

plane of Si, N(2), C(5); deviation 0.010 (6) Å for C(2) from the plane of N(2), C(3), C(4)]. Some conjugation of the lone pair of N(1) with the phenyl ring is, however, evident in the short N(1)—C(5) bond and the near coplanarity of the phenyl ring [r.m.s. deviation 0.009 (6) Å] with the coordination plane of N(1) [dihedral angle 11.9 (8)°].

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## Structure of 6-Kestose Monohydrate,\* C<sub>18</sub>H<sub>31</sub>O<sub>16</sub>·H<sub>2</sub>O

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**Abstract.**  $M_r = 521.45$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.718$  (2),  $b = 11.317$  (2),  $c = 23.386$  (3) Å,  $U = 2307.3$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.501$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 1.13$  mm<sup>-1</sup>,  $F(000) = 1108$ ,  $T = 298$  K. Final  $R = 0.039$  for 1381 observed reflections. Molecules are associated in the crystal by an extended network of hydrogen bonds where most O atoms are both donors and acceptors. Moreover, there are four bifurcated intramolecular hydrogen bonds. Ring conformation is discussed in terms of puckering-coordinate analysis and the conformation of the glucose-fructose linkage of the sucrose subunit in terms of the potential-energy map calculated in the atom-atom potential approximation.

**Introduction.** Kestoses are non-reducing trisaccharides present in several plant extracts which are synthesized by enzymatic action of invertase on sucrose (Gross, 1962). The sucrose:sucrose-fructosyltransferase isolated from plants or yeast invertase is able to transfer fructose from a donor sucrose molecule to one of the

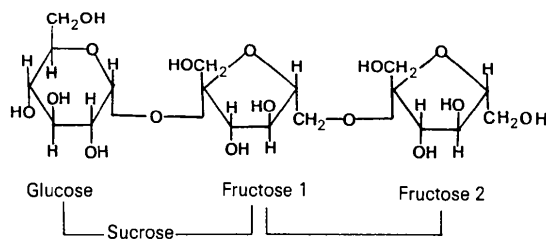
primary alcoholic groups of an acceptor sucrose molecule giving kestoses and glucose. Three different kestoses are reported, that is 1-kestose, 6-kestose and neo-kestose. They can be written, respectively, as 1<sup>F</sup>-fructosyl-sucrose, 6<sup>F</sup>-fructosyl-sucrose, 6<sup>G</sup>-fructosyl-sucrose, where the suffix F or G indicates that the bond links the fructose or glucose part of sucrose. 1- and 6-kestose are believed to act as the smallest possible nuclei for the synthesis of polyfructosanes which can be considered kestoses extended by progressive addition of other fructose units (Binkley, Horton & Bhacca, 1969; Lewis, Cyr & Smith, 1967) by action of the fructan:fructan-fructosyltransferase. The polysaccharide inulin, one of the main reserve carbohydrates of plants, derives from 1-kestose while 6-kestose gives the polyfructosan levan, which is mainly produced in particular non-physiological conditions, for instance in frost-damaged sugar-beets.

At present only the crystal-structure determination of 1-kestose has been reported (Jeffrey & Park, 1972) and that of 6-kestose is reported here. Apart from the intrinsic interest in the conformational aspects of these sugars the present crystal-structure determination has been undertaken in the frame of a wider research

\* *O*- $\alpha$ -D-Glucopyranosyl-(1 $\rightarrow$ 2)-*O*- $\beta$ -D-fructofuranosyl-(6 $\rightarrow$ 2)- $\beta$ -D-fructofuranoside monohydrate.

dealing with the effect of several oligosaccharides in small quantities on the crystal growth of sucrose in a practical industrial environment.

The chemical formula of 6-kestose is shown below. It consists of one glucose and two fructose condensed molecules and contains as subunits the sucrose moiety and a disaccharide which has not been observed as a separate molecule.



