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Note

Methyl 6-deoxy-6-iodo-α-D-glucopyranoside: crystal structure and high-resolution NMR spectroscopy

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ABSTRACT

Single-crystal X-ray diffraction and high-resolution ^{1}H and ^{13}C NMR spectral data for methyl 6-deoxy-6-iodo-α-D-glucopyranoside are reported. The $^{4}C_{1}$ conformation was found to be the preferred form for this compound, both in the crystal lattice and in solution. The rotational preferences of all the groups bound to the pyranose ring are presented. The stabilization of the crystal structure by a network of O–H···O intra- and intermolecular interactions as well as the short contacts of the iodine atoms is discussed.

6-Deoxy-6-iodohexoses are an important and useful class of compounds for both chemical and biological applications. Since iodide is a good leaving group, deoxy iodo sugars are amenable to chemical transformations such as substitution and elimination. Dehydrohalogenation of 6-deoxy-6-iodohexopyranosides has been widely used to produce 6-deoxyhex-5-enopyranosides—compounds of great interest as substrates in the preparation of chiral substituted cyclohexanones,[1–4] 3-amino-2,3,6-trideoxyhexopyranosides,[5–7] and iminosugars.[8] 6-Deoxy-6-iodohexopyranosides may also undergo reductive elimination, which generates carbohydrate-derived dienes that are subsequently converted into carbocycles by ring-closing olefin metathesis.[9] Additionally, terminal deoxyiodo sugars have been successfully used to produce *N*-(D,L-ribitol-5-yl)trimethylammonium iodide[10] and 6-deoxy-6-diethoxyphosphinyl derivatives, the intermediates in the preparation of phospho sugars.[11]

Glucose,[12] methyl α- and β-D-glucopyranosides,[13] labeled with radioactive iodine in position 6, have been proposed as tracers of glucose transport in vivo.

Methyl 6-deoxy-6-iodo-α-D-glucopyranoside was synthesized, and its crystal structure and high-resolution NMR spectroscopy are presented here. We focus our attention on the three-dimensional structure of this compound with respect to the pyranose ring conformation, orientation of the iodomethyl, hydroxy and methoxy groups, as well as intra- and intermolecular interactions. All this is prerequisite to an understanding of the chemical and biological functions of this compound.

The first procedure for obtaining methyl 6-deoxy-6-iodo-α-D-glucopyranoside that we examined involved the reaction of α-D-glucopyranoside with triphenylphosphine–carbon tetraiodide reagent in anhydrous pyridine.[14] This procedure was not very effective, however, so we tested another one using triphenylphosphine, imidazole, and iodine in toluene at reflux temperature.[15] Separation of the product without further acetylation yielded crystalline methyl 6-deoxy-6-iodo-α-D-glucopyranoside.

In the crystal, methyl 6-deoxy-6-iodo-α-D-glucopyranoside adopts the $^{4}C_{1}$ conformation[16,17] (Fig. 1) with ring-puckering parameters[18,19] $Q = 0.562(5)$ Å, $\theta = 5.5(5)$ Å, and $\varphi = 380(5)°$. The ^{1}H and ^{13}C NMR spectra confirm the structure and also the $^{4}C_{1}$ conformation of this compound in methanol solution ($J_{2,3}$ 9.77, $J_{3,4}$ 8.79, $J_{4,5}$ 9.77 Hz). The relatively small chemical shift of the C-6 carbon in the ^{13}C NMR spectra of the methyl 6-deoxy-6-iodo-α-D-glucopyranoside (δ 6.10) is noteworthy; it is characteristic of a carbon atom bound to iodine (heavy-atom effect).[20]

X-ray analysis revealed that the 6-iodomethyl group in the crystal lattice exists in the *gg* (*gauche–gauche*) conformation, which is reflected by the C4–C5–C6–I8 torsion angle of 57.7(5)° (Table 3, see Fig. 2). Such an orientation is also preferred by the hydroxymethyl group in glucopyranose derivatives, both in crystals and in solution; it is due to the network of O–H···O interactions between the C4–OH, C6–OH and ring oxygen atoms.[21,22] The stability of the *gg* conformation in the case of the hydroxymethyl group may also be due to the '*gauche* effect'.[23] This requires the hydrogen atom to be oriented antiperiplanarly to the electronegative atoms (F and O). The stability of the *gg* conformation in the case of the iodomethyl group cannot be explained either by O–H···I interactions, which are not detected (Table 4), or by the '*gauche* effect', because the electronegativity of the iodine atom is relatively small.

