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## The Crystal and Molecular Structure of Planteose Dihydrate

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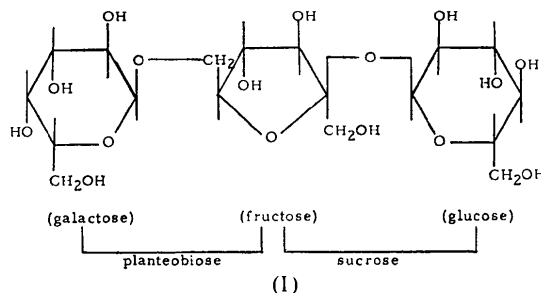
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The crystal structure of the nonreducing trisaccharide planteose dihydrate, *O*- $\alpha$ -D-galactopyranosyl-(1 $\rightarrow$ 6)-*O*- $\beta$ -D-fructofuranosyl-(2 $\rightarrow$ 1)- $\alpha$ -D-glucopyranoside ( $C_{18}H_{32}O_{16} \cdot 2H_2O$ ), has been determined using a combination of Patterson superposition techniques and tangent-phase refinement. Three-dimensional intensities were measured on a Picker FACS-I diffractometer using Ni-filtered Cu  $K\alpha$  radiation. The crystals are orthorhombic with space group  $P2_12_12_1$ . Unit-cell constants are  $a = 32.43$  (1),  $b = 8.152$  (2), and  $c = 8.711$  (2) Å. Measured density,  $D_m = 1.547$  g.cm $^{-3}$ , is consistent with the calculated density,  $D_x = 1.531$  g.cm $^{-3}$ , for a unit cell containing four sugar molecules and eight water molecules. The final  $R$  is 3.6% for 2197 reflections. The molecule has a circular conformation with O(6) of the glucose and O(6') of the galactose, at the opposite end, both hydrogen bonded to the same hydroxyl, O(2)H, of an adjacent molecule. Both pyranosyl rings have the expected  ${}^4C_1$  ( $C1$ ) conformation. The fructofuranosyl ring has a twisted  ${}_3T^4$  conformation, which places the O(3')H hydroxyl in the equatorial plane of the ring. Conformational similarities of the (1 $\rightarrow$ 2) linkage in the sucrose moieties of planteose and raffinose are more easily recognized using the pseudotorsional angles between C(1) and C(2'), defined herein, than using the torsional angles involving O(1). The largest difference in the pseudotorsional angles between the two molecules is only 12° compared to differences as large as 36° in the torsional angles involving O(1). The (1 $\rightarrow$ 6) linkage between the fructose and galactose portions has antiperiplanar conformation similar to the other two known crystal structures containing this type of linkage. Most of the hydroxyls both donate and accept a hydrogen bond with the fructofuranosyl ring oxygen atom also acting as a hydrogen-bond acceptor. One water oxygen atom both accepts and donates two hydrogen bonds, while the other water oxygen atom only accepts and donates one hydrogen bond.

### Introduction

Planteose, *O*- $\alpha$ -D-galactopyranosyl-(1 $\rightarrow$ 6)-*O*- $\beta$ -D-fructofuranosyl-(2 $\rightarrow$ 1)- $\alpha$ -D-glucopyranoside ( $C_{18}H_{32}O_{16}$ ), is a nonreducing trisaccharide first isolated from the seeds of *Plantago major* and *Plantago ovata* (Wattiez & Hans, 1943). It is a member of the raffinose family of oligosaccharides, which occur in a variety of plants and are found primarily in seeds, roots, and underground stems, where they probably act as reserve carbohydrates (French, 1954). As shown in (I), the configuration of planteose can be subdivided into two disaccharide portions: sucrose and planteobiose. Raffinose and planteose are structural isomers having the  $\alpha$ -D-galactopyranosyl portion linked to C(6') of the fructose in planteose, seen in (I) below, whereas in raffinose, it is linked to O(6) of the glucose portion. The structure of

sucrose has been accurately determined, crystallographically, as sucrose itself (Brown & Levy, 1963), in raffinose pentahydrate (Berman, 1970), in 1-kestose (Jeffrey & Park, 1971), and now in planteose dihydrate. No previous crystallographic study relating to the planteobiose part of the molecule has been made.



*Crystal data*Planteose dihydrate, C<sub>18</sub>H<sub>32</sub>O<sub>16</sub>·2H<sub>2</sub>O

M.W. 504.4, m.p. 123 °C

Orthorhombic

Space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, from systematic absences *h*00, 0*k*0, and 00*l* = 2*n* + 1*a* = 32.43 (1), *b* = 8.152 (2), *c* = 8.711 (2) Å*Z* = 4*D<sub>m</sub>* = 1.547 g.cm<sup>-3</sup>, *D<sub>x</sub>* = 1.531 g.cm<sup>-3</sup>*μ<sub>Cu Kα</sub>* = 12.2 cm<sup>-1</sup> (*λ* = 1.5418 Å)**Experimental**

Large prismatic crystals of planteose dihydrate were kindly provided by Dr Dexter French of the Department of Biochemistry and Biophysics, Iowa State University. The density was determined to be 1.547 g.cm<sup>-3</sup> using the flotation technique in a CHCl<sub>3</sub>/CBr<sub>4</sub> solvent mixture. The dimensions of the crystal used for data collection were 0.25 × 0.36 × 0.47 mm. The unit-cell parameters and intensity data were measured on a Picker FACS-I diffractometer, using Ni-filtered Cu *Kα* radiation and the *θ*-2*θ* scan method for data collection. Of the 2314 independent data, which were collected to a

maximum 2*θ* value of 130°, 102 were determined to be unobserved by the criterion of the measured intensity not exceeding two standard deviations, calculated from intensity counting statistics. The data were reduced to structure-factor amplitudes and *E*'s using an IBM 1130 program (Shiono, 1969), without applying absorption corrections.