**Experimental.** Crystals obtained by recrystallization from methanol; the recrystallization proved very difficult and only a small crystal of dimensions  $0.20 \times 0.03 \times 0.28$  mm was produced and successfully submitted to crystal analysis. Cell parameters obtained from least-squares refinement of positions of 15 reflections in range  $20 < \theta < 25^\circ$ . Siemens AED automatic diffractometer, Ni-filtered Cu K $\alpha$  radiation,  $\omega/2\theta$  scan technique ( $\theta < 70^\circ$ ). Out of 2364 independent reflections collected ( $h$  0–10,  $k$  0–13,  $l$  0–28), only 1381 having  $I_o > 3\sigma(I_o)$  used in refinement. One standard reflection monitored at 50 reflection intervals, no appreciable decay observed. Structure solved by direct methods (MULTAN74, Main, Woolfson, Lessinger, Germain & Declercq, 1974). All H atoms located in difference map carried out after preliminary refinement. Final blocked-matrix (three blocks) refinement on  $F$  with anisotropic non-H atoms gave  $R = 0.039$ ,  $R_w = 0.041$ . H atoms linked to O atoms refined isotropically, others given calculated positions (C–H 1.08 Å). Weights and  $(\Delta/\sigma)_{\max}$  for last cycle  $1.47/w = \sigma_F^2 + 0.00089|F_o|^2$  and 0.3.  $\Delta\rho = -0.19$ – $0.21$  e Å $^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). Most calculations performed with SHELX76 (Sheldrick, 1976) and PARST (Nardelli, 1980).

**Discussion.** Final atomic coordinates and isotropic thermal parameters (Hamilton, 1959) are given in Table 1.\* An ORTEP (Johnson, 1971) view of the molecule is reported in Fig. 1. Bond distances and angles are given in Table 2, selected torsion angles in Table 3.

**Bond distances and angles.** C–C bond distances do not differ significantly in the three rings [1.524 (7,4) in

GP and 1.517 (3,6) Å in FF\*] and are in good agreement with values from the literature (Fries, Rao & Sundaralingam, 1971). C–O bond distances [1.424 (3,21) Å] fit the value of 1.426 Å calculated by Avenel, Neuman & Gillier-Pandraud (1976) as an average over 23 glucosyl residues. The average C–O distance of the C–O–C bridges [1.422 (3,4) Å] is not very different from that value. The endocyclic angle at the endocyclic C atoms is  $110.6$  (9,5) $^\circ$  in GP but considerably narrower [ $103.7$  (7,8) $^\circ$ ] in FF. Accordingly the endocyclic C–O–C angles are  $115.2$  (4) and  $110.0$  (3,2) $^\circ$  in GP and FF respectively.

Endocyclic C–O bonds show the usual shortening of the bond connected with the anomeric C as a consequence of the so-called anomeric effect (Stoddard, 1971; Jeffrey & French, 1978). In fact C(1)–O(5) is slightly shorter than C(5)–O(5) in GP [1.411 (6) against 1.428 (6) Å] and the difference is even larger in FF, where C(2)–O(2) and C(5)–O(2) average to 1.427 (4,2) and 1.451 (7,2) Å. Connected with the same effect is the fact that the O(1)–C(1)–O(5) angle of  $113.3$  (4) $^\circ$  is larger than the O(1)–C(1)–C(2) one [ $105.0$  (4) $^\circ$ ], which is systematically observed in  $\alpha$ -anomers of GP (Avenel *et al.*, 1976, and references therein).

**Ring conformation.** A complete puckering analysis (Cremer & Pople, 1975) of the ring conformations of 6-kestose, sucrose and of the four known trisaccharides containing sucrose as a subunit is reported in Table 4. The conformation of the glucose ring in the saccharose subunit is always very close to  ${}^4C_1$ . This is not surprising as both the anomeric effect and steric repulsion contribute to stabilize this conformation with respect to  ${}^1C_4$  in D-glucose (Stoddard, 1971). The pseudorotation wheel for FF built up using data from Table 4 is shown in Fig. 2. In spite of the differences in inter- and intramolecular environment the ring displays a remarkable conformational stability, the conformation being mostly limited to the range  $E_3$ – ${}^4T_3$ . Several factors determine this arrangement. First, the anomeric effect, which forces the C'(2)–O(1) and C''(2)–O'(6) bonds at the anomeric C atoms to be almost perpendicular to the planes of the rings; second, the need for the C'(3)–O'(3) and C''(3)–O''(3) bonds to be encompassed by the C'(1)–C'(2)–O(1) and C''(1)–C''(2)–O'(6) angles and, third, the mutual *transoid* arrangements of the bonds C'(3)–O'(3), C'(4)–O'(4) and C'(5)–C'(6) and C''(3)–O''(3), C''(4)–O''(4) and C''(5)–C''(6) for the two FF rings respectively. Only in 1-kestose does the intermediate FF ring appear to be perturbed to assume the enantiomeric  ${}^3T_4$  conformation with a smaller puckering amplitude  $Q$ .

