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THE CRYSTAL AND MOLECULAR STRUCTURE OF α-LAMINARIBIOSE OCTA-ACETATE

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ABSTRACT

The crystal and molecular structure of octa-*O*-acetyl-α-laminaribiose is compared with those of disaccharides, and their acetylated derivatives, related to polysaccharides of the laminarin and curdlan type. Marked differences are found in the endo- and exo-cyclic torsion angles as well as in the molecular geometry of the glycosidic linkage. The conformation of AcO-6′ provides the first experimental evidence of the theoretically predicted *gauche–trans–gauche*$^-$ conformation. This conformational change, together with the α-orientation of AcO-1, alters the overall shape of the molecule and influences the packing features. The effect of the acetylation is also examined in terms of calculated conformational energy maps.

INTRODUCTION

One approach to the determination of the conformational features of a polymer is the systematic study of the crystal structures of related small molecules or oligomers. This idea has not yet been fully exploited for polysaccharides because of the difficulty of preparing, purifying, and obtaining suitable single crystals of the oligosaccharide fragments. Nevertheless, results have been reported on the crystalline structures of oligosaccharides related to the conformations of such naturally occurring polysaccharides as cellulose[1], amylose[2], curdlan[3], and, more recently, mannan, glucomannan, and galactomannan[4–6].

There are also several reports of structural determinations of acetylated oligosaccharides[7–13] which are of interest not only in relation to the conformational data of fully acetylated polymeric derivatives such as cellulose acetate[14], but also because many naturally occurring polysaccharides (particularly those of microbial origin) are partially acetylated[15]. Although the biological functions of these acetyl groups are not well understood, it is known that, in some instances, *e.g.*, gellan, their presence greatly affects the rheological properties of aqueous solutions[16]

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which are important in technological applications of these polysaccharides. Therefore, it is of interest to acquire stereochemical data concerning acetylated carbohydrate derivatives and to consider factors such as the influence of acetyl groups on the geometry of the sugar ring and glycosidic torsion angles, as well as the molecular packing and changes that occur from alterations in hydrogen-bonding capabilities.

Analysis of the crystalline conformations by X-ray diffraction has shown that the chain symmetries of unsubstituted and acetylated polysaccharides differ significantly[17,18], and, in some instances, the role played by the substituents on the local conformation appears to be a determining factor in enzymic recognition[19].

We now report on the crystal and molecular structure of α-laminaribiose octa-acetate (**1**), a disaccharide related to the laminarin- and curdlan-type polysaccharides.

Of prime interest is the distortion of the ring arising from the introduction of the acetyl substituents and the effects of the suppression of the intramolecular hydrogen-bond which is present in the crystal and molecular structure of α,β-laminaribiose[3]. We have also compared the effects of the acetylation on the values of the conformational angles ϕ and ψ about the linkage oxygen and on the molecular packing, with those found[10,13] in the crystal and molecular structures of methyl β-laminaribioside hepta-acetate (**2**) and β-laminaribiose octa-acetate (**3**).

EXPERIMENTAL

1,2,4,6-Tetra-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranose (**1**, α-laminaribiose octa-acetate) was prepared[20] from laminarin. Crystals were grown by slow concentration of an aqueous ethanolic solution. A crystal (0.58 × 0.29 × 0.18 mm) was sealed in a Lindeman glass capillary and set on an Enraf-Nonius CAD-4F diffractometer. Accurate unit-cell parameters were determined by least-squares fit from measurements of 20 reflections with $24° < \theta < 26°$. The crystal data are given in Table I.

The intensity data were collected in the ω–2θ scan mode using nickel-filtered Cu-K_α radiation up to $\theta = 57°$ for a total of 9962 reflections (h 0 to 10, k −15 to 15,

