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THE CRYSTAL AND MOLECULAR STRUCTURE OF A 3:2 MIXTURE OF LAMINARABIOSE AND *O*-α-D-GLUCOPYRANOSYL-(1 → 3)-β-D-GLUCOPYRANOSE

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ABSTRACT

The crystal and molecular structure of a 3:2 mixture of laminarabiose and 3-*O*-α-D-glucopyranosyl-β-D-glucopyranose has been determined by X-ray diffraction. The crystal belongs to the monoclinic system, space group P2, a 14.778(1), b 4.794(1), c 10.516(1) Å and β 98.10(1)°, Dm 1.54 g.cm^{-3}, Z 2. The structure was solved by the direct method and refined by the block-diagonal, least-squares procedure to R 0.057 for 1034 observed reflections. Difference synthesis showed all hydrogen atoms and indicated a partial (~39%), random substitution of the β anomer molecules by the α anomer molecules, which are accompanied by water molecules on the crystallographic two-fold axis (~19%). The molecule shows a conformation, different from the fully-extended one, which is stabilized by an intramolecular hydrogen-bond between O-4–H and O-5 [2.786(7) Å]. The ring-to-ring conformation can be described as (Φ, Ψ) = (27.9°, −37.5°), according to the definition of Sathyanarayana and Rao, and it is located in the comparatively low-energy region of the energy-contour diagram of laminarabiose. Four intermolecular hydrogen-bonds hold molecules together to form infinite sheets, which are approximately parallel to the ab-plane and linked by additional hydrogen-bonds in the c-direction.

INTRODUCTION

Among the naturally occurring polysaccharides composed of D-glucose residues, little is known about the structure of those having a β-D-(1 → 3) linkage. Recently, Harada and associates[1] have succeeded in producing, in good yield, a curdlan-type polysaccharide with the bacteria *Alcaligenes faecalis var. myxogenes* 10C3K. This polysaccharide is essentially a linear polymer, almost exclusively composed of β-(1 → 3)-linked D-glucose residues.

In connection with X-ray structural studies of the polymeric (1 → 3)-β-D-glucan, we have undertaken the X-ray crystal structure analysis of *O*-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranose (laminarabiose) in order to obtain information

about the intra- and inter-molecular hydrogen-bonding schemes and also about the ring and linkage conformations.

EXPERIMENTAL

Laminarabiose was purified, by charcoal chromatography, from the degradation products obtained by partial acid hydrolysis of the curdlan-type polysaccharide (polysaccharide 13140). Colorless, thin-platelet crystals were grown by slow evaporation of a 90% ethanol solution.

Preliminary photographic data showed that the crystals belong to the monoclinic system. No systematic absence of reflections was observed. The space group was, therefore, determined to be P2 (and not Pm), since the molecule contains asymmetric carbon atoms. Accurate, unit-cell dimensions were determined by the least-squares method from 13 reflections measured on a Rigaku automated, four-circle diffractometer with Ni-filtered CuKα radiation (λ 1.5418 Å). The crystal data are summarized in Table I.

TABLE I

CRYSTAL DATA

Molecular formula	$C_{12}O_{11}H_{22}\cdot 0.19H_2O$
Molecular weight	345.4
Crystal system	monoclinic
Space group	P2
Cell dimensions	a 14.778(1) Å
	b 4.794(1)
	c 10.516(1)
	β 98.10(1)°
Cell volume	737.5 Å^3
	Z 2
Density	D_m 1.54 g cm^{-3}
	D_c 1.555
μ (CuKα)	7.70 cm^{-1}

The intensity data were collected on the single-crystal diffractometer by the ω-scanning, stationary counter-mode. The integrated intensity 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 15 s at both ends of a scan. The ω-scan width was $(2.8+0.15\times\tan\theta_c)°$, where θ_c denotes the calculated Bragg angle for CuKα (λ 1.5418 Å)*. The crystal used had the dimensions of $0.25\times0.13\times0.02$ mm^3. A total of 1247 independent reflections were measured to a 2θ value of 120° (CuKα), of which 1034 had intensities significantly larger than the background [$|F|>3\sigma(F)$]. Of these, 11 reflections, each of which had a very high background on

*This unusually wide scan-width probably resulted from the disorder due to the presence of about 39% of α-anomer molecules in the crystal lattice.

the higher angle-side, were omitted from the structure determination. 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 (μ 7.70 cm^{-1}).

Computations throughout the present study were performed on a NEAC 2200-700 computer and the figures were drawn on a NUMERICON 7000 system with a local version of ORTEP[2].

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by the direct method. A set of 151 E's ($|E| \geqq 1.5$) was used with the MULTAN program[3] to establish the phase relationship. Of the 16 E-maps computed, the map corresponding to the second largest "figure of merit" revealed all the non-hydrogen atoms of the β-laminarabiose in the asymmetric unit. These atoms were subjected to the block-diagonal, least-squares refinement[4].

After three cycles of isotropic refinement, the temperature factor of the O-1′ atom was unusually large, suggesting the existence of a disorder due to the presence of a small amount of the α-anomer in the crystal. Re-examination of the Fourier map led to the location of the α-anomeric oxygen atom on the remaining peak at the position expected. A weaker peak on the two-fold axis close to this α-anomeric oxygen atom could also be assigned to the oxygen atom of the water of crystallization. The occupancy parameters of these oxygen atoms, O-1′α, O-1′β, and O-W were determined in the next least-squares cycle by the KRFINE (a local version of RFINE[5]) program independent of the constraints. When the refinement converged, these parameters were 0.385(32), 0.605(25), and 0.191(19) for O-1′α, O-1′β, and O-W, respectively, hence indicating the presence of about 39% of the α anomer accompanied by about 19% of water of crystallization in the crystal structure.

The difference Fourier map computed after 3 cycles of refinement, assuming anisotropic temperature factors for non-hydrogen atoms, except for the disordered oxygen atom, located 18 hydrogen atoms. Hydrogen atoms attached to anomeric oxygen and C-1′ atoms were also found on successive difference maps; however, those of the water of crystallization could not be located. An additional 3-cycle refinement, which included these hydrogen atoms, was performed: the occupancy of each disordered hydrogen atom was taken as equal to that of the heavy atom to which it is attached, and the temperature factor of each hydrogen atom as equal to that of the parent atom. During the refinement, the H(O-3)–O-3 bond length was found to be unusually short, which suggested a disorder of the H(O-3) atom related to the water of crystallization. Two locations of the disordered H(O-3) atom were then included in the refinement.

