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Molecular and crystal structure of methyl hepta-*O*-acetyl-α-laminarabioside

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ABSTRACT

The molecular and crystal structure of methyl 2,3,4,6,2′,4′,6′-hepta-*O*-acetyl-α-laminarabioside (methyl α-laminarabioside heptaacetate) was determined by the X-ray diffraction method. The crystal belongs to the monoclinic system, space group $P2_1$, $a = 13.179(3)$, $b = 22.832(3)$, $c = 5.555(2)$ Å, $\beta = 95.91(3)°$, $D_{obsd} = 1.32$ g/cm^3, $D_{calcd} = 1.300$ g/cm^3, $Z = 2$. The structure was obtained by the direct method and refined by the full-matrix least-squares procedure to $R = 0.061$ for 2097 observed reflections with $|F_o| \geq 2\sigma(F_o)$. The difference Fourier synthesis showed all the hydrogen atoms except those of the methyl moieties. The linkage conformation angles, $\phi = \Theta$(O-5–C-1–O-1–C-3′) and $\psi = \Theta$(C-1–O-1–C-3′–C-2′), are −85.5 and −111.9°, respectively. These are similar to those of other β-(1 → 3)-linked acetylated disaccharide compounds. The acetate substituent at C-6 of the reducing residue was in the *gg* conformation, while the *gt* conformation was observed in the nonreducing residue. The conformational analysis using the bond lengths and angles obtained revealed that the energy map for ϕ and ψ angles was independent of the orientation of the C-6 acetate. In the crystal structure D-glucopyranose rings are amassed along the *c* axis and parallel to the *ab*-plane. These molecules interact with their surrounding molecules only by van der Waals forces.

INTRODUCTION

Conformational studies of macromolecules have been strongly supported by the systematic studies of crystal structures of related small molecules. Because of the difficulty of preparation, purification, and crystallization of oligosaccharides, the number of single-crystal analyses of these compounds has been limited. Acetylated derivatives of oligosaccharides crystallize more easily compared with untreated carbohydrates in many cases. A number of crystal structures of acetate derivatives of mono-, di, and tri-saccharides has been reported[1–10]. Many of these conforma-

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TABLE I

Crystal data for methyl α-laminarabioside heptaacetate

Molecular formula	$C_{27}H_{38}O_{18}$	
Molecular weight	650.6	
Space group	$P2_1$	
Crystal system	monoclinic	
Cell dimension	a	13.179(3) Å
	b	22.832(3) Å
	c	5.555(2) Å
	β	95.91(3)°
Cell volume		1662.6(6) Å^3
Number of molecules in a cell	Z	2
Density	D_{calcd}	1.300 g/cm^3
	D_{obsd}	1.32 g/cm^3
μ (Cu $K\alpha$)	8.6 cm^{-1}	

tions have been also analyzed by the semiempirical potential energy method to get a better understanding of the observed conformations[11].

In this paper, we report on the molecular and crystal structure of methyl α-laminarabioside heptaacetate, an acetylated disaccharide with (1 → 3)-linked β-D-glucopyranosyl residues. Laminarabiose consists of a simple repeating unit of (1 → 3)-linked poly(β-D-glucose), such as curdlan, laminaran, lentinan, and schizophyllan. The introduction of acetate substituents to the laminarabiose removes the possibility of an intramolecular hydrogen bond between O-4′ and O-5 observed in the structures of laminarabiose[12] and methyl β-laminarabioside[13]. The obtained linkage angles (ϕ and ψ) were compared with those of the related compounds.

EXPERIMENTAL

X-ray experiments.—Specimen crystals were obtained from an ethanolic solution by slow evaporation of the solvent. The X-ray intensities were measured by a four-cycle diffractometer (RASA 5R-II, Rigaku Co.) with graphite monochromatized Cu $K\alpha$ radiation (λ = 1.5418 Å). A crystal with the dimensions of 0.6 × 0.2 × 0.1 mm was used for the intensity measurement. Accurate unit-cell parameters were determined by the least-squares fit from measurements of 19 reflections with 2θ range of 55–60°. Crystal data are given in Table I.

