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THE CRYSTAL AND MOLECULAR STRUCTURE OF METHYL 2,4,6-TRI-*O*-ACETYL-3-*O*-(2,3,4,6-TETRA-*O*-ACETYL-β-D-GLUCOPYRANOSYL)-β-D-GLUCOPYRANOSIDE (METHYL 2,3,4,6,2′,4′,6′,-HEPTA-*O*-ACETYL-β-D-LAMINARABIOSIDE)*

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ABSTRACT

The crystal and molecular structure of methyl 2,3,4,6,2′,4′,6′-hepta-*O*-acetyl-β-laminarabioside has been determined by X-ray diffraction. The crystal belongs to the orthorhombic system, space group $P2_12_12_1$, a 10.471(1), b 22.482(1), c 13.647(1) Å, D_m 1.33 g.cm^{-3}, Z 4. The structure was established by the direct method and refined by the block-diagonal, least-squares procedure to R 0.093 for 2043 observed reflections. Difference synthesis showed all the hydrogen atoms except the methyl hydrogen ones. The molecule shows a fully-extended conformation and has no intra-molecular hydrogen bond. The ring-to-ring conformation can be described. as $(\Phi,\Psi) = (42.5, 4.7°)$, according to the definition of Sathyanarayana and Rao, and it is compared with $(\Phi, \Psi) = (27.9, -37.5°)$ of laminarabiose. There is no inter-molecular hydrogen bond. The D-glucopyranose rings of the molecule are piled up along the a axis and approximately parallel to the bc-plane. Each of the acetyl groups is approximately perpendicular to the D-glucopyranose ring.

INTRODUCTION

In connection with the X-ray structural studies of a β-(1→3)-D-glucan, the X-ray crystal-structure analysis of *O*-β-D-glucopyranosyl-(1→3)-β-D-glucopyranose (β-laminarabiose) has been performed in order to elucidate the intra- and inter-molecular, hydrogen-bonding schemes, and the ring and linkage conformations[2]. As part of a series on laminarabiose, this paper describes the crystal and molecular structure determination of methyl 2,4,6-tri-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (methyl 2,3,4,6,2′,4′,6′-hepta-*O*-acetyl-β-laminarabioside).

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*A preliminary communication has been presented[1].

TABLE I

CRYSTAL DATA

Molecular formula	$C_{27}H_{38}O_{18}$
Molecular weight	650.6
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Cell dimensions (Å)	
a	10.471 (1)
b	22 482 (1)
c	13.647 (1)
Cell volume (Å^3)	3212.6 (1)
Z	4
Density (D_m, g.cm^{-3})	1.33
(D_c, g.cm^{-3})	1 34
μCu$K\alpha$ (cm^{-1})	6.9

EXPERIMENTAL

Methyl 2,3,4,6,2′,4′,6′-hepta-*O*-acetyl-β-laminarabioside was prepared by the method described by Bächli and Percival[3] starting from laminarabiose which was obtained by partial acid hydrolysis of β-(1→3)-D-glucan (polysaccharide 13140). Two types of crystals (m.p. 164.5° and 180°) were obtained from ethanol solution. The high melting-point crystals, which are colorless, very thin, and long tabular, were used for X-ray structure analysis.

Preliminary photographic data showed that the crystal belongs to the orthorhombic system and the space group is $P2_12_12_1$ (systematic absence of reflections, $h00$: $h = 2n + 1$, $0k0$: $k = 2n + 1$, and $00l = 2n + 1$). Accurate unit-cell dimensions were determined by the least-squares fit from 2θ values of 17 high-angle reflections measured on a Rigaku automated, four-circle diffractometer with Ni-filtered Cu-$K\alpha_1$ radiation ($\lambda = 1.5405$ Å). The crystal data are given in Table I.