TABLE I

DATA FOR α-LAMINARIBIOSE OCTA-ACETATE

Molecular formula	$C_{28}H_{38}O_{19}$	Cell volume (Å^3)	3457.2
Molecular weight	678.5	Z	4
Crystal system	Orthorhombic	$F(000)$ (e)	1432.0
Space group	$P2_12_12_1$	$\mu(CuK_\alpha)$ (cm^{-1})	9.19
Cell dimensions (Å)		D_c (kg.m^{-3})	1.303
a	9.287(1)		
b	13.790(2)		
c	26.995(3)		

l −29 to 29) of which 6867 were non-zero. The control reflection 4 4 3 was measured every hour of exposure time (179 measurements) with an average value of 537 counts and a standard deviation (of the distribution) of 48.9 (9.1%). These measurements showed crystal damage during the data collection with a 20.0% decrease in intensity. Lorentz and polarisation corrections were applied, but no absorption correction was made. The data were merged using the SHELX suite[21] to give 2368 unique reflections, merging $R = 0.08$, of which 2096 with $F_o > 3\sigma(F_o)$ were used in the following calculations.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct methods using the MULTAN-80 suite of programs[22].

The normalised structure factors were calculated according to Main[23], with the assumption that the groups of atoms were in random positions and orientations. This computation was performed with the molecular geometry provided by the crystal and molecular structure of the hepta-acetate **2**.

The development of 448 sets of phases was required. Among the different solutions, only the E-map based on the phases produced for the set with the second highest combined figure of merit showed the location of a recognisable fragment of 40 atoms. The remaining atoms were obtained by Karle-recycling and weight-Fourier procedures.

The structure was then refined isotropically ($R = 0.145$, unit weights) and anisotropically, minimising the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1.8862/[\sigma^2(F_o) + 0.001282(F_o)^2]$, together with the anisotropic refinement of the overall scale factor. The hydrogen atoms could not be located from difference Fourier syntheses because of the relatively large thermal motion affecting the molecule. These were included in the later refinement in the geometrically calculated positions. The methyl groups were set up in the staggered conformation and then refined as rigid groups. The hydrogen atoms attached to the glucopyranose rings were fixed positionally and isotropically with the U_{iso} values equal to those of the carrier atoms. The final R and R_w values were 0.0735 and 0.0844, respectively. In the final cycle of SFLS refinement, the average shift/e.s.d. was 0.053. The final difference Fourier synthesis showed maximum and minimum electron densities of 0.34 and −0.24 eÅ^{-3}, respectively. The atomic scattering factors used were taken from the International Tables for X-Ray Crystallography[24].

Table II lists the positional parameters of the heavy atoms and the U_{eq} values. Hydrogen atom coordinates, anisotropic thermal vibration parameters, and the observed and calculated structure factors have been deposited*.

*The vibrational parameters U_{ij} of the heavy atoms, the coordinates and U_{iso} values of the H atoms, tables of bond lengths and angles, and a list of F_o and F_c structure factors are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/339/*Carbohydr. Res.*, 153 (1986) 205–216.