The final cycles of the refinement gave an R value of 0.057 for observed (0.097 for all) reflections. The function minimized was $\Sigma w(|F_o|-k|F_c|)^2 = 0.056$, where k is a single scale factor, and $w = [\sigma^2(F_o) + a|F_o| + b|F_o|^2]^{-1}$ for $F_o \neq 0$, $w = 0.52$ for $F_o = 0$, $a = -0.017$, and $b = 0.0024$. The atomic scattering factors were taken from

TABLE II

ATOMIC FRACTIONAL COORDINATES AND ANTISOTROPIC 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	1961(3)	6554(12)	6518(5)	16(2)	239(33)	65(5)	−18(15)	15(6)	−42(24)
C-2	1223(3)	7293(14)	7336(5)	18(2)	294(33)	74(6)	12(16)	14(6)	−68(25)
C-3	1552(3)	9523(14)	8283(5)	24(2)	352(35)	68(6)	−3(17)	18(6)	−81(26)
C-4	2440(3)	8630(13)	9114(5)	29(2)	230(31)	54(5)	−11(17)	4(6)	−55(24)
C-5	3142(3)	7812(14)	8218(5)	20(2)	320(36)	74(6)	−33(16)	−0(6)	−80(26)
C-6	4002(3)	6657(16)	8964(5)	25(2)	514(45)	69(6)	−8(18)	25(6)	−81(28)
O-1	1685(2)	4323(9)	5716(3)	23(2)	291(21)	57(4)	−36(10)	23(4)	−69(16)
O-2	0449(2)	8303(9)	6488(4)	22(2)	325(22)	93(4)	23(11)	−8(4)	−66(18)
O-3	0891(2)	10139(12)	9104(4)	29(2)	698(33)	75(4)	89(14)	30(4)	−101(21)
O-4	2774(2)	10987(11)	9860(3)	45(2)	420(26)	59(4)	−33(14)	12(5)	−65(19)
O-5	2769(2)	5656(9)	7353(3)	17(1)	292(21)	66(3)	37(11)	10(4)	−1(16)
O-6	4675(2)	6048(11)	8127(4)	24(2)	416(26)	108(4)	−3(13)	25(4)	−14(20)
C-1′	1685(3)	1655(13)	2388(5)	19(2)	383(40)	67(6)	−5(17)	−10(6)	42(27)
C-2′	1356(3)	2225(14)	3683(5)	14(2)	310(32)	58(5)	27(15)	15(5)	−62(23)
C-3′	2001(3)	4203(13)	4492(5)	21(2)	251(32)	62(5)	−9(15)	29(6)	23(23)
C-4′	3002(3)	3179(15)	4603(5)	12(2)	407(36)	70(6)	−29(16)	8(6)	−27(26)
C-5′	3236(3)	2625(14)	3253(5)	25(2)	322(35)	70(6)	−7(17)	12(6)	4(26)
C-6′	4180(3)	1310(16)	3318(5)	24(3)	482(42)	69(6)	−17(19)	17(6)	−55(30)
O-2′	0466(2)	3376(9)	3516(4)	15(1)	328(22)	102(4)	14(11)	15(4)	−2(18)
O-4′	3626(2)	5251(11)	5165(4)	27(2)	529(30)	86(4)	−72(13)	28(4)	−137(20)
O-5′	2603(2)	0654(10)	2610(3)	22(2)	414(23)	77(4)	−22(12)	21(4)	−72(19)
O-6′	4446(2)	1045(11)	2063(4)	35(2)	454(27)	95(4)	12(14)	53(5)	−38(21)
O-1′β[b]	1123(4)	−178(15)	1716(6)	2.99(12)[c]					
O-1′α[b]	1611(6)	3628(26)	1573(10)	3.44(21)[c]					
O-W[b]	0	5950(50)	0	6.39(46)[c]					

[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. [b]Occupancy parameters of O-1′β, O-1′α, and O-W are 0.01, 0.39, and 0.19, respectively. [c]Isotropic thermal parameters.

TABLE III

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

Atom	*x*	*y*	*z*
H(C-1)	211(4)	836(15)	611(6)
H(C-2)	101(4)	551(17)	778(5)
H(C-3)	169(4)	1129(15)	784(5)
H(C-4)	231(4)	679(14)	967(5)
H(C-5)	337(4)	956(15)	775(6)
H(C-6-1)	390(4)	469(17)	942(6)
H(C-6-2)	416(4)	800(18)	964(6)
H(C-2')	135(4)	49(17)	406(5)
H(C-3')	202(4)	638(16)	407(5)
H(C-4')	305(4)	139(15)	519(5)
H(C-5')	317(4)	464(15)	279(6)
H(C-6'-1)	420(4)	−69(16)	376(5)
H(C-6'-2)	459(4)	260(18)	383(6)
H(O-2)	6(4)	673(15)	639(6)
H(O-4)	291(4)	1074(16)	1055(6)
H(O-6)	478(4)	763(18)	798(6)
H(O-2')	5(4)	203(15)	347(6)
H(O-4')	359(4)	532(18)	595(6)
H(O-6')	466(4)	273(17)	192(6)
Hβ(C-1)a[b]	146(6)	370(20)	176(9)
Hα(C-1')b[b]	121	14	190
H(O-1'α)b[b]	145(10)	340(40)	65(15)
H(O-1'β)a[b]	95(6)	77(27)	114(8)
H(O-3α)b[b]	64	860	963
H(O-3β)a[b]	46	1108	960

[a]Estimated standard deviations in parentheses. The hydrogen atoms of the water of crystallization could not be located, and are therefore omitted from this Table. The temperature factor of each hydrogen atom is fixed equal to the corresponding isotropic factor of the parent atom. [b]Occupancy parameters: a, 0.61; b, 0.39.

