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THE CRYSTAL AND MOLECULAR STRUCTURE OF *O*-α-D-MANNOPYRANOSYL-(1→3)-*O*-β-D-MANNOPYRANOSYL-(1→4)-2-ACETAMIDO-2-DEOXY-α-D-GLUCOPYRANOSE

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ABSTRACT

The crystal structure of α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-α-D-GlcNAc*p* has been determined by the direct method using the multi-solution, tangent formula, and "magic integer" procedures. The space group is $P2_1$, and 2 molecules are in the unit cell with $a = 9.894$ (5), $b = 10.372$ (6), $c = 11.816$ (6) Å, and $\beta = 95.03°$ (6). The structure was refined to R 0.059 for 2099 reflections measured with Mo Kα radiation. Difference synthesis showed all the hydrogen atoms, and indicated a partial (~30%) substitution of the α-anomer molecules by the β-anomer molecules. The D-mannopyranose and the D-glucopyranose have the normal $^4C_1$ conformation; an intramolecular hydrogen-bond O-3″–H.....O-5′ (2.703 Å) stabilises the GlcNAc in relation to β-D-mannopyranose.

INTRODUCTION

The trisaccharide α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-D-GlcNAc*p* is a sequence found in the common pentasaccharide-core, α-D-Man*p*-(1→3)-[α-D-Man*p*-(1→6)]-β-D-Man*p*-(1→4)-β-D-GlcNAc*p*-(1→4)-β-D-GlcNAc*p*, present in most of the glycans N-glycosylically linked to asparagine[1]. As the spatial conformation of the two "antennae", neuraminyl- (or fucosyl)-*N*-acetyl-lactosamine, or oligomannoside residues conjugated to the pentasaccharide core, depends on the spatial conformation of the oligosaccharide situated at the branching position, we have investigated the spatial conformation of the trisaccharide α-Man*p*-(1→3)-β-Man*p*-(1→4)-GlcNAc*p*. Molecular models suggested the possibility of T- or Y-conformations, according to the orientation of the terminal mannose residue[2].

EXPERIMENTAL

The free trisaccharide, which was first characterised in the urine of patients

TABLE I

CRYSTALLOGRAPHIC DATA (AT 21 °)

Molecular formula $C_{20}H_{35}O_{16}N$; molecular weight 545.49;

Crystal system, monoclinic; space group $P2_1$, $Z = 2$; density D_M 1.50 g.cm^{-3}; λ MoKα, 0.7107 Å;

Cell dimensions: $a = 9.894\,(5)$ Å, $b = 10.372\,(6)$ Å, $c = 11.816\,(6)$ Å, $\beta = 95.03°\,(6)$, V = 1208.8 Å^3.

having mannosidosis[3], was isolated from urine according to the procedure of Strecker *et al.*[4].

From the oligosaccharide (0.2–0.3 g), transparent crystals (0.2 × 0.4 × 0.7 mm^3) of α-Man*p*-(1→3)-β-Man*p*-(1→4)-GlcNAc*p* were obtained by slow concentration of a solution in *p*-dioxane–water.

The crystallographic data are reported in Table I. Intensities for 4246 reflections were collected on an automatic Philips diffractometer, using Mo Kα radiation. A θ–2θ scanning mode with a minimum rate of 1 °/min and with an invariant scan-width of 1.2 was used. Of the recorded data, 2099 reflections were considered, based on a cut-off criterion that the observed intensity I should be $>3\sigma(I)$, where $\sigma(I)$ is the standard deviation in the observed intensity. The data were corrected for the Lorentz and polarisation factor. No absorption and extinction corrections were applied.

STRUCTURE DETERMINATION AND REFINEMENT

The structure could not be solved by straightforward application of the *MULTAN* programme[5]. This programme often gives a fragment of 12 atoms, but the whole molecule could not be obtained by tangent-formula recycling and Fourier methods. A substantialisation technique with *MULTAN* was also applied without success[6]. The structure was solved by the application of "magic integers"[7]; 499 normalised E_{hkl}'s $\geqslant 1.48$ were used with this procedure. From the 50 possible solutions, the 35th highest combined figure of merit gave a clear fragment of 25 out of the 37 non-hydrogen atoms. The classical Fourier-procedure led directly to the solution, which was first refined by the rigid-body, least-squares programme *ORION*[8] with an isotropic thermal factor. After five cycles of isotropic refinement, the temperature factor of the O-1″α atom was unusually large (>10 Å^2), suggesting the existence of a disorder due to the presence of a small amount of the β anomer in the crystal. Re-examination of the Fourier map permitted the β-anomeric oxygen atom to be located on the remaining peak at the position expected. The occupancy parameters of these oxygen atoms, O-1″α and O-1″β were 0.70 (α) and 0.30 (β). The *R* value was then 0.108. At this stage, the positional parameters of the non-hydrogen atoms and the anisotropic thermal factors were refined by the full-matrix, least-squares method to an *R* factor of 0.073. The hydrogen atoms were positioned from difference Fourier