The intensity data were collected by the ω-scan mode. The integrated intensity of each reflection was obtained by scanning over the peak at a rate of 6°/min, and the scan width of $\Delta\omega = (1.4 + 0.14 \tan \theta)°$, where θ denotes the calculated Bragg angle. A total of 2372 independent reflections was measured up to 2θ value of 120°, of which 2097 with $|F_o| \geq 2\sigma(F_o)$ were used for the following analysis. Three standard reflections were measured every 100 reflections and their intensities remained constant within ±2% throughout the data collection. Lorentz and polarization corrections were made as usual, but no absorption correction was made (μ = 8.6 cm^{-1}).

The density of the crystal was measured by the flotation method using a mixture of carbon tetrachloride and hexane.

Solution and refinement of the structure.—The structure was solved by the direct method with the SHELX-86 program[14]. The direct method and the following Fourier procedure revealed 42 out of 45 nonhydrogen atoms. The locations of these atoms with isotropic temperature factors were refined three cycles by the full-matrix least-squares procedure. The following difference Fourier map revealed three remaining nonhydrogen atoms.

The structure was further refined isotropically ($R = 0.13$). The difference Fourier map calculated after two cycles of anisotropic refinement showed 14 hydrogen atoms. Hydrogen atoms of the methyl moieties, however, could not be located. After three additional cycles, including 14 hydrogen atoms with equivalent temperature factors (B_{eq}) of the corresponding parent atoms, the final R value of 0.061 was obtained for observed 2097 reflections. The final atomic parameters are given in Table II. The final anisotropic temperature factors and observed and calculated structure factors have been deposited *.

The atomic scattering factors were taken from the International Tables for X-ray Crystallography, Vol. IV[15]. Computations were performed on an A-70 minicomputer with the help of the CRYSTAN program in a RASA-5RII system (Rigaku Corporation).

Conformational analysis.—The potential energy was calculated by considering the van der Waals interactions and electrostatic interactions between nonbonded atoms and torsion energies[16]. The van der Waals interactions were evaluated by using the Lennard–Jones 6–12 potential function with the parameters proposed by Scott and Scheraga[17]. For the electrostatic interactions, the parameters proposed by Scheraga et al.[18] were used. Using the molecular structure obtained in this study, the angles ϕ and ψ were varied systematically with 5° intervals. The coordinates of hydrogen atoms of the methyl moieties were included and fixed to the staggered conformation. They were calculated by using the C–H bond length of 1.1 Å and an H–C–H bond angle of 109.5°.

RESULTS AND DISCUSSION

The chemical structure of methyl α-laminarabioside heptaacetate with observed bond lengths and bond angles are given in Fig. 1 together with the atomic numbering. The atoms in the acetate moieties have been labeled CA, CM, and OA. These abbreviations stand for the carbonyl C, the methyl C, and carbonyl O, respectively. All bond lenghts and angles are similar to those found in other carbohydrates[20]. An ORTEP[19] plot is given in Fig. 2.

* Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

TABLE II

Fractional coordinates and equivalent isotropic temperature factors (Å^2) of methyl α-laminarabioside heptaacetate, with estimated standard deviations in parentheses. $B_{eq} = (4/3) \times \{B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2(B_{12}ab + B_{23}bc + B_{31}ca)\}$