**Structure determination and refinement**

The crystal structure of planteose dihydrate was solved by combining Patterson superposition techniques and tangent-phase refinement. A Patterson superposition program (Seeman, 1970) was used to locate seven possible atomic positions from an (*E*<sup>2</sup> - 1) Patterson map. Phases calculated from these seven positions for the 100 reflections with highest *E* values were refined, using the tangent formula and the phase-extension method of Hall (1967). Ten cycles of refinement, which expanded the number of reflections to 328, resulted in an *E* map showing all the nonhydrogen atoms, except one of the water oxygen atoms. A comparison of these coordinates with the seven starting positions revealed that only four of the seven were correct. This reconfirms (Karle, 1968)

Table 1. Fractional atomic parameters and anisotropic thermal parameters (× 10<sup>5</sup>) in planteose dihydrateTemperature-factor expression used was exp [-(*h*<sup>2</sup>*β*<sub>11</sub> + *k*<sup>2</sup>*β*<sub>22</sub> + *l*<sup>2</sup>*β*<sub>33</sub> + 2*hkβ*<sub>12</sub> + 2*hlβ*<sub>13</sub> + 2*klβ*<sub>23</sub>)].

Numbers in parentheses refer to the e.s.d. of that parameter.

	<i>x</i> × 10 <sup>5</sup>	<i>y</i> × 10 <sup>4</sup>	<i>z</i> × 10 <sup>4</sup>	<i>β</i> <sub>11</sub>	<i>β</i> <sub>22</sub>	<i>β</i> <sub>33</sub>	<i>β</i> <sub>12</sub>	<i>β</i> <sub>13</sub>	<i>β</i> <sub>23</sub>
C(1)	15393 (7)	1969 (3)	5025 (3)	38 (2)	700 (37)	619 (33)	3 (8)	-22 (7)	61 (33)
C(2)	16976 (8)	924 (3)	3702 (3)	58 (2)	625 (38)	609 (33)	7 (8)	-33 (8)	4 (32)
C(3)	21595 (8)	1114 (3)	3558 (3)	54 (2)	778 (42)	524 (32)	51 (8)	-16 (8)	-70 (33)
C(4)	22701 (8)	2908 (3)	3395 (3)	43 (2)	834 (41)	576 (32)	26 (8)	4 (7)	54 (33)
C(5)	20785 (8)	3939 (3)	4679 (3)	42 (2)	704 (40)	631 (33)	15 (8)	-11 (7)	12 (33)
C(6)	21383 (9)	5733 (4)	4340 (4)	68 (3)	753 (42)	849 (38)	1 (9)	25 (9)	15 (37)
O(1)	17130 (5)	1419 (2)	6423 (2)	36 (2)	889 (29)	480 (22)	3 (6)	2 (5)	88 (24)
O(2)	16007 (6)	-757 (2)	3923 (3)	67 (2)	581 (28)	1170 (32)	6 (6)	-65 (7)	-75 (26)
O(3)	23026 (6)	221 (3)	2240 (2)	63 (2)	1099 (35)	616 (24)	118 (7)	-20 (6)	-212 (27)
O(4)	27048 (6)	3132 (3)	3438 (2)	40 (2)	1308 (36)	759 (25)	4 (7)	22 (6)	-41 (29)
O(5)	16451 (6)	3632 (2)	4775 (2)	40 (2)	553 (26)	740 (24)	32 (6)	19 (6)	49 (23)
O(6)	19854 (7)	6731 (2)	5565 (2)	98 (2)	728 (31)	807 (27)	75 (7)	-69 (7)	-210 (27)
C(1')	13277 (8)	-676 (3)	7682 (3)	54 (2)	658 (38)	752 (36)	5 (9)	25 (8)	-80 (34)
C(2')	14446 (7)	1122 (3)	7711 (3)	36 (2)	605 (38)	617 (32)	15 (8)	22 (7)	9 (31)
C(3')	16660 (8)	1699 (3)	9149 (3)	34 (2)	621 (39)	656 (32)	28 (8)	3 (7)	27 (31)
C(4')	15634 (8)	3518 (3)	9192 (3)	46 (2)	631 (39)	680 (33)	16 (8)	-34 (7)	-57 (32)
C(5')	11148 (8)	3503 (3)	8661 (3)	47 (2)	578 (36)	628 (33)	12 (8)	-19 (8)	-170 (32)
C(6')	9961 (8)	5027 (3)	7815 (4)	45 (2)	666 (39)	1089 (43)	14 (8)	-67 (9)	-20 (37)
O(1')	11062 (6)	-1134 (2)	9018 (2)	59 (2)	742 (30)	820 (27)	-17 (7)	25 (6)	138 (25)
O(2')	10840 (5)	2078 (2)	7646 (2)	33 (1)	592 (25)	638 (24)	12 (5)	-30 (5)	-114 (22)
O(3')	20917 (6)	1322 (3)	9142 (2)	42 (2)	974 (32)	719 (25)	71 (6)	-39 (6)	-47 (26)
O(4')	16125 (6)	4125 (3)	10698 (2)	75 (2)	896 (32)	808 (27)	29 (7)	-98 (7)	-285 (27)
O(6')	5736 (5)	4934 (2)	7356 (2)	41 (2)	637 (28)	892 (27)	28 (6)	-41 (6)	46 (26)
C(1'')	4375 (8)	6439 (3)	6727 (3)	57 (2)	696 (39)	785 (36)	49 (8)	-22 (8)	-12 (35)
C(2'')	-98 (8)	6277 (4)	6232 (3)	49 (2)	1042 (45)	810 (37)	51 (9)	1 (8)	64 (38)
C(3'')	-505 (8)	5057 (4)	4923 (3)	51 (2)	1096 (47)	899 (39)	-28 (9)	-21 (9)	50 (41)
C(4'')	2318 (9)	5501 (4)	3604 (3)	61 (3)	993 (46)	806 (39)	-34 (9)	8 (9)	-46 (40)
C(5'')	6671 (8)	5728 (4)	4198 (4)	57 (3)	813 (42)	936 (40)	3 (9)	3 (9)	-76 (38)
C(6'')	9710 (9)	6294 (4)	3004 (4)	64 (3)	1253 (52)	1250 (48)	-58 (11)	32 (10)	-61 (46)
O(2'')	-2573 (6)	5791 (3)	7506 (2)	52 (2)	1710 (43)	820 (29)	78 (8)	29 (6)	202 (33)
O(3'')	-4611 (6)	5012 (4)	4343 (3)	47 (2)	2474 (57)	920 (30)	-88 (9)	-29 (6)	0 (40)
O(4'')	1054 (6)	6969 (3)	2866 (3)	73 (2)	1272 (38)	1015 (32)	0 (8)	-45 (7)	326 (33)
O(5'')	6783 (6)	6902 (2)	5440 (2)	54 (2)	651 (27)	841 (27)	-11 (6)	-14 (6)	25 (25)
O(6'')	9339 (6)	7977 (3)	2585 (3)	61 (2)	1469 (40)	1192 (34)	-57 (8)	-56 (7)	481 (34)
O( <i>W</i> 1)	32438 (7)	2428 (3)	5712 (3)	78 (2)	1207 (37)	896 (29)	2 (7)	2 (7)	140 (30)
O( <i>W</i> 2)	4470 (11)	735 (5)	4350 (3)	197 (5)	2611 (71)	1167 (41)	172 (16)	-111 (12)	-317 (51)