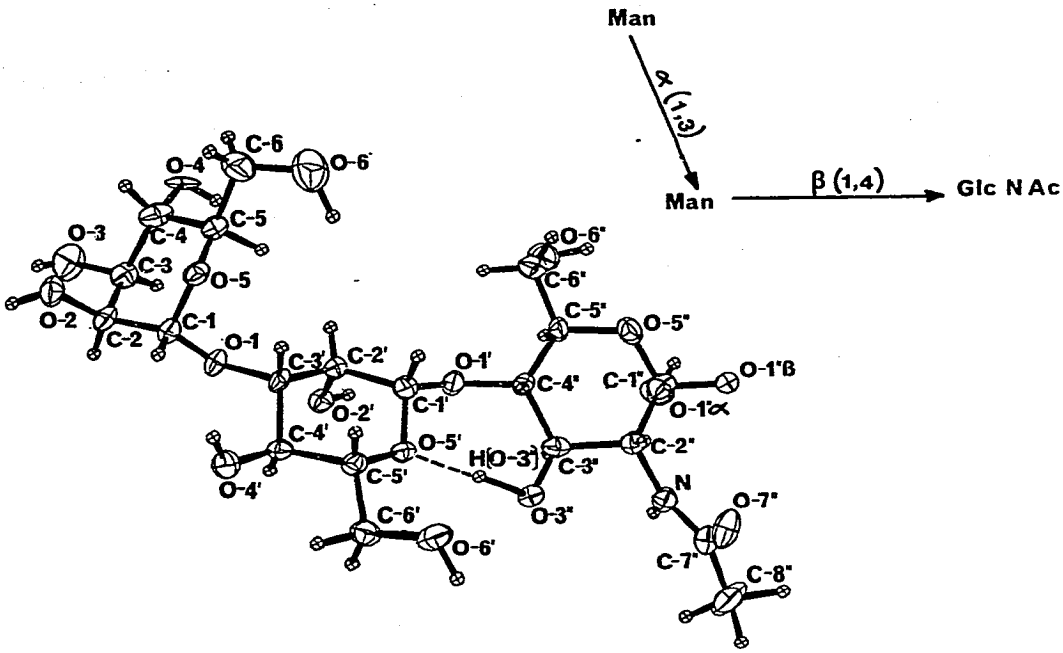


Fig. 1. Molecular conformation and atomic numbering in α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-α/β-D-GlcNAc*p*.

