The Crystal and Molecular Structure of a Dimeric Form of 5-*keto*-D-Fructose; D-*threo*-Hexo-2,5-diulose Dimer

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Crystals of the 5-*keto*-D-fructose dimer $C_{12}H_{20}O_{12}$ are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 12.094(3)$ Å, $b = 21.700(6)$ Å, $c = 5.329(3)$ Å and $Z = 4$.

X-Ray data were collected on a Siemens AED diffractometer using MoKα radiation and the five-value scan technique. The structure was solved by direct methods (MULTAN) and refined by full matrix least squares.

The dimer consists of α-D-fructose in the furanose form and α-L-sorbose in the pyranose form; the latter appears as a result of the dimerization. The two dimeric partners are interconnected through ether bridges from C(5) of sorbose to C(4) and C(5), respectively, of fructose, thus forming a dioxolane ring. The latter, as well as the furanosyl ring, has the envelope conformation.

Average values for C−C, C−O(hydroxyl) and C−O(ether) bond lengths are found to be 1.525(2), 1.419(2) and 1.422(2) Å, respectively.

All the hydroxyl groups and one of the four ether oxygens participate in hydrogen bonding. Three hydrogen bonds are intramolecular.

The present compound (5KF) is the first dicarbonyl sugar to be isolated from natural material. It was discovered by Weidehagen and Bernsee[1] in 1960 in connection with studies on the metabolic product of acetic acid bacteria utilizing sucrose; the same product was later obtained directly from fructose using the same bacteria.

Weidehagen and Bernsee assumed that the fructose molecule had been dehydrogenated in the 6-position and transferred to 6-*aldo*-D-fructose which they report to have isolated in crystalline form. The specific rotation of the metabolic product was found to be almost equal to that of fructose itself,

and this fact was used as an argument for the proposed structure; D(−)-fructose and 6-*aldo*-D-fructose have namely the same number of asymmetric carbons with almost equal configurations.
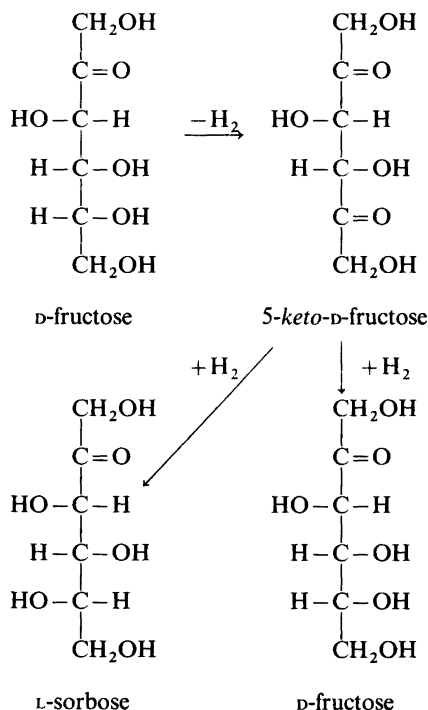

D(−)-fructose   6-*aldo*-D-fructose
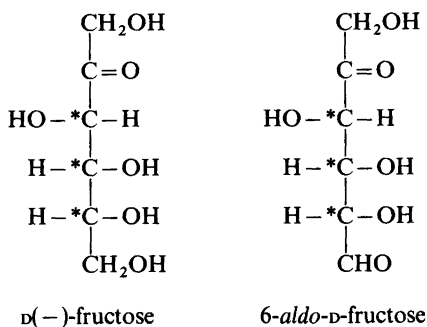
Although the proposed structure later was found to be incorrect (see below), it is interesting to note that Weidehagen and Bernsee at that point had an IR-spectrum which they thought indicated the presence of a pyranose ring as well as a furanose ring in the molecule.

The title compound was also isolated (in 1960) by Terada et al.[2] in the course of their studies on the utilization of fructose by ketogenic bacteria. However, their conclusion was that fructose had been dehydrogenated in the 5-position.

