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The crystal and molecular structure of β-D-fructofuranosyl α-D-xylopyranoside hemihydrate

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ABSTRACT

The crystal and molecular structure of β-D-fructofuranosyl α-D-xylopyranoside (xylosucrose) hemihydrate, $C_{11}H_{20}O_{10}\cdot 0.5H_2O$, is orthorhombic, $P2_12_12$, with $a = 20.919(5)$, $b = 18.727(2)$, $c = 7.071(1)$ Å, $V = 2770.1(2)$ Å^3, $Z = 8$, and $D_x = 1.541$ g·cm^{-3}. The structure was solved by direct methods and refined to $R = 0.040$ for 2564 observed reflections. Two independent xylosucrose molecules exist in the unit cell, and their conformations about the $1 \rightarrow 2'$ glycosidic bond are similar to sucrose. The orientations of the primary hydroxyl groups in the two molecules differ. An O-1′ · · · O-2 intramolecular hydrogen bond was observed in the one molecule, while an O-6′ · · · O-5 intramolecular hydrogen bond was observed in the other involving disorder of O-6′.

INTRODUCTION

β-D-Fructofuranosyl α-D-xylopyranoside (xylosucrose) strongly inhibits the synthesis of D-glucans from sucrose by D-glucosyltransferases. It has consequently received attention as an anti-carious food additive[1,2]. The chemical structure of xylosucrose is related to that of sucrose through replacement of the $-CH_2-OH$ group of the glucose residue in sucrose by an H atom. In the present X-ray study, we determined the crystal structure of xylosucrose hemihydrate and compared it with that of sucrose[3,4].

EXPERIMENTAL

Xylosucrose hemihydrate was crystallized as colorless prisms by slow evaporation of an $EtOH-H_2O$ solution. The crystal data, details of data collection, and refinement are given in Table I. The structure was solved by direct methods using

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TABLE I

Crystal and structure determination data for xylosucrose hemihydrate

Molecular formula	$C_{11}H_{20}O_{10}\cdot 0.5H_2O$
Molecular weight	321.28
Crystal system	Orthorhombic
Space group	$P2_12_12$
Cell dimensions	
a(Å)	20.919(5)
b(Å)	18.727(2)
c(Å)	7.071(1)
Volume (Å^3)	2770.1(2)
Z	8
Calculated density (g/cm^3)	1.541
Crystal dimension (mm)	0.25×0.20×0.20
Temperature (K)	295
Diffractometer	Rigaku AFC-5RU
Radiation	Cu $K\alpha$
Wavelength (Å)	1.54178
2θ max (°)	120
Range of h	$0 \rightarrow 24$
k	$0 \rightarrow 22$
l	$0 \rightarrow 8$
Number of reflections measured	2734
Least-squares refiment	full-matrix
Number of refined parameters	528
Number of reflections used ($F > 3\sigma$)	2564
Weighting scheme	$[\sigma^2(F)+(0.023F)^2]^{-1}$
R-factors (R; R_w)	0.040, 0.0466
Goodness of fit	2.67
Max shift/esd	0.8
$\Delta\rho$ (eÅ^{-3})	$-0.24 \sim 0.28$

MULTAN78[5], and refined by a combination of difference Fourier syntheses and least-squares methods. There were two independent xylosucrose molecules, designated as "A" and "B", in the asymmetric unit of the crystal. It was found that both molecules had disordered hydroxyl groups at the 6′ position. The disordered atoms were located in the difference Fourier map; their occupancy factors were estimated from the peak heights. The positions of the disordered methylene H atoms were calculated in the standard geometry. The other hydrogen atoms were located in the difference Fourier map. The structure was refined with anisotropic temperature factors for nonhydrogen atoms except for the disordered atoms. Isotropic temperature factors were assumed for hydrogen atoms and disordered oxygen atoms. The occupancy factor of 0.5 was assigned to the disordered hydrogen atoms in the molecule A. The occupancy factors of the disordered groups in the molecule B were estimated in the last several cycles of the full-matrix least-squares computations, giving 0.63 for the O-6′Ba group and 0.37 for the O-6′Bb group. Atomic scattering factors used were obtained from the International Tables for X-ray

Crystallography[6]. All computations were performed on a FACOM M780 computer in the Data Processing Center of Kyoto University, using the programs KP-PXRAY[7].