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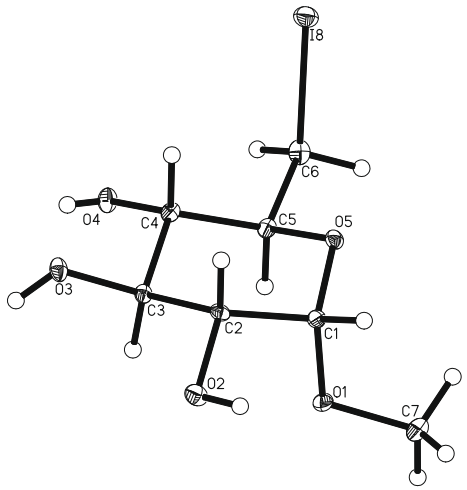

Figure 1. Structure of methyl 6-deoxy-6-iodo-α-D-glucopyranoside showing 25% probability displacements for ellipsoids.

Interestingly, the intramolecular distance between the H4 hydrogen atom and the iodine atom is very short indeed at 2.98 Å (Table 4), but the sum of their van der Waals radii is 3.2 Å.[19]

Rotation of the 4-OH group around the O4–C4 bond prefers the staggered conformation as shown in Figure 2. Such an arrangement is probably the most favourable because it allows an intramolecular hydrogen bond to form between the C4–OH and C3–OH hydroxyl groups (O4–H4A···O3, Table 4). It was recently argued that vicinal hydroxyl groups in glucopyranose are not linked by intramolecular hydrogen bonding.[24] However, an apparent D–H···A donor–hydrogen–acceptor sequence is seen here with an H···A distance of 2.55(7) Å and with a D–H···A angle of 121(8)° (Table 4). Since, as far as we are aware of, no one has suggested a new name for this evident attraction of the hydroxyl hydrogen by the vicinal oxygen, we shall continue to use the traditional term 'hydrogen bond' for this kind of interaction.

One might expect that methyl 6-deoxy-6-iodo-α-D-glucopyranoside, like α-D-glucopyranose,[21,25] would exhibit a counterclockwise network of the following intramolecular hydrogen interactions: O5–H5A···O4, O4–H4A···O3, and O3–H3A···O2. In fact, only the first of these hydrogen bonds is detected in the crystal lattice of the 6-deoxyiodoglucoside in question. The second one cannot be formed, because the rotation around the O3–C3 bond in the compound unexpectedly prefers one of the eclipsed conformations (Fig. 2). Such an eclipsed conformation is not found among the geometry-optimized structures of α-D-glucopyranose, which exhibits a network of intramolecular hydrogen interactions. In all probability, the crystal packing forces dictate that the eclipsed conformation is to be adopted in the case of rotation around the O3–C3 bond, even though it is less favourable than the staggered conformation and causes the loss of intramolecular hydrogen bonding.

In spite of the favourable staggered conformations resulting from the rotations around the O2–C2 and O1–C1 bonds (Fig. 2), the O2–H2A···O1 intramolecular hydrogen bond is not formed in the crystal structure of methyl 6-deoxy-6-iodo-α-D-glucopyranoside. If we apply the widely accepted criteria for hydrogen bonds,[21] we find that the 2.78(7) Å distance between the H2A and O1 atoms is acceptable for an H-bond, but that the 88(8)° O2–H2A···O1 angle is not. The O2–H2A···O1 hydrogen bond would be formed if another staggered conformation, resulting from rotation around the O2–C2 bond, were adopted with the H2A hydrogen atom oriented antiperiplanarly to the H2 hydrogen atom. Here, too, there is no intramolecular hydrogen bonding in the crystal lattice of this compound, probably because of the crystal packing arrangement.

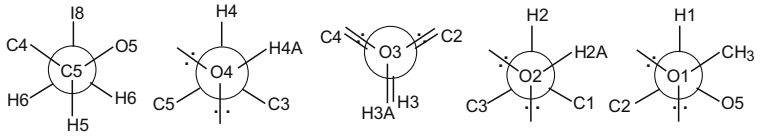

Figure 2. Rotational preferences of the groups bound to the pyranose ring in the crystal lattice of methyl 6-deoxy-6-iodo-α-D-glucopyranoside.

