a] The biggest difference between the same geometry parameter for three molecules in an asymmetric part of the unit cell of **11**.

To recapitulate, two crystal structures of new precursors of sugar amino acids are presented to provide geometric parameters for these compounds. The respective valence and torsion angles indicate that the methoxycarbonyl group is planar and that the azido group is linear as a consequence of their resonance structures. The aglycone methyl group is oriented in accordance with the *exo*-anomeric effect.

EXPERIMENTAL

Diffraction data were collected at rt (295 K) on a Gemini R-Ultra diffractometer[17] with MoKα radiation ($\lambda = 0.71073$ Å). The initial phase angle determination was performed using SHELXS.[18] All H atoms that participate in the hydrogen bonds were located on a Fourier difference map and refined using a riding model with $U_{iso}(H) = 1.5U_{eq}(O)$ and $U_{iso}(H) = 1.2U_{eq}(C(alkyl))$, and $U_{iso}(H) = 1.2U_{eq}(C(methyl))$. All other H atoms were located geometrically and refined using a riding model with C−H = 0.97–0.98 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$ (C−H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl H atoms). Table 2 summarizes the crystallographic data, data collection, and structure refinement; Table 3 sets out the coordinates of the atoms and their isotropic temperature factors; Table 4 gives selected crystals' geometric parameters; and Tables 5 and 6 summarize the hydrogen interactions.

The crystal structure of **10** was refined to $R_1 = 0.0834$ (21,854 reflections–all unique) and $R_1 = 0.0369$ (1193 reflections with $F_0 > 2\sigma(F_0)$) using the full-matrix least-squares method and the SHELXL-97 program[19] based on 162 parameters. The crystal structure of **11** was refined to $R_1 = 0.0675$ (12,891 reflections—all unique) and $R_1 = 0.0300$ (3162 reflections with $F_0 > 2\sigma(F_0)$) using the full-matrix least-squares method and the SHELXL-97 program based on 462 parameters. The structures of the compounds showing the conformations and atom numbering system are illustrated in Figures 1 (**10**) and 2 (**11**).[20] The molecular packing in the crystals, illustrated in Figures 4 (**10**) and 5 (**11**), was prepared with the aid of PLUTO-78.[21] The computational material for this publication was prepared using the PLATON program.[14]

SUPPLEMENTARY MATERIALS

Full crystallographic details, excluding structures features, have been deposited (deposition No. CCDC 756578 and 756579) with the Cambridge Crystallographic Data Center. These data may be obtained, on request, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

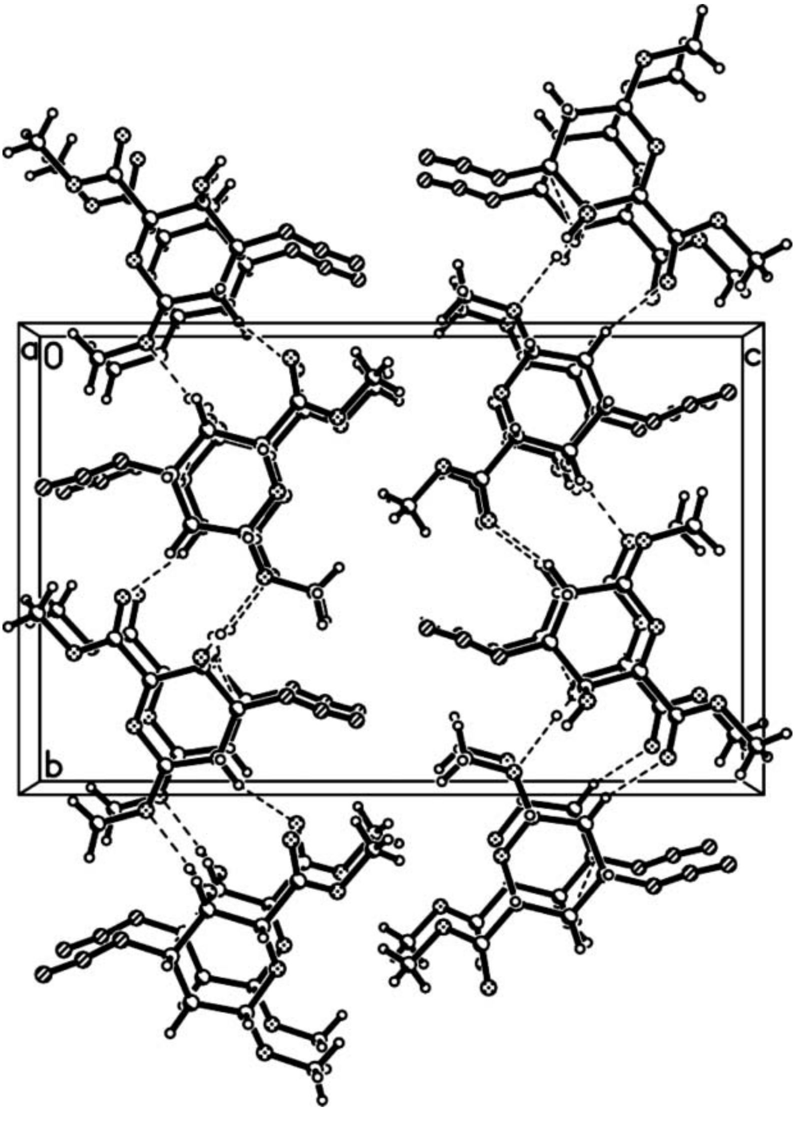


Figure 4: Molecular packing of **10** (view along *a*-axis).