The intensity data were collected with the same diffractometer by the $\theta - 2\theta$ scan technique on a crystal having the dimensions of 0.2 × 0.12 × 0.12 mm. The integrated intensity of each reflection was measured by scanning over the peak at a rate of 4°/min, and subtracting the background count obtained by averaging the two values measured for 7.5 s at both ends of a scan. The scan width was $\Delta(2\theta) = (2.0 + 0.3 \tan\theta_c)°$, where θ_c denotes the calculated Bragg angle for Cu-$K\alpha_1$ radiation. The starting angle of the scan was $[2\theta_c - \Delta(2\theta)/2]°$. A total of 2305 independent reflections was measured out to a 2θ value of 110°, of which 2043 had intensities larger than the background $[|F| \geqq 3\sigma(F)]$. Four standard reflections were measured after every 60 reflections: their intensities remained constant within ±2% throughout the data collection. Lorentz and polarization corrections were made in the usual way. No absorption correction was made ($\mu = 6.9$ cm^{-1}).

Computations throughout the present study were performed with a NEAC 2200–700 computer at the Osaka University and Figs. 2 and 5 were drawn on a NUMERICON 7000 system with a local version of ORTEP[4].

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by the direct method. A set of 371 *E*'s ($|E| \geq 1.35$) was used with the ASS program (a modified program of MULTAN[5]) to establish the phase relationship. Of the 32 *E*-maps computed, the map corresponding to the largest "figure of merit" (ABS FOM = 1.2135) revealed 19 non-hydrogen atoms*, which located all the non-hydrogen atoms of the two pyranose rings and substituents. The locations of these atoms were refined by two cycles of the block-diagonal, least-squares procedure, the HBLS V program[7] being used. The Fourier map computed at this stage revealed all the remaining non-hydrogen atoms.

The structure was then refined isotropically through seven cycles ($R = 0.17$ for non-zero reflections). The difference Fourier map computed after seven cycles of the anisotropic refinement located 14 hydrogen atoms attached to the D-glucopyranose rings. Hydrogen atoms of the methyl groups, however, could not be located exactly, because of relatively large thermal-motions of the methyl carbon atoms. Two additional cycles of refinement including 14 non-methyl hydrogen atoms gave the final *R* value of 0.093 for observed (0.114 for all) reflections. This high *R* value seems to be due to large thermal-motions of the acetyl groups which do not allow the location of all 24 methyl hydrogen atoms. The function minimized was $\sum w(|F_0| - k|F_c|)^2$, where *k* is a single scale factor, and $w = [\sigma^2(F_0) + a|F_0| + b|F_0|^2]^{-1}$ for $|F_0| \neq 0$, $a = 0.06067$, $b = -0.00072$, and $w = 1.23583$ for $|F_0| = 0$. The atomic scattering factors used for the hydrogen and non-hydrogen atoms were taken from Stewart *et al.*[8] and Cromer and Waber[9], respectively. The final, atomic parameters are listed in Tables II and III**.

RESULTS AND DISCUSSION

The molecular structure of methyl 2,3,4,6,2',4',6'-hepta-*O*-acetyl-β-laminarabioside with the bond lengths and bond angles is given in Fig. 1, and the stereoscopic drawing in Fig. 2. The estimated standard deviation of the bond lengths is 0.015–0.019 and 0.012–0.017 for ring C–C and C–O bonds; and 0.019–0.022, 0.016–0.021, and 0.014–0.018 Å for C–C, C=O, and C–O bonds of acetyl groups, respectively.

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*The phase relationship was redetermined with the MULTAN 74 program[6].

	ABS FOM	PSI ZERO	RESID	COMBINED FOM
Max	1.1419	.3261E + 03	52.62	2.9113
Min	.6672	.2187E + 03	46.20	.9248
Best set of phases	1.1044	.2198E + 03	46.20	2.9113

The *E*-map corresponding to the largest COMBINED FOM revealed 35 non-hydrogen atoms.

**The table of structure-factors is deposited with, and can be obtained from: Elsevier Scientific Publishing Company, BBA Data Deposition P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/068, *Carbohydr. Res.*, 62 (1978) 27–37.