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38979 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Averages and their standard error are calculated by  $x_m = \sum f_i x_i / \sum f_i$  and  $\sigma_m = \{\sum f_i (x_i - x_m)^2 / ((N-1) \sum f_i)\}^{1/2}$  where  $f_i = 1/\sigma_i^2$  and the summation is from 1 to  $N$ . They are indicated as  $x_m(\sigma_m, N)$ . GP and FF indicate the glucopyranoside and fructofuranoside rings respectively.

This is not surprising in view of the fact that both the glucose and the other fructose units are connected in this sugar by the same C(2) atom of the intermediate fructose.

Another point concerns the actual values of torsion angles in GP and FF rings (Table 3). In GP the mean torsion angle around C—O bonds, 56 (5,2)°, does not differ significantly from that around C—C bonds,

Table 1. Positional ( $\times 10^4$ ,  $\times 10^3$  for H) and isotropic thermal ( $\text{\AA}^2 \times 10^3$ ) parameters with e.s.d.'s in parentheses

	x	y	z	$U_{eq}/U$
C(1)	9763 (6)	2042 (5)	1447 (2)	22 (3)
C(2)	9915 (5)	2192 (5)	802 (2)	21 (2)
C(3)	8568 (6)	2898 (5)	590 (2)	22 (3)
C(4)	7063 (5)	2278 (5)	753 (2)	22 (2)
C(5)	7025 (6)	1902 (5)	1382 (2)	23 (3)
C(6)	5807 (6)	962 (6)	1458 (2)	34 (3)
C'(1)	11996 (6)	3289 (5)	2260 (2)	25 (3)
C'(2)	10247 (6)	3472 (4)	2228 (2)	22 (3)
C'(3)	9696 (6)	4714 (4)	2358 (2)	22 (3)
C'(4)	8079 (6)	4485 (5)	2564 (2)	25 (3)
C'(5)	8331 (5)	3412 (4)	2942 (2)	24 (3)
C'(6)	6917 (6)	2664 (5)	3030 (2)	30 (3)
C''(1)	4858 (7)	800 (5)	3508 (2)	36 (3)
C''(2)	6169 (6)	1375 (5)	3816 (2)	26 (2)
C''(3)	7031 (6)	631 (5)	4254 (2)	27 (3)
C''(4)	7676 (6)	1555 (5)	4655 (2)	29 (3)
C''(5)	6451 (6)	2510 (5)	4652 (2)	32 (3)
C''(6)	7072 (7)	3741 (5)	4688 (3)	37 (3)
O(1)	9709 (4)	3207 (3)	1667 (1)	22 (2)
O(2)	11343 (4)	2686 (4)	649 (2)	28 (2)
O(3)	8663 (4)	3067 (4)	-19 (1)	28 (2)
O(4)	5834 (4)	3103 (4)	652 (2)	33 (2)
O(5)	8431 (4)	1379 (3)	1567 (1)	25 (2)
O(6)	5599 (5)	625 (4)	2036 (2)	35 (2)
O'(1)	12570 (5)	3669 (4)	2802 (2)	37 (2)
O'(2)	9517 (4)	2742 (3)	2645 (1)	24 (2)
O'(3)	9794 (4)	5458 (3)	1875 (1)	30 (2)
O'(4)	7506 (5)	5446 (4)	2879 (2)	34 (2)
O'(6)	7311 (4)	1760 (3)	3429 (1)	34 (2)
O''(1)	3686 (5)	395 (5)	3878 (2)	50 (3)
O''(2)	5573 (4)	2346 (3)	4135 (1)	33 (2)
O''(3)	8115 (5)	-135 (3)	4011 (2)	35 (2)
O''(4)	7905 (6)	1133 (4)	5223 (2)	47 (2)
O''(6)	5834 (5)	4555 (4)	4743 (2)	51 (3)
O(H)	1705 (6)	2528 (5)	3794 (2)	60 (3)
H(2)	1144 (7)	344 (6)	82 (2)	38 (19)
H(3)	806 (11)	282 (9)	-18 (3)	80 (37)
H(4)	520 (9)	287 (7)	49 (3)	45 (27)
H(6)	610 (11)	15 (7)	208 (3)	57 (39)
H'(1)	1280 (19)	447 (12)	278 (5)	56*
H'(3)	1001 (7)	610 (5)	201 (2)	24 (16)
H'(4)	673 (7)	542 (5)	290 (2)	20 (20)
H''(1)	410 (9)	-32 (7)	393 (3)	76 (26)
H''(3)	860 (11)	1 (8)	371 (3)	91 (35)
H''(4)	905 (12)	90 (10)	531 (4)	146 (38)
H''(6)	598 (17)	501 (12)	497 (5)	76*
H(H)	205 (10)	300 (7)	406 (3)	80 (35)
H(H')	188 (24)	149 (19)	385 (7)	90*

