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Crystal structure of methyl 3-*O*-β-D-glucopyranosyl-β-D-glucopyranoside (methyl β-D-laminarabioside) monohydrate

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ABSTRACT

Crystals of methyl 3-*O*-β-D-glucopyranosyl-β-D-glucopyranoside (methyl β-D-laminarabioside) belong to the orthorhombic system, space group $P2_12_12$, with $a = 14.548(2)$, $b = 24.252(7)$, $c = 4.938(1)$ Å, and $Z = 4$. The crystal structure was solved by the direct method and refined by the full-matrix least-squares procedure to an R-value of 0.062 for 1099 observed reflections in the X-ray data. The molecular structure is similar to that of β-D-laminarabiose. The torsional angles around the glycosidic bonds are influenced by both the existence of an intramolecular hydrogen bond at O-4′ · · · O-5 and the exo-anomeric effect. In the nonreducing residue, the exocyclic O-5–C-5–C-6–O-6 and C-4–C-5–C-6–O-6 torsional angles are (+)*gauche* and *trans*, respectively, whereas the corresponding torsional angles in the reducing residue are (−)*gauche* and (+)*gauche*. One water molecule cocrystallizes with each disaccharide, and the crystal structure is stabilized mainly by intra- and inter-molecular hydrogen bonds involving water molecules.

INTRODUCTION

Polysaccharides such as curdlan, lentinan, shizophyllan, scleroglucan, and grifolan, contain a main chain of (1 → 3)-linked β-D-glucopyranosyl residues. Except for curdlan, they all have branches at C-6; however, the degree of branching is different in each polymer. Curdlan is a linear polymer almost exclusively composed of (1 → 3)-β-D-glucose residues. Many researchers[1–5] have reported that most of the above polysaccharides have antitumor activities that may be correlated to their molecular structures.

In order to obtain structural information about the intra- and inter-molecular hydrogen bonding schemes, together with the ring and linkage conformations of a (1 → 3)-β-D-glucan, Takeda et al.[6] carried out X-ray structure analyses of 3-*O*-β-

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D-glucopyranosyl-β-D-glucopyranose (β-D-laminarabiose), a disaccharide related to curdlan-type polysaccharides. In this paper, we report the molecular and crystal structure of methyl 3-*O*-β-D-glucopyranosyl-β-D-glucopyranoside (methyl β-D-laminarabioside). The linkage conformation and the molecular packing are compared with those found in other related saccharides.

EXPERIMENTAL

Methyl β-D-laminarabioside was prepared by a method that has been reported elsewhere[7]. Colorless, thin, single, platelets were grown by slow evaporation of a ~70% ethanolic solution. Determination of the unit-cell dimensions and collection of the diffraction intensities were performed on a Rigaku four-circle diffractometer with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). A crystal with dimensions of $0.5 \times 0.2 \times 0.1$ mm^3 was used for the X-ray measurements. The lattice parameters were obtained by a least-squares procedure using 20 reflections with 2θ in the range 45–50°. The intensity data were collected by the ω-scan mode with a scanning rate of 4°/min with an ω-scanning width of $\Delta\omega = (2.0 + 0.14 \tan \theta)°$. Three reference reflections that were measured after every 100 reflections showed no significant intensity deterioration during the data collection. The observed intensities were corrected by a Lorentz-polarization factor. No absorption correction was made. A total of 1662 independent reflections were measured up to $2\theta = 120°$, of which 1099 reflections with F_0 greater than 2σ (F_0) were used in the structure analysis. The density of the crystal was measured by the flotation method using a mixture of carbon tetrachloride and toluene. The observed density (1.425 g/cm^3) suggested the existence of one water molecule for each disaccharide so that the unit cell contains four disaccharide and four water molecules.