TABLE II

FRACTIONAL COORDINATES AND U_{eq} (Å^2) OF THE NON-HYDROGEN ATOMS

Atom	*Reducing residue*				*Non-reducing residue*			
	x	*y*	*z*	U_{eq}*	*x*	*y*	*z*	U_{eq}*
C-1	0.1899(9)	0.5439(6)	0.5180(3)	0.0546	0.0188(8)	0.2752(6)	0.6015(3)	0.0479
C-2	0.1823(9)	0.4366(5)	0.5270(3)	0.0486	0.0353(9)	0.1651(5)	0.6062(3)	0.0531
C-3	0.1540(8)	0.4151(5)	0.5816(3)	0.0411	−0.1033(10)	0.1183(5)	0.6269(3)	0.0558
C-4	0.2695(8)	0.4637(5)	0.6120(3)	0.0460	−0.1697(9)	0.1778(7)	0.6692(3)	0.0627
C-5	0.2806(9)	0.5703(5)	0.6000(3)	0.0534	−0.1713(9)	0.2860(6)	0.6584(3)	0.0544
C-6	0.4093(10)	0.6171(5)	0.6254(3)	0.0636	−0.2187(11)	0.3476(7)	0.7022(4)	0.0748
O-1	0.0520(7)	0.5860(4)	0.5300(2)	0.0637	—	—	—	—
O-2	0.0653(6)	0.3966(4)	0.4976(2)	0.0516	0.0548(6)	0.1316(4)	0.5557(2)	0.0616
O-3	0.1553(6)	0.3132(3)	0.5909(2)	0.0491	−0.0696(7)	0.0265(4)	0.6475(2)	0.0667
O-4	0.2323(6)	0.4550(4)	0.6627(2)	0.0564	−0.3179(7)	0.1452(5)	0.6737(2)	0.0753
O-5	0.2984(7)	0.5841(4)	0.5474(2)	0.0600	−0.0224(6)	0.3120(4)	0.6482(2)	0.0564
O-6	0.3842(7)	0.7205(4)	0.6225(2)	0.0715	−0.2039(10)	0.4470(6)	0.6854(3)	0.1065
CA-1	0.0116(15)	0.6642(9)	0.5047(6)	0.1033	—	—	—	—
OA-1	0.0828(13)	0.6933(9)	0.4705(5)	0.1775	—	—	—	—
CM-1	−0.1291(14)	0.7047(9)	0.5193(6)	0.1244	—	—	—	—
CA-2	0.0963(11)	0.3193(7)	0.4680(3)	0.0565	0.1501(2)	0.0605(7)	0.5473(5)	0.0805
OA-2	0.2132(7)	0.2847(5)	0.4652(2)	0.0689	0.2171(9)	0.0241(6)	0.5793(4)	0.1121
CM-2	−0.0337(11)	0.2886(8)	0.4404(4)	0.0794	0.1607(15)	0.0345(8)	0.4936(4)	0.1001
CA-3	—	—	—	—	−0.0811(15)	−0.0532(7)	0.6199(4)	0.0863
OA-3	—	—	—	—	−0.1250(12)	−0.0505(5)	0.5781(3)	0.1298
CM-3	—	—	—	—	−0.0303(19)	−0.1423(8)	0.6444(5)	0.1183
CA-4	0.3090(14)	0.3957(8)	0.6920(4)	0.0795	−0.3722(14)	0.1343(9)	0.7197(6)	0.0978
OA-4	0.4188(10)	0.3590(8)	0.6777(3)	0.1279	−0.3031(12)	0.1452(9)	0.7568(4)	0.1545
CM-4	0.2426(14)	0.3841(7)	0.7417(3)	0.0883	−0.5301(13)	0.1129(10)	0.7199(5)	0.1140
CA-6	0.4863(17)	0.7754(8)	0.6437(5)	0.1013	−0.1487(16)	0.5103(11)	0.7114(8)	0.1243
OA-6	0.5948(11)	0.7397(6)	0.6604(4)	0.1255	−0.1267(25)	0.4940(9)	0.7550(6)	0.2569
CM-6	0.4563(19)	0.8788(9)	0.6398(7)	0.1509	−0.1208(17)	0.6042(9)	0.6887(7)	0.1365

*$U_{eq} = 1/3\Sigma_i\Sigma_j\ U_{ij}\ a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

RESULTS AND DISCUSSION

The molecular structure of **1** with the numbering of the atoms is shown in Fig. 1[25]. As previously observed for the hepta-acetate **2** and the octa-acetate **3**, the accuracy of the structural parameters obtained for **1** is not high. A common feature is the relatively high thermal motion affecting these molecules.

Molecular geometry. — Tables of bond lengths and valence angles involving the non-hydrogen atoms have been deposited*. The values conform to those tabulated for other oligosaccharides[26].

The average bond distances and angles of the acetate groups are in good agreement with the values observed for other acetylated carbohydrate derivatives (Fig. 2).

The relative orientation of contiguous pyranose rings is described by the torsion angles ϕ and ψ around the interglycosidic bond[27], where ϕ = O-5–C-1–O-3′–C-3′ and ψ = C-1–O-3′–C-3′–C-2′. These values, as found for laminaribiose and for the acetylated derivatives, are compared in Table III. The trend in (ϕ,ψ) values has been related to the exo-anomeric effect and its resulting conformational bias at the glycosidic linkage that make the ϕ angle more resistant to stereochemical adjustment than the ψ angle[28].

The removal of the intramolecular hydrogen-bond between O-4 and O-5′, as found in laminaribiose, is evidently responsible for the variation of the angle ψ.

A further important feature is the glycosidic valence angle τ [C-3–O-3–C-1′].