Hanson *et al.*[6]. The final, atomic parameters are listed in Tables II and III. The observed and calculated structure-factors are listed in Table IV*.

RESULTS AND DISCUSSION

The molecular structure of laminarabiose is illustrated in Fig. 1 and the stereo drawing in Fig. 2. The bond lengths and bond angles involving carbon and oxygen atoms are given in Table V. The accuracy of the present analysis is not as high as those for other carbohydrate molecules[7–15], because of the disorder due to the presence of about 39% of α-anomer molecules in the crystal.

*Table IV 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/052/*Carbohydr. Res.*, 53 (1977) 137–152.

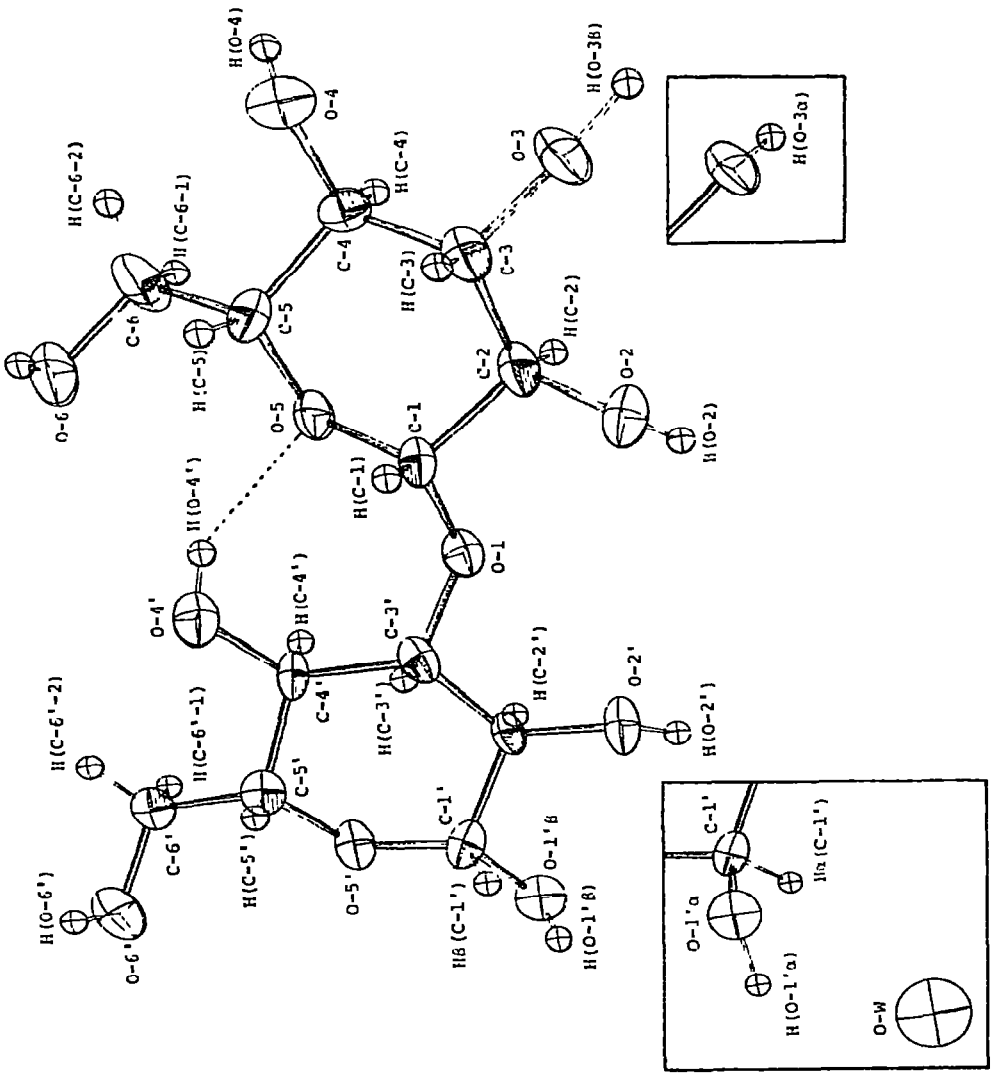

Fig. 1. Molecular structure of luminarabiose. The 50% probability thermal ellipsoids are shown for carbon and oxygen atoms. The hydrogen atoms are represented by the temperature factor 0.75 Å^2. Atoms that are related to the α-anomer molecule and include water of crystallization are shown in squares.

