dependence of the P–N bond length on the angle P–N–P in cyclophosphazenes. This may be a bit disappointing, because it would be possible to explain qualitatively such a relationship by considering the hybridization of the atomic orbitals at nitrogen and the π bonding capability of the s–p lone pair hybrid as a function of the size of the angle P–N–P. Apparently, such an argument would be too simple to explain adequately the relevant structural features of the cyclophosphazenes.

The authors are indebted to Professor Aafje Vos for her interest in this work.

Table 6. *Intramolecular distances and angles in the* $N_4P_4Br_8$ *molecule*

Standard deviations in parentheses

P(1)——N(1)	1·576 (6) Å	P(1)—N(1′)–P(1′)	131·0 (4)°
P(1)——N(1′)	1·574 (6)	N(1) –P(1)—N(1′)	120·1 (4)
P(1)——Br(1)	2·166 (2)	Br(1)–P(1)—Br(2)	103·9 (1)
P(1)——Br(2)	2·176 (2)	N(1) –P(1)—Br(1)	112·2 (3)
Br(1)···Br(2)	3·418 (1)	N(1) –P(1)—Br(2)	104·6 (2)
P(1) ···P(1′)	2·865 (3)	N(1′)–P(1)—Br(1)	105·8 (3)
N(1) ···N(1′)	2·729 (9)	N(1′)–P(1)—Br(2)	109·2 (2)
N(1) ···Br(1)	3·123 (6)		
N(1) ···Br(2)	2·991 (6)		
N(1′)···Br(1)	3·004 (6)		
N(1′)···Br(2)	3·075 (6)		

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The Crystal and Molecular Structure of 1-Kestose

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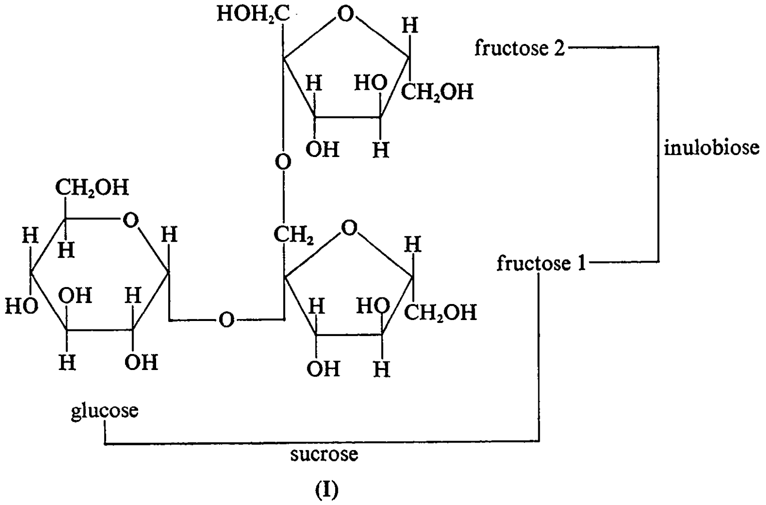
The crystal structure of 1-kestose, O-α-D-glucopyranosyl-(1 → 2)-O-β-D-fructofuranosyl-(1 → 2)-β-D-fructofuranoside, $C_{18}H_{32}O_{16}$, has been determined by direct methods using the tangent formula for phase determination. The space group is $P2_12_12_1$, 4 molecules in a unit cell with $a=7{\cdot}935$ (5), $b=9{\cdot}994$ (8), $c=26{\cdot}699$ (9) Å. The structure was refined to $R=0{\cdot}039$ for 2089 reflections measured with Cu $K\alpha$ radiation. The α-D-glucopyranoside unit of the molecule has the normal $C1$ chair conformation, with a primary alcohol group that is disordered over two orientations. Fructofuranoside units have puckered rings with different conformations: C′(4) is the principal out-of-plane atom in one, while C″(3) is the principal out-of-plane atom in the other. The conformation of the 1 → 2 linkage in the sucrose moiety is different from that in the trisaccharides planteose and raffinose, and is closer to that observed in sucrose. The 1 → 2 linkage of the inulobiose moiety is *anti*, with the four atoms C′(2), C′(1), O′(1) and C″(2) forming a planar chain. All hydrogen bonding is intermolecular, with the majority of the hydroxyls functioning as both donor and acceptor groups. The exception is O′(4), which is a donor only. Of the five ether oxygen atoms, only the ring oxygen atom O″(2) accepts a hydrogen bond.

Introduction

Three non-reducing trisaccharides are synthesized through the enzymatic action of invertase on sucrose by transfructosylation, *i.e.*, the transfer of a β-D-fructofuranosyl radical from one molecule of sucrose to one of the three primary alcoholic groups of another sucrose molecule (Bacon & Bell, 1953; Gross, 1962;

Stanek, Černý & Pacák, 1965). These are 1-kestose, 6-kestose, and neo-kestose. The repetition of this process on the new terminal D-fructofuranosyl group of 1-kestose gives the tetrasaccharide, nystose. The polysaccharide inulin, which is the main reserve carbohydrate of plants, can be regarded as resulting from an extension of the process exemplified by the series sucrose → 1-kestose → nystose → and so on to the linear fructosan, inulin (Binkley, Horton & Bhacca, 1969).

1-Kestose is the principal trisaccharide of the kestose group, with the chemical name O-α-D-glucopyranosyl-(1 → 2)-*O*-β-D-fructofuranosyl-(1 → 2)-β-D-fructofuranoside (Aspinall, Percival, Rees & Rennie, 1967). It contains sucrose and inulobiose moieties, as shown in (I). Apart from the intrinsic interest in the conformation of 1-kestose, a primary purpose of this investigation was to compare the conformation of the sucrose unit in different intramolecular environments, *i.e.*, in sucrose itself (Brown & Levy, 1963) and in sucrose linked: *via* the glucose unit to α-D-galactose in raffinose (Berman, 1970), *via* the fructose unit to α-D-galactose in planteose (Rohrer, 1971), and *via* the fructose unit to β-D-fructose in this molecule. Since the polysaccharide inulin consists of about 35 β-D-1 → 2 linked fructofuranose residues terminating in sucrose, this structure determination should give data which are useful for extrapolation to model structures for the macromolecular polysaccharide.



(I)

Experimental

Large transparent prismatic crystals of 1-kestose were provided by Dr W. W. Binkley of the New York Sugar Trade Laboratory, Inc.

Crystal data are as follows:

1-kestose, $C_{18}H_{32}O_{16}$, M.W. 504·44, m.p. ~ 184°
Space group $P2_12_12_1$, from systematic absences,
$h00$ with h odd, $0k0$ with k odd, $00l$ with l odd.
$a = 7{\cdot}935\ (5)$ Å
$b = 9{\cdot}994\ (8)$
$c = 26{\cdot}699\ (9)$ (values in parentheses are estimated standard errors)
$\lambda_{\text{Cu}\,K\alpha} = 1{\cdot}5418$ Å
$Z = 4$
$D_x = 1{\cdot}582$ g.cm^3
$D_m = 1{\cdot}574$ g.cm^3
$\mu_{\text{Cu}\,K\alpha} = 12{\cdot}38\ \text{cm}^{-1}$.