TABLE II

Fractional coordinates ($\times 10^4$) and B_{eq} (Å^2) ($\times 10$) of nonhydrogen atoms

Atom	x	y	z	B_{eq} [a]
C-1	6267(2)	2686(2)	4219(5)	23(2)
C-2	6419(2)	3475(2)	3880(5)	25(2)
C-3	6646(2)	3843(2)	5686(5)	22(2)
C-4	6166(2)	3714(2)	7229(5)	26(2)
C-5	6083(2)	2910(2)	7470(5)	28(2)
C-1′	7074(2)	1856(2)	1389(5)	29(2)
C-2′	6925(2)	1665(2)	3431(5)	21(2)
C-3′	7422(2)	1222(2)	4478(5)	23(2)
C-4′	7018(2)	826(2)	5919(5)	24(2)
C-5′	6395(2)	704(2)	4891(6)	28(2)
C-6′	5817(2)	786(2)	6159(7)	39(2)
O-1	6836(1)	2295(1)	4543(3)	21(2)
O-2	6889(1)	3544(1)	2434(4)	31(2)
O-3	6696(1)	4596(1)	5391(4)	29(2)
O-4	6365(1)	4005(1)	9000(4)	35(2)
O-5	5845(1)	2606(1)	5754(4)	28(2)
O-1′	7584(1)	2368(1)	1273(4)	37(2)
O-2′	6374(1)	1237(1)	3388(4)	25(2)
O-3′	7944(1)	1598(1)	5231(4)	28(2)
O-4′	7291(1)	170(1)	6520(4)	33(2)
O-6′	5229(1)	686(2)	5261(6)	59(2)
C-1B	9598(2)	1908(2)	7178(5)	21(2)
C-2B	9485(2)	1132(2)	6594(5)	21(2)
C-3B	9115(2)	719(2)	8074(5)	22(2)
C-4B	9431(2)	799(2)	9984(5)	26(2)
C-5B	9492(2)	1588(2)	10425(5)	27(2)
C-1′B	8954(2)	2997(2)	4383(5)	26(2)
C-2′B	8973(2)	2971(2)	6532(5)	21(2)
C-3′B	8404(2)	3311(2)	7541(5)	24(2)
C-4′B	8713(2)	3557(2)	9368(5)	28(2)
C-5′B	9338(2)	3854(2)	8626(6)	30(2)
C-6′B	9886(2)	3913(2)	9949(6)	38(2)
O-1B	9000(1)	2251(1)	7161(3)	20(2)
O-2B	9178(1)	1114(1)	4795(3)	26(2)
O-3B	9097(1)	−23(1)	7605(4)	32(2)
O-4B	9050(2)	432(1)	11322(4)	40(2)
O-5B	9871(1)	1939(1)	9016(3)	25(2)
O-1′B	8944(1)	3717(1)	3756(4)	38(2)
O-2′B	9516(1)	3365(1)	7119(4)	26(2)
O-3′B	7870(1)	2852(1)	7689(4)	30(2)
O-4′B	8335(2)	4062(2)	10327(4)	45(2)
O-6′Ba	10021(2)	3279(3)	10796(7)	45(2)
O-6′Bb	10457(4)	4234(5)	9360(10)	51(2)
O-W	7459(2)	5149(2)	9704(5)	51(2)

[a] $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$

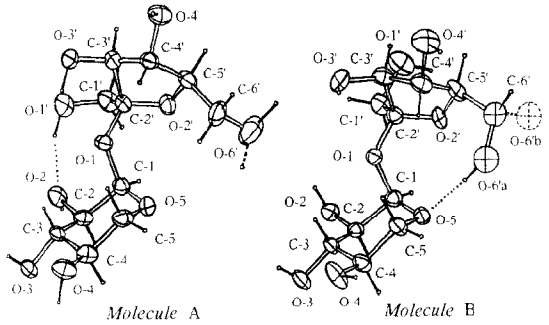


Fig. 1. View of the two independent molecules A and B of xylosucrose with numbering scheme. (Thermal ellipsoids at 50% probability; intramolecular hydrogen bonds indicated by dotted lines; and disordered portions "b" at C-6′ of A and B are given by broken lines.)