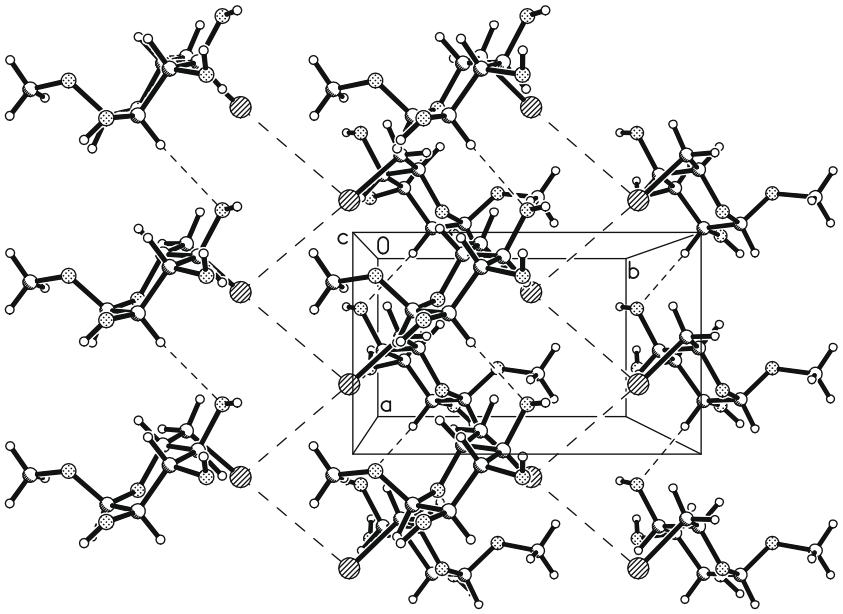

Figure 3. Molecular packing of methyl 6-deoxy-6-iodo-α-D-glucopyranoside (view along *c*-axis).

Table 1
Crystal data and structure refinement for methyl 6-deoxy-6-iodo-α-D-glucopyranoside

Empirical formula	$C_7H_{13}O_5I$
Formula weight	304.07
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	5.267(1)
b (Å)	8.286(2)
c (Å)	22.820(5)
V (Å^3)	995.9(4)
Z	4
D_{calcd} (Mg m^{-3})	2.028
Absorption coefficient (mm^{-1})	3.206
Absorption correction type	Empirical (DIFABS)
F(000)	592
Crystal size (mm)	0.6 × 0.3 × 0.2
Θ Range for data collection (°)	2.62–25.00
Limiting indices	$-6 \leqslant h \leqslant 1$, $0 \leqslant k \leqslant 9$, $-24 \leqslant l \leqslant 0$
Reflections collected/unique	1218/1109 [R_{int} = 0.0897]
Completeness 2Θ = 50.24° (%)	97.6
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1218/0/130
Goodness-of-fit on F^2	1.055
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0300
	wR_2 = 0.0680
R indices (all data)	R_1 = 0.0245
	wR_2 = 0.0646
Absolute structure parameter	0.01(4)
Extinction coefficient	0.0030(6)
Largest difference in peak and hole (e Å^{-3})	0.517 and −0.496

The nearly antiperiplanar orientation of the methyl group to the C2 carbon atom resulting from the rotation around the O1–C1 bond with the C2–C1–O1–C7 torsion angle of −160.3(4)° is typical of glycosides, and is due to the *exo*-anomeric effect.

Analysis of the intermolecular interactions shows that three hydrogen bonds are formed in the crystal lattice of methyl 6-deoxy-6-iodo-α-D-glucopyranoside: O2–H2A···O3, O3–H3A···O1, and O4–H4A···O2, undoubtedly with the proper lengths and angles (Table 4). Worthy of notice is the very short distance between two iodine atoms (Fig. 3)—4.073(1) Å. The sum of the van der Waals radii of these two iodine atoms is 3.98 Å,[19] which means that these bulky atoms almost touch each other.

