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Molecular and crystal structure of (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1 → 3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1 → 6)]-(2,4-di-*O*-acetyl-β-D-glucopyranosyl)-(1 → 3)-1,2,4,6-tetra-*O*-acetyl-β-D-glucopyranose

Keiichi Noguchi [a], Eiichi Kobayashi [a], Kenji Okuyama [a,*], Shinichi Kitamura [b], Kenichi Takeo [b], Shigeru Ohno [c]

[a] *Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan*
[b] *Department of Agricultural Chemistry, Kyoto Prefectural University, Shimogamo, Kyoto 606, Japan*
[c] *Japan Synchrotron Radiation Research Institute, 1-9-1 Minatojima Nakamichi, Kobe 650, Japan*

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Abstract

Crystals of the tetrasaccharide, (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1 → 3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1 → 6)]-(2,4-di-*O*-acetyl-β-D-glucopyranosyl)-(1 → 3)-1,2,4,6-tetra-*O*-acetyl-β-D-glucopyranose, belong to the monoclinic system, space group $P2_1$, with $a = 12.709(4)$, $b = 27.767(9)$, $c = 9.567(4)$ Å, $\beta = 105.07(2)°$, and $Z = 2$. The crystal structure was solved by the direct method and refined by the full-matrix least-squares procedure to an *R*-value of 0.071 for 3029 observed reflections in the X-ray data. All the four D-glucopyranose residues have the usual $^4C_1$ chair conformations. The torsional angles at two (1 → 3)-β-linkages were ϕ(O-5–C-1–O-1–C-3) = −74° and ψ (C-1–O-1–C-3–C-2) = −122° between the nonreducing and the middle residues, and $\phi = -67°$, $\psi = -111°$ between the middle and the reducing residues. The orientation about the (1 → 6)-β-linkage was found to be ϕ (O5–C1–O-1–C-6) = −77°, θ(C1–O-1–C-6–C-5) = 160°, and χ (O-1–C-6–C-5–O-5) = 63° (*gt* conformation). The primary acetate groups at C-6 of the reducing and the (1 → 6)-branched residues were in the *gt* conformations (O-5–C-5–C-6–O-6 = 81° and 84°, respectively). On the other hand, the *gg* conformation was observed for the primary acetate group in the nonreducing residue (O-5–C-5–C-6–O-6 = 78°).

* Corresponding author.

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1. Introduction

The (1 → 6)-branched (1 → 3)-β-D-glucans have attracted increasing attention because of their physiological activities such as, antitumor activity, radioprotective activity, antiviral activity, and immunomodulating activities. Schizophyllan, a polysaccharide produced extracellularly by the fungus, *Schizophllum commune*, is one of the water-soluble (1 → 6)-branched (1 → 3)-β-D-glucans. Its repeating unit consists of linearly linked (1 → 3)-βD-glucose residues with one (1 → 6)-β-D-glucose side chain for every three main chain residues. It is well known that schizophyllan dissolves as a rigid triple-helical structure in an aqueous solution and random coils in dimethyl sulfoxide Me_2SO [1]. In mixture solutions of water and Me_2SO, this polysaccharide shows two thermally induced conformational transitions for most of the solvent composition ratios [2]. These were assigned to an internal change of the triple helix [3], and a triple-helix–single-coil transitions [4]. Molecular cyclizations of schizophyllan were observed in the electron micrographs after the denaturation–renaturation process [5]. The X-ray fiber diffraction study on schizophyllan indicated the presence of a triple-helical structure in the solid state [6]. The relationships between conformation and physiological activities have been investigated by many researchers [7–9]. It was reported that the triple-helical structure of schizophyllan was essential for some antitumor activity [8].

Tetrasaccharide, (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1 → 3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1 → 6)]-(2,4-di-*O*-acetyl-β-D-glucopyranosyl)-(1 → 3)-1,2,4,6-tetra-*O*-acetyl-β-D-glucopyranose, is an acetylated derivative of the repeating unit of schizophyllan. So far, there are only two tetrasaccharides (stachyose [10] and nystose [11,12]) whose crystal structures were determined by X-ray diffraction. Although structure analyses of several kinds of disaccharides with either a (1 → 3)-β or a (1 → 6)-β-linkage have been performed [13–19], there is no structural information about oligosaccharides with both (1 → 3)-β- and (1 → 6)-β-linkages.

This work is a part of the series of structure analyses for oligosaccharides to obtain conformational details of (1 → 6)-branched (1 → 3)-β-D-glucans.