Atom	x	y	z	B_{eq}
C-1	−0.0482(4)	0.7105(−)	0.4678(9)	5.61(13)
C-2	0.0086(3)	0.7608(3)	0.6074(9)	5.32(13)
C-3	0.0997(4)	0.7810(4)	0.4865(9)	5.53(13)
C-4	0.1666(4)	0.7300(3)	0.4236(9)	5.78(14)
C-5	0.0966(4)	0.6829(3)	0.2902(10)	5.94(17)
C-6	0.1517(4)	0.6287(3)	0.2178(10)	7.15(16)
CA-2	−0.0781(4)	0.8330(3)	0.8162(11)	6.47(19)
CA-3	0.1599(4)	0.8763(3)	0.6226(12)	7.34(20)
CA-4	0.3352(4)	0.7467(3)	0.3091(13)	7.78(20)
CA-6	0.2692(4)	0.5572(3)	0.4002(14)	8.10(20)
CM-2	−0.1370(4)	0.8914(3)	0.7756(12)	8.85(19)
CM-3	0.2036(4)	0.9079(3)	0.8384(10)	8.48(22)
CM-4	0.3952(4)	0.7704(3)	0.1050(12)	9.56(22)
CM-6	0.3340(4)	0.5412(4)	0.6254(12)	9.64(16)
O-1	−0.3067(2)	0.6886(2)	0.6171(15)	6.07(9)
O-2	−0.0603(2)	0.8111(2)	0.6052(6)	5.79(9)
O-3	0.1587(2)	0.8175(2)	0.6618(6)	6.35(10)
O-4	0.2347(3)	0.7516(2)	0.2524(6)	7.08(10)
O-5	0.0250(2)	0.6654(2)	0.4457(6)	6.21(9)
O-6	0.2155(3)	0.6074(3)	0.4284(6)	7.20(11)
OA-2	−0.0564(3)	0.8103(3)	1.0071(7)	9.37(14)
OA-3	0.1271(4)	0.8977(3)	0.4760(8)	9.62(15)
OA-4	0.3718(3)	0.7233(3)	0.4904(9)	11.93(21)
OA-6	0.2609(4)	0.5323(3)	0.2099(9)	11.40(18)
C-1′	−0.3938(4)	0.6525(3)	0.4069(10)	6.46(16)
C-2′	−0.2985(4)	0.6886(3)	0.4941(9)	6.05(14)
C-3′	−0.2003(4)	0.6549(3)	0.4893(8)	5.50(13)
C-4′	−0.2080(4)	0.5964(3)	0.6226(9)	5.64(13)
C-5′	−0.3015(4)	0.5652(3)	0.5050(8)	6.14(15)
C-6′	−0.3204(4)	0.5061(3)	0.6192(11)	6.95(17)
CA-2′	−0.3183(4)	0.7905(3)	0.4080(13)	7.44(19)
CA-4′	−0.0567(4)	0.5442(3)	0.7745(14)	7.80(20)
CA-6′	−0.4465(5)	0.4323(4)	0.5005(15)	9.47(25)
CM-1′	−0.4895(4)	0.6138(4)	0.0552(11)	9.16(21)
CM-2′	−0.3067(4)	0.8358(3)	0.2150(10)	8.38(19)
CM-4′	0.0339(4)	0.5139(3)	0.6820(13)	9.24(21)
CM-6′	−0.5144(5)	0.4085(4)	0.2940(13)	11.18(27)
O-1′	−0.3955(3)	0.6439(3)	0.1587(6)	7.33(11)
O-2′	−0.2911(3)	0.7378(3)	0.3363(6)	7.03(11)
O-4′	−0.1193(3)	0.5622(2)	0.5845(6)	6.43(10)
O-5′	−0.3901(3)	0.5997(3)	0.5371(6)	6.74(10)
O-6′	−0.3925(3)	0.4771(3)	0.4423(7)	9.15(13)
OA-2′	−0.3430(4)	0.7974(3)	0.6030(10)	12.37(20)
OA-4′	−0.0739(4)	0.5527(4)	0.9753(9)	13.22(22)
OA-6′	−0.4396(5)	0.4180(3)	0.7003(12)	16.94(29)
H(C-1)	−0.082(3)	0.724(2)	0.278(9)	
H(C-2)	0.034(3)	0.742(2)	0.784(9)	
H(C-3)	0.075(4)	0.801(2)	0.323(9)	
H(C-4)	0.200(4)	0.716(2)	0.590(9)	

TABLE II (continued)

Atom	x	y	z	B_{eq}
H(C-5)	0.068(4)	0.696(2)	0.101(9)	
H(C-6A)	0.189(4)	0.636(2)	0.068(10)	
H(C-6B)	0.102(4)	0.593(3)	0.119(10)	
H(C-1′)	−0.464(4)	0.673(2)	0.443(9)	
H(C-2′)	−0.308(4)	0.704(2)	0.675(9)	
H(C-3′)	−0.166(3)	0.654(2)	0.300(9)	
H(C-4′)	−0.203(3)	0.602(2)	0.829(9)	
H(C-5′)	−0.298(3)	0.557(2)	0.290(9)	
H(C-6′A)	−0.352(4)	0.514(2)	0.808(10)	
H(C-6′B)	−0.247(4)	0.486(3)	0.647(9)	