TABLE II

ATOMIC FRACTIONAL COORDINATES, AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) FOR NON-HYDROGEN ATOMS[a]

Atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C-1	7046(10)	2401(4)	5190(7)	93(10)	19(2)	49(6)	4(8)	11(14)	18(5)
C-2	7668(9)	1818(4)	5066(6)	93(9)	24(2)	46(5)	−4(8)	−6(13)	9(6)
C-3	6913(9)	1331(4)	5611(7)	85(9)	20(2)	67(6)	−14(7)	−33(13)	16(6)
C-4	6592(8)	1517(4)	6660(7)	71(8)	21(2)	59(5)	−17(7)	1(12)	23(6)
C-5	6160(9)	2151(4)	6725(7)	92(9)	19(2)	69(6)	−4(8)	4(14)	21(6)
C-6	6037(10)	2350(5)	7773(8)	107(11)	28(3)	61(7)	23(9)	43(15)	−3(7)
O-1	7760(6)	2847(3)	4764(5)	96(6)	20(1)	72(4)	7(5)	22(10)	22(4)
O-2	7636(6)	1657(3)	4026(4)	92(6)	27(2)	53(4)	−9(5)	−1(9)	15(4)
O-3	7722(6)	0809(2)	5608(5)	119(7)	16(1)	60(4)	−15(5)	−9(10)	−2(4)
O-4	5578(6)	1152(3)	7015(5)	98(6)	26(2)	62(4)	3(6)	−4(9)	27(5)
O-5	7034(7)	2525(3)	6207(5)	114(7)	19(1)	59(4)	1(5)	−2(10)	12(4)
O-6	7191(7)	2233(3)	8297(5)	127(8)	28(2)	55(4)	−0(6)	6(11)	9(4)
C-1′	6199(9)	4034(4)	3242(7)	92(9)	25(2)	49(6)	2(7)	33(13)	8(6)
C-2′	6909(9)	3453(4)	3450(7)	112(10)	20(2)	49(5)	21(8)	27(13)	5(6)
C-3′	7105(10)	3382(4)	4559(7)	105(10)	19(2)	59(5)	4(8)	28(13)	12(6)
C-4′	7760(10)	3926(4)	4962(7)	122(11)	19(2)	52(6)	14(9)	3(15)	8(6)
C-5′	7148(9)	4494(4)	4644(7)	103(9)	17(2)	76(6)	5(8)	8(15)	4(6)
C-6′	8011(11)	5031(5)	4915(10)	134(12)	27(3)	122(10)	8(9)	−61(21)	11(8)
O-1′	6058(7)	4101(3)	2269(5)	134(8)	32(2)	54(4)	12(6)	−9(10)	22(5)
O-2′	6119(6)	2986(3)	3119(5)	107(7)	22(2)	76(5)	−7(6)	−16(11)	16(5)
O-4′	7668(7)	3917(3)	6004(5)	125(8)	28(2)	55(4)	11(7)	7(10)	3(4)
O-5′	6992(6)	4512(3)	3588(5)	126(7)	22(1)	76(4)	−9(6)	19(10)	16(4)
O-6′	7216(7)	5546(3)	4962(6)	129(8)	22(2)	82(5)	−10(6)	8(12)	−1(5)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C-2A	8668(10)	1415(5)	3634(8)	131(11)	30(3)	63(7)	4(10)	46(16)	−25(8)
C-2M	8467(14)	1196(6)	2613(8)	210(18)	39(3)	67(7)	39(15)	−22(21)	−18(9)
O-2A	9652(8)	1356(7)	4051(8)	113(8)	96(6)	113(8)	59(12)	−46(14)	−94(12)
C-3A	7203(12)	0290(5)	5460(10)	178(13)	29(3)	80(9)	−34(12)	28(21)	−5(9)
C-3M	8236(16)	−0218(5)	5472(13)	200(21)	15(2)	128(12)	12(13)	46(26)	4(9)
O-3A	6109(10)	0205(4)	5357(10)	228(13)	30(2)	218(12)	−27(10)	−60(23)	−18(9)
C-4A	5849(10)	0689(5)	7631(8)	126(11)	26(3)	67(7)	5(10)	37(16)	30(7)
C-4M	4629(11)	0376(5)	7922(10)	138(12)	27(3)	92(9)	−25(9)	12(19)	18(8)
O-4A	6879(7)	0559(4)	7859(7)	124(8)	47(3)	121(8)	9(8)	−7(13)	89(8)
C-6A	7139(13)	1929(5)	9115(8)	212(16)	30(3)	58(7)	−8(12)	6(21)	11(8)
C-6M	8431(15)	1812(6)	9556(10)	183(19)	44(4)	112(8)	1(15)	−95(22)	29(10)
O-6A	6165(12)	1783(6)	9487(8)	181(16)	79(4)	142(8)	−50(15)	−9(21)	107(11)
C-1′M	5003(10)	4487(6)	2004(10)	112(11)	37(3)	82(9)	30(11)	−47(19)	17(9)
C-2′A	6636(12)	2632(5)	2408(8)	201(15)	23(2)	54(6)	11(11)	−45(18)	29(6)
C-2′M	5600(12)	2165(6)	2098(10)	158(14)	28(3)	113(9)	−28(12)	−62(22)	−16(9)
O-2′A	7659(8)	2658(4)	2110(6)	199(11)	32(2)	76(5)	−18(8)	54(14)	0(5)
C-4′A	8678(13)	3881(5)	6559(8)	207(16)	32(3)	70(6)	58(13)	36(18)	23(8)
C-4′M	8306(15)	3917(8)	7637(8)	200(18)	57(5)	59(7)	55(18)	39(19)	14(10)
O-4′A	9735(8)	3824(6)	6261(7)	125(9)	92(5)	70(6)	33(13)	9(13)	50(10)
C-6′A	7746(14)	6072(6)	4903(8)	187(17)	35(3)	79(7)	−32(13)	−36(21)	25(8)
C-6′M	6942(18)	6565(5)	5070(12)	288(26)	23(2)	100(13)	44(13)	18(26)	−22(9)
O-6′A	8934(10)	6110(4)	4654(9)	193(14)	35(2)	188(10)	−25(10)	−35(22)	42(8)