2. Experimental

X-ray measurement.—The title compound was prepared by a method that has been reported elsewhere [20]. Single crystals suitable for X-ray work were grown by slow evaporation of a ca. 90% ethanolic solution. Determination of the unit cell dimensions and collection of the diffraction intensities were carried out using a four-circle diffractometer (RASA 5R-II, Rigaku Co.) with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). A crystal with dimensions of $0.6 \times 0.2 \times 0.2$ mm^3 was used for the X-ray measurements. The lattice constants were obtained by a least-squares procedure using 20 reflections with 2θ in the range of 40–50°. At first, the X-ray measurements were performed at room temperature (293 K). Although the atomic positions were obtained by the direct method, the tempera-

Table 1
Crystal data

Molecular formula	$C_{52}H_{70}O_{35}$
Molecular weight	1254.4
Crystal system	monoclinic
Space group	$P2_1$
Z	2
a (Å)	12.709 (4)
b (Å)	27.767 (9)
c (Å)	9.567 (4)
β (°)	105.07 (2)
V (Å^3)	3260
D_{calcd} (g/cm^3)	1.278
D_{obsd} (g/cm^3)	1.28

ture factors of a few atoms in the C-6 acetate groups were unusually large in the refinement cycle. Therefore, the intensity data were recollected at 243 K. No significant difference of the unit cell dimensions was observed. The ω-scanning technique was used throughout the data collection with a scanning rate of 10°/min and a scanning width of $\Delta\omega = (2.0 + 0.14 \tan \theta)°$. Three reference reflections (measured after every 100 reflections) showed no significant intensity change during data collection (less that 2%). The observed intensities were corrected by a Lorentz-polarization factor. No absorption correction was made ($\mu = 8.47$ cm^{-1}). A total of 3517 independent reflections were measured up to $2\theta = 120°$, of which 3029 reflections with $F_o \geq 2\sigma(F_o)$ were used for the following calculations. The density of the crystal was measured by the flotation method using a mixture of carbon tetrachloride and toluene.

3. Structure analysis

On the basis of the measured density and the unit cell volume, a unit cell contains two oligosaccharide molecules. The systematic absences for $0k0$ reflections when k is odd, identify the space group as $P2_1$. Crystal data are shown in Table 1. The initial atomic coordinates of 48 of the 87 nonhydrogen atoms in the asymmetric unit (one molecule) were obtained by the direct method with the SAPI85 program [21]. The remaining atoms, with the exception of the CM-6‴ atom, were obtained by the weighted Fourier procedure. After several cycles of full-matrix least-squares refinement with isotropic thermal factors, the difference Fourier synthesis revealed the CM-6‴ atom. After an additional refinement cycles for all the nonhydrogen atoms with anisotropic temperature factors, bond lengths of the C-6‴ acetate group deviated significantly from the standard values. Therefore, these were fixed to the standard values during the refinement cycle by using the SHELX-76 program [22]. In the final refinement cycle, these constraints were released. The locations of 37 of 70 hydrogen atoms were found in the difference

Table 2
Fractional coordinates and equivalent isotropic temperature factors for nonhydrogen atoms, with estimated standard deviations in parentheses. $B_{eq} = 4/3[B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2(B_{12}ab + B_{23}bc + B_{31}ca)]$