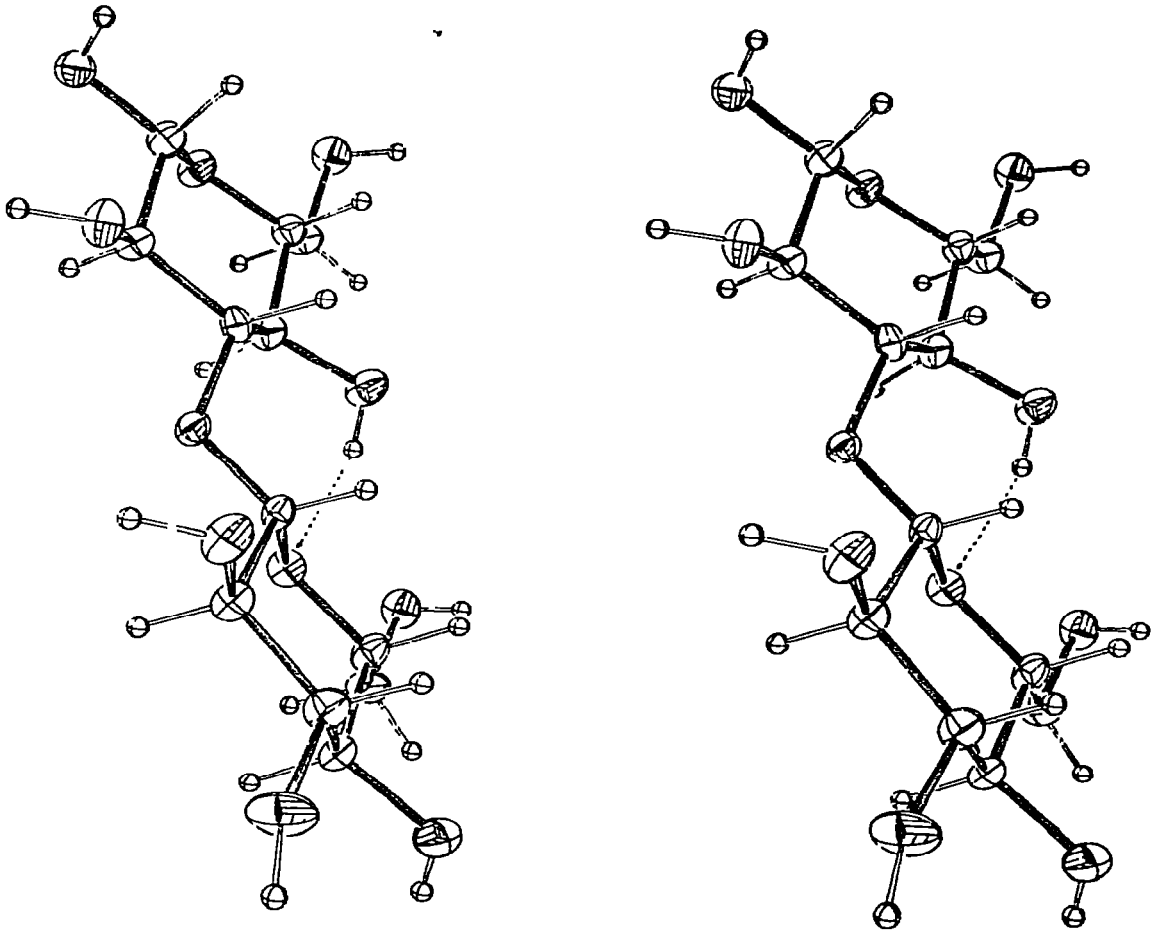

Fig. 2 Stereodrawing of a β-laminarabiose molecule. The upper ring is the reducing D-glucose residue. Shaded and non-shaded ellipsoids, and small spheres represent oxygen, carbon, and hydrogen atoms, respectively. The intramolecular hydrogen bond is shown by a broken line.

Bond lengths. — The bond lengths for both D-glucose residues are all in agreement with the values reported in accurately determined pyranosides[7–15]. The length of the ring C–C bonds is in the range 1.495–1.546 Å (average 1.524 Å) for the reducing residue, and 1.517–1.548 Å (average 1.532 Å) for the nonreducing residue. Although the difference between the two average values is less than 1σ, it is of interest to compare these values with those for cellobiose[12] (1.530 and 1.522 Å for the average, ring C–C bond-lengths for the reducing and nonreducing residues, respectively).

The exocyclic C-5–C-6 bond is slightly shorter than the average, ring C–C bond, and this shortening of the C-5–C-6 bond associated with D-glucopyranose rings has been pointed out by Ham and Williams[16].

TABLE V

BOND LENGTHS AND BOND ANGLES OF NON-HYDROGEN ATOMS[a]

Bond length (Å)		*Bond length* (Å)	
C-1–C-2	1.524(9)	C-1′–C-2′	1.533(9)
C-2–C-3	1.495(9)	C-2′–C-3′	1.517(9)
C-3–C-4	1.531(9)	C-3′–C-4′	1.548(9)
C-4–C-5	1.546(9)	C-4′–C-5′	1.531(10)
C-5–C-6	1.502(10)	C-5′–C-6′	1.524(10)
C-1–O-1	1.387(7)	C-1′–O-1′α	1.271(14)
		C-1′–O-1′β	1.340(10)
C-2–O-2	1.432(8)	C-2′–O-2′	1.415(8)
C-3–O-3	1.424(9)	C-3′–O-1	1.431(7)
C-4–O-4	1.423(8)	C-4′–O-4′	1.426(9)
C-5–O-5	1.435(8)	C-5′–O-5′	1.431(8)
C-1–O-5	1.445(7)	C-1′–O-5′	1.428(8)
C-6–O-6	1.447(9)	C-6′–O-6′	1.435(9)

Bond angle (°)				*Bond angle* (°)			
i	*j*	*k*	<(*ijk*)	*i*	*j*	*k*	<(*ijk*)
C-2	C-1	O-1	110.5(5)	C-2′	C-1′	O-1′β	109.6(6)
C-2	C-1	O-5	108.8(5)	C-2′	C-1′	O-1′α	117.3(8)
O-1	C-1	O-5	106.7(4)	C-2′	C-1′	O-5′	109.1(5)
C-1	C-2	C-3	110.5(5)	O-5′	C-1′	O-1′β	111.7(6)
C-1	C-2	O-2	107.4(5)	O-5′	C-1′	O-1′α	110.5(7)
C-3	C-2	O-2	109.3(5)	C-1′	C-2′	C-3′	110.9(5)
C-2	C-3	C-4	110.7(5)	C-1′	C-2′	O-2′	111.4(5)
C-2	C-3	O-3	111.4(5)	C-3′	C-2′	O-2′	109.0(5)
C-4	C-3	O-3	108.5(5)	C-2′	C-3′	C-4′	111.2(5)
C-3	C-4	C-5	108.5(5)	C-2′	C-3′	O-1	105.7(5)
C-3	C-4	O-4	107.2(5)	C-4′	C-3′	O-1	112.0(5)
C-5	C-4	O-4	109.1(5)	C-3′	C-4′	C-5′	108.9(6)
C-4	C-5	C-6	111.5(6)	C-3′	C-4′	O-4′	111.5(6)
C-4	C-5	O-5	109.8(5)	C-5′	C-4′	O-4′	106.7(6)
C-6	C-5	O-5	106.7(5)	C-4′	C-5′	C-6′	110.8(6)
C-5	C-6	O-6	111.1(6)	C-4′	C-5′	O-5	109.6(6)
C-1	O-5	C-5	112.5(5)	C-6′	C-5′	O-5′	106.3(6)
C-1	O-1	C-3′	118.2(5)	C-5′	C-6′	O-6′	111.3(6)
				C-1′	O-5′	C-5′	113.5(5)

[a]Estimated standard deviations in parentheses.