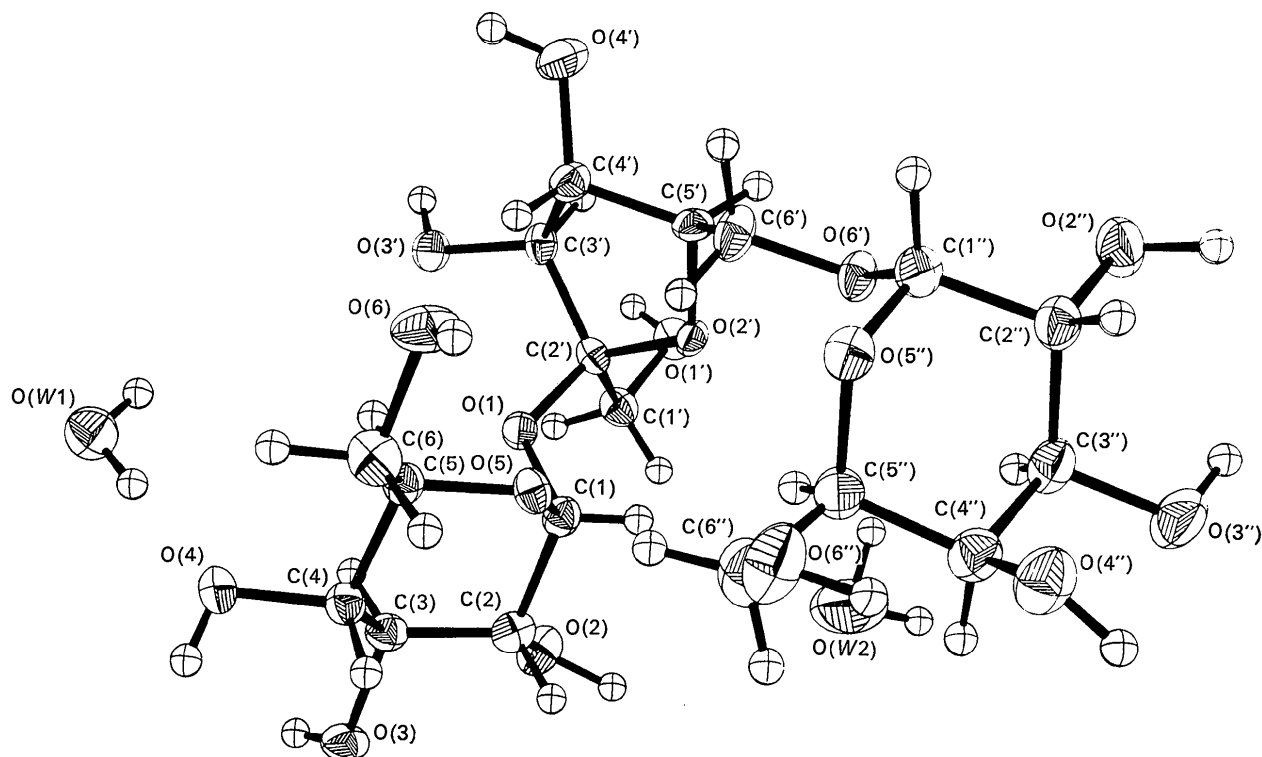


Fig. 1. Molecular conformation and numbering of atoms in planteose dihydrate.

that tangent-refinement procedures can overcome relatively large errors in the starting phase set.

Structure factors, calculated with the 35 atomic positions obtained from the  $E$  map, resulted in an  $R$  ( $= \sum ||F_o| - |F_c|| / \sum |F_o|$ ) of 34%. Two cycles of isotropic full-matrix least-squares refinement, followed by the calculation of a difference Fourier map, revealed the

location of the missing water oxygen atom. Two more cycles of refinement with this atom included lowered  $R$  to 9.4%. Successive cycles of anisotropic block-diagonal least-squares refinement and difference map calculations were necessary to locate the 36 hydrogen atoms. The hydrogen atoms were assigned the isotropic thermal parameter of their parent atoms and were included in the refinement, varying positional parameters but holding thermal parameters fixed. Additional cycles of mixed-mode block-diagonal refinement resulted in an  $R$  of 3.9%. At this point, 15 reflections with very large structure-factor amplitudes were removed from the data because they appeared to be affected by secondary extinction. Two final cycles of full-matrix refinement, holding all hydrogen parameters fixed, resulted in no significant parameter shifts and gave an  $R$  of 3.6% for the observed reflections and 4.5% for all reflections. The final atomic parameters are listed in Tables 1 and 2. Final structure factors are given in Table 3. A Hughes (1941) weighting scheme was used throughout with an  $F_{\min}$  of 4.0. The scattering factors used for carbon and oxygen were those of Cromer & Waber (1965); and for hydrogen, those of Stewart, Davidson & Simpson (1965).