The presence of two carbonyl groups was shown by the hydroxylamine hydrochloride titration method. Furthermore, reaction with periodate yielded twice as much glycolic and glyoxylic acid as did fructose itself and these results, together with the fact that the compound was stable to bromine

oxidation, suggested the presence of two CH_2OH- $CO-$ radicals in the molecule. In addition, stepwise reduction with borohydride gave ketoses with R_F values of fructose and sorbose, and not those of tagatose and psicose. One should note in this connection that hydrogenation of 5-keto-D-fructose at positions 2 or 5 gives the same products, namely D-fructose or L-sorbose.

$$
\begin{array}{ccc}
CH_2OH & & CH_2OH \\
| & & | \\
C=O & & C=O \\
| & & | \\
HO-C-H & \xrightarrow{-H_2} & HO-C-H \\
| & & | \\
H-C-OH & & H-C-OH \\
| & & | \\
H-C-OH & & C=O \\
| & & | \\
CH_2OH & & CH_2OH
\end{array}
$$

D-fructose   5-keto-D-fructose

$$+H_2 \quad\quad +H_2$$

$$
\begin{array}{ccc}
CH_2OH & & CH_2OH \\
| & & | \\
C=O & & C=O \\
| & & | \\
HO-C-H & & HO-C-H \\
| & & | \\
H-C-OH & & H-C-OH \\
| & & | \\
HO-C-H & & H-C-OH \\
| & & | \\
CH_2OH & & CH_2OH
\end{array}
$$

L-sorbose   D-fructose

Whiting and Coggings[3] found that bromine oxidation of L-sorbose, D-glucitol or D-fructose at 50 °C in the presence of freshly precipitated strontium carbonate yielded a dicarbonyl compound which they identified and named 2,5-D-*threo*-diketohexose.

The IR spectrum of this compound was identical to those of the metabolic products mentioned above, and mixed melting point determinations showed no depressions. It was therefore concluded that the three compounds were, in fact, identical.

Unequivocal proof that the mentioned dicarbonylhexose is indeed 5-keto-D-fructose has been given by England et al.[4] through enzymatic degradation of 5-tritiated D-fructose, obtained by stereospecific enzymatic reduction of the dicarbonylhexose.

A molecular structure proposal by Englard et al. is shown in Fig. 1. It is based on previously presented IR and NMR spectra which show that the molecule does not contain free carbonyl groups.[4] Furthermore, molecular weight determination by a freezing point depression method had indicated that the molecule was a monomer.[2] The proposed structure, cf. Fig. 1, is seen to contain two boat-shaped pyranose rings and one boat-shaped 1,4-dioxane ring, and may in addition have twofold symmetry.

More recent IR, NMR and MS studies carried out by Jantzen[5] indicated that 5-keto-D-fructose probably occurs in a dimeric form, and a series of possible dimeric structures might be thought of.

We found a challenging task in this structural problem which we now have solved. Preliminary results from the structure study have been published,[6] and a more detailed description of the structure is given here.

STRUCTURE ANALYSIS

Crystals of the title compound (5KF) were generously supplied by Jantzen.[5] The crystals are colourless needles elongated in the c-axis direction.

Crystal data. $C_{12}H_{20}O_{12}$; F.W. 356.28.
Space group: $P2_12_12_1$; $a=12.094(3)$ Å, $b=21.700(6)$ Å, $c=5.329(3)$ Å;
$V=1398.54$ Å^3; $D_c=1.692$ g/cm^3, D_m(flotation)= 1.68 g/cm^3;
$Z=4$; $\mu=1.66$ cm^{-1} (MoKα).

A crystal of approximate dimensions $0.20\times 0.15\times 0.40$ mm was used for the X-ray analysis which was carried out on a papertape controlled Siemens AED diffractometer using MoKα radiation ($\lambda=0.71069$ Å).

The unit cell dimensions were determined from the 2θ values of 17 high order reflections in the range $26° < 2\theta < 42°$ measured at room temperature,
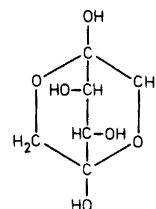

Fig. 1. The structure of the title compound as proposed by Englard et al.[4]