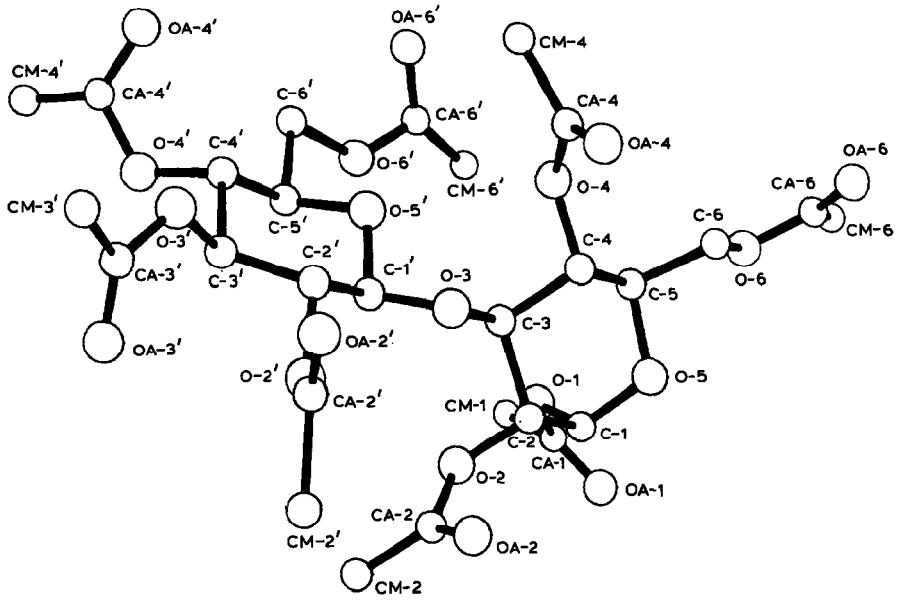

Fig. 1. Conformation and atom numbering of α-laminaribiose octa-acetate (**1**); CA, CM, and OA refer to the carbonyl C, methyl C, and carbonyl O of the acetyl groups.

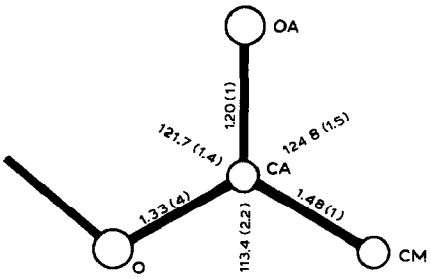

Fig. 2. Average bond lengths (Å) and valence angles (°) for the acetate groups in **1**.

The values in Table III indicate that the linkage valence angle might depend on the molecular size of the substituent at C-1′ and on the degree of substitution, decreasing from OH to OAc.

As expected, for laminaribiose, **2**, and **3**, the $^4C_1$ chair conformation is found for both sugar residues in **1**.

A comparison of the various torsion angles around the skeletal bonds and of the molecular geometry of the pyranose rings is given in Table IV. Significant effects on the conformation of the ring due to the acetylation are shown by the variation of the endo- and exo-cyclic torsion angles. As shown in Table IV, the values of the intracyclic torsion angles of the non-reducing residues have a wider range than those of the reducing residues. The relevant differences, particularly in the exo-cyclic torsion angles, might be due to the non-bonded interaction of the acetate groups. A quantitative evaluation of the degree to which the pyranose rings deviate from the ideal symmetry is given[29] in terms of the asymmetry parameter ΔC_s.

Furthermore, the displacement of C-3 and O-5 from the least-squares plane defined by C-1,2,4,5 suggests that acetylation results in a flattening of the chair

TABLE III

MOLECULAR GEOMETRY OF THE GLYCOSIDIC BRIDGE

	Laminaribiose	**2**	**3**	**1**
Glycosidic valence angle (°)				
C-3–O-3–C-1′ (τ)	118.2(4)	116.1(7)	113.5(1.2)	113.4(5)
Glycosidic bond lengths (Å)				
C-3–O-3	1.431(6)	1.413(12)	1.461(20)	1.427(9)
C-1′–O-3	1.387(6)	1.379(12)	1.457(22)	1.401(9)
Glycosidic torsion angles (°)				
O-5–C-1′–O-3–C-3 (ϕ)	−93.6(5)	−83.4(9)	−81.2(1.5)	−69.1(7)
C-1′–O-3–C-3–C-2 (ψ)	−161.0(4)	−108.4(9)	−107.3(1.5)	−109.1(7)
Intramolecular O–O distances (Å)				
O-2–O-2′	3.920(6)	3.603(9)	3.606(16)	3.979(8)
O-4–O-5′	2.785(6)	3.211(10)	3.200(16)	3.105(8)