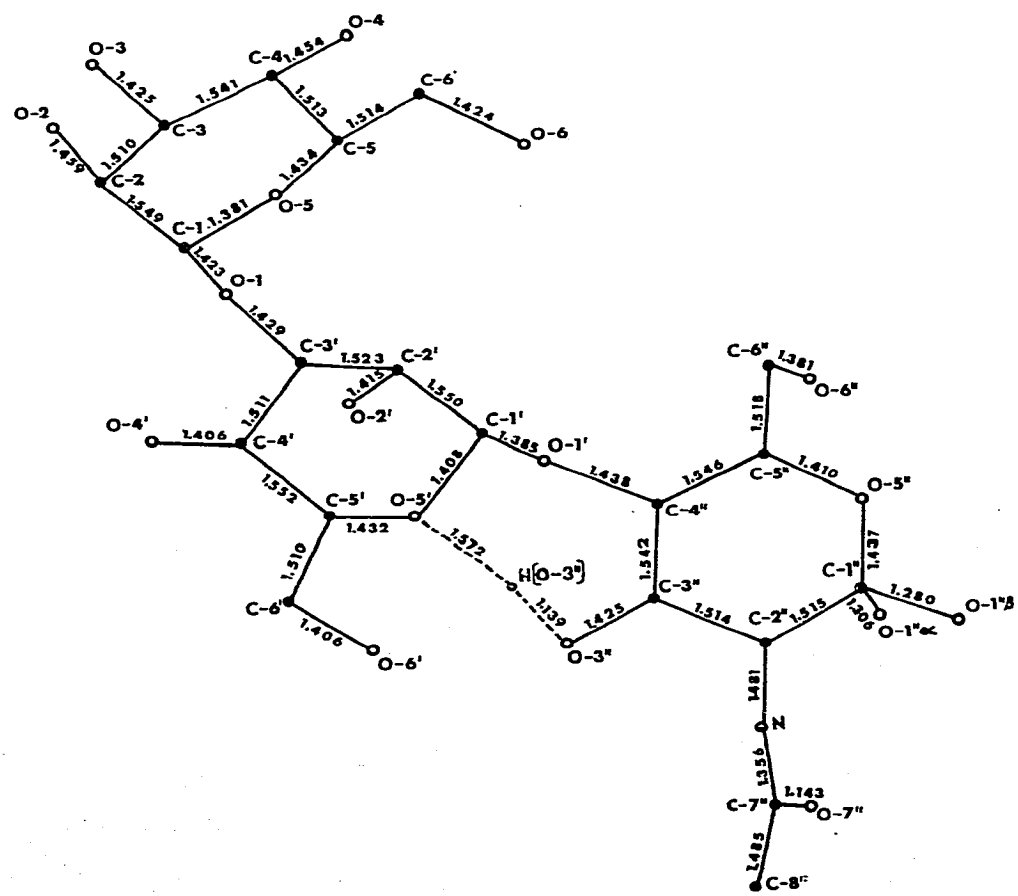


Fig. 2. Intramolecular bond distance (Å) in α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-α/β-D-GlcNAc*p*; average e.s.d. is 0.01 Å.

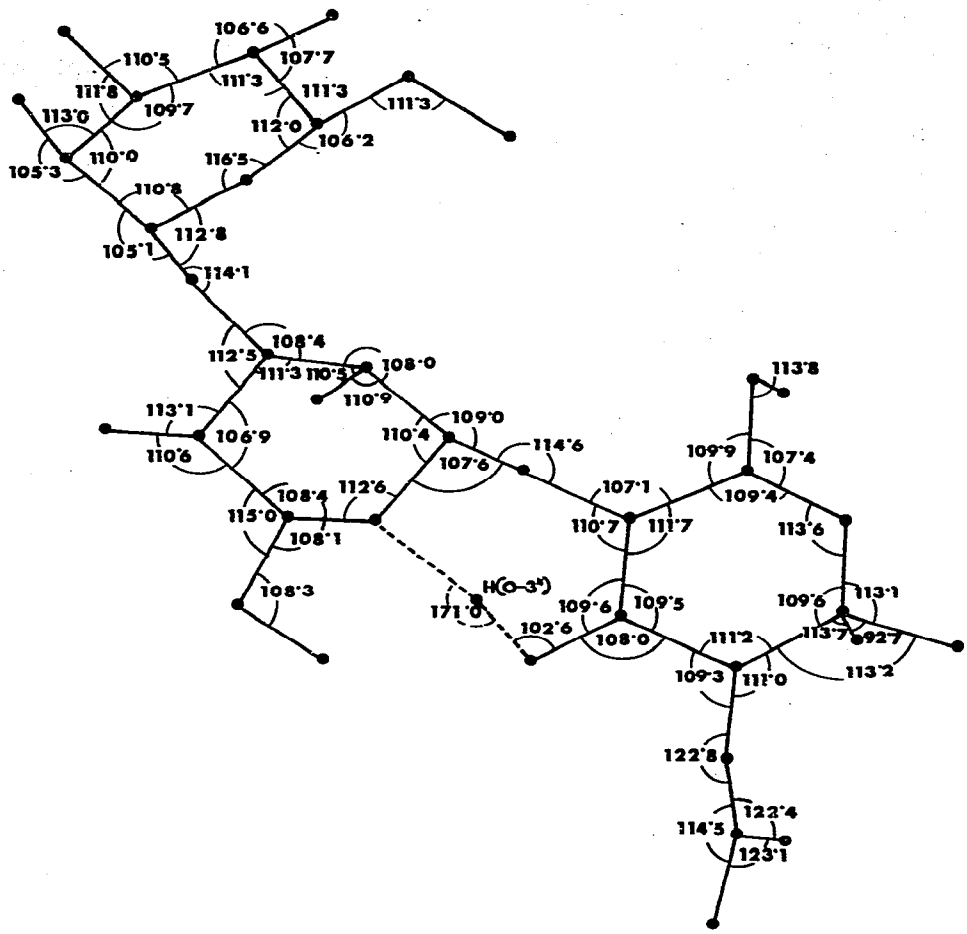


Fig. 3. Bond angles in α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-α/β-D-GlcNAc*p*; average e.s.d. is 0.7°.

maps. A last refinement of the parameters of the non-hydrogen atoms gave the final R factor of 0.059 for 2099 reflections with $I \geqslant 3\sigma(I)$. The temperature factor of each hydrogen atom is fixed equal to the corresponding isotropic factor of the parent atom. The scattering factors for all the atoms were those of Hanson *et al.*[9]. A final electron-density map showed no significant residual density, the extreme fluctuations being 0.17 and -0.3 eA^{-3}.

RESULTS AND DISCUSSION

The molecular structure of α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-α/β-D-GlcNAc*p* is illustrated in Fig. 1. The D-mannopyranosyl and D-glucopyranosyl residues have the normal $^4C_1$ conformation.

The bond lengths and bond angles involving carbon and oxygen atoms are drawn in Figs. 2 and 3.