Table 2
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for methyl 6-deoxy-6-iodo-α-D-glucopyranoside; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
C-1	1572(10)	8394(5)	1514(2)	33(1)
C-2	1406(9)	7214(6)	2024(2)	29(1)
C-3	3747(9)	6175(6)	2071(2)	28(1)
C-4	4355(9)	5433(6)	1480(2)	30(1)
C-5	4520(9)	6734(6)	1013(2)	31(1)
O-1	3336(8)	9602(4)	1645(2)	41(1)
O-2	1060(7)	8015(5)	2571(2)	40(1)
O-3	3259(7)	4891(3)	2476(1)	37(1)
O-4	6734(7)	4633(4)	1478(2)	38(2)
O-5	2153(7)	7576(4)	987(1)	32(1)
C-6	5154(10)	6126(7)	416(3)	41(1)
C-7	3034(14)	11,017(6)	1297(2)	52(2)
I-8	2587(1)	4363(1)	76(1)	49(1)
H-1	−94	8905	1467	39
H-2	−58	6507	1959	35
H-2A	100	8630	2500	61
H-3	5186	6824	2207	33
H-3A	4260	4840	2730	56
H-4	3018	4664	1375	35
H-4A	6660	4240	1720	50
H-5	5837	7504	1130	37
H-6A	5198	7035	148	49
H-6B	6843	5661	426	49
H-7A	2804	10,716	894	78
H-7B	1573	11,607	1430	78
H-7C	4518	11,682	1333	78

1. Experimental

1.1. General methods

The melting point was uncorrected. The optical rotation was determined at rt with a Perkin–Elmer polarimeter in a 1-dm tube

Table 3
Selected bond lengths (Å), valence angles (°), and torsion angles (°) for methyl 6-deoxy-6-iodo-α-D-glucopyranoside

Bond length (Å)	
C-1–O-1	1.398(6)
C-1–O-5	1.414(6)
C-1–C-2	1.523(7)
C-2–C-3	1.508(7)
C-3–O-3	1.433(6)
C-3–C-4	1.516(7)
C-4–O-4	1.417(6)
C-4–C-5	1.519(7)
C-5–O-5	1.430(5)
C-5–C-6	1.491(7)
C-6–I-8	2.136(6)
C-7– O-1	1.424(6)
Valence angles (°)	
O-1–C-1–O-5	112.4(4)
O-1–C-1–C-2	109.5(4)
O-5–C-1–C-2	110.8(4)
C-3–C-2–C-1	111.9(4)
O-3–C-3–C-2	108.8(4)
O-3–C-3–C-4	108.1(4)
C-1–O-5–C-5	112.8(3)
C-2–C-3–C-4	110.0(4)
O-4–C-4–C-3	112.3(4)
O-4–C-4–C-5	106.2(4)
C-3–C-4–C-5	110.2(4)
O-5–C-5–C-6	108.8(4)
O-5–C-5–C-4	109.0(4)
C-6–C-5–C-4	114.9(4)
C-5–C-6–I-8	114.9(3)
C-1–O-1–C-7	113.4(4)
Torsion angles (°)	
O-1–C-1–O-5–C-5	63.1(5)
C-2–C-1–O-5–C-5	−59.9(5)
O-1–C-1–C-2–O-2	49.9(5)
O-5–C-1–C-2–O-2	174.5(4)
C-1–C-2–C-3–O-3	−168.2(4)
C-1–C-2–C-3–C-4	−50.0(5)
C-2–C-1–O-1–C-7	−160.3(4)
O-2–C-2–C-3–O-3	67.7(4)
O-2–C-2–C-3–C-4	−174.0(4)
C-2–C-3–C-4–C-5	53.2(5)
C-2–C-3–C-4–O-4	171.5(4)
O-3–C-3–C-4–O-4	−69.7(5)
O-3–C-3–C-4–C-5	171.9(4)
O-5–C-5–C-6–I-8	−64.5(5)
C-4–C-5–C-6–I-8	57.7(5)
C-1–O-5–C-5–C-6	−171.5(4)
O-1–C-1–C-2–C-3	−71.7(5)
O-5–C-1–C-2–C-3	52.8(5)
O-5–C-1–O-1–C-7	76.0(5)
C-1–O-5–C-5–C-4	63.0(5)
O-4–C-4–C-5–O-5	179.2(3)
C-3–C-4–C-5–O-5	−58.8(5)
O-4–C-4–C-5–C-6	57.1(5)
C-3–C-4–C-5–C-6	179.1(4)
H-1–C-1–C-2–H-2	51.7
H-2–C-2–C-3–H-3	−169.6
H-3–C-3–C-4–H-4	171.7
H-4–C-4–C-5–H-5	178.7

Table 4
Intramolecular (*) and intermolecular hydrogen bonds and short contacts for methyl 6-deoxy-6-iodo-α-D-glucopyranoside with distances (*d*): *d*(D···A) ∠R(D) + R(A) + 0.50 Å; *d*(H···A) ∠R(H) + R(A) − 0.12 Å and angle (∠) ⟨D-H···A⟩ 100.0°[a]