TABLE IV

MOLECULAR GEOMETRY OF THE PYRANOSE RINGS

	Laminaribiose		**2**		**3**		**1**	
	Reducing residue	*Non-reducing residue*	*Reducing residue*	*Non-reducing residue*	*Reducing residue*	*Non-reducing residue*	*Reducing residue*	*Non-reducing residue*
Endocyclic torsion angles (°)								
C-5–O-5–C-1–C-2 (ν_0)	−62.5(5)	−62.3(5)	−65.2(9)	−70.7(9)	−71.6(1.7)	−70.7(1.6)	−59.3(8)	−72.5(7)
O-5–C-1–C-2–C-3 (ν_1)	55.0(6)	58.1(6)	61.9(9)	60.6(9)	66.2(1.7)	62.4(1.7)	58.0(8)	55.0(8)
C-1–C-2–C-3–C-4 (ν_2)	−51.8(6)	−56.0(6)	−54.3(1.0)	−48.4(1.0)	−60.5(1.8)	−54.4(1.9)	−55.9(8)	−41.7(9)
C-2–C-3–C-4–C-5 (ν_3)	52.3(6)	54.5(6)	49.3(1.1)	42.4(1.0)	54.2(1.7)	51.1(1.9)	53.5(8)	43.7(9)
C-3–C-4–C-5–O-5 (ν_4)	−56.7(6)	−56.7(5)	−51.6(1.0)	−48.9(1.0)	−57.8(1.8)	−60.4(1.8)	−53.1(8)	−56.2(9)
C-4–C-5–O-5–C-1 (ν_5)	64.4(5)	62.5(5)	60.3(9)	64.9(9)	66.0(7)	71.5(1.7)	57.1(8)	72.3(7)
Asymmetry parameter ΔC_s (°)	1.5	1.1	7.2	8.4	6.9	2.3	3.4	1.3
Displacement (Å) from the plane defined by C-1,2,4,5								
C-3	0.642(6)	0.666(7)	−0.643(10)	−0.571(9)	−0.706(15)	−0.633(16)	−0.675(7)	−0.540(9)
O-5	−0.662(5)	−0.670(4)	0.681(7)	0.698(7)	0.740(11)	0.800(11)	0.607(6)	0.754(5)
Orientation of the rings (°)	14.5(5)		51.0(1.2)		52.8(1.4)		63.7(8)	
Exocyclic torsion angles (°)								
O-5–C-1–O-1–CA-1 (χ_1)	—	—	—	—	−84.4(1.8)	—	90.8(1.0)	—
C-1–C-2–O-2–CA-2 (χ_2)	—	—	120.1(9)	138.2(8)	115.8(1.7)	143.7(1.6)	128.0(7)	140.6(8)
C-2–C-3–O-3–CA-3 (χ_3)	—	—	—	−139.7(9)	—	−136.6(1.9)	—	145.7(8)
C-3–C-4–O-4–CA-4 (χ_4)	—	—	116.7(1.0)	101.4(9)	125.5(1.7)	108.5(1.7)	109.2(8)	139.4(9)
C-4–C-5–C-6–O-6 (χ_5)	−174.0(4) t	−176.7(4) t	−157.5(8) t	52.7(1.1) g	−162.7(1.4) t	49.0(2.2) g	−164.2(6) t	176.5(6) t
C-5–C-6–O-6–CA-6 (θ_6)	—	—	160.9(1.0) t	−126.7(1.0) g⁻	−163.5(1.7) t	−176.5(1.9) t	179.2(8) t	−135.2(1.2) g⁻
O-1–C-1–C-2–O-2	−60.8(6)	−66.0(5)	64.1(9)	−68.0(9)	−70.1(1.7)	−74.1(1.6)	56.9(8)	−73.8(7)
O-2–C-2–C-3–O-3	63.4(5)	65.1(6)	63.6(9)	73.2(8)	67.6(1.6)	73.0(1.4)	63.9(7)	87.1(7)
O-3–C-3–C-4–O-4	−72.2(6)	−65.3(5)	69.4(1.0)	−80.6(9)	−78.6(1.4)	−80.7(1.7)	−66.4(7)	−79.1(8)
O-4–C-4–C-5–C-6	65.8(6)	68.9(6)	71.8(1.0)	68.4(1.0)	71.4(1.7)	67.9(1.9)	68.7(8)	70.4(9)
O-5–C-5–C-6–O-6	67.0(6) g	63.5(6) g	81.9(1.0) g	−69.5(1.0) g⁻	77.8(1.8) g	−71.3(1.7) g⁻	74.6(8) g	60.6(9) g

conformation of the non-reducing residue; the reducing residue is also slightly flattened.