Table 1. Fractional atomic coordinates and temperature parameters U_{ij} (Å²) for oxygen and carbon, and U (Å²) for hydrogen. The expressions used are $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots 2hka^*b^*U_{12} + \cdots)]$ and $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$, respectively. Standard deviations in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
O(1)	.2269(3)	.08296(19)	.4186(8)	.0232(13)	.0333(15)	.0454(18)	−.0088(12)	.0109(15)	−.0074(16)
O(2)	.3278(3)	.10699(17)	.8721(7)	.0221(14)	.0370(15)	.0251(16)	.0047(13)	−.0047(13)	−.0015(13)
O(3)	.4475(3)	−.00254(15)	.9442(8)	.0349(16)	.0277(14)	.0357(17)	−.0150(13)	.0091(14)	−.0067(16)
O(4)	.65642(29)	.04563(17)	1.0215(8)	.0238(14)	.0331(15)	.0392(18)	−.0018(12)	.0184(14)	−.0019(13)
O(5)	.67359(26)	.17659(14)	.9496(7)	.0189(10)	.0255(21)	.0208(12)	−.0050(10)	−.0046(11)	.0048(12)
O(6)	.44250(26)	.13458(15)	.5382(7)	.0245(12)	.0239(12)	.0287(15)	−.0064(11)	−.0069(13)	−.0042(13)
O(11)	.7032(3)	.29329(17)	.7346(8)	.0311(16)	.0256(14)	.0445(18)	.0061(12)	.0057(14)	.0029(15)
O(12)	.86477(25)	.16227(14)	.9522(7)	.0236(12)	.0278(12)	.0171(12)	.0075(11)	−.0032(11)	−.0046(11)
O(13)	.68143(25)	.11438(14)	.6059(6)	.0172(10)	.0214(11)	.0218(13)	−.0042(10)	−.0050(10)	.0024(11)
O(14)	.95350(29)	.17111(17)	.4332(8)	.0224(13)	.0434(15)	.0248(14)	−.0055(12)	.0039(14)	.0017(13)
O(15)	.8715(3)	.05518(16)	.8852(8)	.0252(15)	.0241(13)	.0359(17)	.0025(12)	.0063(12)	−.0015(14)
O(16)	1.0931(3)	.16673(19)	.8339(8)	.0347(15)	.0372(16)	.0394(19)	−.0107(13)	.0079(16)	−.0127(15)
C(1)	.3253(3)	.05028(20)	.4823(9)	.0251(20)	.0268(19)	.0258(23)	−.0043(18)	−.0017(18)	.0013(19)
C(2)	.3935(3)	.08492(18)	.6743(8)	.0158(16)	.0222(17)	.0212(20)	−.0011(14)	.0009(17)	.0028(17)
C(3)	.4863(3)	.04471(18)	.7834(9)	.0212(18)	.0182(17)	.0245(21)	−.0017(14)	.0045(16)	.0045(17)
C(4)	.5659(3)	.08214(18)	.9441(9)	.0180(17)	.0236(17)	.0203(18)	.0025(15)	.0000(17)	.0017(18)
C(5)	.6097(3)	.13612(18)	.7939(8)	.0205(16)	.0178(16)	.0196(17)	−.0035(15)	−.0009(16)	.0017(15)
C(6)	.5133(3)	.17252(20)	.6845(10)	.0236(19)	.0204(18)	.0311(23)	−.0015(16)	.0027(18)	.0000(19)
C(11)	.7929(3)	.25966(18)	.8365(10)	.0201(19)	.0197(19)	.0197(19)	−.0028(15)	−.0011(18)	.0031(19)
C(12)	.7728(3)	.19047(17)	.8263(7)	.0158(16)	.0188(17)	.0188(17)	.0029(14)	.0007(14)	−.0003(16)
C(13)	.7654(3)	.15906(17)	.5705(8)	.0179(16)	.0168(16)	.0168(16)	.0007(14)	.0029(16)	−.0027(17)
C(14)	.8764(3)	.12755(19)	.5353(8)	.0192(16)	.0238(18)	.0238(18)	−.0034(15)	−.0014(15)	−.0007(16)
C(15)	.9108(3)	.11348(19)	.8058(8)	.0195(17)	.0208(17)	.0208(17)	.0025(15)	−.0031(16)	−.0002(16)
C(16)	1.0356(4)	.11001(21)	.8631(10)	.0246(19)	.0246(18)	.0246(18)	.0048(17)	−.0006(19)	−.0062(18)