\* Fixed as 50% greater than the mean thermal parameter of the connected atom.

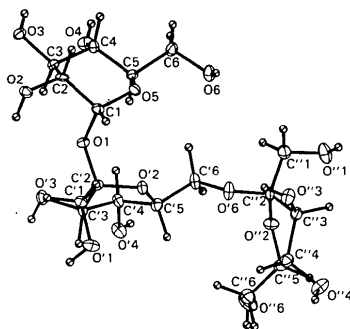


Fig. 1. An ORTEP (Johnson, 1971) view of the molecule.

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

C(1)—C(2)	1.522 (7)	C'(3)—O'(3)	1.410 (6)
C(1)—O(1)	1.417 (6)	C'(4)—C'(5)	1.517 (7)
C(1)—O(5)	1.411 (6)	C'(4)—O'(4)	1.405 (7)
C(2)—C(3)	1.504 (7)	C'(5)—C'(6)	1.509 (7)
C(2)—O(2)	1.411 (6)	C'(5)—O'(2)	1.458 (6)
C(3)—C(4)	1.536 (7)	C'(6)—O'(6)	1.427 (6)
C(3)—O(3)	1.440 (6)	C''(1)—O''(2)	1.500 (8)
C(4)—C(5)	1.533 (7)	C''(1)—O''(1)	1.415 (7)
C(4)—O(4)	1.441 (7)	C''(2)—C''(3)	1.524 (7)
C(5)—C(6)	1.513 (8)	C''(2)—O''(6)	1.414 (6)
C(5)—O(5)	1.428 (6)	C''(2)—O''(2)	1.427 (6)
C(6)—O(6)	1.416 (7)	C''(3)—C''(4)	1.513 (7)
C'(1)—C'(2)	1.541 (7)	C''(3)—O''(3)	1.403 (7)
C'(1)—O'(1)	1.430 (6)	C''(4)—C''(5)	1.519 (8)
C'(2)—C'(3)	1.517 (7)	C''(4)—O''(4)	1.425 (6)
C'(2)—O'(1)	1.426 (5)	C''(5)—C''(6)	1.497 (8)
C'(2)—O'(2)	1.427 (6)	C''(5)—O''(2)	1.444 (6)
C'(3)—C'(4)	1.513 (7)	C''(6)—O''(6)	1.425 (7)
C(2)—C(1)—O(1)	105.0 (4)	C'(3)—C'(4)—C'(5)	100.9 (4)
C(2)—C(1)—O(5)	109.2 (4)	C'(3)—C'(4)—O'(4)	111.4 (4)
O(1)—C(1)—O(5)	113.3 (4)	C'(5)—C'(4)—O'(4)	111.5 (4)
C(1)—C(2)—C(3)	108.6 (4)	C'(4)—C'(5)—C'(6)	114.2 (4)
C(1)—C(2)—O(2)	111.9 (4)	C'(4)—C'(5)—O'(2)	104.0 (4)
C(3)—C(2)—O(2)	113.2 (4)	C'(6)—C'(5)—O'(2)	110.7 (4)
C(2)—C(3)—C(4)	110.0 (4)	C'(5)—C'(6)—O'(6)	107.2 (4)
C(2)—C(3)—O(3)	110.7 (4)	C'(2)—O'(2)—C'(5)	109.9 (3)
C(4)—C(3)—O(3)	110.8 (4)	C'(6)—O'(6)—C''(2)	118.0 (4)
C(3)—C(4)—C(5)	112.5 (4)	C''(2)—C''(1)—O''(1)	113.4 (4)
C(3)—C(4)—O(4)	107.4 (4)	C''(1)—C''(2)—C''(3)	117.3 (4)
C(5)—C(4)—O(4)	108.7 (4)	C''(1)—C''(2)—O''(6)	111.2 (4)
C(4)—C(5)—C(6)	108.8 (4)	C''(1)—C''(2)—O''(2)	108.0 (4)
C(4)—C(5)—O(5)	112.8 (4)	C''(3)—C''(2)—O''(6)	104.7 (4)
C(6)—C(5)—O(5)	106.0 (4)	C''(3)—C''(2)—O''(2)	104.7 (4)
C(5)—C(6)—O(6)	113.0 (4)	O'(6)—C''(2)—O''(2)	110.7 (4)
C(1)—O(1)—C'(2)	121.3 (4)	C''(2)—C''(3)—C''(4)	102.6 (4)
C(1)—O(5)—C(5)	115.2 (4)	C''(2)—C''(3)—O''(3)	113.7 (4)
C'(1)—O'(1)—O''(1)	110.4 (4)	C''(4)—C''(3)—O''(3)	115.4 (4)
C'(1)—C'(2)—C'(3)	115.4 (4)	C''(3)—C''(4)—C''(5)	103.2 (4)
C'(1)—C'(2)—O'(1)	110.0 (4)	C''(3)—C''(4)—O''(4)	113.4 (4)
C'(1)—C'(2)—O'(2)	109.3 (4)	C'(5)—C'(4)—O''(4)	110.0 (4)
C'(3)—C'(2)—O'(1)	105.9 (4)	C''(4)—C''(5)—C''(6)	114.0 (5)
C'(3)—C'(2)—O'(2)	105.0 (4)	C''(4)—C''(5)—O''(2)	106.6 (4)
O(1)—C'(2)—O'(2)	111.2 (4)	C''(6)—C''(5)—O''(2)	111.0 (4)
C'(2)—C'(3)—C'(4)	101.5 (4)	C'(5)—C'(6)—O''(6)	109.4 (5)
C'(2)—C'(3)—O'(3)	112.0 (4)	C''(2)—O''(2)—C''(5)	110.1 (4)
C'(4)—C'(3)—O'(3)	114.4 (4)		