The C-1–O-5 bond of the nonreducing residue [1.445(4) Å] is slightly longer than the C-5–O-5 [1.435(8) Å] bond, although the difference is not significant. In the reducing residue, the corresponding bond-lengths C-1′–O-5′ [1.428(8) Å] and C-5′–O-5′ [1.431(8) Å] are found to be equal. However, the reverse observation was made for the nonreducing residue in cellobiose[12], C-1–O-5 [1.425(4) Å]<C-5–O-5 [1.436(4) Å]. In the reducing residue, the C-1′–O-5′ bond [1.435(4) Å] is equal to the C-5′–O-5′ bond [1.437(4) Å].

Excluding the anomeric and bridge C–O bonds, the exocyclic C–O bond-lengths have normal values falling in the range 1.415–1.432 Å (average 1.424 Å). The C-1′–O-1′β bond-length [1.340(10 Å] was found to be shorter, and the anomeric C-1′–O-1′α bond shorter still [1.271(14) Å]. The same relationship was observed for the structure of α-lactose monohydrate[10] in which the α anomer coexists with about 7% of β anomer.

The bond-lengths of the bridge C-3′–O-1 and C-1–O-1 are 1.431(7) and 1.387(7) Å, respectively, which are slightly shorter than the corresponding bonds in cellobiose[12]. These values are shorter than the normal C–O bond-length.

The C–H bond-lengths are in the range 0.92–1.19 Å (average 1.05 Å), and the O–H bonds in the range 0.73–1.02 Å (average 0.88 Å), in agreement with the normal values.

Bond angles. — No unusual deviations from the values typically found in carbohydrates[7–15] were observed for the internal, ring angles. The largest deviations were for angles involving the ring-oxygen atoms. The exocyclic angles show a wide range, from 105.7 to 111.7°. The pairs of exocyclic angles of the ring atoms are, in general, unequal, the greatest difference occurring at C-3′. The C-4–C-3′–O-1 angle is larger than the C-2′–C-3′–O-1 angle; it may be affected to some extent by the intramolecular hydrogen-bond O-4′–H···O-5.

Of particular interest are the bond-angles involving the bridge-oxygen atoms. The value of 118.2° for the C-1–O-1–C-3′ angle is significantly larger than the values of 116.5° and 116.1° for the β-(1 → 4)-linked disaccharides of β-lactose[15] and cellobiose[12], respectively, and slightly smaller than the mean value of 119.1° for cyclohexaamylose[17]. Depending on the type of linkage, either β-D-(1 → 3) or β-D-(1 → 4), the bridge, valency angle varies somewhat from the mean value.

Molecular conformation. — The torsional angles of the nonreducing residue vary from 54.5° to 62.5° (average 58.4°) and from 51.9° to 64.4° (average 57.2°) in the reducing residue (see Table VI). The torsional angle adjacent to the ring C–O bonds are generally the largest, whereas those adjacent to the C-2–C-3, C-3–C-4, C-2′–C-3′, and C-3′–C-4′ bonds, which are opposite to the ring C–O bonds, are the smallest. This may be due to the smaller puckering effect near the C-5–O-5 and C-1–O-5 bonds. The exocyclic torsional angles adjacent to the C-5′–C-6′ and C-3′–C-4′ bonds in the reducing residue are considerably larger than the corresponding ones in the nonreducing residue. Both exocyclic C-5–C-6 and C-5′–C-6′ bonds have the (+)*synclinal* conformation.

The conformational twist along the bridge bonds C-1–O-1 and O-1–C-3′ is of particular interest. The two pyranose rings are roughly parallel, the dihedral angle between their least-squares planes being 16.4°. The values of the dihedral angles (Φ and Ψ) describing the ring-to-ring conformation[19], which correspond to the torsional angles H(C-1)–[C-1–O-1]–C-3′ and C-1–[O-1–C-3′]–H(C-3′), respectively, are 27.9° and −37.5°. It is noteworthy that the observed values [(Φ, Ψ) ≃ (28°, −38°)] are clearly in a low-energy region that is only ~0.5 kcal/mol above the global

TABLE VI

TORSIONAL ANGLES

Intracyclic torsional angles (°)			
C-1⟶C-2	58.1	C-1′⟶C-2′	55.0
C-2⟶C-3	−56.0	C-2′⟶C-3′	−51.9
C-3⟶C-4	54.5	C-3′⟶C-4′	52.3
C-4⟶C-5	−56.7	C-4′⟶C-5′	−56.8
C-5⟶O-5	62.5	C-5′⟶O-5′	64.4
O-5⟶C-1	−62.3	O-5′⟶C-1′	−62.5
Exocyclic torsional angles (°)			
O-5–[C-5–C-6]–O-6	63.5	O-5′–[C-5′–C-6′]–O-6′	67.0
C-4–[C-5–C-6]–O-6	−176.7	C-4′–[C-5′–C-6′]–O-6′	−174.0
O-1–[C-1–C-2]–O-2	−66.0	O-1′*β*–[C-1′–C-2′]–O-2′	−60.8
O-2–[C-2–C-3]–O-3	65.2	O-2′–[C-2′–C-3′]–O-1	63.4
O-3–[C-3–C-4]–O-4	−65.3	O-1–[C-3′–C-4′]–O-4′	−72.1
O-4–[C-4–C-5]–C-6	68.9	O-4′–[C-4′–C-5′]–C-6′	65.8
Torsional and pseudotorsional angles of the β-D-(1→3) linkage (°)			
Torsional angles			
O-5–[C-1–O-1]–C-3′	−93.6	ψ_1[a]	
C-2–[C-1–O-1]–C-3′	148.3	ψ_1'	
C-1–[O-1–C-3′]–C-2′	−161.0	ψ_2	
C-1–[O-1–C-3′]–C-4′	77.7	ψ_2	
H(C-1)–[C-1–O-1]–C-3′	27.9	Φ[b]	
C-1–[O-1–C-3′]–H(C-3′)	−37.5	υ	
Pseudotorsional angles[c]			
O-5–C-1·····C-3′–C-2′	121.6		
O-5–C-1·····C-3′–C-4′	−15.8		
C-2–C-1·····C-3′–C-2′	−18.9		
C-2–C-1·····C-3′–C-4	−156.3		

[a]Ref. 18. [b]Ref. 19. [c]Ref. 21.

minimum in the energy-contour diagram of laminarabiose prepared by Sathyanarayana and Rao[19] as a result of conformational studies of *β*-D-glucans. These results and those for other torsional[18] and pseudotorsional[21] angles (see Table VI) suggest that the intramolecular hydrogen bond (O-4′–H···O-5) strongly affects the conformation of the bridge bond and also plays an important role in determining the molecular conformation.