Structure analysis.—Consistent with the systematic absences for the $h00$ and $0k0$ reflections when h and k are odd, the space group was assigned to be $P2_12_12$. Crystal data are shown in Table I. The initial positions of 23 of the 24 nonhydrogen atoms in the disaccharide unit were obtained by the direct method with SAPI-85 program[8] for the $P2_12_12$ space group, and the remaining atoms by the weighted Fourier procedure. After several cycles of full-matrix least-squares refinement with isotropic thermal factors, the difference Fourier synthesis revealed the oxygen atom of the water molecule. In the difference Fourier map obtained after several refinement cycles with anisotropic thermal factors, the locations of 22 hydrogen atoms were found. Among the four hydrogen atoms which could not be found, those attached to the methyl carbon and O-4′ oxygen were located at the calculated positions. Further refinement was performed including the hydrogen atoms. The isotropic temperature factor of each hydrogen atom was calculated from the anisotropic temperature factors of the corresponding parent atom at each refinement cycles. One hydrogen atom of the water molecule [H(O-W-A)] was found in the final refinement procedure. The final discrepancy factor (R-value) was 0.062 and the R_w value was 0.059, for all the non-hydrogen atoms with

TABLE I

Crystal data for methyl β-D-laminarabioside

Molecular formula	$C_{13}H_{24}O_{11} \cdot H_2O$
Molecular weight	374.34
Crystal system	orthorhombic
Space group	$P2_12_12$
Z	4
a (Å)	14.548(2)
b (Å)	24.252(7)
c (Å)	4.938(1)
V (Å^3)	1742.4(7)
D_{calcd} (g/cm^3)	1.426
D_{obsd} (g/cm^3)	1.425

anisotropic temperature factors and 25 hydrogen atoms with isotropic temperature factors, for the observed 1099 reflections. The final atomic parameters are given in Tables II and III. 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 (ref. 9). Computations were performed on an A-70 minicomputer with the help of the CRYSTAN program in a RASA-5RII system (Rigaku Corporation).

RESULTS AND DISCUSSION

The molecular structure of methyl β-D-laminarabioside is shown in Fig. 1 together with the atomic numberings.

Bond lengths and angles.—The bond lengths for both nonreducing and reducing residues (Table IV) are in agreement with the previously reported values[6,10–18]. The endocyclic C–C bonds in the nonreducing residue are in the range 1.51 to 1.55 Å with an average of 1.52 Å, and those in the reducing residue are in the range 1.48 to 1.54 Å with an average of 1.52 Å. The C-1–O-5 bond (1.42 Å) is slightly shorter than the C-5–O-5 bond (1.45 Å) in the nonreducing residue, but in the reducing residue, the two are nearly equal (C-1′–O-5′ = 1.44 Å and C-5′–O-5′ = 1.45 Å).

Excluding the bridge C–O bonds, the lengths of the exocyclic C–O bonds range from 1.40 to 1.46 Å with an average of 1.43 Å. At the bridge, the C-1–O-1 bond (1.39 Å) is shorter and the C-3′–O-1 bond (1.46 Å) is slightly longer than the normal C–O bond length. This trend is the same as that in β-D-laminarabiose[6].

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* These data have been deposited with, and may be obtained from, Elsevier Science Publishers B.V., B.B.A. Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/509/*Carbohydr. Res.* 237 (1992) 33–43.

TABLE II

Fractional coordinates and equivalent isotropic temperature factors for nonhydrogen atoms of methyl β-D-laminarabioside, 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	0.3743(6)	0.1587(4)	0.5379(29)	3.95
C-2	0.4694(6)	0.1866(4)	0.4980(28)	3.82
C-3	0.4859(6)	0.2254(4)	0.7327(26)	4.15
C-4	0.4066(6)	0.2657(4)	0.7670(24)	3.55
C-5	0.3171(6)	0.2343(4)	0.7936(28)	3.96
C-6	0.2334(7)	0.2723(5)	0.8009(29)	4.38
C-1′	0.2370(6)	−0.0004(4)	0.0947(25)	4.09
C-2′	0.3089(6)	0.0452(4)	0.1077(27)	3.75
C-3′	0.2907(6)	0.0814(4)	0.3427(27)	3.79
C-4′	0.1923(6)	0.1034(4)	0.3511(28)	3.98
C-5′	0.1232(6)	0.0562(4)	0.3051(32)	4.89
C-6′	0.0264(7)	0.0790(5)	0.2369(33)	4.90
C-M	0.2003(11)	−0.0816(6)	−0.1479(45)	6.75
O-1	0.3562(4)	0.1267(3)	0.3119(16)	3.92
O-2	0.5396(4)	0.1456(3)	0.5015(18)	4.96
O-3	0.5686(5)	0.2570(4)	0.6711(19)	5.10
O-4	0.4178(4)	0.2945(3)	1.0181(18)	4.92
O-5	0.3064(4)	0.2008(3)	0.5529(16)	3.75
O-6	0.1512(4)	0.2400(4)	0.8258(18)	4.89
O-1′	0.2520(5)	−0.0312(3)	−0.1424(19)	5.39
O-2′	0.3949(4)	0.0191(3)	0.1223(23)	6.27
O-4′	0.1673(5)	0.1235(3)	0.6102(20)	5.52
O-5′	0.1480(4)	0.0245(3)	0.0663(17)	4.62
O-6′	0.0271(5)	0.1144(3)	0.0101(20)	5.36
O-W	0.5493(4)	0.0873(3)	0.0026(19)	5.40