A marked difference is observed in the orientation of the two pyranose rings of the molecule, along the pseudo axis passing through C-1′ and C-3, as shown in Fig. 3[30]. In laminaribiose, both the pyranose rings have approximately the same orientation, whereas the orientations are quite different in the acetylated derivatives.

As in other acetylated carbohydrate derivatives, the secondary acetate groups are so arranged that the carbonyl O nearly eclipses the axial H at the corresponding ring C. These torsion angles are in the range 8.4–29.1° (average, 19.1°), which are consistent with those observed in **2** and **3**.

The orientation of the primary acetate groups, AcO-6,6′, falls into the theoretically predicted range of conformations for acetyl groups in glucosaccharides[11]. The data in Table IV show that the major conformational differences for **1–3** occur at AcO-6′. Also of note are the values of the torsion angles at C-5 (χ_5) and at C-6 (θ_6).

The present crystallographic study provides the first experimental evidence of the theoretically predicted *gauche–trans–gauche*$^-$ conformation at a primary acetate group in glucosaccharides. This conformational change, together with the α-orientation of AcO-1, alters the overall shape of the molecule and influences the packing features as described below.

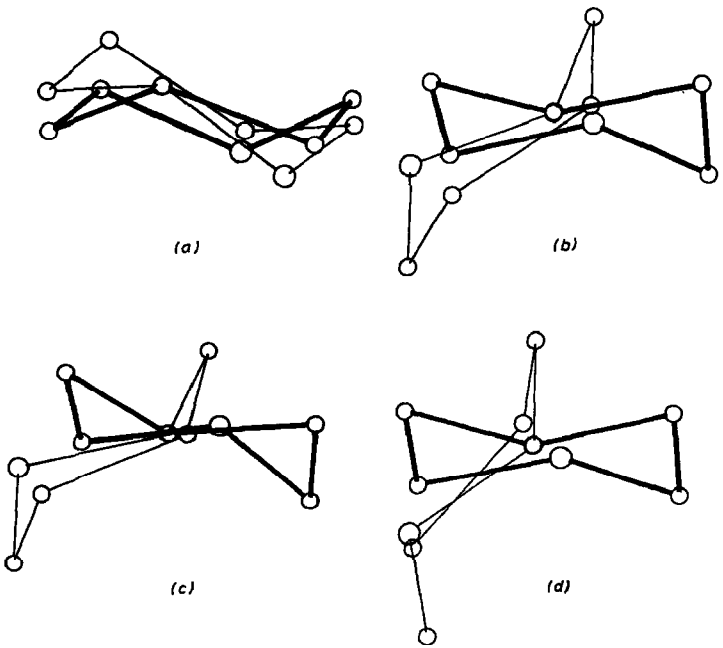

Fig. 3. Projections of the (1→3)-linked β-D-pyranose rings along the C-1–C-3′ pseudo-axis. Thin and thick lines represent the non-reducing and reducing residues, respectively: (*a*) laminaribiose, (*b*) hepta-acetate **2**, (*c*) octa-acetate **3**, (*d*) **1**.

Conformational analysis. — The potential energy was calculated by the ENERGY suite of programs[31], including the partitioned contributions arising from the Van der Waals interactions of non-bonded atoms, evaluated using the Lennard-Jones 6-12 potential function with the parameters proposed by Scott and Sheraga[32], and the torsion energies about the different torsion angles. Only for laminaribiose was a hydrogen-bond potential considered.