Unit-cell parameters and three-dimensional intensity data were obtained on a Picker FACS I diffractometer using Ni-filtered Cu *Kα* radiation with a crystal of dimensions 0·20 × 0·20 × 0·20 mm mounted along the a^* axis. A 2θ scanning mode with varying interval was used up to the maximum value of $2\theta = 130°$. Of the 2089 recorded data, 107 reflections whose intensities were below two standard deviations, based on counting statistics, were considered to be unobserved. The data were reduced to structure amplitudes using an IBM 1130 program (Shiono, 1969), without absorption corrections. The crystal density was measured by the flotation method in a mixture of hexane and bromoform.

Determination and refinement of the structure

The structure was solved by the application of the tangent formula (Karle & Hauptman, 1956; Karle & Karle, 1966) using an IBM 7090 version of the Hall (1968) direct-phasing methods. The following four reflections were selected as starting phases:

h	k	l	φ	$\|E\|$
0	5	21	0·5π	3·65
1	0	16	1·0π	2·56
2	0	15	0·5π	2·38
0	3	20	0·5π	1·99

The tangent-formula refinement was applied to 340 reflections with $E > 1{\cdot}30$. The 34 highest peaks on the resulting E map corresponded to 18 carbon and 16 oxygen atoms of a stereochemically reasonable model for the molecule. One cycle of block-diagonal least-squares refinement on the IBM 1130 (Shiono, 1968) gave $R = 0{\cdot}28$ for all reflections, which was reduced to 0·11 by a full-matrix isotropic least-squares cycle. Successive difference Fourier synthesis maps were then used to locate positions of the hydrogen atoms. The first difference map revealed hydrogen atoms attached to all carbon atoms except C(6) and some of the hydroxyl hydrogen atoms. The highest peak on the map was located at a stereochemically reasonable position for an atom to form another primary bond with C(6); its electron density was three times those of the other peaks, which were associated with the hydrogen atoms. The peak was interpreted as a second position for the primary alcohol group O(6)H, which was taken to be twofold disordered. A similar example was found in the structure of α-L-sorbose (Kim & Rosenstein, 1967), in which the primary alcohol group

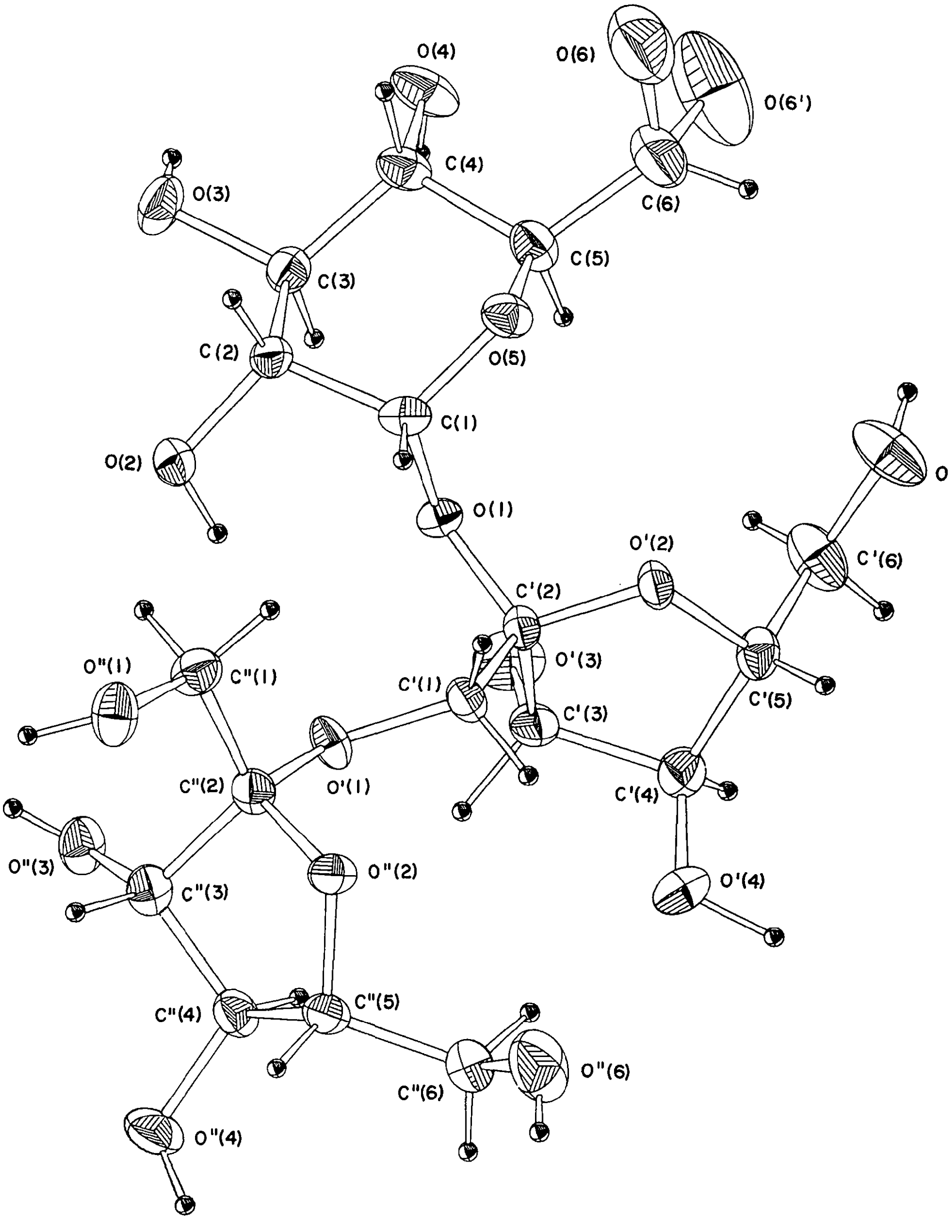


Fig. 1. Molecular conformation and atomic numbering in 1-kestose. The 50% probability thermal ellipsoids (Johnson, 1965) are shown for the carbon and oxygen atoms.

is also disordered. Inclusion of this disorder in the model resulted in no significant change in the agreement index, but this was not unexpected due to the small contribution of the scattering from O(6) relative to that of the whole molecule. All the hydrogen atoms, except for one on C(6) and those on O(6) and O′(3), were then located on the successive difference Fourier maps. They were assigned thermal parameters of the atoms to which they were bonded, and these parameters were not refined.