Atom	x	y	z	U
H(O1)	.243(3)	.1155(17)	.352(7)	.027(12)
H(O2)	.277(3)	.1186(17)	.799(7)	.036(14)
H(O3)	.406(3)	−.0206(15)	.889(7)	.013(11)
H(O4)	.638(3)	.0204(19)	1.110(10)	.028(12)
H(O11)	.660(4)	.2957(20)	.841(10)	.073(20)
H(O14)	.921(6)	.1720(28)	.270(14)	.074(17)
H(O15)	.809(4)	.0536(19)	.903(10)	.047(15)
H(O16)	1.081(3)	.1800(20)	.705(8)	.031(13)
H(1C1)	.300(3)	.0079(16)	.555(8)	.006(8)
H(2C1)	.373(4)	.0402(20)	.340(10)	.028(11)

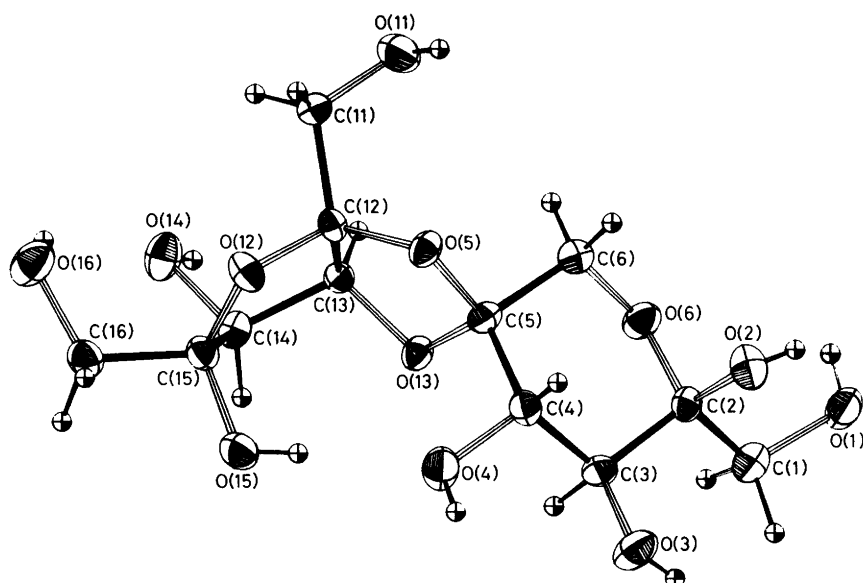| Atom	x	y	z	U
H(C3)	.533(3)	.0244(18)	.640(9)	.015(9)
H(C4)	.530(4)	.0973(21)	1.090(11)	.022(10)
H(1C6)	.476(3)	.1931(18)	.831(8)	.009(8)
H(2C6)	.540(4)	.2037(21)	.565(10)	.028(10)
H(1C11)	.814(3)	.2701(16)	1.018(8)	.010(9)
H(2C11)	.857(4)	.2689(21)	.743(10)	.032(11)
H(C13)	.746(3)	.1865(18)	.442(8)	.007(8)
H(C14)	.870(3)	.0873(13)	.424(6)	.010(6)
H(1C16)	1.062(4)	.0731(24)	.747(11)	.040(12)
H(2C16)	1.038(4)	.0995(21)	1.057(11)	.037(11)

Fig. 2. ORTEP[12] drawing of the molecular structure of the title compound with numbering of atoms.

Table 2. Bond lengths and angles in the pyranose part of the title compound (I) as compared with those in α-L-sorbose (II) and β-D-fructose (III). Standard deviations in parentheses.