Table 3. A selection of torsion angles ( $^\circ$ ) with e.s.d.'s in parentheses

Pyranose ring		(6 $\rightarrow$ 2) Fructose 1—fructose 2 linkage	
O(5)—C(1)—C(2)—C(3)	63.6 (5)	C'(5)—C'(6)—O'(6)—C''(2)	145.6 (4)
C(1)—C(2)—C(3)—C(4)	-57.4 (5)	C'(6)—O'(6)—C''(2)—C''(1)	64.3 (5)
C(2)—C(3)—C(4)—C(5)	48.2 (5)	C'(6)—O'(6)—C''(2)—O''(2)	-55.8 (5)
C(3)—C(4)—C(5)—O(5)	-43.5 (5)	C'(6)—O'(6)—C''(2)—C''(3)	-168.1 (4)
C(4)—C(5)—O(5)—C(1)	51.3 (5)		
C(5)—O(5)—C(1)—C(2)	-61.3 (5)		
Furanose ring 2		Furanose ring 1	
O''(2)—C''(2)—C''(3)—C''(4)	-34.6 (5)	O(2)—C(1)—O(1)—C'(2)	-151.4 (4)
C''(2)—C''(3)—C''(4)—C''(5)	33.5 (5)	O(5)—C(1)—O(1)—C'(2)	89.6 (5)
C''(3)—C''(4)—C''(5)—O''(2)	-21.2 (5)	C(1)—O(1)—C'(2)—C'(1)	66.7 (5)
C''(4)—C''(5)—O''(2)—C''(2)	-0.6 (5)	C(1)—O(1)—C'(2)—O'(2)	-54.5 (5)
C''(5)—O''(2)—C''(2)—C''(3)	22.2 (5)	C(1)—O(1)—C'(2)—C'(3)	-168.0 (4)
Primary alcohol groups		Furanose ring 1	
C(4)—C(5)—C(6)—O(6)	-175.2 (4)	O(2)—C(1)—O(1)—C'(2)	-34.1 (4)
O(5)—C(5)—C(6)—O(6)	63.2 (5)	C'(2)—C'(3)—C'(4)—C'(5)	42.6 (4)
C(3)—C(2)—C'(1)—O'(1)	54.2 (5)	C'(3)—C'(4)—C'(5)—O'(2)	-36.2 (4)
O(2)—C'(2)—C'(1)—O'(1)	-63.8 (5)	C'(4)—C'(5)—O'(2)—C'(2)	15.7 (4)
O'(6)—C''(2)—C''(1)—O''(1)	-179.8 (4)	C'(5)—O'(2)—C'(2)—C'(3)	11.5 (4)
O''(2)—C''(2)—C''(1)—O''(1)	-58.5 (5)		
C''(3)—C''(2)—C''(1)—O''(1)	59.3 (6)		
C''(4)—C''(5)—C''(6)—O''(6)	-173.9 (4)		
O''(2)—C''(5)—C''(6)—O''(6)	65.7 (6)		