The crystal structure coordinates were used and only ϕ and ψ were allowed to vary; this accords with the suggestion that, in acetylated oligosaccharides, the orientation of the 6-substituent does not have any influence on the energetically allowed conformational space[12]. The iso-energy contour maps, computed as a

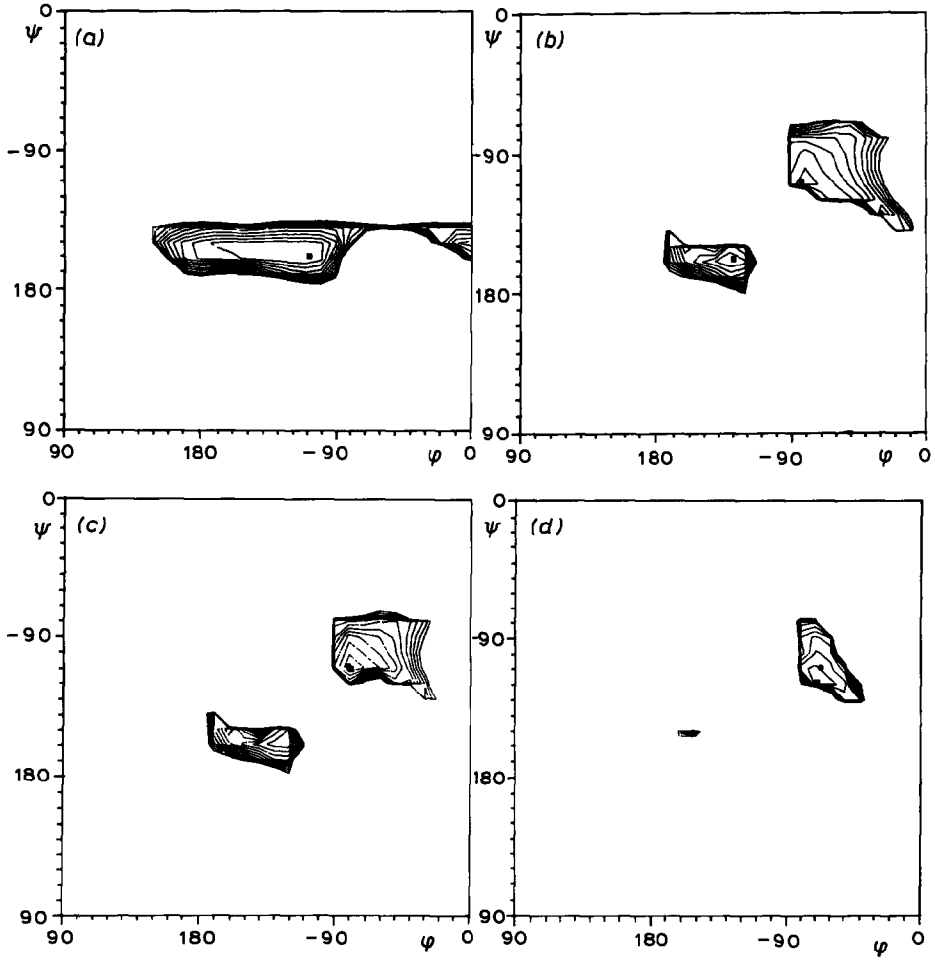

Fig. 4. Iso-energy contour maps computed as a function of the rotations about the ϕ and ψ angles at intervals of 10°: (*a*) laminaribiose, (*b*) hepta-acetate **2**, (*c*) octa-acetate **3**, (*d*) **1**; ● indicates the crystalline conformation and ■ the global energy minima; these being −11.2, −10.1, −10.0, and −11.8 kcal.mol^{-1}, respectively. Contour levels plotted at intervals of 2.0 kcal.mol^{-1}.

function of the rotations about ϕ and ψ at intervals of 10°, are given in Fig. 4. Identical iso-energy contour maps, obtained from calculations carried out for both anomers of laminaribiose, show that HO-1 has little effect on the molecule. Accordingly, laminaribiose will be discussed solely as the β anomer.

All of the regions of minimum energy correlated well with the crystallographically determined molecular conformations. There is an obvious trend for the acetylated derivative structures to move to a potential well, different to that of laminaribiose, whilst still showing an energetically allowed region like that of the non-acetylated disaccharide. Laminaribiose exhibits only one region of low energy in which both the global energy minimum and the crystallographically determined structure are found to be in close agreement. This region still appears in the hepta-acetate **2**, and is the site of the global minimum, but another region around ($-60°$, $-100°$) contains the crystal structure values for ϕ and ψ. The energy here is only 1.0 kcal.mol^{-1} above the global minimum and is therefore acceptable. The (ϕ,ψ) plot for the octa-acetate **3** is nearly identical to that of the hepta-acetate **2**, except that both the global minimum and the crystal structural values are found in the non-laminaribiose region.