TABLE II

FRACTIONAL ATOMIC CO-ORDINATES AND ANISOTROPIC THERMAL PARAMETERS IN α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-α/β-D-Glc*p*NAc[a]

				β					
Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C-1	10906(8)	3780(10)	0326(6)	56(7)	64(7)	30(4)	−4(6)	10(4)	−0(4)
C-2	11774(8)	4464(10)	−524(6)	67(7)	51(7)	29(4)	−2(6)	15(4)	−7(5)
C-3	10917(8)	5425(10)	−1227(7)	67(7)	48(7)	43(5)	−9(6)	5(4)	0(4)
C-4	9648(10)	4749(11)	−1798(7)	95(9)	61(9)	38(5)	−11(8)	−4(5)	−7(6)
C-5	8900(8)	4011(10)	−0941(6)	61(7)	57(7)	37(4)	−2(6)	3(4)	−14(4)
C-6	7826(9)	3138(12)	−1522(9)	74(8)	109(10)	69(7)	−28(8)	−1(6)	−1(7)
C-1′	7826(8)	4836(9)	3097(7)	47(6)	51(5)	37(4)	3(5)	2(46)	−1(48)
C-2′	8665(7)	5319(10)	2133(6)	45(6)	65(7)	29(4)	5(5)	2(40)	2(45)
C-3′	9761(8)	4323(10)	1964(6)	57(7)	46(7)	24(3)	−7(6)	14(44)	5(44)
C-4′	10618(8)	4059(9)	3062(6)	48(6)	49(7)	29(4)	−6(5)	−4(40)	−5(46)
C-5′	9646(8)	3590(9)	3938(6)	52(6)	46(6)	29(4)	−3(5)	1(44)	6(45)
C-6′	10327(9)	3240(10)	5091(7)	53(8)	75(7)	42(4)	−10(7)	−7(52)	13(53)
C-1″	3558(9)	6121(12)	5181(7)	71(8)	113(10)	43(5)	13(7)	7(5)	−33(6)
C-2″	4817(8)	5596(10)	5847(7)	55(5)	55(7)	32(4)	−7(5)	2(3)	−6(4)
C-3″	6073(8)	5856(11)	5238(6)	54(7)	82(8)	34(4)	−4(6)	−8(4)	−12(5)
C-4″	5849(7)	5360(10)	4006(5)	44(6)	63(7)	26(3)	9(6)	6(3)	4(4)
C-5″	4500(7)	5860(10)	3403(6)	33(6)	57(8)	34(4)	7(6)	8(3)	8(5)
C-6″	4214(8)	5189(11)	2265(7)	54(6)	99(9)	41(4)	9(6)	−7(4)	−5(5)
C-7″	4938(9)	5458(13)	7958(8)	58(6)	136(11)	43(6)	−10(7)	15(4)	−4(6)
C-8″	5232(13)	6194(13)	9029(6)	164(13)	130(11)	30(4)	−42(10)	24(5)	−4(5)
O-1	10549(5)	4765(5)	1084(4)	63(5)	49(5)	32(3)	−2(4)	18(3)	2(3)
O-2	12272(6)	3434(8)	−1219(4)	61(4)	70(5)	53(3)	−14(4)	22(3)	−14(3)
O-3	11662(7)	6034(9)	−2057(5)	119(6)	105(6)	70(3)	−25(5)	34(4)	31(4)
O-4	8750(7)	5761(8)	−2270(5)	66(5)	27(4)	29(3)	13(3)	−36(3)	4(3)
O-5	9789(5)	3192(7)	−0238(4)	63(4)	43(3)	29(3)	−11(3)	7(2)	−5(2)
O-6	6791(9)	2856(10)	−0795(7)	112(8)	139(7)	108(5)	−33(6)	31(5)	15(3)
O-1′	6920(5)	5790(7)	3350(4)	51(4)	54(4)	34(2)	5(3)	11(2)	2(2)
O-2′	9254(5)	6535(7)	2407(4)	57(4)	37(3)	36(2)	−4(3)	5(2)	−4(2)
O-4′	11643(6)	3144(8)	2938(5)	60(4)	60(5)	49(3)	9(4)	5(2)	−2(3)
O-5′	8681(5)	4591(8)	4090(4)	47(4)	57(4)	25(2)	7(3)	−1(2)	1(3)
O-6′	9353(7)	2673(9)	5733(4)	92(5)	111(6)	34(3)	−18(5)	−5(3)	2(4)
O-1″α	3486(7)	7378(9)	5179(4)	74(7)	72(8)	66(5)	8(6)	−5(5)	−22(5)
O-3″	7180(6)	5183(9)	5823(4)	51(4)	14(6)	29(2)	14(4)	7(7)	−3(3)
O-5″	3426(5)	5558(8)	4066(5)	37(4)	88(5)	51(3)	4(4)	1(1)	18(3)
O-6″	4124(7)	3864(8)	2345(5)	64(5)	80(5)	61(3)	9(4)	2(2)	−20(3)
O-7″	4658(7)	4389(9)	7937(5)	112(6)	79(6)	66(3)	−19(5)	37(3)	27(4)
N	4993(7)	6167(9)	6999(5)	58(5)	67(6)	36(3)	−14(4)	9(3)	−7(4)
O-1″β	2486	6005	5705	1.62 Å^2					