RESULTS AND DISCUSSION

The final atomic coordinates and temperature factors are listed in Table II*. Fig. 1 shows the two independent xylosucrose molecules, with the atomic-numbering scheme. The bond distances and angles except for the disordered atoms are in the usual range. The C-1–O-1–C-2′ glycosidic bond angle is 116.6(3)° for A and 118.1(3)° for B, and the C-1–O-5–C-5 and C-2′–O-2′–C-5′ ring angles are 113.2(3)° and 110.5(3)° for A, and 113.3(3)° and 109.7(3)° for B, respectively. They are comparable with the values observed in sucrose[4,5] and related compounds[8–15]. The pyranose rings of both molecules have the $^4C_1$ conformation. The molecular dimensions of the xylose moieties are comparable with those observed in methyl α-D-xylopyranoside[16] and α-L-xylopyranose[17], and are close to the standard structure for the α-D-$^4C_1$ pyranoside[18]. The furanose ring of molecule B has the C3′*endo* form with the puckering values Q = 0.43 Å and $\psi = 277°$ as defined by Cremer and Pople[19], while molecule A has the C2′*exo* form with Q = 0.35 Å and $\psi = 253°$, which is similar to sucrose with Q = 0.35 Å and $\psi = 265°$. Comparisons of selected torsion angles with sucrose are given in Table III. The conformation of molecule A has a close similarity to that of sucrose except for the conformation around the 6′ primary hydroxyl group. Molecule A has a *gauche–trans* conformation, whereas sucrose has a *gauche–gauche* conformation. On the other hand, molecule B has a great difference in torsion angles about the 1 → 2′ glycosidic bond, and the orientation of the 1′ primary hydroxyl group is also different. The 6′ primary hydroxyl group of B is disordered. One conformation corresponds to that found in A and the other is as found in sucrose. Different conformations of the 1′ and 6′ primary hydroxyl groups, as observed here, have been found also in other

* List of hydrogen atom coordinates, anisotropic temperature factors, bond distances and angles and observed and calculated structure factors have been deposited with, and can be obtained from, Elsevier Sciences Publishers, B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/524/*Carbohydr. Res.*, 241 (1993) 63–69.

TABLE III

Selected torsion angles (°) in comparison with those observed in sucrose

Torsion angles	Molecule A	Molecule B	Sucrose [3]
Glycosidic linkage			
O-5–C-1–O-1–C-2′	108.2(3)	96.9(3)	107.8(1)
C-1–O-1–C-2′–O-2′	−46.9(4)	−37.2(4)	−44.8(1)
O-1′ group			
O-1′–C-1′–C-2′–O-2′	172.8(2)	−56.6(3)	171.4(1)
O-1′–C-1′–C-2′–C-3′	−70.4(4)	61.0(3)	−72.1(1)
O-1′–C-1′–C-2′–O-1	50.7(3)	−178.5(2)	50.6(1)
O-6′ group			
O-6′–C-6′–C-5′–O-2′	61.4(4)	−63.3(4), 66.9(6)	−56.4(1)
O-6′–C-6′–C-5′–C-4′	179.3(3)	54.7(5), −175.2(5)	64.4(1)

fructofuranose oligosaccharides[8–15]. These primary hydroxyl groups are more flexible than an aglycon at the glycosidic bond, and molecular packing-forces, especially hydrogen bonding in the crystal, may determine the orientations.

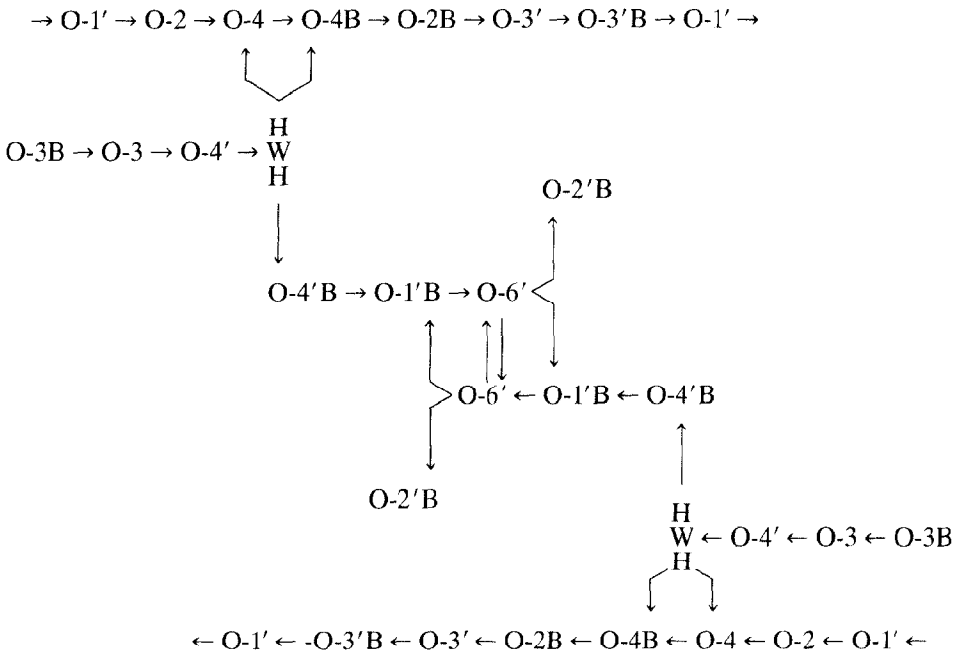
The hydrogen-bond distances and angles observed in the crystal are listed in Table IV. As shown in Fig. 1, molecule A forms an intramolecular hydrogen bond