Glycosidic linkage.—The relative orientation of contiguous pyranosides is usually described by the torsion angles around the glycosidic bonds, C-1–O-1 and O-1–C-3′, and they are denoted as the conformational angles ϕ and ψ[21]. These values obtained in this study were $\phi = \Theta$(O-5–C-1–O-1–C-3′) = −85.5° and $\psi = \Theta$(C-1–O-1–C-3′–C-2′) = −111.9°. Another important parameter, the bridge angle τ = C-1–O-1–C-3′, was found to be 113.9°. These torsion and bridge angles are

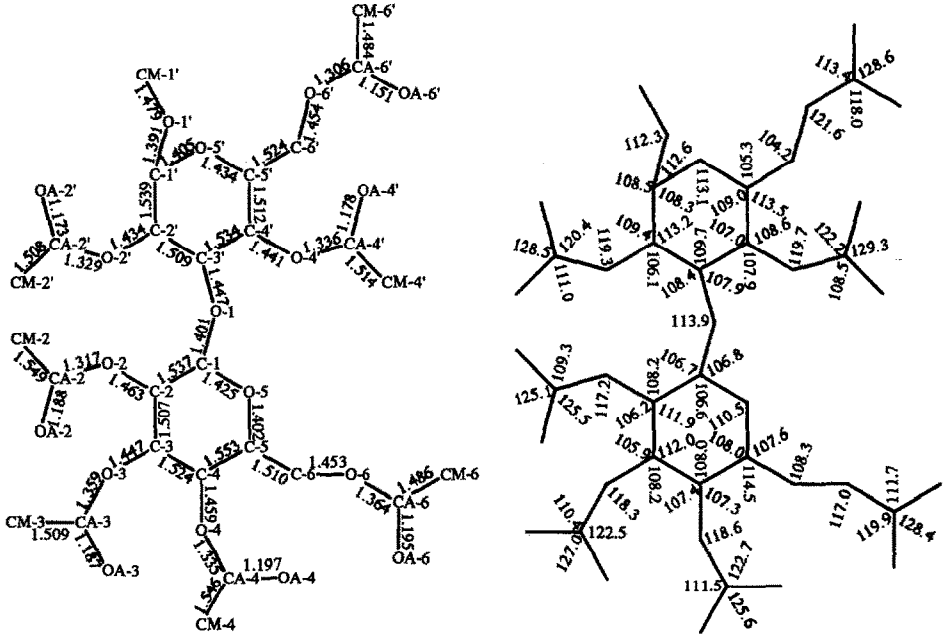

Fig. 1. A schematic drawing of methyl α-laminarabioside heptaacetate with observed bond lengths and angles, together with atomic numbering. The estimated standard deviations for the lengths of ring C–C and C–O bonds are less than 0.010 and 0.009 Å, respectively, while those for C–C, C=O, and C–O in acetyl moieties are less than 0.01 Å. The estimated standard deviation of the bond angles is 0.3–0.6° for the D-glucopyranose rings and 0.5–0.8° for acetyl moieties.

TABLE III

Comparison of torsion angles of β-(1 → 3)-linked disaccharides, with estimated standard deviations in parentheses. 1, Methyl α-laminarabioside heptaacetate (this work); 2, β-laminarabiose[12]; 3, methyl β-laminarabioside[13]; 4, methyl β-laminarabioside heptaacetate[8]; 5, β-laminarabiose octaacetate[9], and 6, α-laminarabiose octaacetate[10]