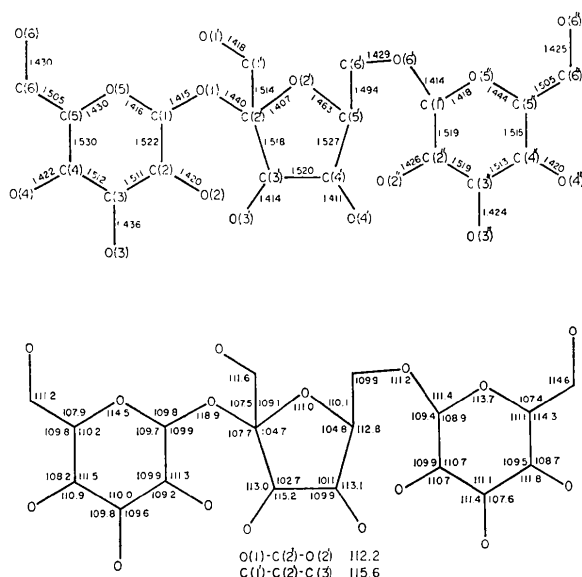


Fig. 2. Bond lengths (Å) and bond angles (°) in planteose dihydrate.

### Molecular conformation

The structural and conformational features of the planteose molecule are illustrated in Fig. 1. The glucose, fructose, and galactose portions of the molecule are

denoted by unprimed, single-primed, and double-primed atom designators respectively. The molecule has a circular conformation, with the glucopyranosyl and galactopyranosyl portions extending away from the central fructofuranosyl ring. However, the terminal primary hydroxyls, O(6)H and O(6'')H, on the pyranosyl rings are close enough to form hydrogen bonds with the same hydroxyl, O(2), on an adjacent molecule, closing the circle.

Table 2. Fractional atomic parameters and isotropic thermal parameters of the hydrogen atoms in planteose dihydrate

The isotropic temperature-factor expression used was  $\exp[-B(\sin \theta/\lambda)^2]$ . Standard deviations are given in parentheses.

	$x \times 10^4$	$y \times 10^3$	$z \times 10^3$	$B$
HC(1)	1274 (12)	192 (5)	505 (5)	1.70 Å <sup>2</sup>
HC(2)	1567 (12)	129 (5)	270 (5)	1.90
HC(3)	2300 (11)	59 (5)	441 (5)	1.7C
HC(4)	2174 (12)	338 (5)	248 (5)	1.90
HC(5)	2197 (12)	358 (5)	567 (5)	1.79
HC(6)	2461 (13)	587 (6)	416 (5)	2.59
H'C(6)	1977 (13)	614 (6)	334 (5)	2.59
HO(2)	1310 (13)	-101 (6)	361 (5)	2.50
HO(3)	2501 (13)	-22 (6)	253 (5)	2.20
HO(4)	2760 (12)	301 (5)	265 (5)	2.09
HO(6)	1881 (13)	759 (6)	512 (5)	2.70
HC(1')	1593 (12)	-130 (5)	750 (5)	1.90
H'C(1')	1151 (12)	-86 (5)	678 (5)	1.90
HC(3')	1530 (12)	118 (5)	1004 (5)	1.79
HC(4')	1736 (12)	400 (5)	841 (5)	2.20
HC(5')	888 (11)	326 (5)	949 (4)	1.59
HC(6')	1193 (12)	510 (5)	685 (5)	2.20
H'C(6')	1049 (12)	597 (5)	848 (5)	2.20
HO(1')	1280 (12)	-141 (5)	970 (5)	2.09
HO(3')	2159 (12)	104 (6)	1005 (5)	2.29
HO(4')	1829 (13)	458 (6)	1074 (5)	2.90
HC(1'')	489 (12)	732 (5)	753 (5)	1.90
HC(2'')	-121 (13)	746 (5)	583 (5)	2.29
HC(3'')	-10 (12)	403 (5)	523 (5)	2.40
HC(4'')	227 (13)	464 (6)	281 (5)	2.40
HC(5'')	759 (12)	466 (5)	469 (5)	2.20
HC(6'')	899 (13)	573 (6)	205 (5)	3.20
H'C(6'')	1250 (14)	615 (6)	337 (5)	3.20
HO(2'')	-518 (14)	635 (6)	733 (5)	2.90
HO(3'')	-656 (14)	471 (6)	520 (6)	3.50
HO(4'')	-105 (13)	677 (6)	227 (5)	3.00
HO(6'')	692 (14)	825 (6)	220 (5)	3.29
HO(W1)	3125 (13)	182 (6)	656 (5)	2.90
H'O(W1)	3083 (14)	253 (6)	495 (6)	2.90
HO(W2)	142 (18)	19 (8)	430 (7)	5.79
H'O(W2)	396 (17)	71 (8)	560 (7)	5.79

The bond lengths and angles for planteose are given in Fig. 2. The estimated errors in the C-C and C-O bond lengths are 0.004 and 0.003 Å, respectively, and the error in the nonhydrogen-containing bond angles is about 0.2°. The average C-C and C-OH bonds in the two pyranosides are 1.517 and 1.426 Å, respectively, which are in good agreement with earlier values (Berman, Chu & Jeffrey, 1967; Jeffrey & Rosenstein, 1964). The C-O bonds in both pyranoside rings show the same type of systematic disproportion observed in other  $\alpha$ -pyranoside structures (Berman *et al.*, 1967): the C(5)-O(5) bonds in the  $\alpha$ -D-glucopyranoside and  $\alpha$ -D-galac-

topyranosyl rings are significantly longer than the corresponding O(5)-C(1) bonds, by 0.014 and 0.026 Å, respectively.