Refinement of the carbon and oxygen parameters, occupancy factors for O(6) and O(6′), and positional parameters of the hydrogen atoms was completed by the least-squares IBM 7090 program. The function minimized was $w_i(K|F_o|-|F_c|)^2$, where $w_i=|F_o|^{-2}$ for $|F_o|\geq 4|F_{\rm min}|$ and $w_i=4|F_{\rm min}|^{-2}$ for $|F_o|<4|F_{\rm min}|$, with $|F_{\rm min}|=10{\cdot}0$. The final cycle gave an R value of 0·039 for all reflections. The final positional and thermal parameters are given in Table 1; corresponding structure factors are listed in Table 2. Occupancy factors for the disordered O(6) and O(6′), when normalized, were 0·66 and 0·34 respectively. The unnormalized factors from the least-squares with variable occupancy totalled 1·10, due to overlap with the hydrogen atoms attached

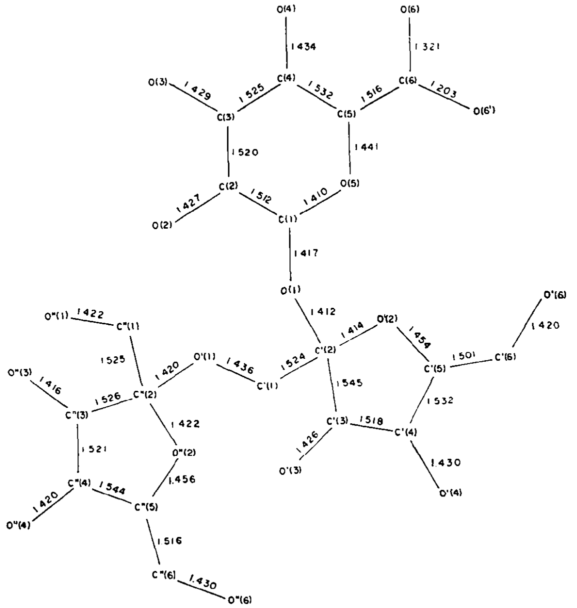


Fig. 2. Intramolecular bond distances (Å) in 1-kestose. Average e.s.d. is 0·005 Å. E.s.d.'s of the C(6)–O(6) and C(6)–O(6′) bond distances are 0·007 and 0·013 Å, respectively.

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters in* 1-*kestose**

Key to atomic numbering is given in Fig. 1. Temperature factor expression used:

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$$

Standard deviations given in parentheses refer to the least significant digits of the parameters. Values for H are × 10³. All others are × 10⁴.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	3809 (4)	6056 (3)	3924 (1)	61 (5)	38 (3)	8 (1)	3 (4)	−3 (0)	2 (1)
C(2)	4639 (4)	5314 (3)	3496 (1)	59 (5)	39 (3)	6 (1)	6 (4)	4 (1)	3 (1)
C(3)	4323 (5)	3816 (3)	3526 (1)	74 (5)	42 (3)	6 (1)	4 (4)	3 (1)	−1 (1)
C(4)	4730 (5)	3298 (3)	4049 (1)	99 (6)	36 (3)	7 (1)	5 (4)	−6 (1)	1 (1)
C(5)	3706 (5)	4100 (4)	4432 (1)	102 (6)	45 (3)	6 (1)	−6 (4)	−1 (1)	3 (1)
C(6)	3969 (7)	3675 (5)	4972 (1)	218 (10)	102 (5)	7 (1)	41 (7)	−1 (2)	4 (1)
C′(1)	1639 (4)	8466 (3)	3876 (1)	83 (5)	40 (3)	4 (1)	1 (4)	−1 (1)	2 (1)
C′(2)	1026 (4)	7070 (3)	4016 (1)	63 (5)	41 (3)	4 (1)	−1 (4)	1 (1)	1 (1)
C′(3)	−9 (4)	6811 (4)	3821 (1)	56 (5)	56 (4)	6 (1)	2 (4)	−3 (1)	1 (1)
C′(4)	−1874 (5)	7185 (4)	4265 (1)	70 (5)	77 (4)	7 (1)	9 (5)	2 (2)	2 (1)
C′(5)	−760 (4)	6886 (4)	4721 (1)	56 (5)	57 (4)	6 (1)	−12 (4)	4 (1)	1 (1)
C′(6)	−1027 (5)	5499 (4)	4922 (1)	120 (7)	75 (4)	8 (1)	−44 (5)	−6 (2)	7 (1)
C″(1)	4470 (5)	9461 (3)	3163 (1)	71 (5)	43 (3)	9 (1)	2 (4)	3 (1)	1 (1)
C″(2)	2568 (5)	9667 (3)	3135 (1)	84 (6)	29 (3)	6 (1)	−2 (4)	2 (1)	1 (1)
C″(3)	1824 (5)	9885 (3)	2614 (1)	95 (6)	35 (3)	6 (1)	−6 (4)	2 (1)	−1 (1)
C″(4)	0131 (5)	10524 (4)	2734 (1)	91 (6)	48 (3)	5 (1)	2 (4)	−2 (1)	−1 (1)
C″(5)	0629 (4)	11466 (3)	3168 (1)	75 (5)	41 (3)	6 (1)	8 (4)	−3 (1)	1 (1)
C″(6)	−705 (5)	11667 (4)	3568 (1)	106 (6)	71 (4)	6 (1)	12 (5)	1 (2)	1 (1)
O(1)	2054 (3)	6035 (2)	3826 (1)	47 (3)	34 (2)	6 (1)	2 (3)	−1 (1)	−1 (1)
O(2)	4094 (4)	5858 (3)	3029 (1)	112 (5)	58 (3)	6 (1)	23 (3)	9 (1)	6 (1)
O(3)	5344 (4)	3209 (2)	3148 (1)	127 (5)	42 (2)	9 (1)	10 (3)	15 (1)	−4 (4)
O(4)	4357 (4)	1896 (2)	4085 (1)	158 (5)	36 (2)	9 (1)	−1 (3)	−13 (1)	4 (1)
O(5)	4212 (3)	5481 (2)	4392 (1)	82 (4)	44 (2)	6 (1)	5 (2)	−6 (1)	−1 (1)
O(6)	5545 (6)	3482 (7)	5114 (2)	128 (9)	194 (9)	10 (1)	−2 (8)	−3 (2)	15 (2)
O(6′)	3612 (18)	2598 (12)	5139 (4)	350 (34)	118 (14)	13 (2)	−118 (19)	1 (6)	12 (4)
O′(1)	1748 (3)	8527 (2)	3339 (1)	97 (4)	38 (2)	4 (1)	−18 (3)	1 (1)	3 (1)
O′(2)	962 (3)	7051 (3)	4545 (1)	53 (3)	66 (3)	4 (1)	−3 (3)	1 (1)	2 (1)
O′(3)	−1063 (4)	5449 (3)	3684 (1)	92 (4)	57 (3)	13 (1)	−22 (3)	−11 (1)	−5 (1)
O′(4)	−2242 (4)	8579 (3)	4214 (1)	133 (5)	92 (3)	12 (1)	63 (4)	12 (1)	5 (1)
O′(6)	7 (4)	5327 (3)	5351 (1)	143 (5)	82 (3)	11 (1)	−47 (4)	−14 (1)	15 (1)
O″(1)	5371 (3)	10562 (2)	2958 (1)	103 (4)	57 (3)	8 (1)	−24 (3)	8 (1)	−2 (1)
O″(2)	2117 (3)	10860 (2)	3392 (1)	76 (4)	37 (2)	6 (1)	10 (3)	−5 (1)	−3 (1)
O″(3)	1649 (3)	8708 (2)	2323 (1)	116 (5)	43 (2)	6 (1)	−7 (3)	3 (1)	−4 (1)
O″(4)	− 542 (4)	11199 (3)	2311 (1)	142 (5)	66 (3)	6 (1)	28 (4)	−11 (1)	−1 (1)
O″(6)	− 90 (5)	12609 (3)	3928 (1)	244 (7)	80 (3)	8 (1)	14 (5)	−1 (2)	−5 (1)