D-H	A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠D-H···A
O-2–H-2A	O-3^{i}	0.74(7)	2.06(8)	2.757(5)	160(8)
O-3–H-3A	O-1^{ii}	0.78(8)	1.92(7)	2.701(5)	177(8)
O-4–H-4A	O-3*	0.64(7)	2.55(7)	2.930(5)	121(8)
O-4–H-4A	O-2^{ii}	0.64(7)	2.26(7)	2.804(5)	144(9)
C-2–H-2	O-4^{iii}	0.98	2.54	3.490(6)	162
C-4–H-4	I-8*	0.98	2.98	3.453(5)	111
C-5–H-5	O-1*	0.98	2.48	2.848(6)	102

[a] Symmetry codes: (i) −*x*, 1/2 + *y*, 1/2 − *z*; (ii) 1 − *x*, −1/2 + *y*, 1/2 − *z*; (iii) −1 + *x*, *y*, *z*.

at the D line of sodium for a solution in CH_3OH. The IR spectrum was recorded as a Nujol mull with a Bruker IFS 66 spectrophotometer, and the ^1H and ^{13}C NMR spectra (CD_3OD, internal Me_4Si) on a Unity Plus 500 (500/125 MHz) instrument; elemental analysis was done on a Carlo Erba EA 1108 instrument. Thin-layer chromatography (TLC) was performed on E. Merck Kieselgel 60 F-254 plates using the eluent system (v/v) A, 3:1 $CHCl_3$–MeOH, and column chromatography on MN Kieselgel 60 (<0.08 mm) with the eluent system (v/v) B, 5:1 $CHCl_3$–MeOH.

1.2. Methyl 6-deoxy-6-iodo-α-D-glucopyranoside

This was synthesized according to the literature procedure (method A, without acetylation).[15] The reaction was stopped after 2 h (TLC, solvent A), after which the reaction mixture was evaporated. Purification of the crude product with column chromatography (solvent B) yielded crystals of the title compound: 83%, mp 146–147 °C, lit[14] 148 °C; $[\alpha]_D^{20}$ +113 (*c* 1, MeOH), lit[14] +107.8 (*c* 1, MeOH); R_f 0.87 (solvent A); IR: *ν* 3296 (OH) cm^{-1}; ^1H NMR (500 MHz, CD_3OD): *δ* 4.67 (d, 1H, $J_{1,2}$ 3.91 Hz, H-1), 3.62 (t, 1H, $J_{3,4}$ 8.79 Hz, H-3), 3.61 (dd, 1H, H-6'), 3.46 (s, 3H, OMe), 3.40 (dd, 1H, $J_{2,3}$ 9.77 Hz, H-2), 3.38 (ddd, 1H, $J_{5,6}$ 7.32, $J_{5,6'}$ 1.95 Hz, H-5), 3.29 (dd, 1H, $J_{6,6'}$ 10.74 Hz, H-6), 3.13 (t, 1H, $J_{4,5}$ 9.77 Hz, H-4); ^{13}C NMR (500 MHz, CD_3OD): *δ* 100.17 (C-1), 74.45 (C-4), 73.43 (C-3), 72.40 (C-2), 71.27 (C-5), 54.69 (OMe), 6.10 (C-6); Anal. Calcd for $C_7H_{13}O_5I$: C, 27.65; H, 4.31. Found: C, 27.79; H, 4.35.

1.3. Description of the crystal structure of methyl 6-deoxy-6-iodo-α-D-glucopyranoside

Diffraction data were collected at room temperature (295 K) on a KUMA KM-4 four-circle diffractometer[26] with MoKα radiation (λ = 0.71073 Å) using the $2\Theta/\omega$ scan mode. Phase angles were initially determined with the SHELXS program.[27] All H atoms bound with C atoms were placed 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) = 1.5 U_{eq}(C) for the methyl H atoms). All H atoms from the O–H groups were located in a difference Fourier map and refined freely with U_{iso}(H) = 1.5 U_{eq}(O). Table 1 summarizes the crystallographic data, data collection, and structure refinement, Table 2 sets out the coordinates of atoms and their isotropic temperature factors, Table 3 lists a selection of the crystal's important geometric parameters, and Table 4 summarizes the intra- and intermolecular hydrogen bonds and short contacts.