The corresponding C-O bonds in the  $\beta$ -D-fructofuranosyl ring show the same type of anomeric effect observed in the pyranosyl rings. However, the disproportion is very much larger (0.056 Å). The anomeric disproportion also seems to affect the C(5')-C(6') bond, causing a shortening of 0.021 Å from the average value. A correlation between the C(3')-C(2')-O(1) angle and the exocyclic C(2')-O(1) bond length involved in the anomeric effect has been reported by Sundaralingam (1965). Using this correlation, the C(2')-O(1) bond length in planteose (1.440 Å) agrees very well with the value of 1.442 Å predicted for a deviation of  $-12.5^\circ$  in the angle away from  $120^\circ$ . The other fructofuranosyl C-C and C-O bonds fall into the range of values normally observed (Sundaralingam, 1968).

The pyranosyl rings have the expected  ${}^4C_1^*$  ( $C_1$ ) chair conformation, with the ring torsional angles ranging from  $52.3$  to  $60.8^\circ$  (Table 4) in the glucopyranosyl ring and from  $52.3$  to  $60.6^\circ$  in the galactopyranosyl ring, with respective averages of  $56.1$  and  $56.4^\circ$ . The furanosyl ring has a twisted  ${}_3T^4$  conformation (Fig. 3), with C(3') primarily displaced on the *exo* side of the ring by 0.402 Å and C(4') secondarily displaced on the opposite side by 0.232 Å (Table 5). The same conformation is observed in raffinose pentahydrate with the relative magnitudes reversed, giving a  ${}^4T_3$  conformation. The effect of this difference is to place O(3') in the equatorial plane of the ring in planteose, rather than O(4') as it is in raffinose. The furanosyl ring in sucrose has a  ${}_3T^4$  conformation very similar to that found in plante-

\* The nomenclature used to denote the conformation of the furanosyl and pyranosyl rings is that proposed by the American Chemical Society Committee on Carbohydrate Nomenclature (1969), with the following modification in the twist-form of the furanosyl ring proposed by Sundaralingam (1971): the number appearing to the left of the  $T$  denotes the primarily displaced atom and the number to the right denotes the secondarily displaced atom. If both atoms are equally displaced, both numbers appear to the right of the  $T$ .

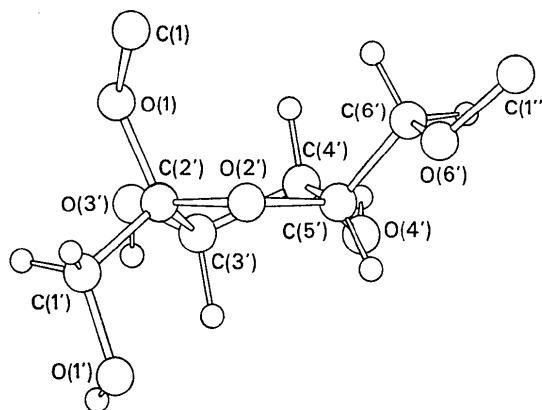


Fig. 3. View of the  ${}_3T^4$  conformation of the  $\beta$ -D-fructofuranosyl ring.

ose, while in the sucrose portion of 1-kestose, it lies between E<sub>4</sub> and 4T<sup>3</sup>.

The greatest degree of conformational freedom in a polysaccharide is in the bonds which link the various

monosaccharide units together. Therefore, the conformational analysis of these linkages in smaller molecules is of primary importance for extrapolation to macromolecules.

Table 3. Observed and calculated structure factors

Columns are: the h index, |0|F<sub>obs</sub>|, |0|F<sub>calc</sub>|. Unobserved reflections are indicated by \*; reflections removed from the final refinement are indicated by †.

Table with multiple columns containing numerical data for structure factors. The table is organized into several vertical sections, each starting with a small header (e.g., h, |0|F<sub>obs</sub>, |0|F<sub>calc</sub>) and followed by rows of data. Some rows are marked with asterisks or daggers to indicate specific reflection types.

Table 4. *Torsional angles for the pyranosyl rings*

Torsional angle  $A(1)-A(2)-A(3)-A(4)$  is viewed down the  $A(2)-A(3)$  bond with a clockwise angle of  $A(1)$  to  $A(4)$  taken to be positive.

(a) $\alpha$ -D-Glucopyranosyl ring	
O(5)-C(1)-C(2)-C(3)	58.2°
C(1)-C(2)-C(3)-C(4)	-55.0
C(2)-C(3)-C(4)-C(5)	52.5
C(3)-C(4)-C(5)-O(5)	-52.3
C(4)-C(5)-O(5)-C(1)	57.5
C(5)-O(5)-C(1)-C(2)	-60.8
Average	56.1
(b) $\alpha$ -D-Galactopyranosyl ring	
O(5'')-C(1'')-C(2'')-C(3'')	56.7
C(1'')-C(2'')-C(3'')-C(4'')	-54.2
C(2'')-C(3'')-C(4'')-C(5'')	52.3
C(3'')-C(4'')-C(5'')-O(5'')	-54.1
C(4'')-C(5'')-O(5'')-C(1'')	60.5
C(5'')-O(5'')-C(1'')-C(2'')	-60.6
Average	56.4

Table 5. *Three atom planes calculated for the fructofuranosyl ring in the four sucrose structures*

	Displacement			
	Planteose	Raffinose	Sucrose	1-Kestose
C(1')	-0.915 Å	-1.050 Å	-0.984 Å	-1.325 Å
C(2')	0.000*	0.000*	0.000*	0.000*
C(3')	-0.402	-0.248	-0.372	0.094
C(4')	0.232	0.409	0.208	-0.389
C(5')	0.000*	0.000*	0.000*	0.000*
C(6')	1.064	0.948	1.049	1.348
O(2')	0.000*	0.000*	0.000*	0.000*
O(3')	-0.019	0.295	0.021	1.423
O(4')	-0.421	0.043	-0.463	-1.805
<i>L</i>	0.3932	-0.1257	0.5768	0.1168
<i>M</i>	0.5351	0.5484	0.7949	-0.9931
<i>N</i>	-0.7476	-0.8266	-0.1878	-0.0087
<i>D</i>	-2.6902	-3.3511	1.2162	-7.0155
Con-formation	${}_3T^4$	${}_4T_3$	${}_3T^4$	$E_4$ or ${}_4T^3$

\* Atoms included in the calculation of the plane. The equation of the plane is of the form  $Lx + My + Nz = D$ , where  $L$ ,  $M$ , and  $N$  are the direction cosines of the normal to the plane, and  $D$  (Å) is the perpendicular distance from the plane to the origin.