Table 1 (*cont.*)

	x	y	z
H(C1)	417	706	396
H(C2)	585	545	350
H(C3)	280	364	345
H(C4)	609	339	416
H(C5)	240	402	437
H(C6)	317	384	522
H(C′1)	260	866	407
H′(C′1)	077	905	401
H(C′3)	−113	739	348
H(C′4)	−293	665	431
H(C′5)	− 88	757	497
H(C′6)	− 85	481	469
H′(C′6)	−234	533	501
H(C″1)	472	853	299
H′(C″1)	482	925	351
H(C″3)	256	1056	242
H(C″4)	− 70	979	288
H(C″5)	93	1233	301
H(C″6)	−109	1079	376
H′(C″6)	−179	1186	341
H(O2)	298	606	305
H(O3)	521	244	318
H(O4)	334	179	393
H(O′4)	−310	889	447
H(O′6)	− 5	445	542
H(O″1)	548	1055	262
H(O″3)	254	868	216
H(O″4)	−097	1204	238
H(O″6)	−048	1322	388

* Positions of one of the disordered hydrogen atoms attached to C(6) and of the hydrogen atoms on O(6), O(6′), and O′(3) were not observed on difference syntheses and are not reported.

to C(6) in the two orientations. The atomic scattering factors used were those of Cromer & Waber (1965) for carbon and oxygen and those of Stewart, Davidson & Simpson (1965) for hydrogen.

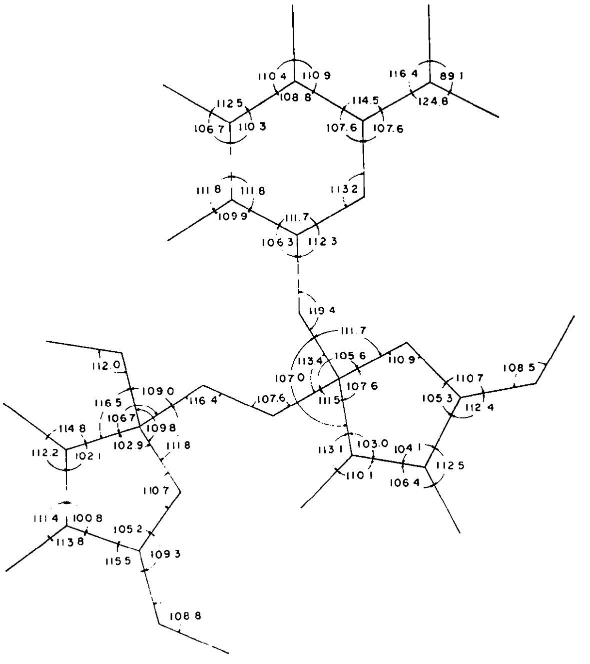


Fig. 3. Bond angles (°) in 1-kestose. Average e.s.d. is 0·3°. E.s.d.'s of angles involving O(6) and O(6′) are 0·7°.

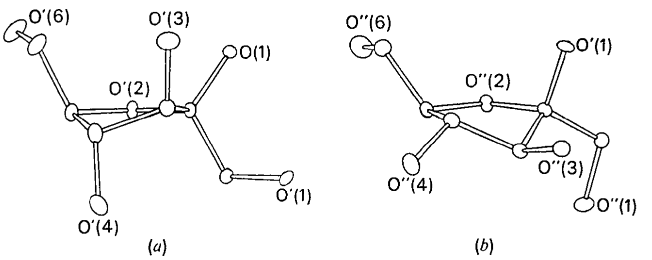


Fig. 4. Comparison of conformations of the two fructofuranoside rings, showing puckering and configurations of hydroxyl groups. (*a*) Fructose 1 (conformation E_4 or $_4T^3$) and (*b*) fructose 2 (conformation E_3).

Molecular conformation

The molecular configuration and conformation of 1-kestose are illustrated in Fig. 1; in atomic numbering on the carbon and oxygen atoms, the letters of the glucose part are unprimed, those of fructose 1 are singly primed, and those of fructose 2 are doubly primed. Corresponding observed bond lengths and valence angles are shown in Figs. 2 and 3. Ring conformations in the molecule are as expected, with a chair-form pyranose ring and two puckered furanose rings. The α-D-glucose part of the molecule has the 'normal' chair conformation, (Eliel, Allinger, Angyal & Morrison, 1966), *i.e.* $^4C_1$ (Hough & Richardson, 1967), with the two possible orientations of the primary alcohol group indicated by O(6) and O(6′) in Fig. 1. The occupancy factors of the two positions for the disordered oxygen give the position O(6) approximately double weight over position O(6′). The large thermal parameters and apparent shortening of the C(6)–O(6) and C(6)–O(6′) distances, given by the least-squares refinement, are consistent with the interpretation of the observed electron density distribution as that of a primary alcohol group with twofold orientational disorder. However, of the three staggered orientations of O(6) about the bond C(5)–C(6), that of O(6′) should be the least favored because of the '*peri*' or '1,3' interaction with O(4).

Dihedral angles of the pyranoside ring are given in Table 3. They show the same range of variation, between 50 and 65°, as found in other pyranose sugar crystal structures, where the rings have the normal chair conformation.

The two fructofuranose rings have different conformations, as shown in Fig. 4. The ring conformation angles and other signed torsion angles (Klyne & Prelog, 1960; Brown & Levy, 1963) are given in Table 3, and Table 4 describes various least-squares best planes. For fructose 1, there are two alternate descriptions: one is an 'envelope' conformation with C′(4) out of the plane (*a*), which contains the other atoms within ±0·02 Å, *i.e.* conformation E_4; the other is a 'twist' conformation, with C′(4) displaced by 0·39 Å and C′(3) displaced by 0·09 Å out of the exact plane (*c*) of C′(2), C′(5), and O′(2), *i.e.* conformation $_4T^3$. The displacement of C(4) is *exo*, and that of C(3) is *endo*, relative to the ring substituents O(1) and C′(6). For fructose 2, the 'envelope' description E_3 with C″(3) 0·63 Å out of the plane (*d*) which contains the other atoms within ±0·004 Å, is unambiguous within the experimental errors of this structure determination. This displacement is *exo* to O′(1) and C″(6). [The ring notation is that recommended by the American Chemical Society Committee on Carbohydrate Nomenclature (Tipson, 1970), in which the superscript and sub-

Table 2. *Observed and calculated structure factors in* 1-*kestose*

Columns are: index *l*, $10|F_{\text{obs}}|$, $10|F_{\text{calc}}|$. Asterisks indicate unobserved reflections.