Table 4. Comparison of ring conformations in the known trisaccharides and in sucrose

$\varphi$ ,  $\theta$  ( $^\circ$ ) and  $Q$  ( $\text{Å}$ ) are the puckering coordinates according to Cremer & Pople (1975). E.s.d.'s for 6-kestose are given in parentheses.

Reference	Ring*	$\varphi$	$\theta$	$Q$	Conformation	Junction
Sucrose I	(a) G	302.8	174.9	0.556	${}^4C_1$	${}^4T_3$
	F	265.2		0.353		
Raffinose	(b) G	29.4	175.7	0.575	${}^4C_1$	${}^4T_3$
	F	274.3		0.397		
1-Kestose	(c) Ga(G)	192.8	179.0	0.555	${}^4C_1$	$\alpha\text{-G-(6}\rightarrow\text{1)-}\alpha\text{-Ga}$
	G	49.1	171.4	0.576	${}^4C_1$	
Melezitose	(d) F	100.6		0.298	${}^1T_4\text{-}E_4$	$\beta\text{-F-(1}\rightarrow\text{2)-}\beta\text{-F}$
	F(F)	254.4		0.416	$E_3$	
Planteose	(e) G	250.9	176.8	0.597	${}^4C_1$	${}^4T_3$
	F	275.7		0.388		
6-Kestose	(f) G	217.4 (2.5)	167.0 (6)	0.553 (5)	${}^4C_1$	$\beta\text{-F-(3}\rightarrow\text{1)-}\alpha\text{-G}$
	F	272.9 (5)		0.422 (5)	${}^4C_1$	
	F(F)	252.3 (8)		0.348 (5)	$E_3$	$\beta\text{-F-(6}\rightarrow\text{2)-}\beta\text{-F}$

References: (a) Brown & Levy (1973). (b) Berman (1970). (c) Jeffrey & Park (1972). (d) Avenel *et al.* (1976). (e) Rohrer (1972). (f) Present work.

\* G = glucose, F = fructose, Ga = galactose. The first two rings refer to the sucrose subunit. The third ring is connected to sucrose through the ring given in parentheses.

56 (5,4) $^\circ$ , while in FF the latter is larger, that is 35 (3,6) $^\circ$  for the torsion angle around C—C and 13 (4,4) $^\circ$  for that around C—O. This effect is known to occur systematically in FF rings.

**Linkages between monosaccharides.** The glucopyranosyl-(1 $\rightarrow$ 2)-O- $\beta$ -D-fructofuranosyl linkage occurs in sucrose (Brown & Levy, 1973) and in the sucrose units of raffinose (Berman, 1970), 1-kestose (Jeffrey & Park, 1972), melezitose (Avenel *et al.*, 1976), planteose (Rohrer, 1972) and 6-kestose. The reciprocal position of the two GP and FF rings can be defined by means of the two torsion angles  $\varphi = \text{O}(5)\text{-C}(1)\text{-O}(1)\text{-C}'(2)$  and  $\psi = \text{O}'(2)\text{-C}'(2)\text{-O}(1)\text{-C}(1)$  and it is found that the total variation range in the six sugars is 25.9 $^\circ$  for  $\varphi$  and 77.2 $^\circ$  for  $\psi$  (see Avenel *et al.*, 1976). A better understanding of the problem can be gained taking into account its energetic aspects. Fig. 3 shows an energy map computed in the atom-atom potential approximation (potentials from Giglio, 1969) for sucrose as a function of the two  $\varphi$  and  $\psi$  angles. Only van der Waals interactions were taken into account and the geometry was fixed to that of Brown & Levy (1973).\* As sucrose forms two intramolecular hydrogen bonds between GP and FF units, which are not