Atoms			Bond lengths (Å)			Bond angles (°)		
i	j	k	(I) $l(ij)$	(II) $l(ij)$	(III) $l(ij)$	(I) $\angle(ijk)$	(II) $\angle(ijk)$	(III) $\angle(ijk)$
O(1)	C(1)	C(2)	1.427(5)		1.422(4)	111.6(3)		110.4(2)
C(1)	C(2)	C(3)	1.514(5)	1.515(6)	1.520(4)	111.8(3)	111.9(3)	112.3(2)
C(1)	C(2)	O(2)				111.7(3)	111.1(3)	110.8(2)
C(1)	C(2)	O(6)				104.9(3)	106.9(3)	104.6(2)
O(2)	C(2)	·O(6)	1.404(4)	1.415(5)	1.411(4)	111.0(3)	110.2(3)	111.2(2)
O(2)	C(2)	C(3)				108.8(3)	107.2(3)	106.8(2)
C(3)	C(2)	O(6)	1.536(5)	1.527(5)	1.540(4)	108.5(3)	109.5(3)	111.2(2)
C(2)	C(3)	C(4)				111.8(3)	112.1(3)	111.2(2)
C(2)	C(3)	O(3)				113.5(3)	109.9(3)	111.1(2)
O(3)	C(3)	C(4)	1.416(4)	1.429(5)	1.425(4)	104.8(3)	108.9(3)	108.8(2)
C(3)	C(4)	C(5)	1.523(5)	1.511(5)	1.518(4)	109.7(3)	110.3(3)	109.3(2)
C(3)	C(4)	O(4)				110.8(3)	108.9(3)	110.2(2)
O(4)	C(4)	C(5)	1.413(4)	1.427(5)	1.415(4)	108.5(3)	110.4(3)	109.6(2)
C(4)	C(5)	C(6)	1.514(5)	1.515(5)	1.524(4)	109.6(3)	110.7(3)	111.1(2)
C(4)	C(5)	O(5)				110.9(3)	108.5(3)	
O(13)	C(5)	C(4)	1.407(4)		1.423(4)	109.4(3)		110.8(2)
O(5)	C(5)	O(13)	1.434(4)	1.426(5)		106.5(3)		
O(5)	C(5)	C(6)				108.4(2)	109.2(3)	
C(6)	C(5)	O(13)	1.523(5)	1.513(6)	1.494(4)	111.9(3)		107.3(2)
O(6)	C(6)	C(5)	1.421(4)	1.440(5)	1.436(4)	111.8(3)	111.8(3)	111.0(2)
C(5)	O(5)	C(12)				108.8(3)		
C(2)	O(6)	C(6)	1.428(4)	1.420(5)	1.413(3)	114.1(3)	114.2(3)	114.6(2)

$t = 22$ °C. A least squares procedure gave the values quoted above.

The intensities of the reflections were measured at $t = 22$ °C by means of the five-value scan technique.[7] 1443 out of 2174 independent reflections in the range $0° < \theta < 27°$, and for which $I > 2\sigma(I)$, were accepted as observed.

Lp corrections were carried out in the usual way, but absorption corrections were considered unnecessary.

The structure was solved by direct methods (MULTAN)[8] and refined by full matrix least squares (see Ref. 9) to an R of 0.04. All the hydrogen atoms were found from a difference map.

Final atomic coordinates and temperature parameters are listed in Table 1. The final structure factor list is available on request.

The scattering factors for oxygen and carbon were taken from the *International Tables*.[10] For hydrogen, the scattering factor curve given by Stewart *et al.*[11] was used.

The calculations mentioned above were carried out on a UNIVAC 1110 computer at the University of Bergen. The programs, with few exceptions, originate from the Weizmann Institute of Science, Rehovoth, Israel.

DISCUSSION

The molecular structure of 5KF as found in the present study is shown in Fig. 2. Bond lengths and angles are given in Tables 2 and 3, and a stereoscopic view of the molecule is given in Fig. 3. It is realized

Table 3. Bond lengths and angles in the furanose part of the title compound. Standard deviations in parentheses.

Atoms			Bonds (Å)	Angles (°)
i	j	k	l(ij)	∠(ijk)
O(11)	C(11)	C(12)	1.416(5)	111.9(3)
C(11)	C(12)	C(13)	1.523(5)	118.8(3)
C(11)	C(12)	O(12)		106.3(3)
O(5)	C(12)	C(11)	1.401(4)	109.4(3)
O(12)	C(12)	O(5)	1.436(4)	110.7(3)
O(12)	C(12)	C(13)		105.8(3)
C(13)	C(12)	O(5)	1.527(5)	105.8(3)
C(12)	C(13)	C(14)		105.1(3)
C(12)	C(13)	O(13)		103.2(3)
O(13)	C(13)	C(14)	1.417(4)	110.0(3)
C(13)	C(14)	C(15)	1.518(4)	102.3(3)
C(13)	C(14)	O(14)		108.9(3)
O(14)	C(14)	C(15)	1.435(4)	108.2(3)
C(14)	C(15)	C(16)	1.531(5)	117.5(3)
C(14)	C(15)	O(15)		111.6(3)
C(14)	C(15)	O(12)		105.1(3)
O(15)	C(15)	O(12)	1.416(4)	111.6(3)
O(15)	C(15)	C(16)		103.1(3)
C(16)	C(15)	O(12)	1.541(5)	108.0(3)
O(16)	C(16)	C(15)	1.422(5)	114.5(3)
C(15)	O(12)	C(12)	1.428(4)	111.3(3)
C(13)	O(13)	C(5)		107.9(2)

that standard deviations in molecular dimensions may be overestimated when based on the standard deviations in positional parameters from the least squares refinement.[13]