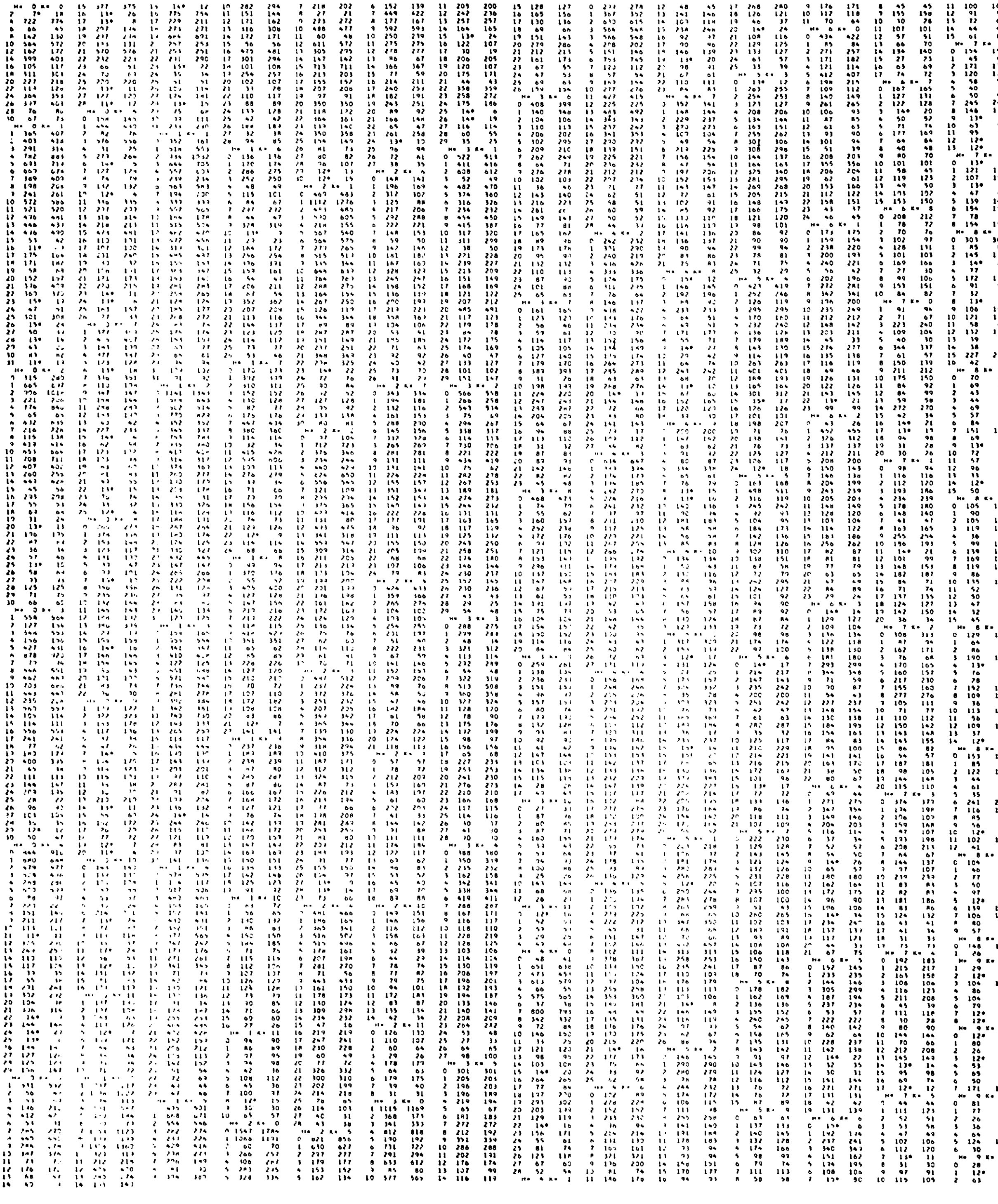


Table 3. *Important conformation angles in* 1-*kestose*

I *J* *K* *L*	
(*a*) Pyranose ring	
O(5) -C(1) -C(2) -C(3)	50·6°
C(1) -C(2) -C(3) -C(4)	−49·8
C(2) -C(3) -C(4) -C(5)	55·4
C(3) -C(4) -C(5) -O(5)	−61·4
C(4) -C(5) -O(5) -C(1)	64·5
C(5) -O(5) -C(1) -C(2)	−59·2
(*b*) 1 → 2 Glucose–fructose 1 linkage	
C(2) -C(1) -O(1) -C′(2)	−152·9
O(5) -C(1) -O(1) -C′(2)	84·7
C(1) -O(1) -C′(2)-C′(1)	53·3
C(1) -O(1) -C′(2)-O′(2)	−65·8
C(1) -O(1) -C′(2)-C′(3)	176·7
(*c*) Furanose ring 1	
O′(2)-C′(2)-C′(3)-C′(4)	21·1
C′(2)-C′(3)-C′(4)-C′(5)	−29·3
C′(3)-C′(4)-C′(5)-O′(2)	28·0
C′(4)-C′(5)-O′(2)-C′(2)	−15·2
C′(5)-O′(2)-C′(2)-C′(3)	−3·7

I *J* *K* *L*	
(*d*) 1 → 2 Fructose 1-fructose 2 linkage	
C′(2) -C′(1) -O′(1) -C″(2)	−169·7°
C′(1) -O′(1) -C″(2)-C″(1)	80·5
C′(1) -O′(1) -C″(2)-O″(2)	−41·1
C′(1) -O′(1) -C″(2)-C″(3)	−152·9
(*e*) Furanose ring 2	
O″(2)-C″(2)-C″(3)-C″(4)	−40·7
C″(2)-C″(3)-C″(4)-C″(5)	40·1
C″(3)-C″(4)-C″(5)-O″(2)	−25·8
C″(4)-C″(5)-O″(2)-C″(2)	0·6
C″(5)-O″(2)-C″(2)-C″(3)	24·9
(*f*) Primary alcohol groups	
C(4)—C(5)—C(6)—O(6)	45·6
C(4)—C(5)—C(6)—O(6′)	−63·3
O(5)—C(5)—C(6)—O(6)	−74·0
O(5)—C(5)—C(6)—O(6′)	177·1
C′(4) -C′(5) -C′(6)-O′(6)	−178·0
O(2)—C′(5) -C′(6) -O′(6)	64·6
O′(1) -C″(2)-C″(1)-O″(1)	179·2
O″(2)-C″(2)-C″(1)-O″(1)	−57·9
C″(3)-C″(2)-C″(1)-O″(1)	58·5
C″(4)-C″(5)-C″(6)-O″(6)	−177·2
O″(2)-C″(5)-C″(6)-O″(6)	64·4

Table 4. *Least squares best planes with atomic displacements for the fructose rings in* 1-*kestose*

Equations of planes $Ax+By+Cz=D$, where x,y,z are in Å.

Plane	*A*	*B*	*C*	*D*
(*a*)	−0·1500	0·9885	−0·0204	6·6243
(*b*)	0·0389	0·9930	0·1117	8·2972
(*c*)	−0·1168	0·9931	0·0088	7·0164
(*d*)	0·5800	0·5268	−0·6213	1·0688
(*e*)	0·6917	0·6349	−0·3442	4·7940
(*f*)	0·5842	0·5295	−0·6151	1·1574
(*g*)	0·9238	−0·3782	0·0598	−1·3349

Displacements in Å from best planes. Atoms whose displacements are in bold-face type were excluded from the calculation of the best plane.

Fructose 1	(*a*)	(*b*)	(*c*)
C′(2)	0·019	−0·052	0·000
C′(3)	−0·011	**−0·423**	**−0·094**
C′(4)	**0·464**	0·047	**0·389**
C′(5)	0·012	−0·079	0·000
O′(2)	−0·020	0·085	0·000

Fructose 2	(*d*)	(*e*)	(*f*)
C″(2)	0·002	−0·133	0·000
C″(3)	**0·632**	0·077	**0·627**
C″(4)	−0·002	**−0·557**	**−0·017**
C″(5)	0·003	−0·085	0·000
O″(2)	−0·004	0·141	0·000

Linkage fructose 1-fructose 2	(*g*)
C′(2)	0·055
C′(1)	−0·045
O′(1)	−0·074
C″(2)	0·063

script positions indicate *endo* and *exo* respectively. We have also used a modification suggested by Sundaralingam (1970) in which the major and minor displacements respectively, are indicated in front and behind the *T* symbol, which stands for *twist*.] As shown in Fig. 4, the orientation of the C–OH bonds, which is very different in the two rings, is more obvious than the ring shape: O′(3) and O′(4) are axial in fructose 1, and O″(3) and O″(4) are equatorial in fructose 2.