Atom	x	y	z	B_{eq}
C-1	1.1440(7)	0.5911	1.0187(8)	4.1(3)
C-2	1.2409(7)	0.5991(4)	1.1521(9)	4.5(3)
C-3	1.3382(6)	0.5707(4)	1.1261(8)	3.7(2)
C-4	1.3097(6)	0.5174(4)	1.0883(9)	4.3(3)
C-5	1.2122(7)	0.5186(4)	0.9563(9)	4.6(3)
C-6	1.1743(8)	0.4710(4)	0.8833(10)	6.1(3)
O-1	1.0513(4)	0.6122(3)	1.0460(5)	4.1(2)
O-2	1.2726(4)	0.6483(4)	1.1600(7)	5.2(2)
O-3	1.4224(4)	0.5729(4)	1.2620(6)	4.9(2)
O-4	1.4011(4)	0.4973(4)	1.0422(6)	4.8(2)
O-5	1.1246(4)	0.5408(3)	0.9982(6)	4.4(2)
O-6	1.1702(6)	0.4350(4)	0.9925(8)	7.1(2)
CA-2	1.2474(8)	0.6781(5)	1.2636(12)	6.2(4)
CA-3	1.5241(7)	0.5826(4)	1.2523(11)	5.7(3)
CA-4	1.4667(8)	0.4674(4)	1.1363(12)	5.9(3)
CA-6	1.1135(11)	0.3939(5)	0.9421(15)	7.9(5)
CM-2	1.2854(9)	0.7277(4)	1.2603(12)	7.2(4)
CM-3	1.6038(8)	0.5848(5)	1.3991(11)	7.8(4)
CM-4	1.5665(7)	0.4556(5)	1.0861(12)	6.6(4)
CM-6	1.1201(10)	0.3590(5)	1.0695(14)	9.6(5)
OA-2	1.1919(5)	0.6619(4)	1.3402(7)	6.5(2)
OA-3	1.5459(5)	0.5893(4)	1.1382(8)	7.5(3)
OA-4	1.4498(7)	0.4534(4)	1.2473(9)	9.9(3)
OA-6	1.0640(11)	0.3887(5)	0.8135(12)	14.8(5)
C-1′	0.8244(6)	0.6750(4)	0.7820(9)	4.5(3)
C-2′	0.9277(6)	0.6690(4)	0.8987(9)	4.1(2)
C-3′	0.9598(6)	0.6166(4)	0.9202(9)	4.4(3)
C-4′	0.8642(6)	0.5892(4)	0.9547(9)	4.1(3)
C-5′	0.7620(6)	0.5984(4)	0.8310(9)	4.2(3)
C-6′	0.6638(7)	0.5732(4)	0.8607(10)	4.7(3)
O-1′	0.7937(4)	0.7235(3)	0.7751(6)	4.4(2)
O-2′	1.0124(4)	0.6947(4)	0.8530(6)	4.8(2)
O-4′	0.8890(4)	0.5385(4)	0.9549(7)	5.5(2)
O-5′	0.7404(4)	0.6493(3)	0.8268(5)	4.2(2)
CA-2′	1.0493(7)	0.7349(5)	0.9255(13)	6.1(4)
CA-4′	0.8679(9)	0.5107(5)	1.0639(15)	6.3(4)
CM-2′	1.1246(9)	0.7617(5)	0.8557(12)	8.4(4)
CM-4′	0.9090(9)	0.4604(5)	1.0590(16)	9.2(5)
OA-2′	1.0300(6)	0.7487(4)	1.0361(8)	7.6(3)
OA-4′	0.8191(7)	0.5271(4)	1.1470(9)	8.7(3)
C-1″	0.6212(7)	0.7837(4)	0.4441(10)	5.0(3)
C-2″	0.7253(7)	0.7657(4)	0.5488(9)	4.7(3)
C-3″	0.6971(6)	0.7352(4)	0.6648(9)	3.8(2)
C-4″	0.6237(7)	0.7659(4)	0.7380(9)	4.5(3)
C-5″	0.5258(7)	0.7848(4)	0.6231(10)	5.0(3)
C-6″	0.4554(7)	0.8184(5)	0.6878(10)	5.7(3)
O-1″	0.6530(5)	0.8164(4)	0.3481(7)	6.0(2)
O-2″	0.7799(5)	0.7342(4)	0.4671(6)	5.8(2)

Table 2 (continued)

Atom	x	y	z	B_{eq}
O-4″	0.5818(5)	0.7342(4)	0.8320(7)	5.4(2)
O-5″	0.5643(4)	0.8126(3)	0.5218(6)	5.1(2)
O-6″	0.3518(6)	0.8199(4)	0.5838(8)	8.0(3)
CA-1″	0.5901(10)	0.8196(5)	0.2120(15)	7.1(4)
CA-2″	0.8818(9)	0.7483(6)	0.4567(13)	6.6(4)
CA-4″	0.6372(10)	0.7335(5)	0.9756(13)	6.5(4)
CA-6″	0.2665(10)	0.8413(5)	0.6262(18)	7.7(5)
CM-1″	0.6306(10)	0.8581(5)	0.1221(12)	7.9(4)
CM-2″	0.9211(13)	0.7138(5)	0.3508(15)	11.1(6)
CM-4″	0.5861(12)	0.6943(5)	1.0526(13)	11.3(6)
CM-6″	0.1629(9)	0.8408(6)	0.5046(15)	9.8(5)
OA-1″	0.5066(7)	0.7951(4)	0.1677(8)	8.3(3)
OA-2″	0.9297(7)	0.7813(4)	0.5212(11)	9.6(4)
OA-4″	0.7101(7)	0.7587(4)	1.0315(8)	8.2(3)
OA-6″	0.2817(7)	0.8563(4)	0.7453(12)	10.3(4)
C-1‴	0.4871(7)	0.5524(4)	0.7242(9)	4.5(3)
C-2‴	0.3880(6)	0.5722(4)	0.6130(9)	4.1(3)
C-3‴	0.2968(7)	0.5355(4)	0.5898(9)	4.4(3)
C-4‴	0.3325(7)	0.4870(4)	0.5398(9)	4.6(3)
C-5‴	0.4375(7)	0.4708(4)	0.6479(9)	4.2(3)
C-6‴	0.4816(8)	0.4262(4)	0.5893(10)	5.2(3)
O-1‴	0.5713(4)	0.5837(3)	0.7379(6)	4.4(2)
O-2‴	0.3491(4)	0.6137(4)	0.6789(5)	4.6(2)
O-3‴	0.2031(4)	0.5521(3)	0.4795(5)	4.4(2)
O-4‴	0.2512(5)	0.4519(4)	0.5545(7)	5.3(2)
O-5‴	0.5169(4)	0.5079(3)	0.6624(5)	4.3(2)
O-6‴	0.5524(5)	0.4024(4)	0.7159(8)	6.8(2)
CA-2‴	0.3696(7)	0.6582(4)	0.6293(11)	5.0(3)
CA-3‴	0.1090(7)	0.5657(5)	0.5168(11)	5.7(3)
CA-4‴	0.1781(11)	0.4350(5)	0.4372(15)	8.3(5)
CA-6‴	0.6614(13)	0.3984(6)	0.7237(17)	10.0(6)
CM-2‴	0.3137(9)	0.6950(5)	0.7033(13)	8.0(4)
CM-3‴	0.0227(8)	0.5783(5)	0.3864(11)	7.2(4)
CM-4‴	0.0939(9)	0.4056(5)	0.4666(12)	8.0(4)
CM-6‴	0.7155(10)	0.3663(5)	0.8553(16)	9.6(5)
OA-2‴	0.4278(5)	0.6657(4)	0.5522(8)	6.0(2)
OA-3‴	0.1070(5)	0.5645(4)	0.6394(8)	8.8(3)
OA-4‴	0.1769(7)	0.4506(5)	0.3177(10)	10.5(4)
OA-6‴	0.6971(8)	0.4201(5)	0.6369(17)	15.5(6)