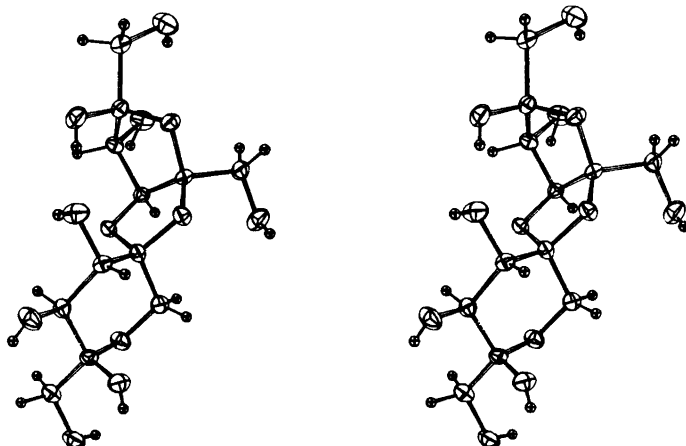Figs. 2 and 3 show that the molecule is a dimeric form of 5KF. It contains a pyranose part, numbered

Fig. 3. A stereoscopic view of the molecule.

1−6, and a furanose part, numbered 11−16; a dioxolane part occurs as a result of dimerization.

The pyranose part occurs as α-L-sorbose with ring conformation *1C*, *cf.* Fig. 2. This structure differs from that of β-D-fructopyranose with respect to the orientation of the hydroxyl group in 5-position which is equatorial in the former and axial in the latter.

Hydrogenation of the title compound at position 5 may, as mentioned above, give either D-fructose or L-sorbose, and the same products may therefore result from dimerization at that position.

One notes from Fig. 2 that C(5) is also bonded to O(13) of the furanose part, and this means that the molecule contains a β-D-fructopyranose configuration as well as the α-L-sorbopyranose configuration.

The present study gives, in fact, the first complete structure description of α-L-sorbose; the crystal structure of α-L-sorbose itself is disordered, with unreasonable values for the length of the C(1)−O(1) bond.[14]

A comparison of bond lengths and angles in the pyranose part of the present molecule with those in α-L-sorbose[14] and β-D-fructose[15] are given in Table 2. The dimensions of the three pyranosyl rings are seen to agree closely. Some differences in C−C−O(hydroxyl) angles occur, but they are probably due to molecular packing in the crystal; C−C−O(hydroxyl) angles in β-D-fructose as found in the pure sugar and in its CaCl₂ and CaBr₂ complexes show similar differences.[15−17]

The equations for three planes through atoms of the pyranosyl ring have been calculated; *A* through C(2), O(6) and C(6), *B* through C(2), C(3), C(5) and C(6), and *C* through C(3), C(4) and C(5). The deviations of atoms from least squares plane *B* are less than 0.002 Å.

The angles between these planes have been calculated and are compared with equivalent angles for α-L-sorbose and β-D-fructose in Table 4; the latter values are based on the atomic coordinates given in Refs. 14 and 15, respectively.

Table 4. A comparison of pyranose ring configurations. See the text for further explanation.

	Angle (°)		
	A/B	*B/C*	*A/C*
Pyranose part of *5KF*	54.1	49.9	5.2
α-L-Sorbose	52.5	47.4	5.2
β-D-Fructose	51.3	48.6	2.8

One notes from Table 4 that the differences in angles are small and the best agreement occurs between α-L-sorbose and the pyranose part of *5KF*. It may therefore be concluded that the dimerization has not affected the configuration of the pyranose part to any noticeable degree.

The furanose part occurs as α-D-fructose, *cf.* Fig. 2 and Table 3. A structure study of fructose in this anomeric form has so far not been carried out.