The glucopyranosyl-(1 → 2)-*O*-*β*-D-fructofuranosyl linkage whose conformation determines the overall shape of the sucrose component of the molecule is shown in Fig. 5(*a*), as viewed in the directions of the C(1)–O(1) bond and of the perpendicular to the plane of C(1)–O(1)–C′(2). The conformation is compared with those about the same links in sucrose (*b*) (Brown & Levy, 1963) and in the sucrose units of planteose (*c*) (Rohrer, 1971) and raffinose (*d*) (Berman, 1970). All four conformations are different, and the differences can be defined by the signed torsion or twist angles of bonds C(1)–O(1) and C′(2)–C′(3) about the bond O(1)–C′(2). These angles are 177° in (*a*), −160° in (*b*), −141° in (*c*), and −105° in (*d*).

The fructofuranosyl-(1 → 2)-*β*-D-fructofuranosyl linkage of the inulobiose unit of the molecule is shown in Fig. 6, with C′(1)–O′(1) parallel and perpendicular to the plane of the diagram. The conformation of the linking chain C′(2)–C′(1)–O′(1)–C″(2) is *anti* (torsion angle of −170°) with respect to the central link, and the atoms lie in one plane within ±0·07 Å [plane (*g*) in Table 4].

The C–C bond lengths over the whole molecule vary between 1·501 and 1·544 Å, with a mean of 1·524 Å over the 15 values. There are no significant differences, except for an indication of marginal significance that bonds of the primary alcohol groups tend to be shorter than the average. Excluding the disordered positions, O(6) and O(6′), the C–O bond lengths vary over a similar range, 1·410 to 1·456 Å with a mean of 1·426 Å over 20 values. However, the C–O bonds associated with the anomeric carbon atoms C(1) and the ring oxygen atoms show systematic trends similar to those pointed out by Berman, Chu & Jeffrey (1967) from a review of distances in other pyranose sugars. Variations from the mean of the bond lengths for C(5)–O(5), O(5)–C(1), and C(1)–O(1) are +0·015, −0·016, −0·009 Å respectively. These compare with values of +0·010, −0·010, −0·013 Å in methyl-α-glucoside (Berman & Kim, 1968), +0·018, −0·011, −0·025 Å in methyl-α-mannoside (Gatehouse & Poppleton, 1970), and +0·012, −0·020, −0·012 in methyl-β-maltoside (Chu & Jeffrey, 1967) for axially oriented C(1)–O(1) bonds. There is also good agreement with the results from sucrose, where the C(5)–O(5), O(5)–C(1), C(1)–O(1) distances are 1·436, 1·408 and 1·420 Å (Brown & Levy, 1963).

Another consistent feature of the C–O bond lengths is the disproportionation of the ring bonds by 0·03 to 0·04 Å in all three rings. The significance level of this observation is low, but there is now sufficient cumulative evidence from a variety of structures to justify a higher-precision analysis of sucrose, or of an appropriate monosaccharide, to establish whether these small variations reflect real features of the electronic structure of the molecules in the vicinity of the ring oxygen atoms and the anomeric carbon atoms, *cf.* Sundaralingam (1965).

The valence angles, shown in Fig. 3, are unremarkable and confirm the general observation that in monosaccharides and oligosaccharides, angles subtended at the ether oxygen atoms are 5 to 10° greater than those at the ring carbon atoms.

Intermolecular packing and hydrogen bonding

The arrangement of the molecules in the structure is shown in Fig. 7. The molecules are linked by an extensive system of hydrogen bonds whose description is given in Table 5. There are two independent systems of hydrogen bonds. One consists of a four-link finite chain

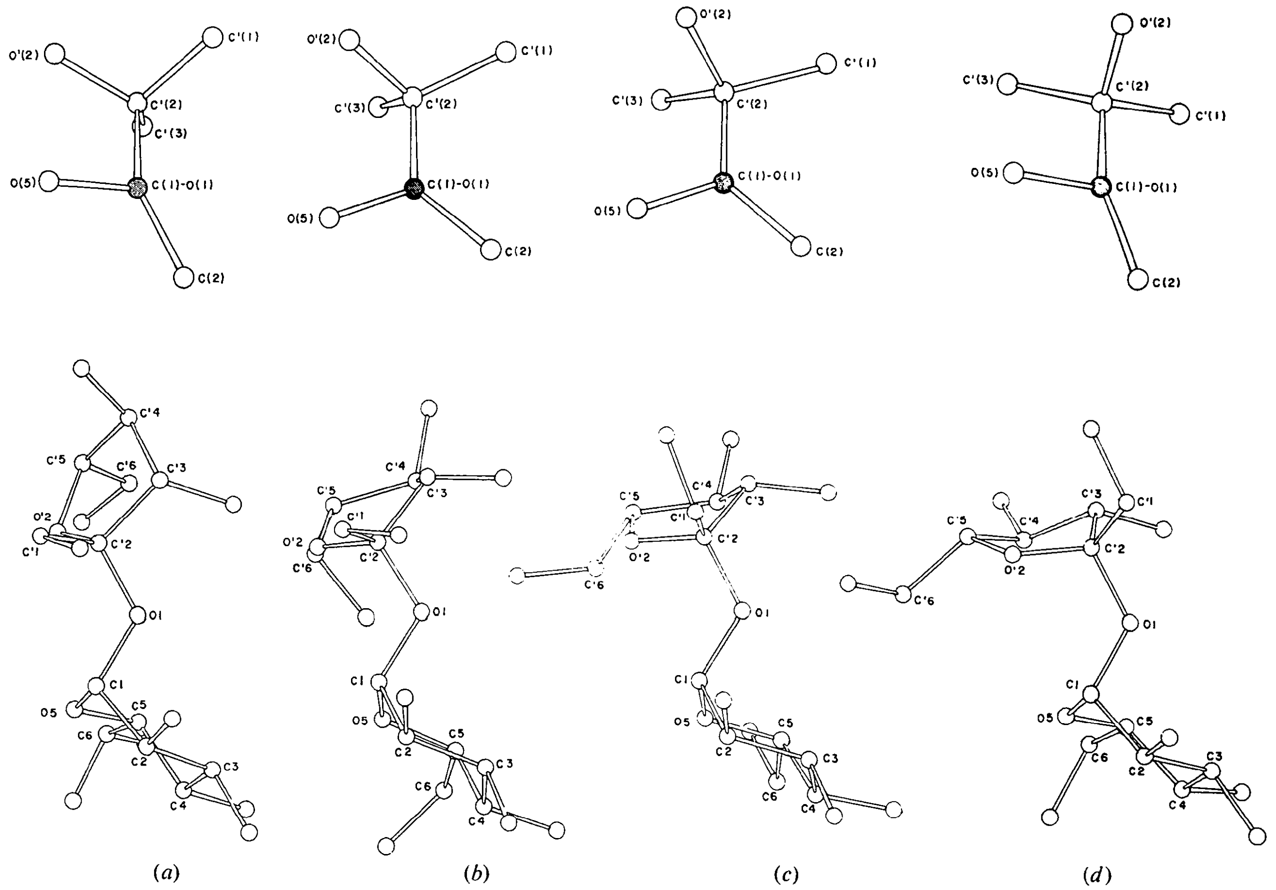


Fig. 5. Conformations of the 1 → 2 links in 1-kestose (*a*), sucrose (*b*), planteose (*c*), and raffinose (*d*): top, view with C(1)–O(1) perpendicular to plane of diagram and the overlapping atoms shaded; bottom, view of the sucrose unit with C(1)–O(1)–C′(2) in the plane of the diagram.