The bond angles of methyl β-D-laminarabioside (Table IV) are in agreement with those typically found in carbohydrates[6,10–18]. The endocyclic angles range from 107.7 to 113.4°, with an average value of 110.1°. As in β-D-laminarabiose[6], the C–O–C ring angle is the largest among the endocyclic angles (111.8° in the nonreducing and 111.5° in the reducing residues).

The exocyclic bond angles range widely from 102.8 to 112.8°, with an average value of 108.4°, excluding the angle at the glycosidic oxygen atom. The 10° variation of the exocyclic bond angles may be due to intermolecular interactions, involving hydrogen bonds[6,13–18].

The bond angle C-1–O-1–C-3′ (117.5°) at the bridge oxygen atom is nearly equal to the corresponding angle in β-D-laminarabiose (118.2°)[6]. In other acetylated derivatives, this angle is 116.1° (methyl hepta-*O*-acetyl-β-D-laminarabioside)[10], 113.5° (octa-*O*-acetyl-β-D-laminarabiose)[11], and 113.4° (octa-*O*-acetyl-α-D-laminarabiose)[12]. These values indicate that the glycosidic bond angle may depend on the stereochemical environment, the size of substituent and the degree of substitution, and on the capability of hydrogen bonding.

TABLE III

Fractional coordinate for hydrogen atoms of methyl β-D-laminarabioside, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
H(C-1)	0.384(7)	0.130(5)	0.746(25)
H(C-2)	0.469(7)	0.207(5)	0.292(27)
H(C-3)	0.501(8)	0.202(5)	0.925(25)
H(C-4)	0.407(7)	0.296(4)	0.606(26)
H(C-5)	0.309(7)	0.202(4)	0.981(27)
H(C-6-A)	0.239(9)	0.293(5)	0.945(28)
H(C-6-B)	0.223(8)	0.297(5)	0.610(27)
H(C-1′)	0.242(8)	−0.026(4)	0.313(26)
H(C-2′)	0.298(7)	0.072(5)	−0.039(28)
H(C-3′)	0.305(7)	0.054(4)	0.507(28)
H(C-4′)	0.180(7)	0.137(5)	0.178(26)
H(C-5′)	0.124(8)	0.024(5)	0.482(27)
H(C-6′-A)	0.018(9)	0.099(5)	0.384(28)
H(C-6′-B)	−0.016(8)	0.043(4)	0.183(27)
H(C-M-A)	0.144(9)	−0.074(6)	−0.206(40)
H(C-M-B)	0.215(11)	−0.097(7)	0.014(36)
H(C-M-C)	0.231(8)	−0.105(5)	−0.287(30)
H(O-2)	0.541(8)	0.118(5)	0.391(29)
H(O-3)	0.588(9)	0.259(6)	0.824(33)
H(O-4)	0.467(7)	0.319(5)	1.000(30)
H(O-6)	0.119(9)	0.236(6)	0.697(32)
H(O-2′)	0.436(8)	0.038(5)	0.106(35)
H(O-4′)	0.199(8)	0.152(5)	0.683(33)
H(O-6′)	0.083(8)	0.110(5)	−0.130(30)
H(O-W-A)	0.417	−0.054	0.009

Conformation.—The torsional angles of methyl β-D-laminarabioside and β-D-laminarabiose are given in Table V. The absolute values of the endocyclic angles in the nonreducing residue are in the range 53.6 to 66.5° with an average value of 59.6°, whereas those in the reducing residue are in the range 47.9 to 65.5° with an average value of 56.3°. The angles around the ring C–O bonds are larger than the others. On the other hand, the angles around the C-2–C-3 and C-3–C-4 bonds are smallest in the nonreducing residue and also smaller than the others in the reducing residue. This tendency has been observed in other saccharide molecules and may be due to the larger puckering effect around the C-5–O-5 and C-1–O-5 bonds[6,13–18]. In addition to this tendency, it was observed that the angle around the C-4′–C-5′ bond is nearly equal to that of C-2′–C-3′.