Table 6. *Torsional angles and pseudotorsional angles for the (1 → 2) linkage in the four sucrose structures*

Torsional angle is taken to be positive if the angle between  $A(1)$  and  $A(4)$  has a clockwise sense when viewed down the  $A(2)-A(3)$  bond. Pseudotorsional angle is defined similarly, except that a line between  $C(1)$  and  $C(2')$  is used in place of a bond.

	Planteose	Raffinose	Sucrose	1-Kestose
(a) Torsional angles				
C(1)-O(1)-C(2')-O(2')	-26.8°	11.4°	-44.4°	-65.8°
C(1)-O(1)-C(2')-C(3')	-141.5	-105.5	-159.6	176.7
C(1)-O(1)-C(2')-C(1')	93.2	129.5	73.9	53.3
O(5)-C(1)-O(1)-C(2')	108.7	81.7	107.6	84.6
C(2)-C(1)-O(1)-C(2')	-130.5	-157.5	-129.2	-152.9
(b) Pseudotorsional angles				
O(5)-C(1)---C(2')-O(2')	70.6	82.1	52.0	15.2
C(2)-C(1)---C(2')-O(2')	-140.8	-139.2	-154.1	157.5
O(5)-C(1)---C(2')-C(3')	-34.2	-21.8	-57.3	-110.7
C(2)-C(1)---C(2')-C(3')	114.3	116.8	96.5	31.6
O(5)-C(1)---C(2')-C(1')	179.1	169.8	158.9	121.4
C(2)-C(1)---C(2')-C(1')	-32.4	-31.1	-47.2	-96.2

The conformational torsion angles of the (1 → 2) linkage of sucrose in the four accurately known structures are given in Table 6(a). Comparison of these results gives the impression that there is very little conformational similarity between these four structures. The closest correlation is between planteose and sucrose. The conformations no longer seem as dissimilar, however, if the bonding oxygen O(1) is ignored and the conformations are examined using a pseudolink between C(1) of the glucose and C(2') of the fructose. As shown in Fig. 4(a) and (b) and Table 6(b), the major difference in the sucrose conformation in planteose and raffinose is the position of oxygen O(1) and not in the relative orientation of the glucose and fructose units. It is also evident that the fructofuranosyl ring in sucrose itself, [Fig. 4(c)], is twisted under the pyranosyl ring more than in either planteose or raffinose. This is probably the result of the two intramolecular hydrogen bonds found in sucrose which are not found in the trisaccharides. Fig. 4(d) shows that the  $\alpha$ -D-fructofuranosyl substituent on O(1') in 1-kestose places a steric strain on the central fructose, forcing it away from the orientation found in the other three sucrose structures. Using the two pseudotorsional angles O(5)-C(1)---C(2')-O(2'),  $\phi'_{OO}$ , and C(2)-C(1)---C(2')-C(3'),  $\phi'_{CC}$ , the conformational similarity between planteose and raffinose is evident from the values for  $\phi'_{OO}$  of 70.6 and 82.1° and for  $\phi'_{CC}$  of 114.3 and 116.8° respectively.

The (6 → 1) linkage to the  $\alpha$ -D-galactopyranosyl portion in planteose, C(5')-C(6')-O(6')-C(1''), has previously been observed only in raffinose. In both structures, it has the antiperiplanar arrangement (see Fig. 5). The planteobiose (1 → 6) linkage of planteose has a torsional angles of 172.5° and a root-mean-square displacement for the four-atom plane (Table 7) of only 0.04 Å. In raffinose, the angle is -169.5° and the r.m.s. displacement is 0.06 Å.

The hydroxymethyl groups also have interesting conformational features. The glucose C(6)-O(6)H has a  $\phi_{OO}$  of 63.4° and a  $\phi_{OC}$  of -176.4° or a *gauche-trans* conformation. This is the most favored form of the

Table 7. Least-squares plane calculated for the four atoms constituting the (1 → 6) linkage

E.s.d.'s are shown in parentheses.

	Displacement	
	Planteose	Raffinose
C(5')	-0.043 (3) Å	0.06 (1) Å
C(6')	0.042 (4)	-0.06 (1)
O(6')	0.047 (2)	-0.06 (1)
C(1'')	-0.046 (3)	0.06 (1)
R.m.s. deviation	0.044 (3)	0.063 (10)
<i>L</i>	0.2758	0.2399
<i>M</i>	-0.3718	0.9690
<i>N</i>	-0.8863	-0.0576
<i>D</i>	-6.7089 Å	5.4452 Å

three noneclipsing conformations (Sundaralingam, 1970). The *trans-gauche* form is the least favorable arrangement due to the 1-3 *peri* interaction with O(4) in  $\alpha$ -D-glucopyranosyls. On the  $\alpha$ -D-galactopyranosyl unit, the C(6'')-O(6'')H group has a *gauche-gauche* conformation with torsional angles  $\varphi_{OO}$  of  $-49.1^\circ$  and  $\varphi_{CO}$  of  $74.6^\circ$ . Using the same criteria, this should be the

least favorable conformation because of the *peri* interaction with O(4''). Presumably, the stabilization gained through intermolecular hydrogen bonding is enough to overcome the intramolecular repulsive forces of the '*peri*' interaction. The fructose C(1')-O(1')H group has a *gauche-gauche* conformation with  $\varphi_{OO} = -65.6^\circ$  and  $\varphi_{CO} = 52.1^\circ$ . This conformation positions the hydroxy under the ring, avoiding both the possible '*peri*' interactions with O(1) and O(3').