[a]Expressed in the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + klB_{23} + hlB_{13})]$. Estimated standard deviations in parentheses.

TABLE III

ATOMIC FRACTIONAL COORDINATES OF HYDROGEN ATOMS ($\times 10^3$)[a]

Atom	*x*	*y*	*z*
H(C-1)	609(8)	234(3)	488(6)
H(C-2)	883(10)	180(4)	533(8)
H(C-3)	600(8)	133(3)	524(6)
H(C-4)	735(10)	142(5)	707(8)
H(C-5)	529(8)	216(4)	641(7)
H(C-6-1)	526(9)	212(4)	812(7)
H(C-6-2)	584(10)	282(5)	779(8)
H(C-1′)	544(9)	405(4)	363(7)
H(C-2′)	778(8)	338(4)	318(6)
H(C-3′)	618(8)	336(3)	482(6)
H(C-4′)	874(9)	392(4)	479(7)
H(C-5′)	628(9)	441(4)	502(7)
H(C-6′-1)	846(12)	495(5)	561(9)
H(C-6′-2)	876	510	435

[a] Estimated standard deviations in parentheses.

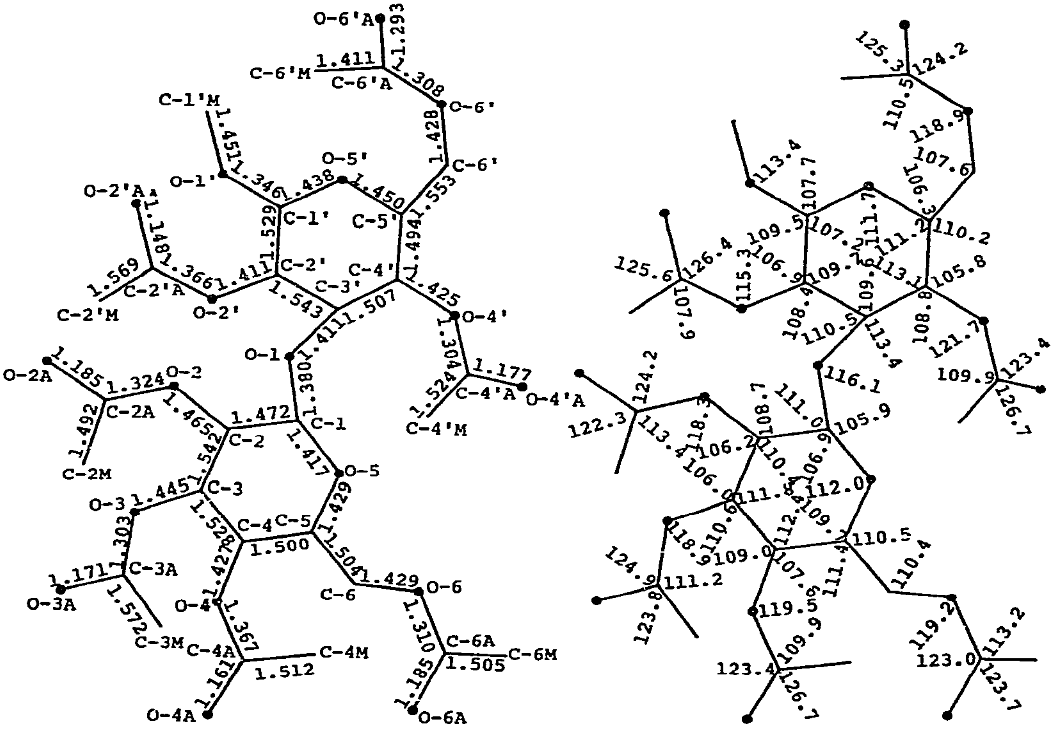

Fig. 1. A schematic drawing of methyl 2,3,4,6,2′,4′,6′-hepta-*O*-acetyl-β-laminarabioside molecule with bond lengths and bond angles. The estimated standard deviation of the bond lengths is 0 015–0.019 and 0 012–0.017 for ring C–C and C–O bonds; and 0.019–0.022, 0.016–0.021, and 0.014–0.018 Å for C–C, C=O, and C–O bonds in acetyl groups, respectively. The estimated standard deviation of the bond angles is 0.8–1.0° for the D-glucopyranose rings and 1.0–1.4° for acetyl groups.