The exocyclic torsional angles around the C-5–C-6 bonds in the β-D-laminarabiose[6] are different from those in the present study. In the case of β-D-laminarabiose, the angle O-5–C-5–C-6–O-6 and C-4–C-5–C-6–O-6 are (+)*gauche* and *trans*, respectively, in both nonreducing and reducing residues (*gauche–trans* conformation). In the present study, those in the nonreducing residue are the same (+)*gauche* and *trans* conformation, while those in the

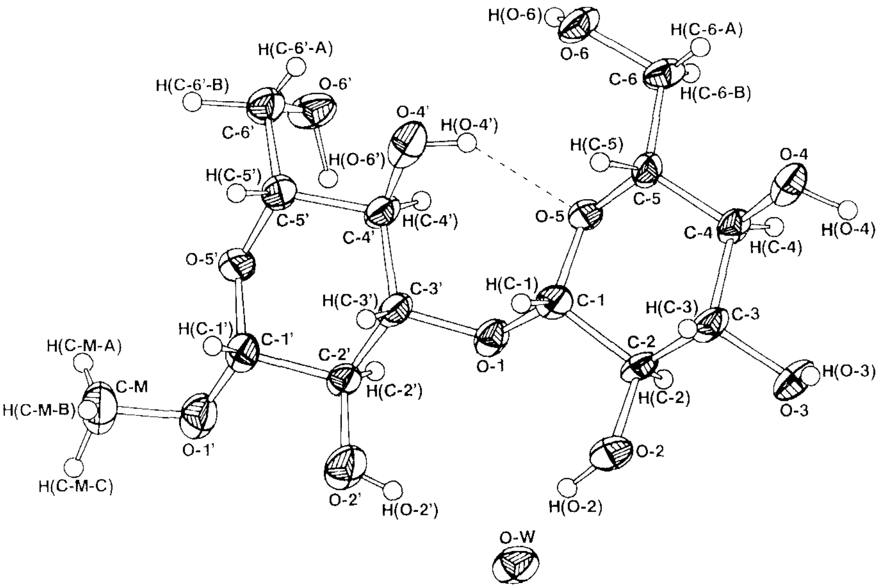

Fig. 1. Molecular structure of methyl β-D-laminarabioside. The 30% probability thermal ellipsoids are shown for carbon and oxygen atoms (ORTEP[26]). The broken line indicates a hydrogen bond.

reducing residue are (−)*gauche* and (+)*gauche* (*gauche–gauche* conformation). The latter may be attributed to the effects of molecular packing and the hydrogen bonding scheme.

Around the glycosidic bonds (Table V), the values of O-5–C-1–O-1–C-3′ (ψ_1)[19] and C-1–O-1–C-3′–C-2′ (ψ_2) are −85.8 and −161.8°, respectively. These are very similar to the corresponding values of −93.6 and −161.0° found in β-D-laminarabiose[6]. Projections of the two pyranose rings of methyl β-D-laminarabioside and β-D-laminarabiose along the pseudo-axis passing through atoms C-1 and C-3′ are shown in Fig. 2. In both disaccharides, pyranose rings have $^{4}C_{1}$ chair conformations in approximately the same orientation. The observed ψ_1 and ψ_2 values in this study are within the low-energy region obtained from the conformational energy calculations for β-D-laminarabiose[20]. Sundaralingam[19] has suggested that (1 → 3)-β-D-linked polysaccharides may exhibit one of two possible intramolecular hydrogen bonds, O-4′ ··· O-5 and O-2′ ··· O-2. In the present study, O-4′ ··· O-5 hydrogen bond (2.77 Å) is observed, which is similar to that seen in β-D-laminarabiose[6].