Fourier map. These hydrogen atoms were not refined. The quantity minimized in the refinement was $\Sigma w(|F_o| - |F_o|)^2$, with $w = 1/\sigma^2(F_o)$, where $\sigma(F_o)$ was the standard deviation of F_o estimated from counting statistics. The final discrepancy factor (R-value) was 0.071 and the Rw value was 0.069, for all the nonhydrogen atoms with anisotropic temperature factors and 37 hydrogen atoms with the isotropic temperature factor of the corresponding parent atom, for the observed 3029 reflections. The final atomic parameters are given in Table 2. The atomic

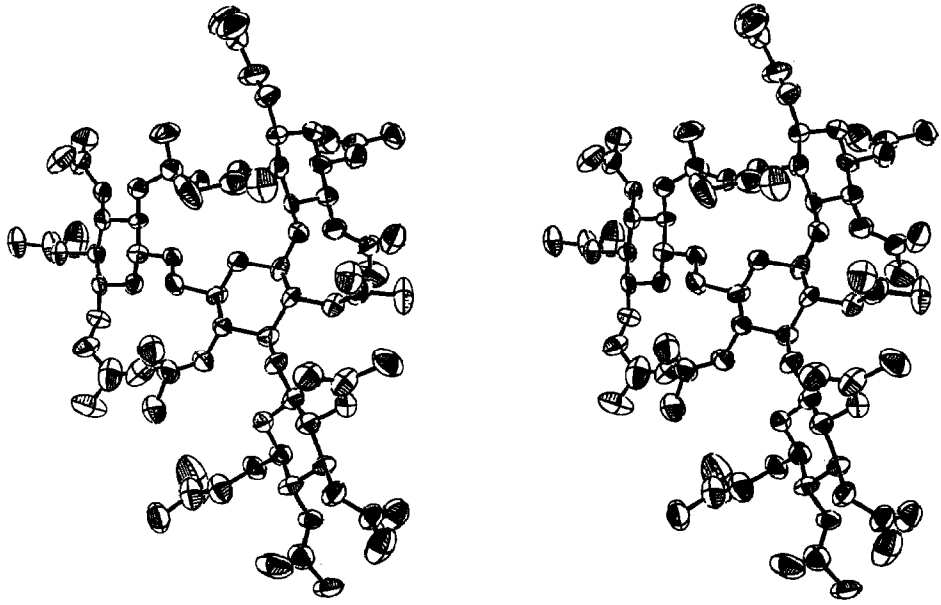

Fig. 1. Stereoscopic view of the backbone conformation. The 50% probability thermal ellipsoids are shown for carbon and oxygen atoms.

coordinates of the hydrogen atoms, 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 (ref 23). Computations were performed on a A-70 minicomputer with the help of the CRYSTAN program in a RASA-5RII system and on an ACOS-3800/8 computer at the Information Processing Center, Tokyo University of Agriculture and Technology.

3. Results and discussion

The molecular conformation of the tetrasaccharide is shown in Fig. 1 (ORTEP [24]). The bond lengths, bond angles, and the numbering system of the molecule are depicted in Fig. 2. The numbering of atoms proceeds from the nonreducing residue (unprimed) to the reducing residue (double primed), and to the (1 → 6)-β-linked glucose residue (triple primed). The estimated standard deviation of the bond lengths ranges from 0.01 to 0.02, and of the bond angles from 0.7 to 1.6°. The

* Data 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.

low accuracy of bond lengths and angles is attributed to the relative paucity of the number of reflections compared with the numbers of parameters being refined.