Molecular packing and hydrogen bonding. — The molecular packing and the hydrogen-bonding schemes are shown in Figs. 3 and 4 and the hydrogen-bond distances and angles listed in Table VII. The molecules are oriented in the cell with the pyranose rings approximately perpendicular to the b axis and with the long axis parallel to the c axis. The molecular packing seems to be determined by the network of hydrogen bonds. All the hydroxyl groups in the asymmetric unit take part in the hydrogen

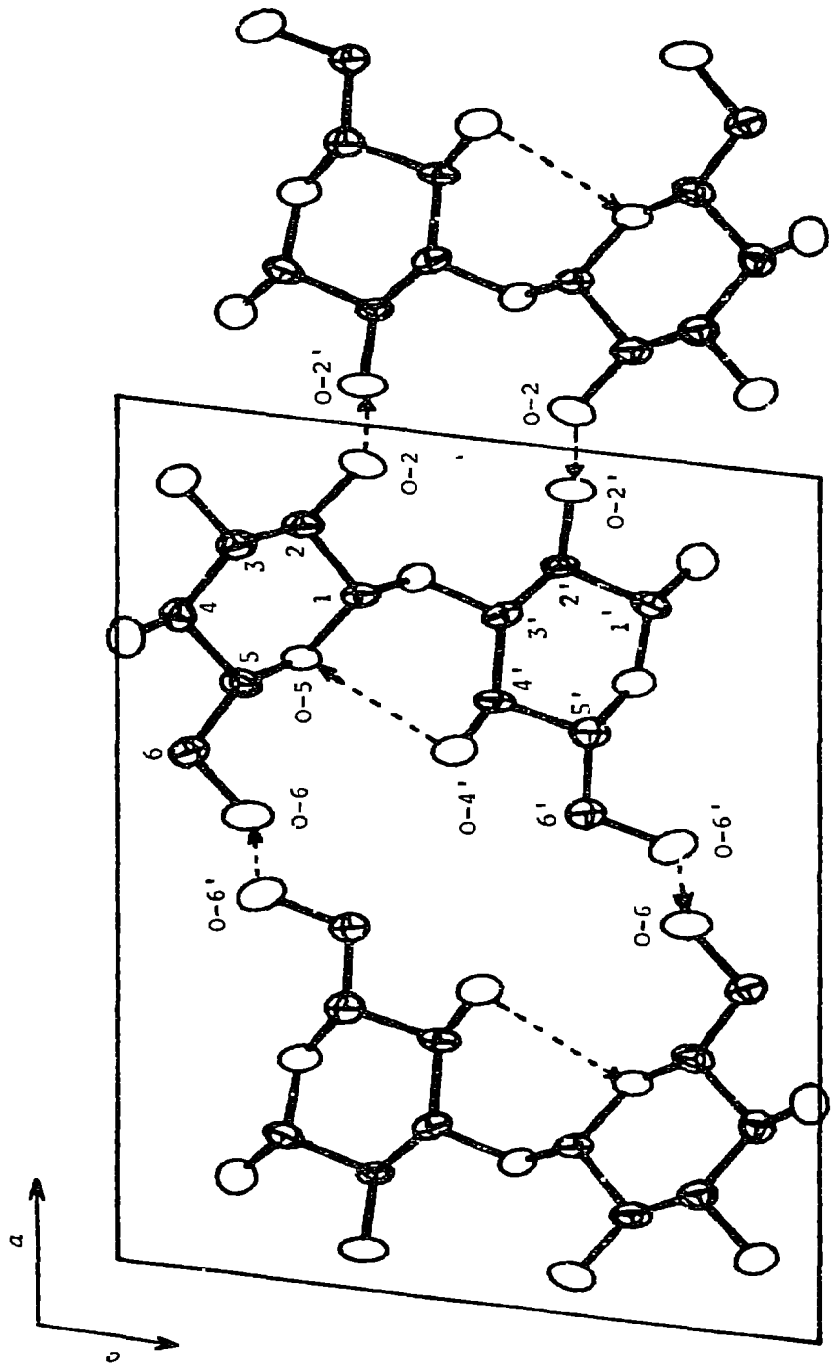

Fig. 3. Molecular packing of β-laminarabiose viewed along the b axis. Hydrogen bonds are shown by broken lines.