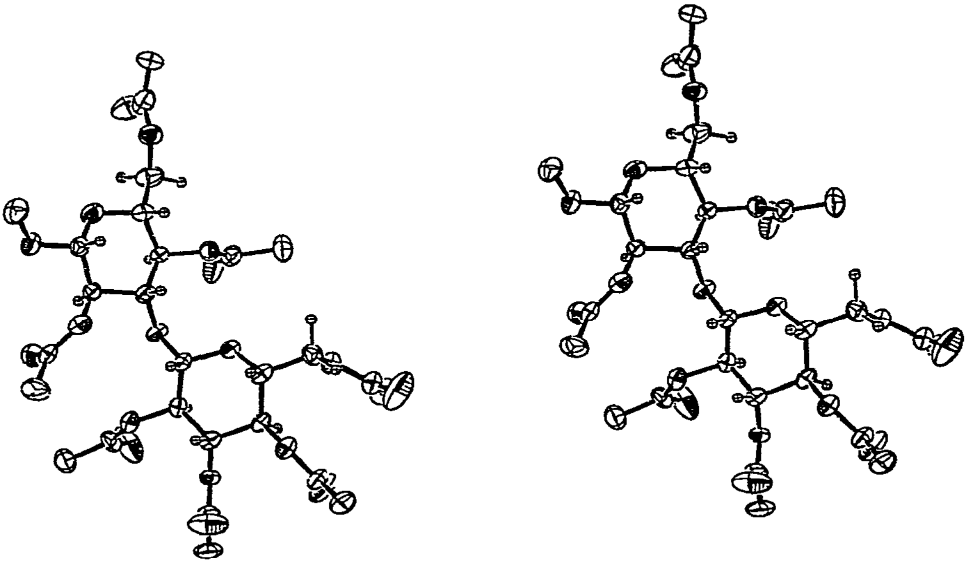

Fig. 2. Stereodrawing of the molecule of methyl 2,3,4,6,2',4',6'-hepta-*O*-acetyl-β-laminarabioside along the *a* axis. The upper ring is the glycosidic residue. Shaded and nonshaded ellipsoids, and small spheres represent oxygen, carbon, and hydrogen atoms, respectively.

The deviation of the bond angles is 0.8–1.0° for the rings and 1.0–1.4° for the acetyl groups.

Bond lengths. — The lengths of the ring C–C bonds are in the range 1.472–1.542 Å (av. 1.511 Å) in the glycosyl group, and 1.494–1.529 Å (av. 1.518 Å) in the glycosidic residue, as compared with 1.495–1.546 Å (av. 1.524 Å) and 1.517–1.548 Å (av. 1.532 Å) in laminarabiose[2], respectively. Similar shortening of the bond was found for β-D-(1→4)-xylobiose hexaacetate[10]: the average ring C–C bond-lengths in the glycosyl group and the glycosidic residue being 1.514 and 1.508 Å, respectively, as compared with 1.520 Å in α-D-xylose[11]. These shortenings, therefore, can be attributed to acetylation.