Among the various compounds with (1 → 3)-β-D-linkage listed in Table VI, the angle ϕ[H(C-1)–C-1–O-1–C-3′][21] varies in a relatively narrow range of 28 to 54° (Table VI). On the contrary, the range for the angle ψ[C-1–O-1–C-3′–H(C-3′)][21] is rather wide (−52 to 14°). In spite of the absence of the intramolecular hydrogen bonds between the O-5 and O-4′ atoms by acetylation, the similar magnitude of the angle ϕ is noteworthy[10–12]. A similar tendency for ϕ was also observed in

TABLE IV

Bond lengths (Å) and bond angles (°) for methyl β-D-laminarabioside, with estimated standard deviations in parentheses

Bond	Length	Bond	Length
C-1–C-2	1.55(1)	C-1′–C-2′	1.52(1)
C-2–C-3	1.51(2)	C-2′–C-3′	1.48(2)
C-3–C-4	1.52(1)	C-3′–C-4′	1.53(1)
C-4–C-5	1.51(1)	C-4′–C-5′	1.54(1)
C-5–C-6	1.53(1)	C-5′–C-6′	1.55(2)
C-1–O-1	1.39(1)	C-1′–O-1′	1.41(1)
C-2–O-2	1.43(1)	C-2′–O-2′	1.40(1)
C-3–O-3	1.46(1)	C-3′–O-1	1.46(1)
C-4–O-4	1.43(1)	C-4′–O-4′	1.43(2)
C-5–O-5	1.45(1)	C-5′–O-5′	1.45(2)
C-1–O-5	1.42(1)	C-1′–O-5′	1.44(1)
C-6–O-6	1.44(1)	C-6′–O-6′	1.41(2)
		C-M–O-1′	1.44(2)

Bond	Angle	Bond	Angle
C-2–C-1–O-1	108.2(10)	C-2′–C-1′–O-1′	108.3(9)
C-2–C-1–O-5	108.2(7)	C-2′–C-1′–O-5′	108.7(7)
O-1–C-1–O-5	108.2(8)	O-1′–C-1′–O-5′	106.4(9)
C-1–C-2–C-3	108.4(9)	C-1′–C-2′–C-3′	109.9(9)
C-1–C-2–O-2	109.4(8)	C-1′–C-2′–O-2′	106.8(8)
C-3–C-2–O-2	108.1(8)	C-3′–C-2′–O-2′	112.8(10)
C-2–C-3–C-4	111.3(8)	C-2′–C-3′–C-4′	113.4(9)
C-2–C-3–O-3	107.3(9)	C-2′–C-3′–O-1	104.3(9)
C-4–C-3–O-3	108.1(8)	C-4′–C-3′–O-1	110.5(8)
C-3–C-4–C-5	109.8(8)	C-3′–C-4′–C-5′	110.3(8)
C-3–C-4–O-4	108.8(8)	C-3′–C-4′–O-4′	112.6(10)
C-5–C-4–O-4	105.6(9)	C-5′–C-4′–O-4′	102.8(9)
C-4–C-5–C-6	112.6(8)	C-4′–C-5′–C-6′	111.1(8)
C-4–C-5–O-5	107.7(9)	C-4′–C-5′–O-5′	110.6(9)
C-6–C-5–O-5	105.8(9)	C-6′–C-5′–O-5′	103.7(11)
C-5–C-6–O-6	109.8(8)	C-5′–C-6′–O-6′	112.5(10)
C-1–O-5–C-5	111.8(8)	C-1′–O-5′–C-5′	111.5(8)
C-1–O-1–C-3′	117.5(8)	C-1′–O-1′–C-M	112.8(11)

three polymorphs of curdlan[22–24]. Perez and Marchessault[25] have pointed out the existence of a conformational bias that restricts rotation around the bond between an anomeric carbon atom and a glycosidic oxygen atom and have related this tendency to the exo-anomeric effect. The angle ϕ is more resistant to the stereochemical environment than the angle ψ, and both of them appear to be influenced by intramolecular hydrogen bonds and the exo-anomeric effect.

It is noteworthy that the angles ϕ and ψ observed in curdlan are similar to those in the acetylated derivatives rather than those in β-D-laminarabiose and this study (Table VI).

The conformation of the methyl group at the reducing end reflects the influence of the exo-anomeric effect[25] (Table V).