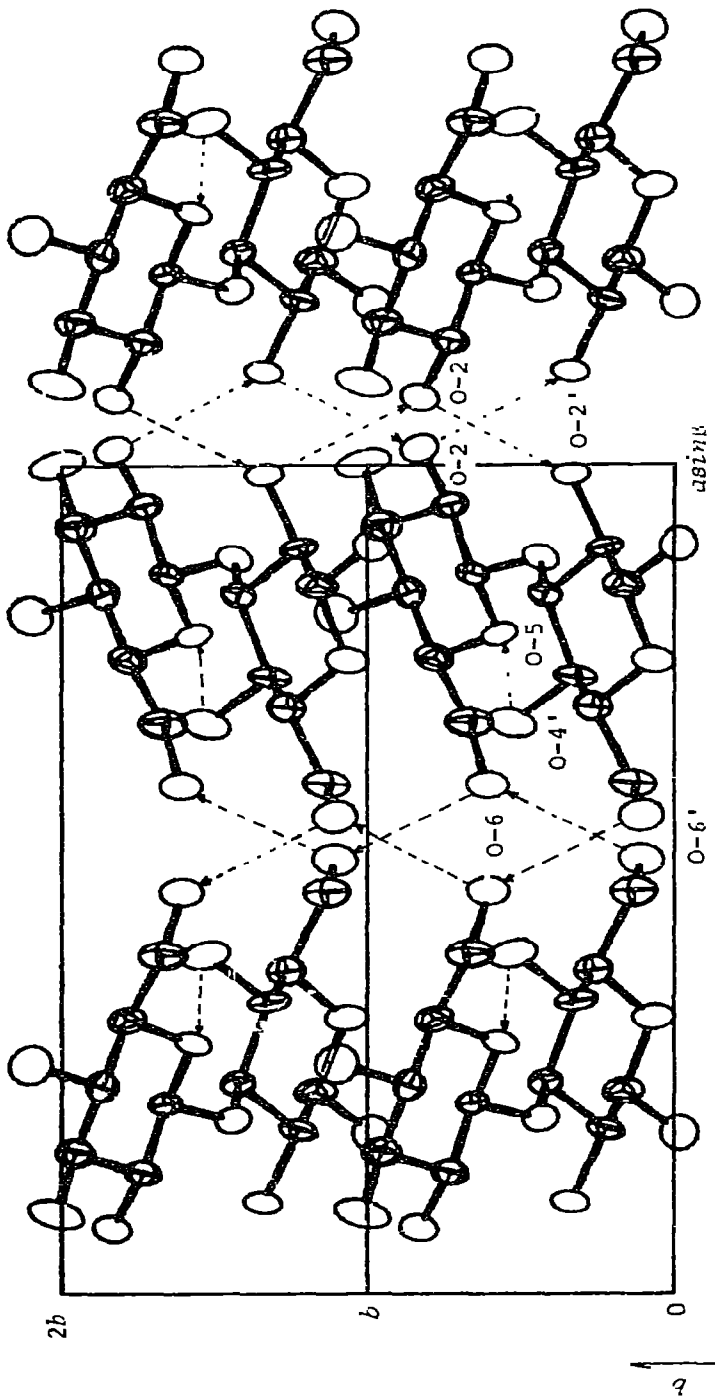

Fig. 4. Molecular packing viewed along the c axis. Hydrogen bonds are shown by broken lines.

bonding, and all the hydroxyl group oxygen atoms, except O-4′, act as both donors and acceptors. The bridge oxygen atom, however, does not take part in the hydrogen bonding.

TABLE VII

HYDROGEN-BOND DISTANCES AND ANGLES

Hydrogen bonds	*Distances and angles*				
	i	*j*	*k*	*i–k* (Å)	$<ijk$ (°)
Intramolecular	O-4′ ——H(O-4′) - - - →	O-5		2.786(7)	147
	[*cf.*O-2′ - - - - -	O-2		3.920(6)]	
Intermolecular[a]	O-6 ——H(O-6) - - - →	O-6′	a	2.746(7)	156
	O-6′ ——H(O-6′) - - - →	O-6	b	2.749(7)	168
	O-2 ——H(O-2) - - - →	O-2′	c	2.721(6)	166
	O-2′ ——H(O-2′) - - - →	O-2	d	2.782(6)	158
	O-4 ——H(O-4) - - - →	O-5′	e	2.943(7)	152
	O-1′β ——H(O-1′β) - - - →	O-3	g	2.723(9)	132
	O-1′β ← - - H(O-3β) ——	O-3	d	2.984(9)	103
Involving the α anomer[b] and water of crystallization[c]	O-W - - - - - - - - - - - →	O-1′α		2.912(28)	
	O-3 ——H(O-3α) - - - →	O-W	f	2.664(26)	160
	O-1′α ——H(O-1′α) - - - →	O-4	g	2.945	107

[a]Symmetry code: a, $1-x$, $1+y$, $1-z$; b, $1-x$, y, $1-z$; c, $-x$, y, $1-z$; d, $-x$, $-1+y$, $1-z$, e, x, $1+y$, $1+z$; f, x, y, $-1+z$; and g, x, $-1+y$, $-1+z$. [b]Occupancy 39%. [c]Occupancy 19%.

The most interesting hydrogen bonding is the intramolecular bond O-4′–H···O-5 [2.786(7) Å]. It has been pointed out that, in β-D-(1 → 3)-linked polysaccharides, of the two possible intramolecular hydrogen bonds O-2′···O-2 and O-4′···O-5 derived by conformational analysis[18], the first one is preferred. In the crystal studied here, however, the second type is found, and the O-2 and O-2′ atoms are engaged in intramolecular hydrogen bonds [the intramolecular length O-2′···O-2 is 3.920(6) Å].

Four major intermolecular hydrogen bonds, O-2–H···O-2′, O-2′–H···O-2, O-6–H···O-6′, and O-6′–H···O-6 link laminarabiose molecules to form infinite sheets, which are piled up roughly parallel to the ab-plane (Fig. 4). These sheets are linked by additional hydrogen bonds, O-4–H···O-5′ and O-1′β–H···O-3, in the c-direction, to form a three-dimensional network.

It is noteworthy that the α anomer accompanied by a water molecule may be accommodated in the lattice with no apparent decrease in the number of hydrogen bonds, the O-3–H···O-W hydrogen bond replacing the O-3···H–O-1′β bond. In addition, although the location of the hydrogen atoms of the water molecule could not be established in the difference Fourier map, the location of the oxygen atom of the water molecule was found within the hydrogen-bond distance from the oxygen atom O-1′α of the hydroxyl group of the neighboring α anomer molecule [O-W···O-1′α