Most of the exocyclic C–O bond-lengths have normal values falling in the range of 1.411–1.445 Å (av. 1.424 Å), except the C-2–O-2 bond [1.465 (12) Å]. The glucosidic C-1'–O-1' bond-length [1.346(13) Å] is slightly shorter than that of the glucosidic C-1–O-1 bond [1.380(13) Å]; these values being close to those observed for laminarabiose[2] [1.340(10) and 1.387(7) Å, respectively]. The other bridge-bond, C-3'–O-1, looks slightly shorter [1.411(13) Å] than the corresponding one in laminarabiose[2] [1.431(8) Å]. Both the C-3'–O-1 [1.411(13) Å] and C-1–O-1 [1.380(13) Å] bonds appear to be shorter than the normal C–O bond-length.

The C–H bond-lengths are in the range 0.96–1.27 Å (av. 1.06 Å), which is in agreement with the normal values, except the C-2–H(C-2) bond-length [1.27(1) Å].

Bond angles. — In general, the widest of the internal ring-angles in many glycosides is the one involving the ring oxygen-atom[12]. This was also observed for laminarabiose[2]. In the present molecule, however, the widest, internal ring-angle is

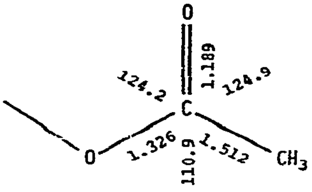

Fig. 3. Average bond lengths (Å) and bond angles (°) of the acetate group.

that involving the C-4 and C-4′ atoms, and the smallest that involving the C-1 and C-1′ atoms (Fig. 1). Other ring angles have normal values. The values of the exocyclic angles show a wide distribution, 105.8–113.4° (av. 108.7°). The glucoside bridge-angle, C-1–O-1–C-3′ is slightly smaller [116.1(8)°] than that in laminarabiose[2] [118.2(5)°]; however, this value is in the normal range for glycosidic angles[12].

The average bond-lengths and bond-angles of acetate groups are given in Fig. 3. These values are slightly smaller than those observed for β-D-(1→4)-xylobiose hexaacetate[10]. They are, however, in good agreement with the normal values observed for other acetate derivatives.

Molecular conformation. — As found for laminarabiose[2], each D-glucopyranosyl ring has the $^4C_1$ chair conformation. A comparison of the torsional angles in the pyranosyl rings with the corresponding angles in laminarabiose[2] is given in Table V.

The values of the intracyclic torsional-angles in the glycosidic residue are in the range 49–65° (av. 57°), whereas those in the glycosyl group ring are in the wider range 42–71° (av. 56°). The torsional angles involving C-2, C-3, and C-4, which are opposite to the ring oxygen atom, are smaller by ~10° than the corresponding angles of laminarabiose. Only the O-5–C-1 torsional angle is larger than the corresponding angle of laminarabiose. This observation suggests that the acetylation resulted in a flattening of the chair conformation of the glycosyl group, such flattening having been observed for 1,2,3,4-tetra-*O*-acetyl-β-D-arabinopyranose[13]. The glycosidic residue also seems to be somewhat flattened. The C-3 and O-5 atoms are displaced by 0.572 and 0.700 Å, respectively, from the least-squares plane defined by C-1, C-2, C-4, and C-5; the corresponding displacements in laminarabiose measure 0.667 and 0.670 Å. On the other hand, the deviations of the C-3′ and O-5′ atoms from the least-squares plane are nearly equal for both disaccharides (0.645 *vs.* 0.649 Å, and 0.680 *vs.* 0.660 Å, respectively).

A marked difference was observed between the exocyclic, torsional angles involving the C-5–C-6 bond in the present disaccharide and those from laminarabiose[2]. The exocyclic C-5–C-6 bond of the present molecule has a (−)*synclinal*[14] conformation, whereas that of laminarabiose has a (+)*synclinal* one. However, both C-5′–C-6′ bonds of the two disaccharides have the same (+)*synclinal* conformation.