Bond lengths and angles.—The mean C–C bond length of 1.53(1) Å and the mean C–O bond length of 1.44(1) Å (except the anomeric C–O bonds) conform to the tabulated values of carbohydrates [25]. The four anomeric C–O bonds are in the normal range observed for an equatorial type of linkage [mean value, 1.39(1)]. Both the internal and exocyclic C–C–C bond angles [mean value, 109.3(8)], except for C-4–C-5–C-6, are close to the tetrahedral angle. The range of the endocyclic and exocyclic C–O–C angles except for the glycosidic linkages are 110.2–113.5°, with a mean value of 111.3(8)° and 115.7–120.6°, with a mean value of 117.6(9)°, respectively. The average bond lengths and angles of the acetate groups [CA–O = 1.37(2) Å, CA–OA = 1.21(2) Å, CA–CM = 1.51(2) Å, O–CA–OA = 122(1)°, O–CA–CM = 111(1)°, and OA–CA–CM = 127(1)°] are in good agreement with the values observed for other acetylated carbohydrate derivatives [15–18,26–28].

Molecular conformation.—The torsional angles at the various skeletal bonds of the pyranose rings and the acetate groups are given in Table 3. The expected $^4C_1$

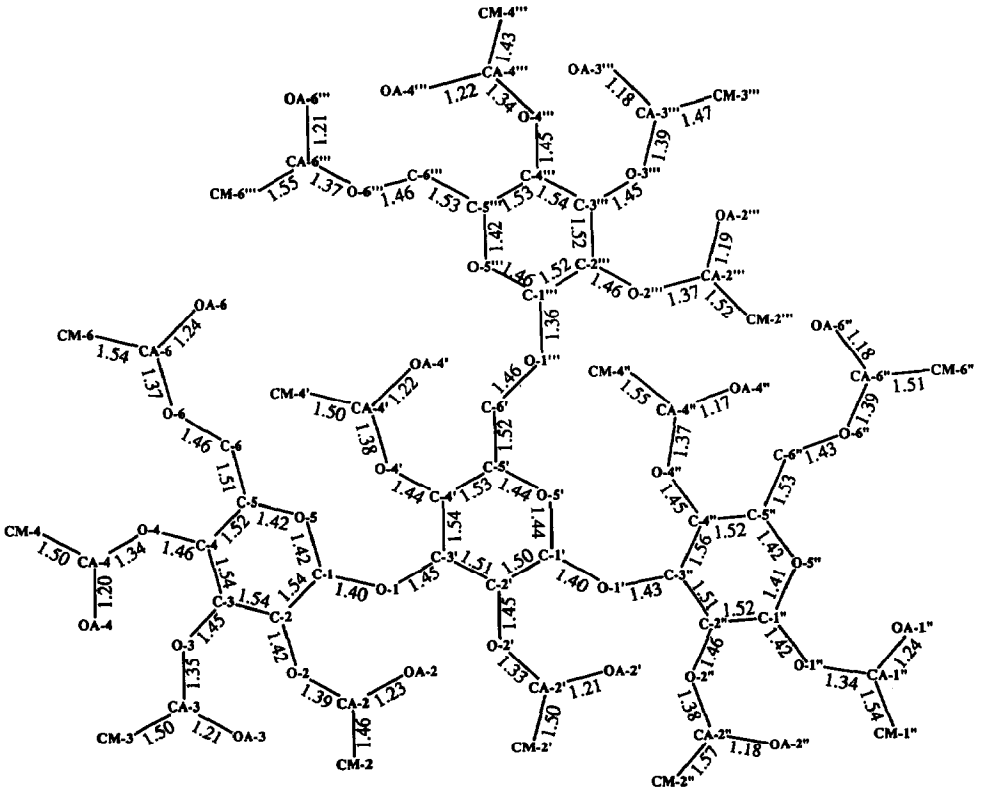

Fig. 2. (a) The numbering of atoms and bond lengths (Å), and (b) bond angles (degrees) of the title compound.