The crystal structure was refined to R_1 = 0.0300 (1218 reflections, all unique) and R_1 = 0.0245 (1109 reflections with $F_0 > 2\sigma(F_0)$) by the full-matrix least-squares method using the SHELXL-97 program[28] based on 120 parameters. Figure 1 illustrates the compound's structure, showing the conformation and atom numbering system.[29] Figure 3 shows the molecular packing in the crystal, prepared by PLUTO-78.[30] The computational material for publication was prepared using the PLATON program.[19]

2. Supplementary data

Full crystallographic details, excluding structural features, have been deposited (deposition No. CCDC 709173) 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).

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References

1. Ferrier, R. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1455–1458.
2. Dubreuil, D.; Cleophax, J.; Viera de Almeida, M. V.; Liaigre, C. V.-S. J.; Vass, G.; Gero, S. D. *Tetrahedron* **1997**, *53*, 16747–16766.
3. Takahashi, H.; Kittaka, H.; Ikegami, S. *Tetrahedron Lett.* **1998**, *39*, 9707–9710.
4. Jia, C.; Pearce, A. J.; Blériot, Y.; Zhang, Y.; Zhang, L.-H.; Sollogoub, M.; Sinaÿ, P. *Tetrahedron: Asymmetry* **2004**, *15*, 699–703.
5. Bovin, J.; Pais, M.; Monneret, C. *Carbohydr. Res.* **1978**, *64*, 271–278.
6. Pelyvas, I.; Sztaricskai, F.; Szilagyi, L.; Bognar, R.; Tamas, J. *Carbohydr. Res.* **1979**, *76*, 79–84.
7. Cheung, T.-M.; Horton, D.; Sorenson, R. J.; Weckerle, W. *Carbohydr. Res.* **1978**, *63*, 77–89.
8. McDonnell, C.; Cronin, L.; O'Brien, J. L.; Murphy, P. V. *J. Org. Chem.* **2004**, *69*, 3565–3568.
9. Skaanderup, P. R.; Madsen, R. *J. Org. Chem.* **2003**, *68*, 2115–2122.
10. Dmochowska, B.; Skorupa, E.; Pellowska-Januszek, L.; Czarkowska, M.; Sikorski, A.; Wiśniewski, A. *Carbohydr. Res.* **2006**, *341*, 1916–1921.
11. Hanaya, T.; Imai, K.; Prikhod'ko, Y. V.; Yamamoto, H. *Carbohydr. Res.* **2005**, *340*, 31–37.
12. Briat, A.; Slimani, L.; Perret, P.; Villemain, D.; Halimi, S.; Demongeot, J.; Fagret, D.; Ghezzi, C. *Eur. J. Nucl. Med. Mol. Imaging* **2007**, *34*, 1756–1764.
13. Koumanov, F.; Henry, Ch.; Ghezzi, C.; Mathieu, J.-P.; Morin, Ch.; Vidal, M.; de Leiris, J.; Comet, M.; Fagret, D. *Nucl. Med. Biol.* **1997**, *24*, 519–525.
14. Whistler, R. L.; Anisuzzman, A. K. M. *Methods Carbohydr. Chem.* **1980**, *VIII*, 227–231.
15. Garegg, P. J.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2866–2868.
16. Evans, G. G.; Boeyens, J. A. *Acta Crystallogr., Sect. B* **1989**, *45*, 581–590.
17. Saenger, W. *Principles of Nucleic Acid Structure*; Springer: New York, 1983. p 19.
18. Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.
19. Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
20. Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 2005. p 225.
21. Jebber, K. A.; Zhang, K.; Cassady, C. J.; Chung-Phillips, A. *J. Am. Chem. Soc.* **1996**, *118*, 10515–10524.
22. Taroška, I.; Taravel, F. R.; Utille, J. P.; Carver, J. P. *Carbohydr. Res.* **2002**, *337*, 353–367.
23. Craig, N. C.; Chen, A.; Suh, K.-H.; Klee, S.; Mellau, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 4789–4790.
24. Klein, R. A. *Chem. Phys. Lett.* **2006**, *433*, 165–169.
25. Appell, M.; Strati, G.; Willett, J. L.; Momany, F. A. *Carbohydr. Res.* **2004**, *339*, 537–551.
26. KUMA KM-4 Software User's Guide. Version 3.1. Kuma Diffraction, Wrocław, Poland, 1989.
27. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
28. Sheldrick, G. M. SHELXL-*97. Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
29. Johnson C. K. ORTEP II; Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976.
30. Mortherwell, S.; Clegg, S. PLUTO-*78. Program for Drawing and Molecular Structure*; University of Cambridge: UK, 1978.