TABLE V

Torsional angles (°) of methyl β-D-laminarabioside with estimated standard deviations in parentheses compared with those in β-D-laminarabiose[6]

	Methyl β-D-laminarabioside	β-D-Laminarabiose
Endocyclic		
O-5–C-1–C-2–C-3	58.3(17)	58.1
C-1–C-2–C-3–C-4	−53.6(11)	−56.0
C-2–C-3–C-4–C-5	54.7(12)	54.5
C-3–C-4–C-5–O-5	−58.1(19)	−56.7
C-4–C-5–O-5–C-1	66.4(8)	62.5
C-5–O-5–C-1–C-2	−66.5(16)	−62.3
O-5′–C-1′–C-2′–C-3′	60.2(16)	55.0
C-1′–C-2′–C-3′–C-4′	−52.7(10)	−51.9
C-2′–C-3′–C-4′–C-5′	47.9(17)	52.3
C-3′–C-4′–C-5′–O-5′	−50.3(18)	−56.8
C-4′–C-5′–O-5′–C-1′	61.2(8)	64.4
C-5′–O-5′–C-1′–C-2′	−65.5(14)	−62.5
Exocyclic		
O-5–C-5–C-6–O-6	62.6(14)	63.5
C-4–C-5–C-6–O-6	179.9(16)	−176.7
O-1–C-1–C-2–O-2	−67.2(22)	−66.0
O-2–C-2–C-3–O-3	69.8(11)	65.2
O-3–C-3–C-4–O-4	−72.5(17)	−65.3
O-4–C-4–C-5–C-6	68.5(21)	68.9
O-5′–C-5′–C-6′–O-6′	−62.5(15)	67.0
C-4′–C-5′–C-6′–O-6′	56.3(11)	−174.0
O-1′–C-1′–C-2′–O-2′	−62.1(16)	−60.8
O-2′–C-2′–C-3′–O-1	68.2(10)	63.4
O-1–C-3′–C-4′–O-4′	−81.2(20)	−72.1
O-4′–C-4′–C-5′–C-6′	74.8(23)	65.8
O-5′–C-1′–O-1′–C-M	−75.2(10)	
C-2′–C-1′–O-1′–C-M	168.2(12)	
(1 → 3)-β-linkage		
O-5–C-1–O-1–C-3′ ψ_1	−85.8(11)	−93.6
C-2–C-1–O-1–C-3′ ψ_1'	157.3(10)	148.3
C-1–O-1–C-3′–C-2′ ψ_2	−161.8(10)	−161.0
C-1–O-1–C-3′–C-4′ ψ_2'	76.0(18)	77.7
H(C-1)–C-1–O-1–C-3 ϕ	43.2(51)	27.9
C-1–O-1–C-3′–H(C-3′) ψ	−51.8(72)	−37.5

Molecular packing.—The crystal structure of methyl β-D-laminarabioside (Fig. 3) is stabilized mainly by intramolecular and intermolecular hydrogen bonds involving water molecules (Table VII).

The disaccharide molecules, arranged along the (120) plane are inclined about 30° to the *ab*-plane (Fig. 3b) and are stacked along the *c* axis.

All the hydroxyl groups take part in hydrogen bonding and act as both proton donors and acceptors, except for atom O-4′ which acts only as a proton donor. The atoms O-1, O-1′, and O-5′ do not take part in the hydrogen bonds. In the case of

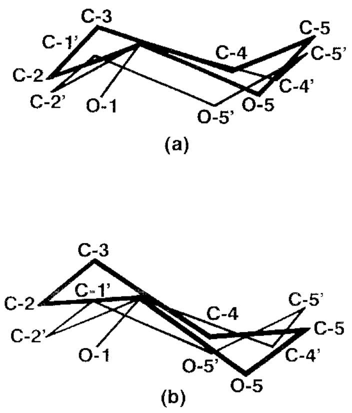

Fig. 2. Projections of (1 → 3)-β-linked pyranose rings along the C-1–C-3' pseudo-axis. Thin and thick lines represent the reducing and nonreducing residue, respectively: (a) methyl β-D-laminarabioside; (b) β-D-laminarabiose.