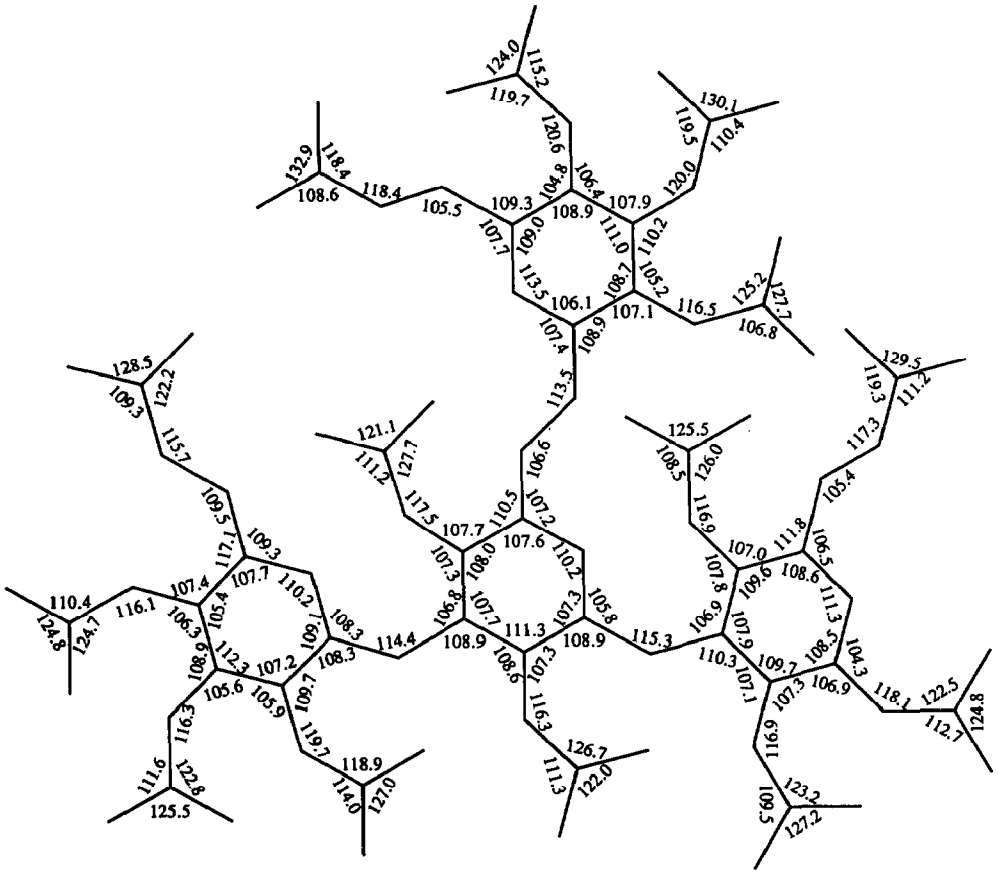

Fig. 2 (continued).

chair conformation is found for each of the four glucopyranose residues. The averaged absolute values of the endocyclic torsional angles are 62°, 62°, 60°, and 60° for the nonreducing, middle, reducing, and (1 → 6)-β-linked residues, respectively.

The orientation at (1 → 3)-β-linkage is described by a set of two torsional angles, ϕ(O-5–C-1–O-1–C-3) and ψ(C-1–O-1–C-3–C-2). The values ϕ and ψ of the title compound, together with those of the related oligosaccharides, are listed in Table 4 (refs 12–17). Two conformations observed in this study ($\phi = -74°, \psi = -122°$ and $\phi = -67°$, $\psi = -111°$) are similar to those of the other acetylated derivatives. The potential energy surfaces for four kinds of acetylated laminarabiose have already been reported in the literature [16–18]. Two crystal conformations of the tetrasaccharide are included in the low-energy domain of the energy contour maps of acetylated derivatives. Therefore, the existence of (1 → 6)-linked D-glucose residue from the middle residue of the trisaccharide does not affect ϕ

Table 3
Torsional angles (degrees) about the various skeletal bonds of the pyranose rings and the acetate groups, with estimated standard deviations in parentheses