	1	2	3	4	5	6
Glycosidic torsion angles (°)						
O-5–C-1–O-1–C-3′(ϕ)	−85.5(7)	−93.6(6)	−85.8(11)	−83.4(9)	−81(1)	−69.0(9)
C-1–O-1–C-3′–C-2′(ψ)	−111.9(7)	−161.0(6)	−161.8(10)	−108.4(13)	−107(2)	−109.3(8)
Glycosidic bridge bond angle (°)						
C-1–O-1–C-3′(τ)	113.9(3)	118.2(4)	117.2(8)	116.1(7)	113(1)	113.4(6)
Glycosidic bond lengths (Å)						
C-1–O-1	1.401(6)	1.387(7)	1.39(1)	1.38(1)	1.46(2)	1.401(9)
C-3′–O-1	1.447(7)	1.431(6)	1.46(1)	1.41(1)	1.46(2)	1.428(8)
Intramolecular O–O distances (Å)						
O-2–O-2′	3.653(6)	3.920(6)	4.16(1)	3.60(1)	3.61(2)	3.978(8)
O-5–O-4′	3.172(7)	2.785(5)	2.77(1)	3.21(1)	3.20(2)	3.104(8)
Endocyclic torsion angles (°)						
C-1–C-2	55.8(6)	58.1(5)	58.1(17)	60.8(11)	62(2)	54.9(10)
C-2–C-3	−49.1(8)	−56.0(5)	−53.6(11)	−48.4(13)	−54(3)	−41.5(10)
C-3–C-4	49.2(6)	54.5(4)	54.7(12)	42.4(11)	51(2)	43.6(11)
C-4–C-5	−59.5(6)	−56.7(5)	−58.1(19)	−48.9(12)	−60(2)	−56.2(12)
C-5–O-5	72.1(8)	62.5(4)	66.4(8)	64.6(7)	71(1)	72.3(8)
O-5–C-1	−68.7(5)	−62.3(8)	−66.5(16)	−70.7(10)	−71(2)	−72.5(7)
C-1′–C-2′	51.9(8)	55.0(5)	60.2(16)	61.9(12)	66(2)	58.1(12)
C-2′–C-3′	−51.5(5)	−51.9(3)	−52.7(10)	−54.3(11)	−61(2)	−56.0(6)

C-3′–C-4′	55.3(6)	52.3(6)	47.9(17)	49.3(11)	54(2)	53.6(7)
C-4′–C-5′	−62.5(7)	−56.8(4)	−50.3(18)	−51.6(10)	−58(2)	−53.2(10)
C-5′–O-5′	68.0(8)	64.4(8)	61.2(8)	60.3(8)	66(2)	57.1(7)
O-5′–C-1′	−59.8(5)	−62.5(9)	−65.5(14)	−65.2(15)	−72(3)	−59.3(11)
Exocyclic torsion angles (°)						
O-5–C-5–C-6–O-6(χ_5)	−69.5(5) g^-	63.5(6) g	62.6(14) g	−69.5(8) g^-	−71(1) g^-	60.6(10) g
C-4–C-5–C-6–O-6	50.5(6) g	−176.7(6) t	179.9(10) t	52.5(8) g	49(2) g	176.4(10) t
O-1–C-1–C-2–O-2	−73.8(7)	−66.0(5)	−67.2(22)	−68.0(13)	−74(2)	−73.7(12)
O-2–C-2–C-3–O-3	75.4(10)	65.2(5)	69.8(11)	73.2(7)	73(1)	87.0(7)
O-3–C-3–C-4–O-4	−79.0(5)	−65.3(10)	−72.5(17)	−80.6(10)	−81(2)	−79.0(8)
O-4–C-4–C-5–C-6	65.2(7)	68.9(6)	68.5(21)	68.4(17)	68(2)	70.5(14)
O-5′–C-5′–C-6′–O-6′($\chi_{5'}$)	76.7(8) g	67.0(10) g	−62.5(15) g	81.9(14) g	78(3) g	74.6(8) g
C-4′–C-5′–C-6′–O-6′	−164.1(7) t	−174.0(8) t	56.3(11) g	−157.5(11) t	−163(2) t	−164.3(7) t
O-1′–C-1′–C-2′–O-2′	47.4(6)	−60.8(5)	−62.1(16)	−64.1(14)	−70(2)	56.9(12)
O-2′–C-2′–C-3′–O-1	71.0(4)	63.4(4)	68.2(10)	63.6(11)	68(2)	63.9(6)
O-1–C-3′–C-4′–O-4′	−70.2(5)	−72.1(12)	−81.2(20)	−69.4(17)	−79(3)	−66.5(11)
O-4′–C-4′–C-5′–C-6′	64.3(8)	65.8(5)	74.8(23)	71.8(10)	71(2)	68.7(10)
C-1–C-2–O-2–CA-2(χ_2)	123.6(6)			138.2(8)	144(2)	140.6(7)
C-2–C-3–O-3–CA-3(χ_3)	−108.2(7)			−139.7(12)	−137(2)	−93.1(14)
C-3–C-4–O-4–CA-4(χ_4)	122.6(7)			101.3(10)	109(3)	139.5(8)
C-5–C-6–O-6–CA-6(θ_6)	178.0(7)			−126.7(15)	−176(3)	−135.3(17)
O-5′–C-1′–O-1′–CA-1′($\chi_{1'}$)					−84(2)	90.7(10)
O-5′–C-1′–O-1′–CM-1′	65.0(6)		−75.2(10)	−87.0(10)		
C-1′–C-2′–O-2′–CA-2′($\chi_{2'}$)	102.7(7)			120.1(14)	116(3)	128.1(8)
C-3′–C-4′–O-4′–CA-4′($\chi_{4'}$)	121.4(11)			116.7(10)	126(2)	109.3(10)
C-5′–C-6′–O-6′–CA-6′($\theta_{6'}$)	−162.0(8)			−160.9(17)	−164(3)	179.2(12)