In the map for **1**, the laminaribiose region has virtually disappeared and the global minimum and the determined crystallographical values are again close together, in the second, now most important region. These trends would be expected for the addition of the acetate groups, as these prevent the formation of the O-4–O-5′ intramolecular hydrogen-bond and increase the steric hindrance. That the addition of one further acetate group at C-1, which is comparatively remote from the interglycosidic bond, should cause such a large change in the region that is common to all species is worthy of note, and is probably more surprising since this region is so prominent in the hepta-acetate **2**. The disappearance of the laminaribiose region in **1**, whilst it still occurs in the acetylated β-disaccharides, shows that acetylation of HO-1 has a large effect on the range of sterically available conformations. This is in contrast to the situation with respect to HO-1 in laminaribiose, which had no effect on the energy map.

Overall, the results correlate with the crystal structures and show that the acetate groups, as expected, have a large effect on the conformation about the glycosidic torsion angles. This finding also demonstrates that the assumptions made in the potential energy calculations do not have a significant effect upon the accuracy of the results, and that they may be used to give an idea of the likely conformations of the oligo- or poly-saccharides, allowing for differences due to crystal packing forces.

Molecular packing. — The molecules of **1** are held in the crystal by Van der Waals forces only; no short atom contacts are observed. The molecules are oriented in the cell with the pyranose rings approximately perpendicular to the *c* axis and with the long axis parallel to the *b* axis (Fig. 5).

Thus, unlike laminaribiose, the hepta-acetate **2**, and the octa-acetate **3**, there is no coincidence of the developing chain axis with the largest unit-cell dimension.

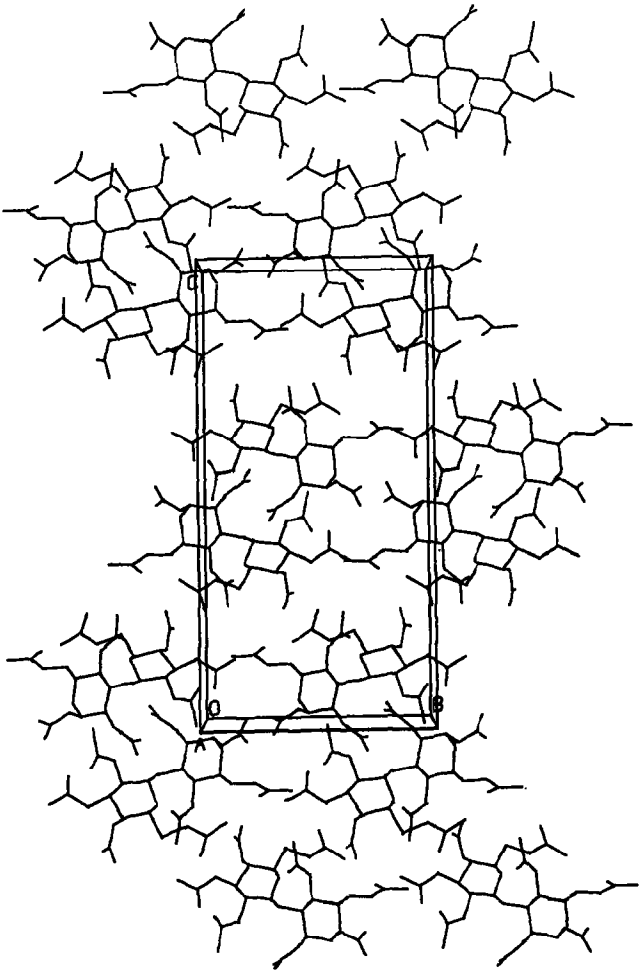

Fig. 5. Molecular packing for **1**.

Furthermore, the three acetylated derivatives, due to the common space-group symmetry, can only be organised in an anti-parallel sheet manner unlike the anti-parallel chain arrangement observed in laminaribiose.

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