	Nonreducing residue	Middle residue	Reducing residue	(1 → 6)-β-Linked residue
Endocyclic				
O-5–C-1–C-2–C-3	56.1(1.2)	60.9(1.7)	61.6(1.3)	60.5(7)
C-1–C-2–C-3–C-4	−53.0(9)	−57.0(1.1)	−55.5(1.4)	−57.8(1.4)
C-2–C-3–C-4–C-5	56.5(1.4)	56.2(1.4)	54.4(1.6)	54.1(9)
C-3–C-4–C-5–O-5	−63.5(9)	−61.8(8)	−58.4(1.0)	−55.2(1.5)
C-4–C-5–O-5–C-1	72.3(1.5)	67.9(8)	65.6(1.2)	64.2(1.2)
C-5–O-5–C-1–C-2	−67.9(1.1)	−66.4(1.4)	−66.8(1.3)	−66.3(1.2)
Exocyclic				
O-1–C-1–C-2–O-2	−71.8(1.4)	−66.3(1.8)	−70.6(1.4)	−70.9(9)
O-2–C-2–C-3–O-3	71.5(1.7)	69.6(1.2) [a]	72.0(1.5) [a]	68.3(1.2)
O-3–C-3–C-4–O-4	−73.1(1.0)	−71.1(1.5)	−70.8(1.4)	−72.6(1.2)
O-4–C-4–C-5–C-6	59.7(9)	65.8(9)	67.7(1.0)	73.8(1.6)
O-5–C-5–C-6–O-6	−77.5(1.3)	63.2(1.5) [b]	80.8(1.4)	83.5(1.1)
C-4–C-5–C-6–O-6	45.4(1.2)	−179.7(1.2) [b]	−160.7(1.6)	−158.2(1.2)
Acetyl group				
O-5–C-1–O-1–CA-1			−96.7(1.4)	
C-1–O-1–CA-1–CM-1			177.1(1.6)	
C-1–O-1–CA-1–OA-1			−0.4(2.0)	
C-1–C-2–O-2–CA-2	106.1(1.5)	109.4(1.7)	117.7(1.6)	106.1(1.3)
C-2–O-2–CA-2–CM-2	179.6(1.4)	−172.0(1.0)	−173.3(1.2)	175.2(1.0)
C-2–O-2–CA-2–OA-2	−4.7(1.3)	10.4(1.7)	7.6(2.1)	−10.3(1.5)
C-2–C-3–O-3–CA-3	−135.3(1.2)			−110.5(1.1)
C-3–O-3–CA-3–CM-3	179.1(1.4)			−176.4(1.6)
C-3–O-3–CA-3–OA-3	−0.0(1.9)			1.6(1.4)
C-3–C-4–O-4–CA-4	106.4(1.8)	137.1(1.3)	96.3(1.4)	106.0(1.5)
C-4–O-4–CA-4–CM-4	−171.0(1.0)	−173.7(1.2)	−174.7(1.4)	−172.2(1.2)
C-4–O-4–CA-4–OA-4	6.7(1.2)	8.1(1.9)	6.2(2.0)	−3.0(1.5)
C-5–C-6–O-6–CA-6	165.1(1.6)		169.1(1.4)	−116.7(1.4)
C-6–O-6–CA-6–CM-6	178.1(1.3)		179.1(1.8)	−172.5(1.8)
C-6–O-6–CA-6–OA-6	−3.9(2.0)		−1.4(1.6)	9.9(1.9)

[a] These torsional angles are designated O-2–C-2–C-3–O-1. [b] These torsional angles are designated O-5–C-5–C-6–O-1 and C-4–C-5–C-6–O-1, respectively.

and ψ values at (1 → 3)-β-linkages. A detailed conformational energy calculation of the tetrasaccharide is now in progress. Since the angle ϕ is influenced by the exo-anomeric effect [29], the C-3 atom is in a (−)-*gauche* orientation with respect to the O-5 atom. A similar tendency is observed in other carbohydrates (Table 4). On the other hand, the angles ψ found in the acetylated derivatives in Table 4 are different from those in β-D-laminarabiose [13] and methyl β-D-laminarabioside [14]. The glycosidic bond angles of the title compound, 114.4° and 115.3°, are in agreement with those observed for other acetylated oligosaccharides in Table 4. These values are slightly smaller than those in β-D-laminarabiose and methyl β-D-laminarabioside. The (1 → 3)-β-linkage conformations are eventually influ-

Table 4
Torsional angles(degrees) and bond angles(degrees) at glycosidic linkages

Compound	(1 → 3)-β-Linkage		
	Torsional angles		Bond angle C-1–O-1–C-3
	O-5–C-1–O-1–C-3 (φ)	C-1–O-1–C-3–C-2 (ψ)	
This work	−74(1)	−122(1)	114.4(7)
	−67(1)	−111(2)	115.3(9)
β-D-Laminarabioside [13]	−94	−161	118.2
Methyl β-D-laminarabioside [14]	−86	−162	117.5
Methyl hepta-*O*-acetyl-β-D-laminarabioside [15]	−83	−108	116.1
Methyl hepta-*O*-acetyl-α-D-lamibarabioside [18]	−86	−112	113.9
Octa-*O*-acetyl-β-D-laminarabiose [16]	−81	−107	113.5
Octa-*O*-acetyl-α-D-laminarabiose [17]	−69	−109	113.4
Curdlan form I [30]	−71	−113	116.5
form II [31]	−85	−111	112.4
form III [32]	−92	−107	110.4

	(1 → 6)-β-linkage			
	Torsional angles			Bond angle C-1–O-1–C-6
	O-5–C-1–O-1–C-6 (φ)	C-1–O-1–C-6–C-5 (θ)	O-1–C-6–C-5–O-5 O-1–C-6–C-5–C-4 (χ)	
This work	−77(1)	160(1)	63(2) 180(1)	113.5(9)
Gentiobiose [19]	−58	−156	−62 60	113.3

enced by intramolecular hydrogen bonding, the acetylation of hydroxyl moieties, and the exo-anomeric effect.