Table 5: Intermolecular hydrogen interactions for **10** with distances (d): d(D . . . A) < R(D)+R(A)+0.50Å; d(H . . . A) < R(H)+R(A)-0.12 Å and angle (<) <D-H . . . A > 100.0°

D-H	A	d(D-H)	d(H..A)	d(D..A)	< D-H . . . A
O-2—H-2C	O-1$^{\mathrm{i}}$	0.98(4)	1.82(4)	2.777(3)	166(4)
C-2—H-2A	O-4$^{\mathrm{ii}}$	0.97(3)	2.50(3)	3.410(5)	156(2)
C-3—H-3	O-2$^{\mathrm{iii}}$	1.99(4)	2.52(4)	3.269(5)	131(3)
C-5—H-5	O-2$^{\mathrm{iii}}$	0.97(4)	2.58(3)	3.278(5)	129(2)

Symmetry codes: (i) –x + 2, y—1/2, –z + 1/2; (ii) –x + 1, y + 1/2, –z + 1/2; (iii) x—1, y, z.

Table 6: Intermolecular hydrogen interactions for **11** with distances (d): d(D . . . A) < R(D)+R(A)+0.50Å; d(H . . . A) < R(H)+R(A)-0.12 Å and angle (<) <D-H . . . A > 100.0°

D-H	A	d(D-H)	d(H..A)	d(D..A)	< D-H . . . A
O-2A—H-2C	O-1C$^{\mathrm{i}}$	0.85(4)	2.17(4)	2.992(3)	165.0(3)
O-2C—H-2I	O-1B$^{\mathrm{i}}$	0.95(4)	2.02(4)	2.946(3)	164(3)
C-1C—H-1C	O-4B$^{\mathrm{i}}$	1.01(4)	2.55(3)	3.434(5)	146(2)
C-11B—H-11E	N-9A$^{\mathrm{ii}}$	1.02(3)	2.60(5)	3.220(7)	117(4)
C-5A—H-5A	O-4C$^{\mathrm{i}}$	1.02(3)	2.45(3)	3.337(3)	144.7(19)

Symmetry codes: (i) –x, y + 1/2, –z + 1; (ii) –x + 1, y—1/2, –z.

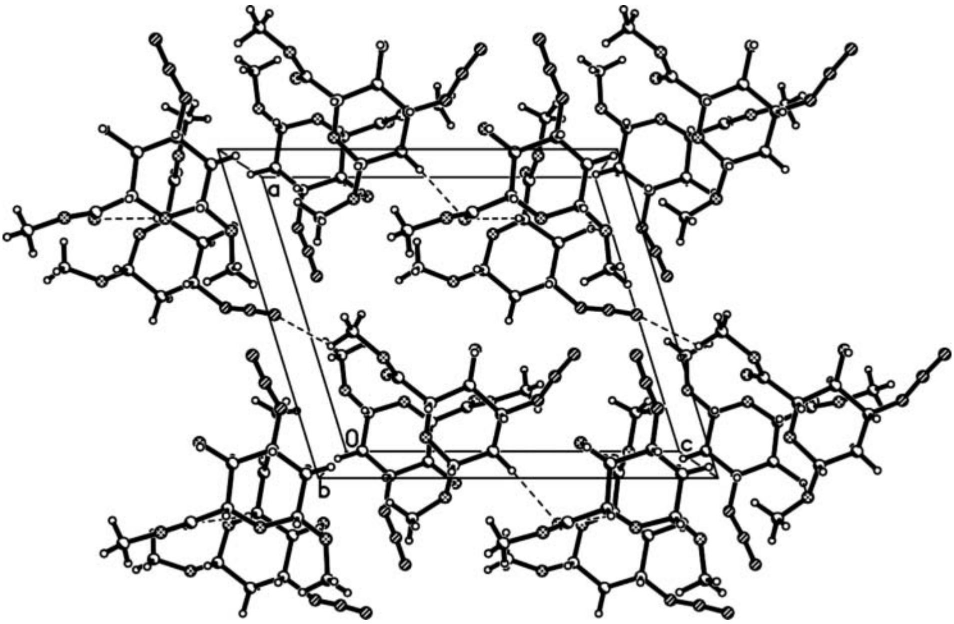


Figure 5: Molecular packing of **11** (view along *b*-axis).

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