The furanosyl ring of the present molecule has very nearly the envelope conformation E_3. This means that four of the ring atoms lie in a plane; the ring carbons are numbered 2−5 in this convention, and subscript 3 points to the atom which lies out of the plane;[18] this numbering is opposite to that on Fig. 2.

The deviations from the least aquares plane through O(12), C(12), C(13), and C(15) are −0.015, 0.023, −0.015, and 0.015 Å, respectively, reckoned in the same order; C(14) lies −0.496 Å from the plane.

Corresponding plane deviations for the atoms of the furanosyl ring in the β-D-fructose moiety of sucrose are, 0.045, −0.028, 0.025, and −0.042 Å, respectively, for O(2), C(2), C(4), and C(5), with C(3) −0.542 Å out of the least squares plane.[19−21]

Looked upon in this way the furanosyl ring in sucrose might be described as being roughly E_3. It is realized, however, that the latter ring is referred to as being twisted (*T*), which means that C(3) and C(4) lie on opposite sides of the plane defined by C(2), O(2) and C(5);[18] the actual deviations are −0.372 and 0.208 Å, respectively. Similar furanosyl ring conformations occur in the β-D-fructose moieties of planteose and raffinose;[18,22] in the latter C(4) shows the greatest plane deviation. In 1-kestose where there are two β-D-fructose moieties the furanosyl ring is almost exactly E_3 in one of them and nearly so in the other,[23] and it might be added that in a carbohydrate derivative[24] where the furanosyl ring is condensed with other rings it is found to be very nearly planar.

This illustrates to which extent the furanosyl ring is able to adjust its structure in order to minimize intramolecular strain and/or crystal energy.

The dioxolane ring which comprises the atoms C(5), O(5), C(12), C(13) and O(13), is a result of the dimerization. A possible route for the actual dimerization reaction is given below, (a)−(c) (Scheme 1.).

The first step (a) is a hemiketal formation in which
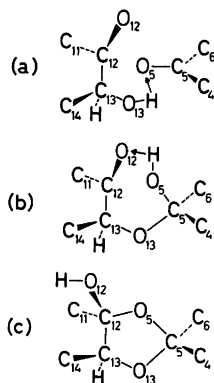
Scheme 1.

the hydroxyl group on C(13) and the keto group on C(5) participate. One should note that due to the symmetry of *5KF*, hemiketal formations between O(13)−H and C(2)−O(2), O(14)−H and C(2)−O(2), and O(14)−H and C(5)−O(5) would be identical to that mentioned above. By this reaction the right hand side molecule, *cf.* Fig. 2, becomes L-sorbose, and the pyranosyl ring closure gives the α-anomer.

The second step (b) too is a hemiketal formation between the O(5)−H hydroxyl group and the C(12)−O(12) keto group. During this reaction the left hand side molecule remains as D-fructose, and subsequent furanosyl ring closure gives the α-anomer.

The deviations from the least squares plane through C(5), O(5), C(12), and C(13) are, −0.012, 0.019, −0.019, and 0.011 Å, respectively, reckoned in the same order; O(13) lies −.386 Å from the plane. This shows that the dioxolane ring of the present compound has an envelope conformation in agreement with the result from structure studies of other compounds containing dioxolane rings. One should note, however, that twist forms have also been reported.[24−26]

The dihedral angle of the O−C−C−O sequence in a free dioxolane ring, corresponding to minimum strain, is assumed to be about 25°.[26] In the present compound this angle is found to be 18.9°.

A comparison of the average values for C−C, C−O(hydroxyl) and C−O(ether) bond lengths in *5KF* dimer with those found in planteose dihydrate,[18] raffinose pentahydrate,[22] l-kestose[23] and sucrose (by X-ray as well as neutron diffrac-

Table 5. A comparison of average C−C, C−O(hydroxyl), and C−O(ether) bond lengths in planteose dihydrate, raffinose pentahydrate, 1-kestose and sucrose with those in *5KF* dimer.

	Ref.	Average bond lengths (Å)		
		C−C	C−O(hydroxyl)	C−O(ether)
Planteose dihydrate	18	1.515(1)	1.422(1)	1.428(1)
Raffinose pentahydrate	22	1.524(2)	1.421(2)	1.429(2)
l-Kestose	23	1.524(1)	1.425(2)	1.428(2)
Sucrose (X-ray)	21	1.523(1)	1.423(1)	1.429(1)
Sucrose (neutron)	20	1.526(1)	1.418(1)	1.425(1)
5KF Dimer	This	1.525(2)	1.419(2)	1.422(2)

Table 6. The hydrogen bonding scheme in crystals of *5KF* dimer.