[a]Key to atomic numbering is given in Fig. 1. Temperature factor expression used, exp − ($h^2\beta_{11}$ + $k^2\beta_{22}$ + $l^2\beta_{33}$ + 2hkβ_{12} + 2hlβ_{13} + 2klβ_{23}). Values for fractional atomic co-ordinates are × 10^4, and temperature factors of the heavy atoms are × 10^4.

TABLE III

FRACTIONAL ATOMIC CO-ORDINATES ($\times 10^4$), ISOTROPIC THERMAL PARAMETERS OF HYDROGEN ATOMS, AND BOND DISTANCES

Atom	x	y	z	*B* (Å^2)	*d* (Å)
H(C-1)	11370	3140	0700	2.09	0.90
H(C-2)	12400	5020	−0150	2.07	0.93
H(O-2)	13050	3330	−1350	2.81	0.80
H(C-3)	10500	6150	−0900	2.29	0.95
H(O-3)	12250	5470	−2150	4.12	0.81
H(C-4)	9810	4220	−2410	3.06	0.93
H(O-4)	8400	6100	−1750	1.17	0.80
H(C-5)	8390	4580	−0290	2.33	1.12
H(C-6)	8160	2380	−1830	3.34	0.93
H(C-6)	7600	3610	−2150	3.34	0.90
H(O-6)	6980	3120	0050	5.65	1.03
H(C-1′)	7310	4040	2790	1.98	1.02
H(C-2′)	8210	5450	1420	1.66	0.93
H(O-2′)	8700	7050	2500	2.03	0.77
H(C-3′)	9370	3390	1580	1.81	1.12
H(C-4′)	11020	4830	3220	1.89	0.90
H(O-4′)	11510	2310	2510	2.64	1.00
H(C-5′)	9290	2860	3540	3.00	0.94
H(C-6′)	11190	2640	4890	2.48	1.09
H(C-6′)	10890	3940	5410	2.48	0.97
H(O-6′)	9500	2720	6510	3.56	0.91
H(O-1″)	2750	7800	4850	1.63	0.90
H(C-2″)	4750	4750	5940	2.09	0.88
H(C-8″)	5340	5920	9720	4.3	0.86
H(C-8″)	4410	6840	9190	4.3	1.07
H(C-8″)	6150	6730	8910	4.3	1.08
H(N)	5290	6950	7100	2.25	0.86
H(C-3″)	6190	6660	5250	2.04	0.84
H(O-3″)	7780	4840	5100	3.00	1.13
H(C-4″)	6020	4430	4120	1.68	0.98
H(C-5″)	4680	6730	3300	2.13	0.92
H(C-6″)	3490	5350	1940	2.70	0.80
H(C-6″)	5010	5420	1860	2.70	0.98
H(O-6″)	3400	3570	2610	3.08	0.86

Bond lengths and bond angles. — The positional and thermal parameters and their standard deviations are given in Tables II and III. The standard deviations of the interatomic distances and angles, derived from the e.s.d. values of the fractional co-ordinates, are 0.01 Å and 0.7°, respectively, for bond distances and angles involving non-hydrogen atoms (0.12 Å for bond distances involving hydrogen atoms).

The bond lengths, bond angles, and numbering system of the molecule are depicted in Figs. 2 and 3, respectively. The numbering of the atoms proceeds from the non-reducing mannose end (unprimed and primed) to the reducing 2-acetamido-2-deoxyglucose end (double primed).

The C–C bond-lengths agree well with each other and with the accepted value, the mean lengths being 1.525 Å with a greatest deviation of 0.02 Å. In three residues, the exocyclic C-5–C-6 bond is consistently shorter than the average C–C ring bond. This feature has already been reported[10–12].

The overall features displayed by the three C-5–O-5–C-1–O-1–C sequences are in good agreement with the coupling of the C–O bond-lengths and bond-angles to the torsional conformation[13–16]. However, a slight departure from that coupling is observed at the reducing 2-acetamido-2-deoxyglucose residue. This difference can be attributed to the persisting $\alpha\beta$ mixture, and the resulting lack of accuracy due to a poor location of disordered atoms O-1″α and O-1″β. Similar observations have been made for laminarabiose[11] and α-lactose monohydrate[17]. The C–H bond-lengths are in the range 0.85–1.11 Å (mean 0.96 Å) and the O–H bond-lengths in the range 0.80–1.13 Å (mean 0.91 Å).