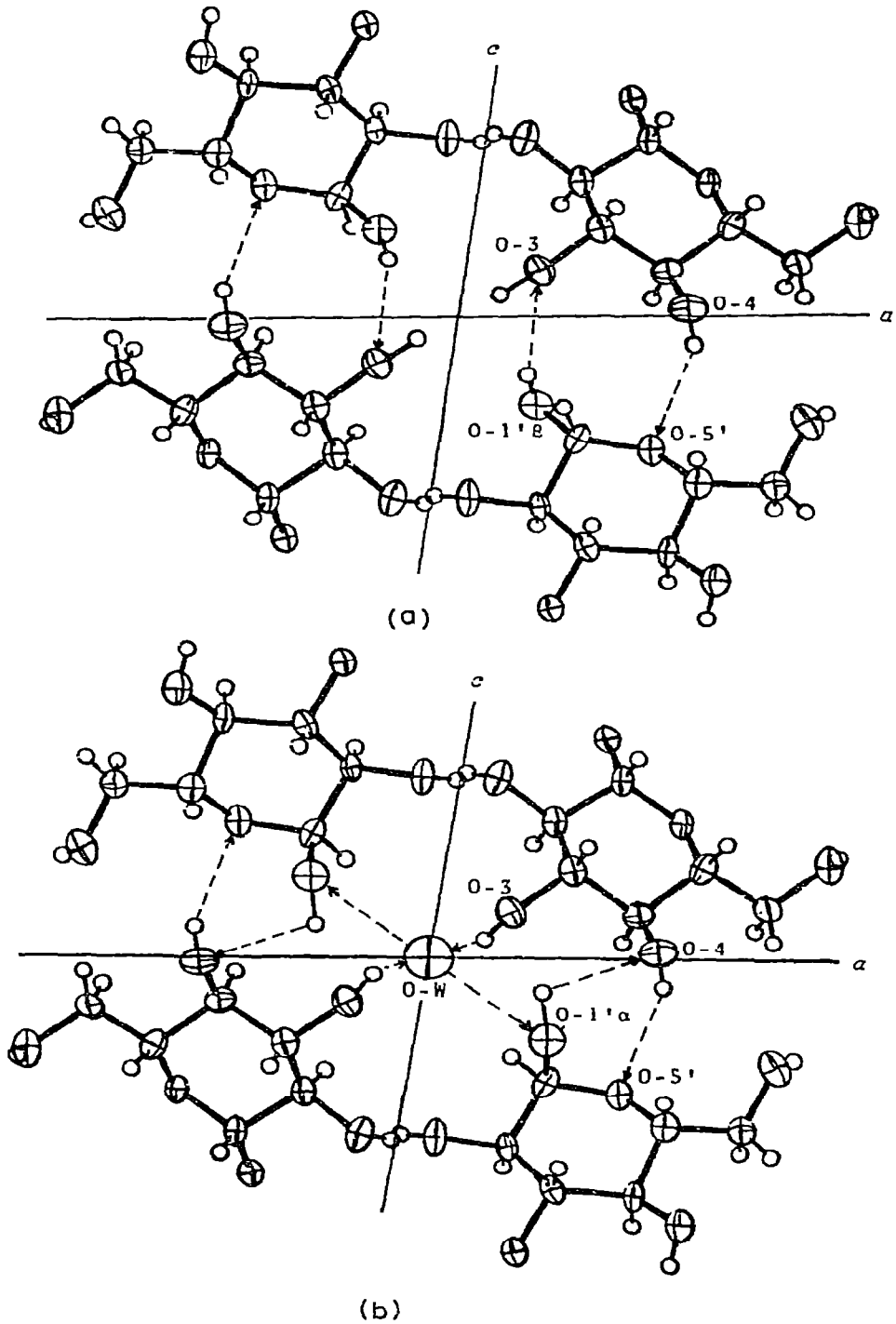

Fig. 5. Hydrogen bonding schemes around the two-fold axis: (a) β anomer; (b) α anomer and water of crystallization (only the oxygen atom is shown).

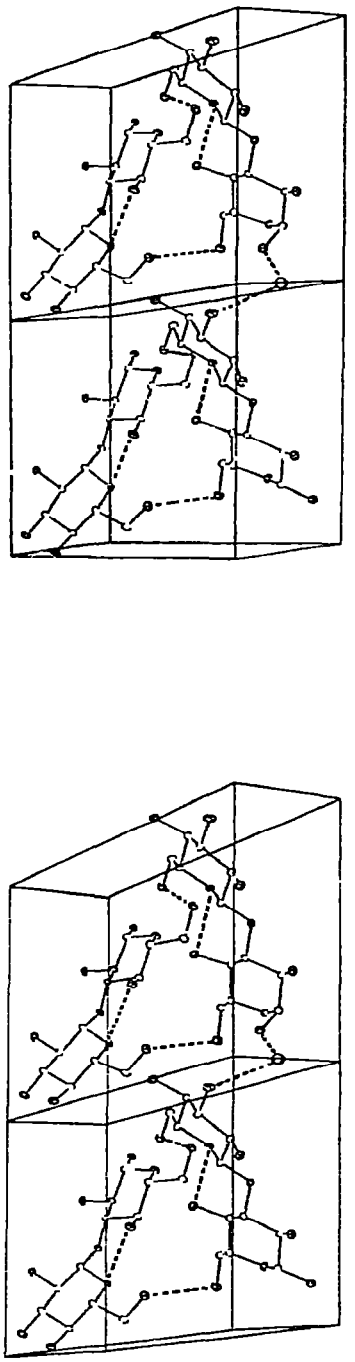

Fig. 6. Stereodrawing of the molecular packing. Four molecules in two unit-cells along the c axis are shown. An α-anomer molecule and water of crystallization (the oxygen atom only) are included in the lower half of the right-hand cell. Hydrogen bonds are shown by broken lines.

= 2.912(28) Å]. The water molecule lies on the two-fold axis and is, therefore, hydrogen-bonded by four different molecules (Fig. 5).

In the packing of molecules that includes the α anomer (see Fig. 6), the large values of $\sigma(y)$, B_{22}, and B_{33} (Table II) can be explained well by the packing disorder.

Ratio of α to β anomer. — The ratio of α to β anomer in the crystal under investigation was determined as 39:61, based on the refined values of the occupancy parameters of the anomeric oxygen atoms. This ratio is in good agreement with those of 43:57 and 2:3 determined by ^{1}H-n.m.r. spectrometry on solutions in deuterium oxide at room temperature and 90°, respectively[20].

The ratios of anomers of other crystalline disaccharides have been determined by X-ray crystal structure analysis, only a small proportion of β anomer being present: they are 93:7, 19:1, and 22:3 for α-lactose monohydrate[10], α-lactose·calcium chloride[22], and lactose·calcium bromide[23], respectively.

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