extending in the **a** direction, consisting of

$$O'(4)\,(5551) \rightarrow O'(6)\,(4663) \rightarrow O(4)\,(4651) \rightarrow O''(2)\,(4551)\,.$$

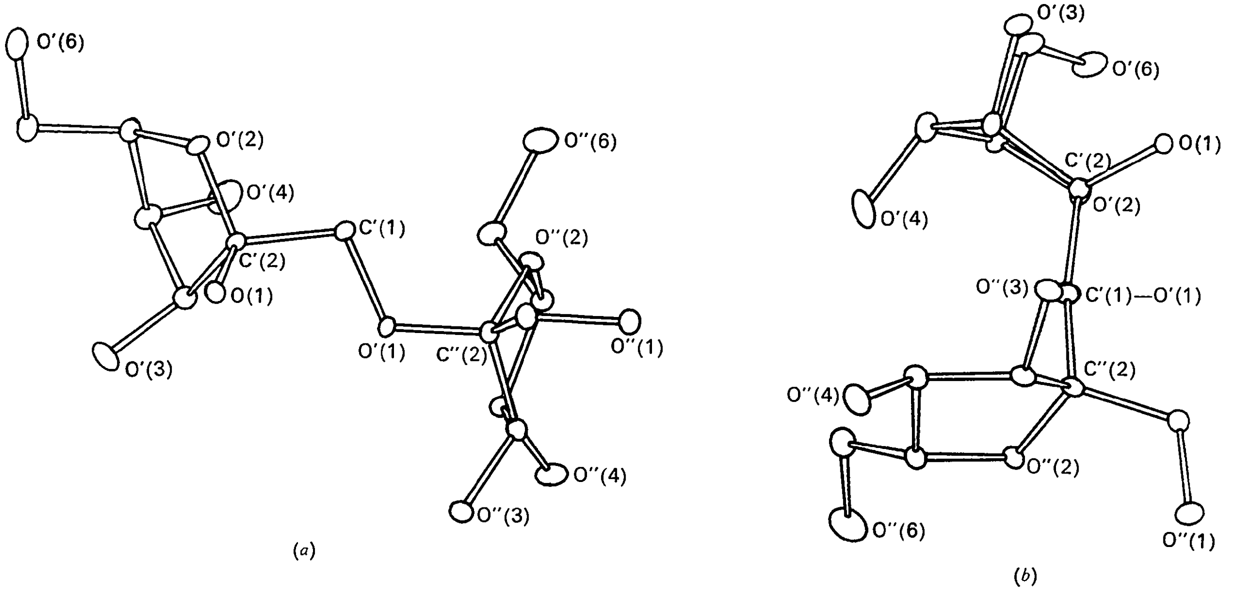
These are all strong bonds with O···O distances ranging from 2·703 to 2·765 Å. The other system is a closed loop with a branched chain, comprising:

Table 5. *Hydrogen bond and* O···O *intermolecular distances and angles in* 1-*kestose*

				Distances		Angles		Symmetry operation
i	*j*	*k*	*l*	*jl*	*jk*	*ijl*	*jkl*	of *l**
C(2)	O(2)	H(O2)	O″(4)	2·980 Å	0·90 Å	126·6°	148°	545·4
C(3)	O(3)	H(O3)	O″(1)	2·693	0·78	123·7	154	545·1
C(4)	O(4)	H(O4)	O″(2)	2·765	0·92	117·0	145	545·1
C′(3)	O′(3)		O″(4)	3·039		85·5		545·4
C′(4)	O′(4)	H(O′4)	O′(6)	2·703	1·01	121·2	154	466·3
C′(6)	O′(6)	H(O′6)	O(4)	2·733	0·89	115·7	145	456·3
C″(1)	O″(1)	H(O″1)	O(2)	2·685	0·91	122·9	167	655·4
C″(3)	O″(3)	H(O″3)	O(3)	2·742	0·83	108·5	166	655·4
C″(4)	O″(4)	H(O″4)	O″(3)	2·830	0·92	105·2	165	555·4
C″(6)	O″(6)	H(O″6)	O′(3)	3·012	0·70	112·8	165	565·1
C″(2)	O″(2)		O(4)	2·765		118·4		565·1
C″(5)	O″(2)		O(4)	2·765		129·9		565·1
C″(6)	O″(6)		O(6)	2·826		114·5		466·3
C″(6)	O″(6)		O(6′)	2·704		116·1		466·3
C(6)	O(6)		O″(6)	2·826		98·5		566·3
C(6)	O(6)		O(6′)	2·744		145·7		556·3
C(6)	O(6′)		O″(6)	2·704		108·6		566·3
C(6)	O(6′)		O(6′)	2·744		118·0		456·3
Intermolecular oxygen–oxygen distances less than 3·5 Å:								
	O(1)		O″(4)	3·266				545·1
	O(4)		O″(1)	3·388				545·1
	O(6′)		O′(6)	3·384				556·3
	O′(1)		O″(4)	3·055				545·4
	O′(3)		O″(3)	3·236				545·4

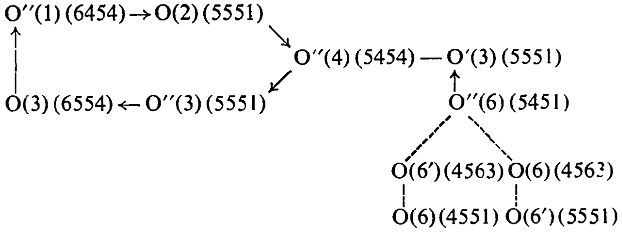
* Reference point is atom *j* at 555·1. The first three digits code a lattice translation, *e.g.* 466·1 is $-a+b+c$ from 555·1. The last digit indicates one of the following operations:

1: $x \quad y \quad z$ 2: $\tfrac{1}{2}-x \quad -y \quad \tfrac{1}{2}+z$
3: $\tfrac{1}{2}+x \quad \tfrac{1}{2}-y \quad -z$ 4: $-x \quad \tfrac{1}{2}+y \quad \tfrac{1}{2}-z$



(*a*) (*b*)

Fig. 6. Conformation of the 1 → 2 linkage of inulobiose moiety in 1-kestose, (*a*) projected on the plane of C′(1), O′(1) and C″(2), (*b*) viewed down the directed bond O′(1)–C′(1).