No unusual deviations from the values commonly found in carbohydrates are observed for the internal ring-angles. The exocyclic bond-angles exhibit a wide range of variation (105–114°). The bond angles involving the bridge oxygen-atom are of particular interest.

This work provides the first determination of the glycosidic angles, C-1–O-1–C-3′, associated with the α-(1→3) linkage. The resulting value is 114.6° (0.7), which is slightly smaller than the usual values found in α-glycosidic bonds except for α-(1→6) linkages.

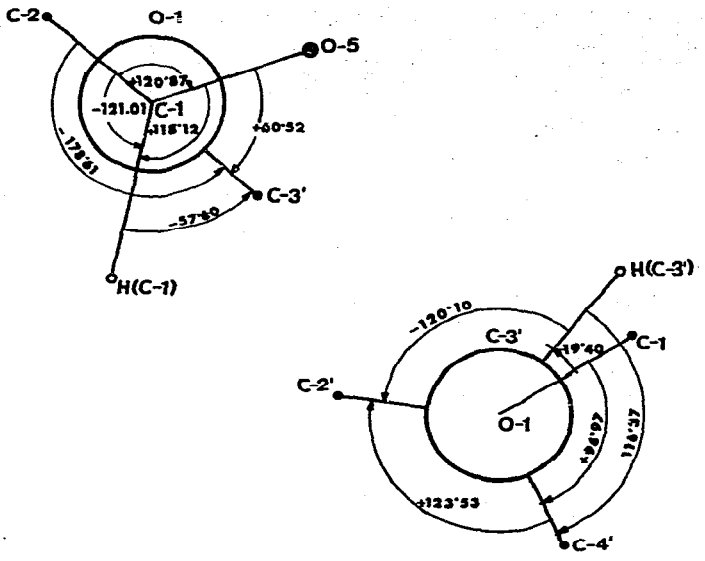
Similarly, the value of the C-1–O-1′–C-4″ angle associated with the β-(1→4) linkage is 114.1° (0.7). This value is again lower than those found for oligosaccharides having an $\alpha\beta$-(1→4) linkage[17–20].

The molecular conformation. — The torsional angles φ_1, φ_1', φ_2, and φ_2' (Sundaralingam)[21] about the bridge bonds C-1–O-1 and O-1–C-3′ for the α-(1→3) linkage, and C-1′–O-1′ and O-1′–C-4″, are given in Table IV and Fig. 4.

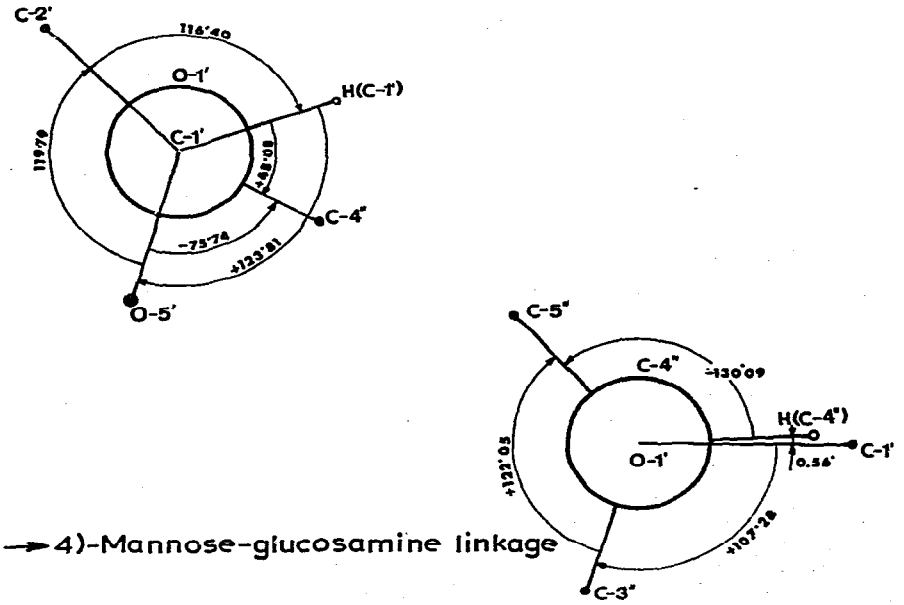
TABLE IV

TORSION ANGLES AROUND THE GLYCOSIDE BONDS

Linkage α-(1→3)		
O-5–C-1–O-1–C-3′	φ_1	+60.52°
C-2–C-1–O-1–C-3′	φ'_1	−178.61°
H-1–C-1–O-1–C-3′	Φ^H	−57.60°
C-1–O-1–C-3′–C-4′	φ_2	+96.97°
C-1–O-1–C-3′–C-2′	φ'_2	−139.50°
C-1–O-1–C-3′–H-3′	Ψ^H	−19.40°
Linkage β-(1→4)		
O-5′–C-1′–O-1′–C-4″	φ_1	−75.74°
C-2′–C-1′–O-1′–C-4″	φ'_1	+164.48°
H-1′–C-1′–O-1′–C-4″	Φ^H	+48.08°
C-1′–O-1′–C-4″–C-5″	φ_2	−130.65°
C-1′–O-1′–C-4″–C-3″	φ'_2	+107.28°
C-1′–O-1′–C-4″–H-4″	Ψ^H	−0.56°