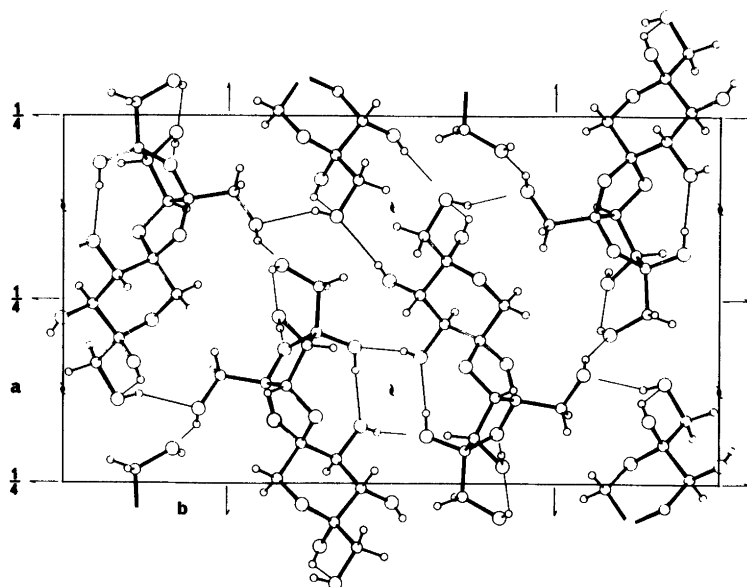| Atoms		Position of atom II	Distances (Å)	
I	II		$O_I \cdots O_{II}$	$H_I \cdots O_{II}$
O(1) →O(11)		$x−\frac{1}{2}, \frac{1}{2}−y, 1−z$	2.821(4)	2.09(4)
O(2) →O(1)		x, y, z	2.757(4)	2.25(4)
O(3) →O(1)		$\frac{1}{2}−x, −y, \frac{1}{2}+z$	2.741(4)	2.11(3)
O(4) →O(15)		$3/2−x, −y, \frac{1}{2}+z$	2.942(4)	2.20(4)
O(11)→O(16)		$x−\frac{1}{2}, \frac{1}{2}−y, 2−z$	2.795(4)	2.08(5)
O(14)→O(12)		$x, y, z−1$	2.786(4)	1.84(5)
O(15)→O(4)		x, y, z	2.708(4)	1.96(4)
O(16)→O(14)		x, y, z	2.724(4)	2.12(3)

Fig. 4. A c-axis projection of the crystal structure showing O···H contacts corresponding to hydrogen bonding.
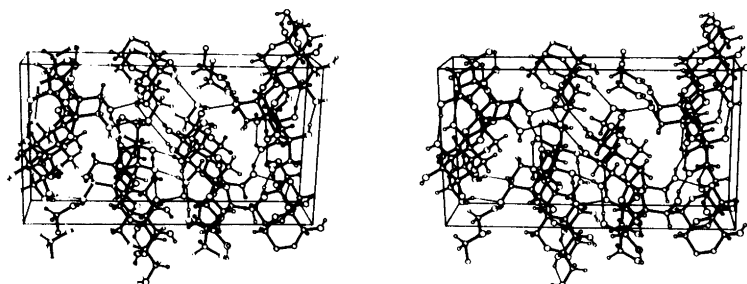

Fig. 5. A stereoview of the crystal structure.

tion),[20,21] is given in Table 5. One notes that the values for *5KF* dimer are in best agreement with the neutron diffraction values for sucrose.

The hydrogen bonding scheme in crystal of *5KF* dimer is given in Table 6 and shown in Fig. 4. Each hydroxyl oxygen donates one hydrogen bond, and apart from O(2) and O(3) each of them also accepts one; O(1) accepts two. There is one rather strong intramolecular hydrogen bond between O(15) and O(4), cf. Figs. 3 and 4.

A stereoscopic view of the crystal structure is given in Fig. 5. One notes that the hydrogen bonds form helixes around the respective screw axes.

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