### Hydrogen bonding

The planteose molecules are arranged in a complex system of hydrogen bonds (Fig. 6). Most of the hydroxyls act as both a donor and an acceptor, except O(4') and O(4'') which act only as donors. There are two separate systems of hydrogen bonds. The first consists of two cross-linked chains [Fig. 7(a)]. One chain is formed by alternating O(3) and O(3') atoms. The other chain consists of six hydroxyl oxygen atoms and the water atom O(W1). The water molecule also acts as the cross link forming a hydrogen bond to O(3), as well as accepting a fourth bond from O(4'). In the second

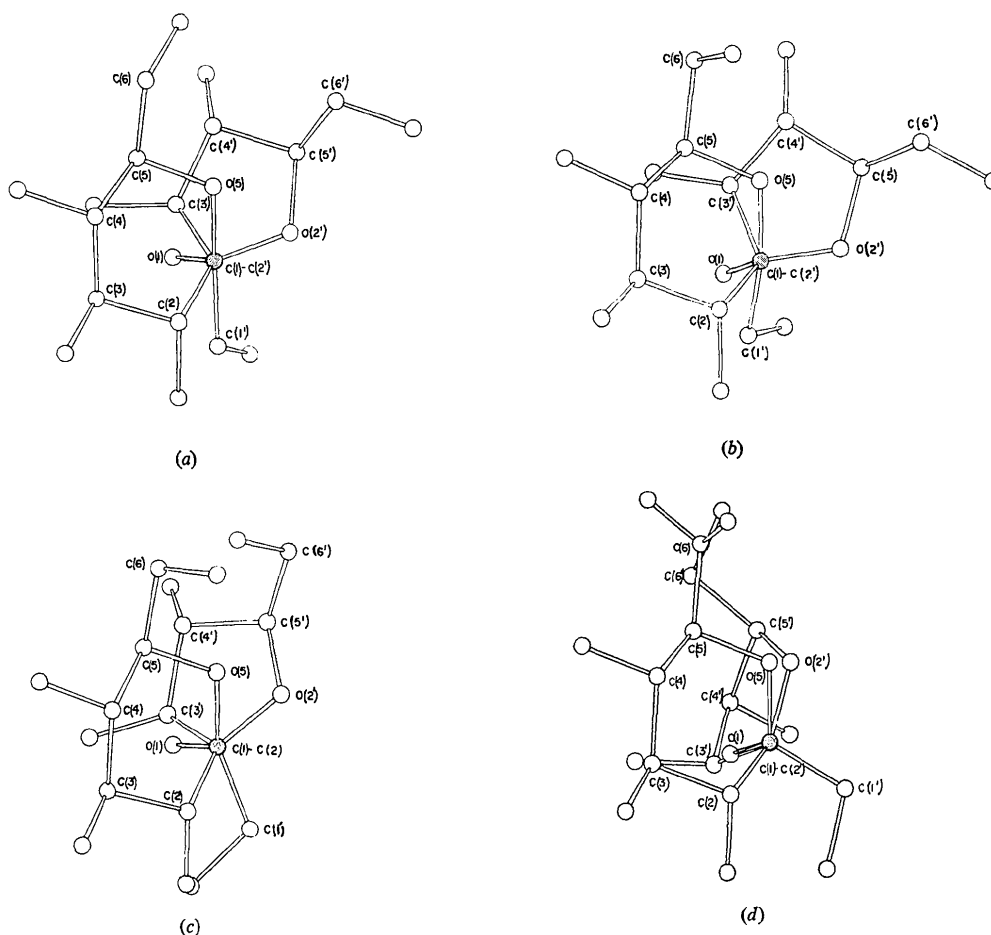


Fig. 4. Conformation of the (1 → 2) linkage in (a) planteose, (b) raffinose, (c) sucrose, and (d) 1-kestose, as viewed down a pseudolinkage between C(1) and C(2).

system, the hydrogen-bonded segment consists only of four oxygen atoms (Fig. 7(b)), including the furanosyl ring oxygen atom. There are no intramolecular hydrogen bonds. However, O(2) of a symmetry-related molecule acts as a bridge between O(6) and O(6'') at opposite ends of the molecule. This closes the circular conformation of the molecule through indirect intramolecular hydrogen bonds. A similar type of indirect intramolecular hydrogen bonding is found in raffinose

and 1-kestose. Hydrogen-bond distances and angles are given in Table 8.

It is also exceptional that O(W2) donates one hydrogen bond and accepts one bond, thereby leaving one water hydrogen atom unbound.

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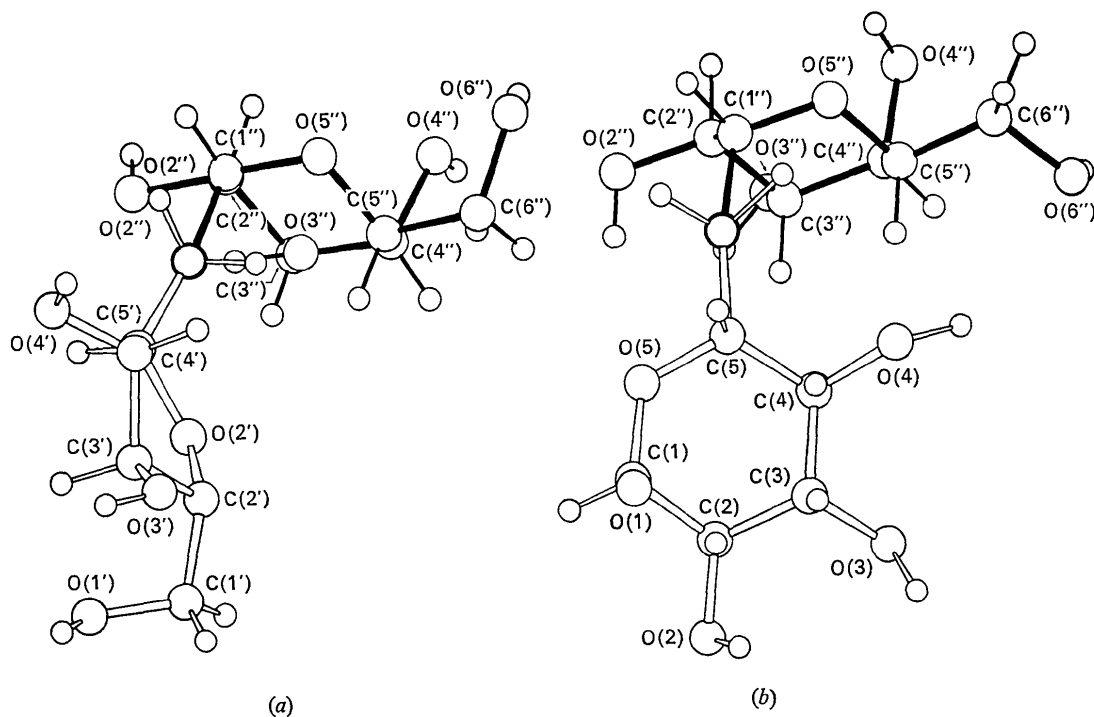