α-(1→3)-Mannose-mannose linkage



β-(1→4)-Mannose-glucosamine linkage

Fig. 4. Torsional angles: mannose–mannose α-(1→3) linkage; mannose–2-acetamido-2-deoxyglucose β-(1→4) linkage.

For the α-(1→3) linkage, the angles φ_1 60.5°, φ_2 96.9°, Ψ^H −58° are in agreement with those for other α-(1→3)-linked oligosaccharides (extreme limits: 58–121°). Furthermore, the molecule exhibits a symmetrical twist about the bridge bonds (φ_1 60.5°, φ_2 96.9°).

TABLE V

IMPORTANT CONFORMATION ANGLES IN α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-α/β-D-GlcNAc*p*

Mannose (ring 1)	
C-5–C-1–C-2–C-3	+56.6°
C-1–C-2–C-3–C-4	−54.2°
C-2–C-3–C-4–C-5	+51.8°
C-3–C-4–C-5–O-5	−49.8°
C-4–C-5–O-5–C-1	+54.3°
C-5–O-5–C-1–C-2	−57°
Mannose (ring 2)	
O′-5–C′-1–C′-2–C′-3	+55.5°
C′-1–C′-2–C′-3–C′-4	−55.2°
C′-2–C′-3–C′-4–C′-5	+57.9°
C′-3–C′-4–C′-5–O′-5	−60.4°
C′-4–C′-5–O′-5–C′-1	+64.9°
C′-5–O′-5–C′-1–C′-2	−62.6°
Glucose (ring 3)	
O″-5–C″-1–C″-2–C″-3	+57.5°
C″-1–C″-2–C″-3–C″-4	−52.5°
C″-2–C″-3–C″-4–C″-5	+50.6°
C″-3–C″-4–C″-5–O″-5	−53.5°
C″-4–C″-5–O″-5–C″-1	+60.3°
C″-5–O″-5–C″-1–C″-2	−62.8°
Primary alcohol groups	
C-4–C-5–C-6–O-6	−156.4°
O-5–C-5–C-6–O-6	+81.3°
C′-4–C′-5–C′-6–O′-6	−172.1°
O′-5–C′-5–C′-6–O′-6	+66.6°
C″-4–C″-5–C″-6–O″-6	+58.8°
O″-5–C″-5–C″-6–O″-6	−60.0°

For the β-(1→4) linkage, the molecule exhibits an asymmetrical twist (φ_1 −75°, φ_2' 107.2°). These values agree with those of other β-(1→4)-linked oligosaccharides (extreme limits −71–+105°). For Ψ^H, the expected value was found. The slight departure from the fully extended conformation for the β-(1→4) linkage is undoubtedly promoted by the intramolecular hydrogen-bond O-3″–H.....O-5′, as is observed in α-lactose[17] and β-cellobiose[18,22].

In this crystal structure, the mean torsional angles about the ring bond in α-mannose (ring 1), β-mannose (ring 2), and 2-acetamido-2-deoxyglucose (ring 3) are, respectively, 54°, 59°, and 56° (Table V). They show the same range of variation (50–65°) as in the crystal structures of other pyranose sugars where the rings have the normal chair conformation. The dihedral angle between the least-squares planes of the two mannopyranose residues is 59.6°, and the dihedral angle between the mannopyranose and the glucopyranose is 40.81°.