TABLE IV

Hydrogen bond distances (Å) and angles (°)

O–H···O	Code [a]	O···O	O–H	H···O	<O–H···O
O-2–HO-2···O-4	ii	2.801(4)	0.99(5)	1.81(5)	177(3)
O-3–HO-3···O-4′	iii	2.733(3)	0.99(4)	1.78(4)	160(3)
O-4–HO-4···O-4B	iv	2.819(3)	0.97(4)	1.90(4)	157(3)
O-1′–HO-1′···O-2	i	2.764(3)	1.00(5)	1.81(5)	157(3)
O-3′–HO-3′···O-3′B	i	2.926(3)	0.99(4)	1.98(4)	158(3)
O-4′–HO-1′···O-W	v	2.721(5)	0.97(5)	1.76(5)	172(3)
O-6′–HO-6′a···O-6′	vi	2.742(5)	1.08(9)	1.71(9)	159(6)
O-6′–HO-6′b···O-1′B	vii	2.993(3)	1.12(9)	2.42(9)	110(5)
O-6′–HO-6′b···O-2′B	vii	2.866(4)	1.12(9)	1.98(9)	132(5)
O-2B–HO-2B···O-3′	i	2.753(3)	0.97(4)	1.78(4)	178(6)
O-3B–HO-3B···O-3	viii	2.784(4)	0.99(5)	1.81(5)	169(2)
O-4B–HO-4B···O-2B	ix	2.781(3)	0.98(5)	1.82(5)	165(2)
O-1′B–HO-1′B···O-6′	x	2.993(3)	1.02(4)	1.99(4)	169(3)
O-3′B–HO-3′B···O-1′	ix	2.757(4)	0.99(5)	1.77(5)	171(3)
O-4′B–HO-4′B···O-1′B	ix	2.814(4)	0.96(6)	1.92(5)	153(3)
O-6′Ba–HO-6′Ba···O-5B	i	2.825(6)	1.21(10)	1.75(9)	145(4)
O-6′Bb–HO-6′Bb···O-2′	x	2.869(8)	1.04(10)	1.91(9)	152(7)
O-W–HO-W1···O-4′B	i	2.774(6)	0.96(6)	1.82(6)	177(3)
O-W–HO-W2···O-4	i	3.174(4)	0.94(6)	2.33(6)	149(3)
O-W–HO-W2···O-4B	iv	3.282(6)	0.94(6)	2.52(6)	138(2)

[a] Symmetry code: i x, y, z; ii $x, y, -1+z$; iii $3/2-x, 3/2+y, 1-z$; iv $3/2-x, 1/2+y, 2-z$; v $3/2-x, -1/2+y, 2-z$; vi $1-x, -y, z$; vii $-1/2+x, 1/2-y, 1-z$; viii $3/2-x, -1/2+y, 1-z$; ix $x, y, 1+z$; x $1/2+x, 1/2-y, 1-z$.



O-6′Ba → O-5B
O-6′Bb → O-2′

Fig. 2. Hydrogen bonding system in xylosucrose hemihydrate crystal.

between O-1′ and O-2, whereas molecule B forms an intramolecular hydrogen bond between O-6′ and O-5. Both types of intramolecular hydrogen bonds have been observed in sucrose. A schematic diagram of the hydrogen bonding in the crystal is given in Fig. 2. Infinite and finite chains are crosslinked in a net by the water molecule forming bifurcated hydrogen bonds. The 6′ hydroxyl group in molecule A locates near the two-fold axis, and one of the disordered hydrogen atoms of the group makes an O-6′ · · · O-6′ hydrogen bond, while another disordered hydrogen atom makes a bifurcated hydrogen bond to O-1′B and O-2′B. The disordered 6′ hydroxyl groups in molecule B make O-6′Ba · · · O-5B and O-6′Bb · · · O-2′ hydrogen bonds separated from the net of the hydrogen bonding.

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