The linear (1 → 3)-β-D-glucan, curdlan, has three crystal forms, namely form I [a right-handed 6/1-single helix, fiber period (f p) 22.8 Å] [30], form II (a right-handed 6/1-triple helix, f p 18.78 Å) [31] and form III (right-handed 6/1-triple helix, f p 5.87 Å) [32]. The angles φ and ψ of three polymorphs of curdlan are similar to each other. In addition, these values resembles those of the acetylated derivatives rather than those of β-D-laminarabiose and methyl β-D-laminarabioside. The

glycosidic linkages' conformations of acetylated compounds appear to be a stable conformation for (1 → 3)-β-linked polysaccharide.

For the (1 → 6)-β-linkage, three torsional angles ϕ, θ, and χ have to be considered to define the conformation. Here, ϕ = O-5–C-1–O-1–C-6, θ = C-1–O-1–C-6–C-5, and χ = O-1–C-6–C-5–O-5. The values are $\phi = -77°$, $\theta = 160°$, and $\chi = 63°$. The corresponding values in the (1 → 6)-β-linked disaccharide, gentiobiose [19], are $\phi = -58.3°$, $\theta = -156.3°$, and $\chi = -61.5°$. So far, gentiobiose was the only example which provided the conformation about (1 → 6)-β-linkage in the solid state. The angle ϕ is influenced by the exo-anomeric effect, and θ is nearly *trans* in both cases. The conformations defining χ in the present study and gentiobiose are *gauche–trans* and *gauche–gauche*, respectively. In this terminology [33], angle O-5–C-5–C-6–O-1 is stated first, and C-4–C-5–C-6–O-1 second. For glucopyranose rings, in general, the orientations for χ are equally distributed between *gauche–gauche* and *gauche–trans* [34]. The glycosidic bond angle C-1–O-1–C-6 (113.5°) is similar to that of gentiobiose [19].

The primary acetate groups on both the reducing and (1 → 6)-β-linked residues exist in a *gauche–trans* conformation. On the other hand, the torsional angles ω (C-5–C-6–O-6–CA-6) are 169° and −117° for reducing and (1 → 6)-β-linked residue, respectively. The latter being a very rare observation for the primary acetate groups with a *gauche–trans* conformation. Similar conformation has been found in octa-*O*-acetyl α-laminarabiose [17]. On the other hand, the primary acetate group on the nonreducing residue corresponds to a *gauche–gauche* type orientation, and the angle ω is 165°. Although the conformations of the three primary acetate groups are different from each other, all of them belong to the theoretically predicted range of the orientations in the glucopyranose ring [35].

The secondary acetate groups take an orientation in which the carbonyl oxygen atom nearly eclipses the axial hydrogen atom at the corresponding ring carbon atom. The absolute values of these torsion angles are in the range of 1–31°

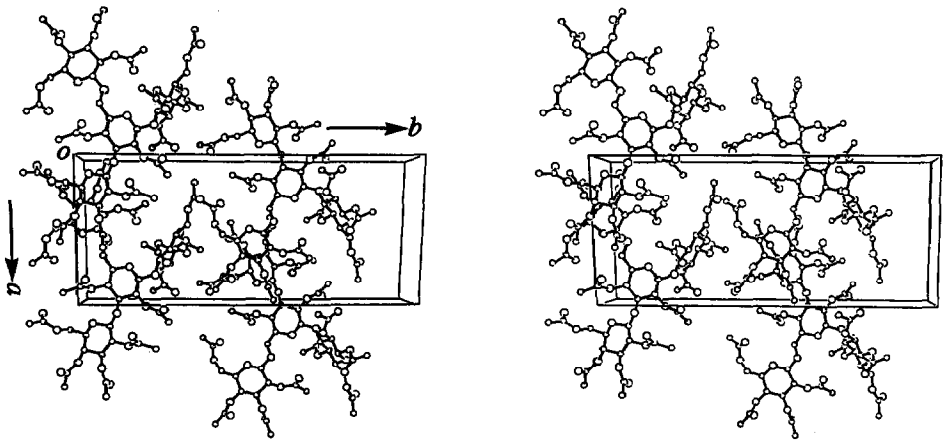

Fig. 3. Packing of the molecules (*c*-projection).

(average 17°; since several hydrogen atoms could not be found in the difference Fourier synthesis, these were fixed at the geometrically expected positions). This range is consistent with those of other acetylated carbohydrates [15–18,26–28].

Molecular packing.—The packing of the molecules in the unit cell is shown in Fig. 3. All the pyranose rings are roughly parallel to the *ab*-plane, except for the reducing residue which is almost perpendicular to the *ab*-plane. The three (1 → 3)-β-linked D-glucose residues are aligned so as to be inclined by ~ 50° to the *b*-axis, and the neighboring molecules are related by 2_1 symmetry along the *b*-axis.

There are no particularly short intermolecular contacts, and the molecules appear to be held together by van der Waals forces, only.

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