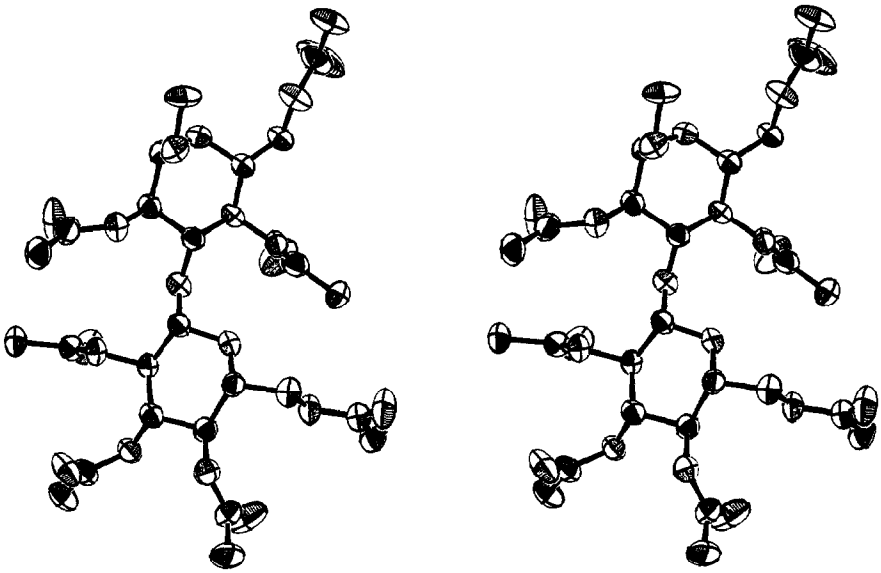

Fig. 2. Stereoscopic view of the methyl α-laminarabioside heptaacetate molecule (drawn with ORTEP[19]). The 30% probability thermal ellipsoids are shown for the carbon and oxygen atoms. The upper ring is the glycosidic residue.

compared with those in several disaccharide compounds with β-(1 → 3)-linkages[8–10,12,13] (Table III). The variation of ϕ is restrained in small region, which can be interpreted by the exo-anomeric effect[22], while those of ψ are classified two groups. One is $\psi \approx -110°$, the other is $\psi \approx -161°$. In the latter case, an intramolecular hydrogen bond was observed between O-4′ and O-5, while there was no hydrogen-bond formation because of introduction of acetate substituents.

Ring torsion angles.—Torsion angles about various skeletal bonds of the pyranose rings are given in Table III. Like other glucose residues, the $^4C_1$ conformation was found for both residues.

Molecular packing.—The packing of the molecule in the unit cell is shown by the stereoscopic pair in Fig. 3. The molecules are held in the crystals by van der Waals forces, only. The small value of the *c* parameter necessarily causes the pyranose rings to lie parallel to the *ab*-plane.

Conformational analysis.—Fig. 4 shows conformational contours for ϕ and ψ angles. With respect to the relative energy minimum, isoenergy contours were drawn with a 1 kcal mol^{-1} interval. The values obtained from the structure analysis (−85.5°, −111.9°) were very close to the energetically minimum position (−85°, −110°).