The dotted lines indicate alternatives involving the two-fold disorder of the glycosidic alcohol group. As shown in Table 5, O(6) and O(6') separations correspond to good intermolecular hydrogen-bond distances with each other and with O''(6). Presumably, this is the primary reason for the disorder, with the especially favorable intermolecular bonding overcoming the unfavorable intramolecular interaction between O(6') and O(4) referred to earlier in the paper.

There is no intramolecular hydrogen bonding as in the dissaccharides, sucrose, cellobiose (Chu & Jeffrey, 1968), or methyl-β-maltoside. All the hydroxyl groups are involved in intermolecular hydrogen bonding, and each functions as single donor and acceptor, except O'(4)H, which is a donor only and O''(4)H, which is a donor and accepts two bonds. Of the ether oxygen atoms, only the ring oxygen O''(2) is a hydrogen-bond acceptor. None of the glycosidic linkage oxygen atoms accepts hydrogen bonds. The O(H)···O distance range is 2·685 to 3·039 Å, which is a similar range to that observed in raffinose pentahydrate (2·664 to 3·000 Å).

There is a considerable difference in the hydrogen-bonding environment of the two furanoside rings, which could be either the cause or the consequence of the differences in their ring conformations. The furanoside unit 2 has a much stronger hydrogen-bond field, involving six hydrogen bonds with O''(4) and O''(3) donating and accepting strong hydrogen bonds, O''(2) accepting a strong bond, and O''(4) accepting a second weaker hydrogen bond. In furanoside 1, there are only three hydrogen bonds: the one from O'(4) is strong, but those to and from O'(3) are relatively weak with O···O separations greater than 3 Å.

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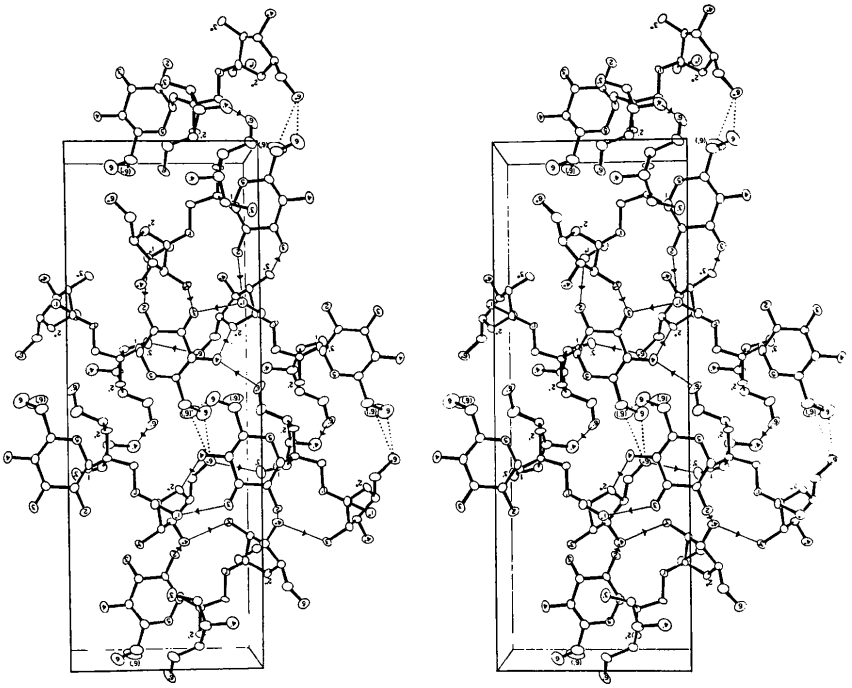

Fig. 7. Stereogram of 1-kestose viewed down the *a* axis showing hydrogen bonding as thin lines with arrows indicating donor direction. Alternative bonding between O(6'') and disordered atoms O(6) and O(6') is indicated by dotted lines. Oxygen atoms only are labelled.

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Synthetic Magnesian Merrihueite, Dipotassium Pentamagnesium Dodecasilicate: a Tetrahedral Magnesiosilicate Framework Crystal Structure

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The compound $K_2Mg_5Si_{12}O_{30}$ was synthesized hydrothermally at 790°C and 2000 bars P_{H_2O}, its composition verified by electron microscope analysis and its crystal structure determined. $K_2Mg_5Si_{12}O_{30}$ is isostructural with milarite: space group $P6/m\ 2/c\ 2/c$, $a=10{\cdot}222$ (2), $c=14{\cdot}152$ (2) Å, $Z=2$. Single-crystal diffractometer data were refined to $R=0{\cdot}028$ for 528 F_{obs}. This phase has the structural formula $Mg_2{}^{[6]}K^{[9]}K^{[12]}Mg_3{}^{[4]}Si_{12}{}^{[4]}O_{30}$, where the coordination number is indicated in brackets. The SiO_4 tetrahedra form hexagonal double rings with the composition $Si_{12}O_{30}$. These double rings are linked by magnesium atoms in tetrahedral four-coordination to form a tetrahedral magnesiosilicate framework structure, the first to be described. One half of the K atoms are located in 9-coordinated sites ($\frac{1}{3},\frac{2}{3},0$ *etc.*) which have not been found to be populated in other milarite-group structures. On the basis of this structure determination, we propose $A_2{}^{[6]}B_2{}^{[9]}C^{[12]}D^{[18]}T2_3{}^{[4]}T1_{12}{}^{[4]}O_{30}$ as a general crystal-chemical formula for milarite-type structures.

Introduction

The compound $K_2Mg_5Si_{12}O_{30}$ was first synthesized by Roedder (1951) while he was studying the phase relations of the system K_2O–MgO–SiO_2. Olsen (1967) analyzed Roedder's material using a microprobe and thus confirmed the composition. Seifert & Schreyer (1969) synthesized the compound under both hydrothermal and dry conditions and determined the lattice constants. These studies established that the compound is isostructural with milarite, $KCa_2Be_2Al(Si_{12}O_{30})\cdot\frac{1}{2}H_2O$ (Ito, Morimoto & Sadanaga, 1952) and osumilite, $(K,Na)(Fe,Mg)_2(Al,Fe)_3(Al,Si)_{12}O_{30}$ (Miyashiro, 1956). Because of the analogy in the chemical formulas it appears that three Mg atoms per formula unit in $K_2Mg_2(Mg_3Si_{12}O_{30})$ should be in tetrahedral 4-coordination. Such coordination is very rare; the only reported case of a silicate with Mg in 4-coordination is melilite $(Ca,Na)_2(Mg,Al)Si_2O_7$ (Smith, 1953), where Mg and Al atoms are statistically distributed over one site. Furthermore $K_2Mg_5Si_{12}O_{30}$ contains twice as much potassium as can be accommodated in the K-sites known from the milarite structure. In order to verify the occurrence of magnesium in 4-coordination and to find out which sites are occupied by the excess potassium atoms the crystal structure of $K_2Mg_5Si_{12}O_{30}$ was determined.

Experimental

The compound $K_2Mg_5Si_{12}O_{30}$ was produced by the decomposition of a synthetic mica, $KMg_3Si_4O_{11}(OH)$, at 790°C and 2000 bars P_{H_2O} (Forbes, 1972). The composition was verified by electron microprobe analysis: $K_2O=9{\cdot}38$, $MgO=19{\cdot}69$, $SiO_2=70{\cdot}82$ weight per cent, as compared with the values of 9·26, 19·82 and 70·91 weight per cent calculated for the ideal composition.