Fig. 5. Conformation of the (6 → 1) linkage as viewed down the C(6')-O(6'') bond in (a) planteose and (b) raffinose.

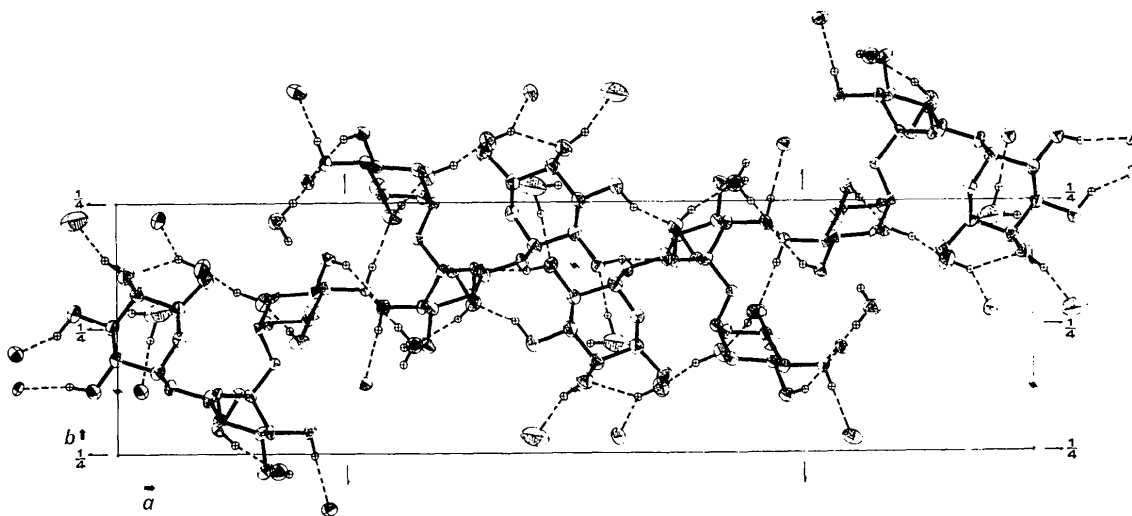


Fig. 6. Molecular packing and hydrogen bonding in planteose dihydrate.



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Table 8. *Hydrogen-bond distances and angles*

<i>i</i>	<i>j</i>	<i>k</i>	<i>d</i> ( <i>jk</i> )	$\angle$ ( <i>ijk</i> )	Symmetry operation on <i>k</i> *
C(2)	O(2)	→ O(6'')	2.664 Å	119.6°	1 545
C(3)	O(3)	→ O(3')	2.925	120.4	1 554
C(4)	O(4)	→ O(6)	2.699	110.5	3 564
C(6)	O(6)	→ O(2)	2.791	100.9	1 565
C(1')	O(1')	→ O(W1)	2.781	98.7	3 555
C(3')	O(3')	→ O(3)	2.861	140.2	3 555
C(4')	O(4')	→ O(W1)	2.849	111.6	3 565
C(2'')	O(2'')	→ O(2')	2.882	112.8	2 556
C(3'')	O(3'')	→ O(1')	2.670	123.1	2 556
C(4'')	O(4'')	→ O(W2)	2.818	101.9	2 555
C(6'')	O(6'')	→ O(3'')	2.815	140.0	2 555
	O(W1)	→ O(3)	3.094		3 555
	O(W1)	→ O(4)	2.704		1 555
	O(W2)	→ O(2'')	2.808		2 546

\* First number indicates symmetry operation performed; the second set of numbers specifies the lattice translation (Johnson, 1965).

1.	<i>x</i>	<i>y</i>	<i>z</i>
2.	- <i>x</i>	$\frac{1}{2}+y$	$\frac{1}{2}-z$
3.	$\frac{1}{2}-x$	- <i>y</i>	$\frac{1}{2}+z$
4.	$\frac{1}{2}+x$	$\frac{1}{2}-y$	- <i>z</i>

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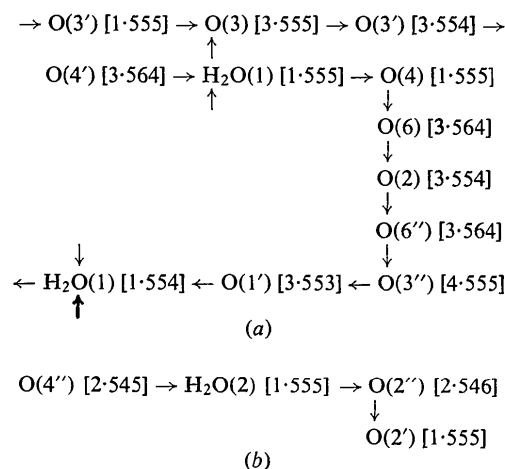


Fig. 7. The two hydrogen bonding systems in planteose dihydrate.