The conformation of the primary acetate substituent at C-6 is described by the torsion angles of $\chi_5 = \Theta$(O-5–C-5–C-6–O-6) and $\theta_6 = \Theta$(C-5–C-6–O-6–CA-6). The conformation of the two primary acetate groups at the nonreducing and reducing residues were found to be ($\chi_5 = -69.5°$, $\theta_6 = 178.0°$) and ($\chi_{5'} = 76.7°$,

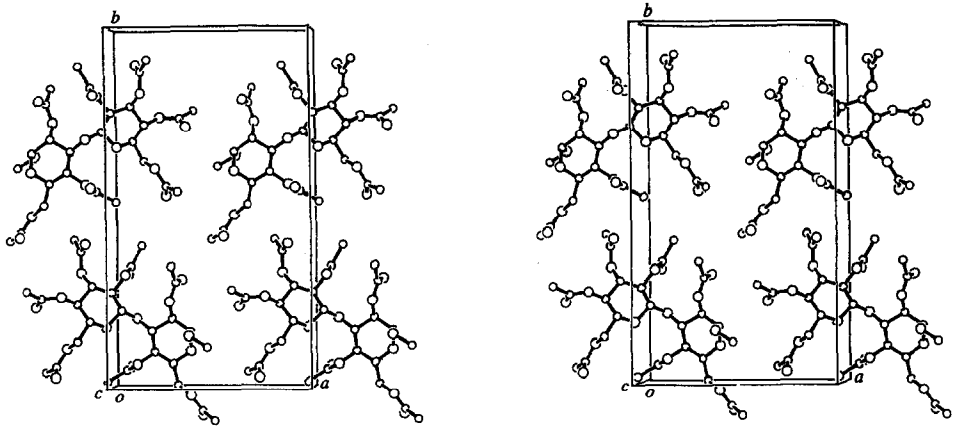

Fig. 3. Stereodrawing of the molecular packing of methyl α-laminarabioside heptaacetate molecules (drawn with ORTEP[19]). Hydrogen atoms are not included.

$\theta_{6'} = -162.0°$), respectively. Two different conformations are observed. According to the terminology proposed by Sundaralingam[21], the conformation about χ_5 is *gauche–gauche* (abbreviated *gg*), whereas the conformation of the C-6′ acetate in the primed residue is *gauche–trans* (*gt*). Table III shows that the major conformational differences for acetylated substituents occur at the C-6 acetoxymethyl group. These two conformations, however, fall into the theoretically predicted range of conformations for acetyl groups in glucosaccharides[11].

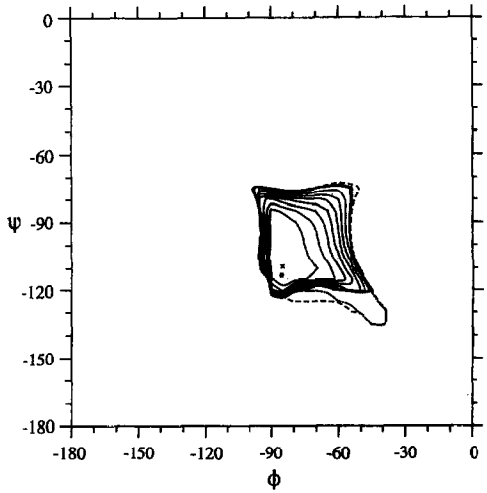

Fig. 4. Energy diagram computed for methyl α-laminarabioside heptaacetate in terms of (ϕ, ψ) angles. Contours were drawn by interpolation of energies computed at 5° for ϕ and ψ. The * indicates the observed position from the X-ray structure analysis, whereas × indicates the energetically minimum position. The 8 kcal mol^{-1} contours are shown as (— — —) and (·–·–·) for *gt* and *tg* conformations of χ_5, respectively.

As in the other acetylated carbohydrate derivatives[1–10], the secondary acetate groups are so arranged that the carbonyl O nearly eclipses the axial H at the corresponding pyranose ring C.

In order to study the influence of the relative orientation of the primary acetate groups on the allowed conformations of methyl α-laminarabioside heptaacetate, energy maps were computed on the conformers of $\chi_5 = 60°$ (gt) and 180° (tg). Only 8 kcal mol^{-1} contours corresponding to these energy diagrams are shown in Fig. 3, which encompass an almost identical area. Therefore, it can be concluded that in the case of acetylated D-glucose residues connected by β-(1 → 3)-linkages, the energetically allowed conformational space is independent of the orientation of the substituent at C-6.

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