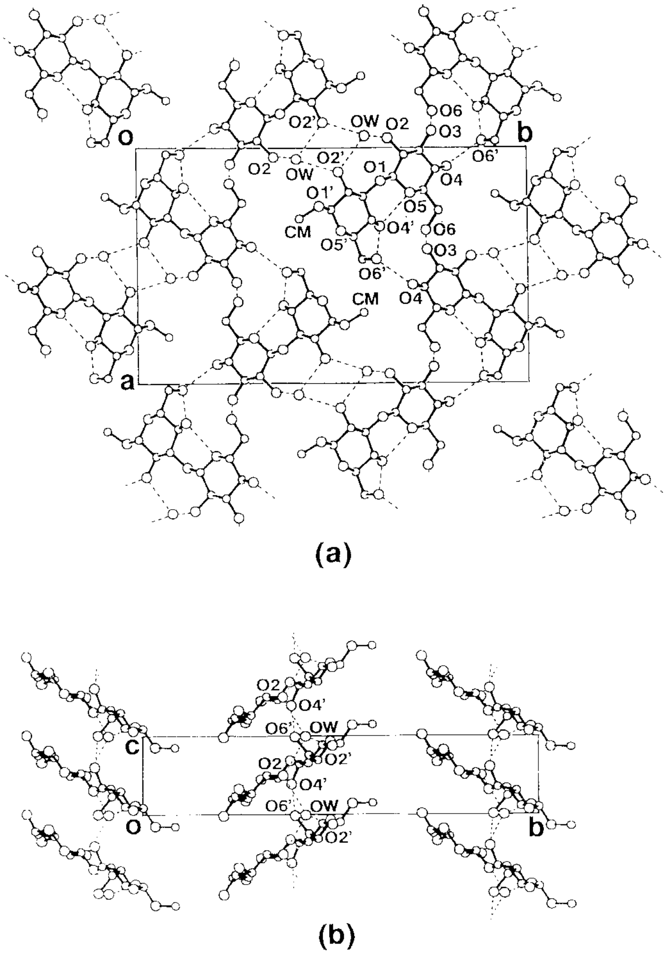

Fig. 3. Crystal structure of methyl β-D-laminarabioside: (a) c projection; (b) a projection; broken lines indicate hydrogen bonds.

TABLE VI

Torsional angles (°) of the glycosidic linkage for (1 → 3)-β-linked disaccharides and polysaccharides

Compound	H(C-1)–C-1–O-1–C-3′ (φ)	C-1–O-1–C-3′–H(C-3′) (ψ)
Methyl β-D-laminarabioside	43	−52
β-D-Laminarabiose[6]	28	−38
Methyl hepta-*O*-acetyl-β-D-laminarabioside[10]	43	5
Octa-*O*-acetyl-β-D-laminarabiose[11]	42	14
Octa-*O*-acetyl-α-D-laminarabiose[12]	54	11
Curdlan form I (ref. 22)	49	6
form II (ref. 23)	35	8
form III (ref. 24)	29	10

β-D-laminarabiose[6], all the oxygen atoms, except for atom O-1, form hydrogen bonds. This difference may be due to the *O*-methylation. Perhaps because of the hydrophobic methyl group, the atoms O-1′ and O-5′ do not participate in hydrogen bonds. Atom O-4 acts only as a proton donor, and, finally, atom O-6′ takes up the previously described *gauche–gauche* conformation in order to avoid a probable short contact with the methyl group (Fig. 3a). Consequently, atom O-6′ participates in the intermolecular hydrogen bonding with atom O-4′. The four water molecules in the unit cell crosslink the disaccharide molecules both as proton donors and acceptors. Three intermolecular hydrogen bonds, O-4–H(O-4) · · · O-6′, O-2′–H(O-2′) · · · O-W and O-W–H(O-W-A) · · · O-2′, connect the disaccharide molecules roughly parallel to the *ab*-plane. The molecules are also linked by the remaining intermolecular hydrogen bonds (Table VII) along the *c*-axis.

TABLE VII

Hydrogen bond distances (Å) and angles (°) in methyl β-D-laminarabioside

	Hydrogen bonds i j k		Distance i-k	Angle ∠ijk
Intramolecular	O-4′–H(O-4′) · · · O-5		2.77(1)	135
Intermolecular [a]	O-3–H(O-3) · · · O-6	a	2.76(1)	173
	O-6–H(O-6) · · · O-3	b	2.73(1)	162
	O-4–H(O-4) · · · O-6′	c	2.73(1)	159
	O-6′–H(O-6′) · · · O-4′	d	2.85(1)	163
Involving water [a]	O-2–H(O-2) · · · O-W		2.84(1)	150
	O-2′–H(O-2′) · · · O-W		2.85(1)	172
	O-W–H(O-W-A) · · · O-2′	e	2.77(1)	155
	O-W–H(O-W-B) · · · O-2	d	2.85(1)	

[a] Symmetry code: a, $1/2+x$, $1/2-y$, $2-z$; b, $-1/2+x$, $1/2-y$, $1-z$; c, $1/2+x$, $1/2-y$, $1-z$; d, x, y, $-1+z$; e, $1-x$, $-y$, z.

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