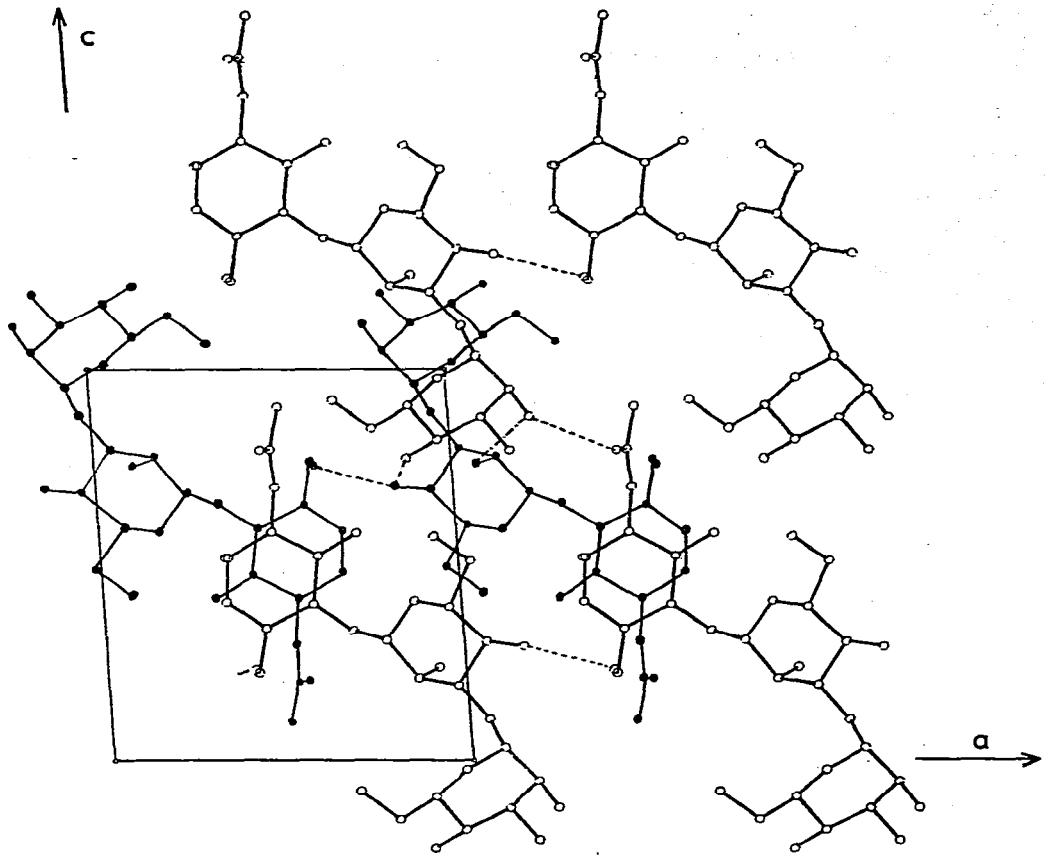


Fig. 5. Molecular packing viewed along the *b* axis; hydrogen bonds are shown by broken lines.

TABLE VI

HYDROGEN-BOND DISTANCES AND ANGLES

Hydrogen bonds	*i*	*j*	*k*	*i–k (Å)*	*j–k (Å)*	*ijk (°)*	*Sym. code*[a]
Intramolecular	O-3″–H-3″		O-5′	2.586(9)	1.563	171.05	
Intermolecular	O-2–H-2		O-7″	2.822(9)	2.160	138.89	*(a)*
	O-6″–H-6″		O-4′	2.716(9)	1.867	167.74	*(b)*
	O-2′–H-2′		O-2	2.787(9)	2.240	127.76	*(c)*
	O-4′–H-4′		O-4	2.690(11)	1.650	159.69	*(c)*
	O-6′–H-6′		O-2′	2.759(10)	2.090	127.99	

[a] *a* $\{x+1, y, z-1\}$, *b* $\{x-1, y, z\}$, *c* $\{\bar{x}, y+\frac{1}{2}, \bar{z}\}$.

The conformations of the primary hydroxyl groups are characterised by the set of torsion angles O-5–C-5–C-6–O-6 and C-4–C-5–C-6–O-6 (Table V).

For the mannose residues, HO-6 exists in a similar *gt* conformation (81°, −156°) (66°, −172°), whereas a *gg* conformation (−60°, 59°) is displayed by HO-6 of the 2-acetamido-2-deoxyglucose residue. These findings agree well with the conclusion of a recent survey on the distribution of the conformations displayed by primary hydroxyl groups in *gluco* carbohydrates[23].

Molecular packing and hydrogen bonding. — The molecular packing is shown in Fig. 5. The hydrogen-bond distances and angles are listed in Table VI. The mannose ring-oxygen is not involved in hydrogen bonding. The most notable of these is the intramolecular hydrogen-bond O-3″–H.....O-5′ = 2.103 Å. A similar hydrogen-bond was observed in α-lactose[17] and in cellobiose[22].

The molecules are oriented approximately perpendicular to the *b* axis. Two major, intermolecular hydrogen-bonds, O-2–H.....O-7″ and O-6″–H.....O-4′, link the molecules to form infinite sheets which are piled up roughly parallel to the *ac*-plane (Fig. 5). These sheets are linked by additional hydrogen-bonds O-2′–H.....O-2, O-4′–H.....O-4, and O-6′–H.....O-2′ in the *b* direction.

Conformation of serotransferrin glycan. — The results obtained show that, in the solid state, the spatial conformation of serotransferrin glycan is of the T type.

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