\* As regards the meaning of a map computed at this low level of approximation, it is generally assumed that it is able to reproduce with reasonable precision the positions of the minima while the relative energies are calculated higher than the true value the further we are from the minimum position. The latter fact is a direct consequence of the rigidity of the molecule which does not allow the relief of the hard-sphere interactions through the lower energy bending of bond angles.

present in the other sugars, before computing the map a preliminary energy minimization was accomplished allowing the rotation around the C'(5)—C'(6) and C'(2)—C'(1) bonds of the sucrose molecule to occur in such a way as to remove the intraring short contacts caused by hydrogen bonding. The filled circles indicate the actual crystal conformations. Sucrose is found to lie almost exactly in the middle of the calculated minimum.

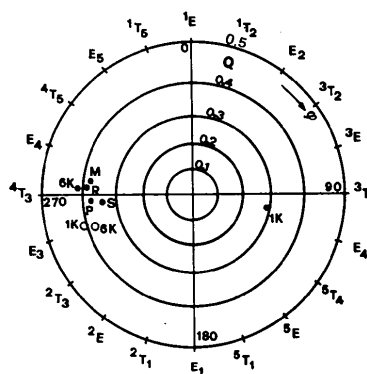


Fig. 2. Pseudorotation wheel of the fructofuranose ring in sucrose (S) and in the trisaccharides raffinose (R), 1-kestose (1K), melezitose (M), planteose (P) and 6-kestose (6K). Filled circles refer to the furanoses of the sucrose unit. The numbering is 1,2,3,4,5, for O(2),C(2),C(3),C(4) and C(5), respectively.  $Q$  in  $\text{Å}$ .

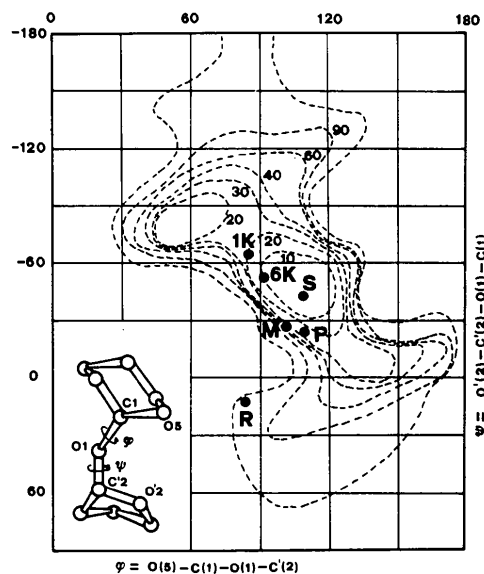


Fig. 3. Intramolecular potential energy ( $\text{kcal mol}^{-1}$ ;  $1 \text{ kcal mol}^{-1} = 4.2 \text{ kJ mol}^{-1}$ ) calculated using atom-atom potentials from Giglio (1969) for the sucrose molecule as a function of the torsion angles  $\varphi$  and  $\psi$  ( $^\circ$ ). The figure shows the only minimum occurring in the range of the variables  $0 \leq \varphi \leq 360^\circ$  and  $0 \leq \psi \leq 360^\circ$ . Filled circles indicate the experimentally determined conformations for sucrose (S), raffinose (R), 1-kestose (1K), melezitose (M), planteose (P) and 6-kestose (6K).

Table 5. Intermolecular and intramolecular hydrogen bonds and O...O intermolecular distances in Å

E.s.d.'s are in the range 0.005–0.008, 0.06–0.13 and 0.06–0.13 Å for O...O, O–H and H...O distances, respectively.