Torsional angles involved in the β-D-(1→3)-linkage are also given in Table IV. The C-1–O-1 bonds of both disaccharides have similar orientations, whereas the O-1–C-3′ bonds have different orientations. Pseudotorsional angles involving the C-1–C-3′ axis are also listed in Table IV.

TABLE IV

TORSIONAL ANGLES (°)

Angle	*Present study*	*Laminarabiose*[a]	*Angle*	*Present study*	*Laminarabiose*[a]
Intracyclic					
C-1–C-2	61	58.1	C-1′–C-2′	62	55.1
C-2–C-3	−49	−56.0	C-2′–C-3′	−54	−51.8
C-3–C-4	42	54.5	C-3′–C-4′	49	52.3
C-4–C-5	−49	−57.7	C-4′–C-5′	−52	−56.8
C-5–O-5	65	62.6	C-5′–O-5′	60	64.4
O-5–C-1	−71	−62.3	O-5′–C-1′	−65	−62.5
Exocyclic					
O-5–[C-5–C-6]–O-6	−70	63.5	O-5′–[C-5′–C-6′]–O-6′	82	67.0
C-4–[C-5–C-6]–O-6	53	−176.7	C-4′–[C-5′–C-6′]–O-6′	−158	−174.0
O-1–[C-1–C-2]–O-2	−68	−66.0	O-1′–[C-1′–C-2′]–O-2′	−64	−60.8
O-2–[C-2–C-3]–O-3	73	65.2	O-2′–[C-2′–C-3′]–O-1	64	63.4
O-3–[C-3–C-4]–O-4	−81	−65.3	O-1 –[C-3′–C-4′]–O-4′	−69	−72.1
O-4–[C-4–C-5]–C-6	69	68.9	O-4′–[C-4′–C-5′]–C-6′	72	65.8
Torsional and pseudotorsional angles of the β-D-(1→3)-linkage (°)					
Torsional					
O-5–[C-1–O-1]–C-3′	−84	−93.6			
ψ_1[b]					
C-2–[C-1–O-1]–C-3′					
ψ_1'	161	148.3			
C-1–[O-1–C-3′]–C-2′					
ψ_2	−108	−161.0			
C-1–[O-1–C-3′]–C-4′					
ψ_2'	128	77.7			
H(C-1)–[C-1–O-1]–C-3′					
Φ[c]	43	27.9			
C-1–[O-1–C-3′]–H(C-3′)					
Ψ	5	−37.5			
Pseudotorsional[d]					
O-5–C-1 . . . C-3′–C-2′	−170	121.6			
O-5–C-1 . . . C-3′–C-4′	35	−15.8			
C-2–C-1 . . . C-3′–C-2′	57	−18.9			
C-2–C-1 . . . C-3′–C-4′	−98	−156.3			

[a] Ref. 2. [b] Ref. 15. [c] Ref. 16. [d] Ref. 17.

A projection of the two pyranose rings of the molecule along the pseudo-axis passing through the C-1 and C-3′ atoms is shown in Fig. 4(a). In laminarabiose [Fig. 4(b)] both pyranose rings have approximately the same orientation along the C-1–C-3′ pseudo-axis; in the present acetate derivative [Fig. 4(a)], however, these two rings have entirely different orientations.

It is also possible to describe[16] the ring-to-ring orientation in relation to the β-D-(1→3)-linkage through the dihedral angles Φ and Ψ, which are 43 and 5°,

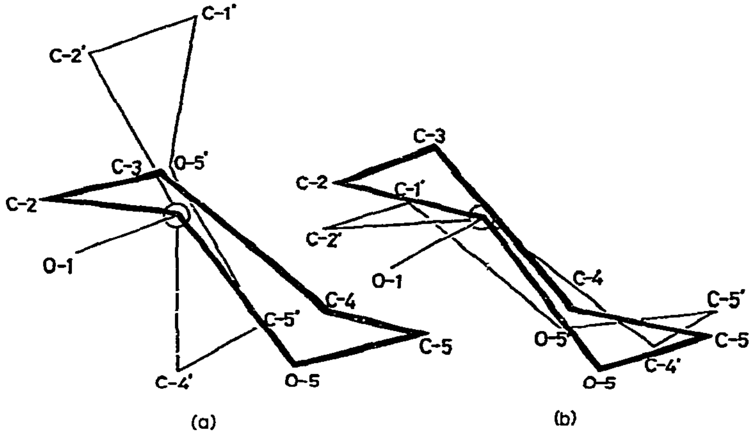

Fig. 4. Projections of β-D-(1 → 3)-linked pyranose rings along the C-1–C-3' pseudo-axis. Thin and thick lines represent the glycosidic residue and glycosyl group, respectively; (a) methyl 2,3,4,6,2',4',6'-hepta-*O*-acetyl-β-laminarabioside, (b) laminarabiose.

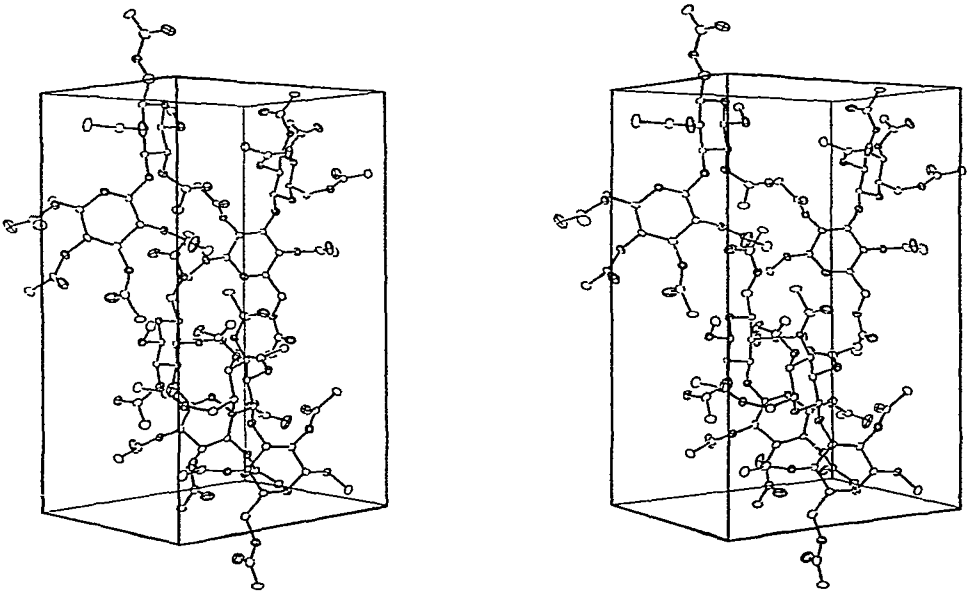

Fig. 5. Stereodrawing of the molecular packing. Each oxygen atom is marked by a cross, and hydrogen atoms are not included.

respectively. Not only are these values different from the corresponding ones of laminarabiose (*Φ* 27.9, *Ψ* −37.5°), but they are also located in a low-energy region different from that of laminarabiose. The latter value is only ~0.5 kcal · mol^{-1} above the global minimum, in the energy contour diagram, for a pair of (1 → 3)-linked β-D-glucose residues. In laminarabiose, an intramolecular hydrogen bond is observed between O-4' and O-5 [2.786(7) Å], and the O-2 · · · O-2' non-bonded distance is

3.920 Å, whereas no hydrogen bond is observed in the present molecule, the nonbonded distance being 3.224 Å for O-4′ · · · O-5 and 3.604 Å for O-2′ · · · O-2. These observations suggest that the β-D-(1→3)-linkage is extended in the present molecule and that the intramolecular hydrogen bond strongly affects the torsion about the bridge bond, and also plays an important role in determining the molecular conformation.

Similar orientations are observed for the acetate groups, except for those at C-6 and C-6′. Each C=O bond is co-planar with respect to the corresponding ring C–H bond. These torsional angles are in the range 2–23° (av. 12°), which is consistent with those of other acetylated pyranose derivatives. The orientation of the substituted groups at C-6, C-6′, and C-1′ is also nearly eclipsed with the corresponding C–H bond [6, 41, and 32°, respectively].

Crystal structure. — A stereoscopic molecular-packing in a unit-cell is illustrated in Fig. 5. Neither hydrogen bonding nor short, intermolecular, atomic contact is found throughout the crystal.

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