	$d_{O...O}$	$d_{O-H}$	$d_{H...O}$	Vector
<b>(a) Intermolecular hydrogen bonds</b>				
O(2)–H(2)...O'(3 <sup>II</sup> )	2.634	0.95	1.70	2, 0, 0
O(3)–H(3)...O(2 <sup>III</sup> )	2.643	0.71	1.94	–1, 0, 0
O(4)–H(4)...O(3 <sup>III</sup> )	2.744	0.72	2.03	–1, 0, 0
O(6)–H(6)...O'(1 <sup>II</sup> )	2.755	0.70	2.05	2, –1, 0
O'(1)–H'(1)...O(6 <sup>II</sup> )	2.755	0.93	1.96	2, 0, 0
O(3)–H'(3)...O'(2 <sup>II</sup> )	2.881	0.81	2.07	2, 0, 0
O'(4)–H'(4)...O(6 <sup>II</sup> )	2.722	0.68	2.05	1, 0, 0
O''(1)–H''(1)...O(4 <sup>II</sup> )	2.848	0.90	2.03	1, –1, 0
O''(3)–H''(3)...O'(3 <sup>II</sup> )	2.840	0.84	2.02	2, –1, 0
O''(4)–H''(4)...O''(6 <sup>III</sup> )	2.671	1.05	1.64	0, 0, 1
O''(6)–H''(6)...O(3 <sup>IV</sup> )	2.783	0.76	2.19	1, 1, 0
O(H')–H(W')...O''(4 <sup>II</sup> )	2.945	0.88	2.07	–1, 0, 1
O(W)–H(W)...O''(1 <sup>I</sup> )	2.974	1.19	2.00	0, 0, 0
<b>(b) Intramolecular hydrogen bonds</b>				
O(2)–H(2)...O(1)	2.836	0.95	2.51	
O(3)–H(3)...O(4)	2.923	0.71	2.78	
O(6)–H(6)...O(5)	2.833	0.70	2.74	
O''(3)–H''(3)...O'(6)	2.635	0.90	2.37	
<b>(c) O...O intermolecular contacts shorter than 3.25 Å</b>				
O(1)...O''(3 <sup>II</sup> )	3.104			2, 0, 0
O(2)...O(4 <sup>II</sup> )	3.202			0, 0, 0
O'(1)...O(W')	2.760			1, 0, 0
O(3)...O'(6 <sup>II</sup> )	3.008			2, 0, 0
O(3)...O(W <sup>II</sup> )	3.105			1, 0, 0

Symmetry operations: (i)  $x, y, z$ ; (ii)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, -z$ ; (iv)  $\frac{1}{2} - x, -y, \frac{1}{2} + z$ .

The experimental conformations of 1-kestose, 6-kestose, melezitose and planteose are lined up along the south-western side of the potential well where it rises too steeply to be climbed. 1-Kestose is more displaced from the sucrose conformation probably in consequence of the higher steric hindrance caused by the linkage of the second fructose unit to the C'(1) atom of the sucrose fructose (see last column of Table 4). Raffinose is the only trisaccharide where the third monose links to the GP moiety of sucrose. This apparently causes a far greater perturbation as the experimental raffinose conformation is displaced in a region of high potential energy from the sucrose molecule.

The fructofuranosyl-(6→2)-β-D-fructofuranoside linkage has not been previously observed in any other polysaccharide. The conformation of the linking chain C'(5)–C'(6)–O'(6)–C''(2) is (+)-*antichiral*, with an actual value of the torsion angle of 145.6 (4)°. A value of 169.7° has been found for the same torsion angle in the (1→2)-fructose–fructose linkage in 1-kestose (Jeffrey & Park, 1972).

**Hydrogen bonding.** Table 5 lists the hydrogen bonds in which the molecule is involved together with O...O intermolecular contacts. A water molecule links together two fructose 2 subunits by two hydrogen bonds donated to the O''(1) and O''(2) atoms. It does not act as an acceptor.

The glucose residue is associated with six neighbouring 6-kestose molecules by means of ten hydrogen bonds, O(2) and O(4) being both donors and acceptors and O(3) and O(6) donors and double acceptors. Moreover, O(2)–H(2), O(3)–H(3) and O(6)–H(6) are donors of intramolecular hydrogen bonds (see Fig. 1) respectively to the O(1), O(4) and O(5) atoms. These bonds are bifurcated as the H atoms are implied as intermolecular donors as well.

In fructose 1 all O atoms are involved in six intermolecular hydrogen bonds with four sugar molecules, O'(2) as acceptor, O'(4) as donor and O'(1), O'(3) and O'(4) both as donors and acceptors.

The fructose 2 subunit links by eight bonds five sugar and two water molecules; all O atoms are both donors and acceptors, with the exception of O''(2). Moreover, O''(3)–H''(3) is a donor of a bifurcated intramolecular hydrogen bond to the bridging O'(6) atom.

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