Carbohydrate Research, 251 (1994) 203–212
Elsevier Science B.V., Amsterdam

The crystal and molecular structure of the trisaccharide erlose trihydrate

Tooru Taga [a,*], Eiji Inagaki [a], Yoshihiro Fujimori [a] and Satoshi Nakamura [b]

[a] *Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606 (Japan)*
[b] *Sugar Institute, Hayashibara Co. LTD., Shimoishi 1-2-3, Okayama 700 (Japan)*

(Received April 29th, 1993; accepted June 21st, 1993)

ABSTRACT

Erlose [β-D-fructofuranosyl *O*-α-D-glucopyranosyl-(1 → 4)-D-glucopyranoside] trihydrate, $C_{18}H_{32}O_{16}\cdot 3H_2O$, $M_r = 558.48$, is orthorhombic, $P2_12_12_1$ with $a = 31.164(7)$, $b = 13.111(5)$, $c = 11.636(5)$ Å, and $Z = 8$. The structure was solved by direct methods, and refined to $R = 0.035$ for 3926 observed reflections. The unit cell contains two independent molecules having a similar conformation. The conformation of the α-(1 → 2) glycosidic linkage is similar to that observed in erlose monohydrate, whereas the conformation of the α-(1 → 4) glycosidic linkage differs significantly. The molecule has no intramolecular hydrogen-bonds except for the minor components of three-center bonds, but indirect intramolecular hydrogen-bonds through the water molecules are formed. The hydrogen-bond system in the crystal structure consists of infinite and finite chains crosslinked by water molecules.

INTRODUCTION

Erlose is a nonreducing trisaccharide having anticarious properties[1,2], and it crystallizes in two hydrated forms. The crystal structure of the monohydrate form has already been determined[3], and the molecular structure, consisting of maltose and sucrose moieties, was compared with other oligosaccharides[4]. In the present X-ray work, we have determined the structure of the trihydrate in order to compare its structure with that of the monohydrate. The differences in the molecular conformations and the hydrogen bonding around the water molecules were of special interest.

EXPERIMENTAL

Erlose trihydrate was crystallized as colorless prisms by slow evaporation of an EtOH–H_2O solution. The crystal data and the details of the intensity-data collection and structure determination are given in Table I. The structure was

* Corresponding author.

SSDI 0008-6215(93)E0219-D

TABLE I

Crystal and structure determination data of erlose trihydrate

Molecular formula	$C_{18}H_{32}O_{16}\cdot 3H_2O$
Molecular weight	558.48
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Z	8
Cell dimension (Å)	
a	31.164(7)
b	13.111(5)
c	11.636(5)
V (Å^3)	4754.4(8)
D_x (g/cm^3)	1.560
T(K)	295
Crystal dimensions (mm)	$0.5\times0.3\times0.25$
Measurement	Rigaku AFC-5RU
Radiation	Cu $K\alpha$
Wavelength (Å)	1.54178
No. of reflections measured	3985
No. of reflections observed ($F_O > 3\sigma$)	3926
Max value of θ (°)	60
Range of h	$0 \rightarrow 34$
k	$0 \rightarrow 14$
l	$0 \rightarrow 13$
Determination	MULTAN88
Refinement	Full-matrix least-squares
No. of reflections used	3926
No. of parameters	578
R	0.035
R_w	0.044
Goodness of fit	2.8
Max. shift/(esd)	0.10
$\Delta\varrho$ (eÅ^{-3})	$-0.34 \sim 0.40$

solved with MULTAN88 (ref. 5) including SAYTAN (ref. 6). The non-H atoms were refined anisotropically, and the H atoms were located in the Fourier difference map. Atomic scattering factors used were obtained from the International Tables for X-ray Crystallography[7]. All computations were performed on a FACOM M780 computer in the Data Processing Center of Kyoto University, using the programs KPPXRAY (ref. 8).

RESULTS AND DISCUSSION

The final atomic coordinates and thermal parameters were listed in Tables II and III *. There are two independent molecules, designated by "A" and "B", in

* Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CV2 1EZ, UK.

the unit cell. Fig. 1 shows the molecular structures with the atomic numbering scheme for the two molecules †. Both molecules have a similar conformation. The pyranose rings have the $^4C_1$(D) conformation, and the furanose rings have the C-3″*exo* puckered conformation. Cremer–Pople puckering parameters[9] for the pyranose and furanose rings are given in Table IV. All the bond distances and angles calculated with the atomic coordinates given in Table II fall in the accepted range. Selected bond distances, bond angles, and torsion angles for erlose trihydrate, together with the monohydrate and other saccharides, are listed in Table V. The C-1–O-1–C-4′ bond angles, 115° for A and 117° for B, are comparable with the value 117° observed in the monohydrate crystal[3]. The C-1′–O-1′–C-2″ bond angles, 118° for A and 116° for B, are also similar to the corresponding angle 117° in the monohydrate, and they are also comparable with 114° observed in sucrose[10]. The conformation of the α-(1 → 4)-glycosidic linkage is different from those observed in the monohydrate and in α-maltose[11]. The O-2 · · · O-3′ intramolecular interresidue hydrogen bond usually observed in maltose moieties is not found in the structure. The α-(1 → 4) linkage conformation is similar to that found in phenyl 6′-deoxy-6′iodo-α-maltoside[12]. In the theoretical calculations of the conformation energy for the isolated maltose molecule[12,13], there are several energy minima in the maps calculated at increments of the torsion angles about the α-(1 → 4) linkage. The conformation observed here corresponds to the most stable conformation calculated by the MM2CARB empirical potential functions without hydrogen-bonding interactions[13]. For the α-(1 → 2)-glycosidic linkage, the torsion angles for the trihydrate are close to those for the monohydrate and sucrose. There are no interresiduel hydrogen bonds around the α-(1 → 2)-glycosidic linkage as in the monohydrate. The molecules A and B have the same conformation about the primary hydroxyl groups. The O-6, O-6′, and O-1″ hydroxyl groups have the *gauche–gauche* conformation, and the O-6″ hydroxyl group has the *gauche–trans* conformation. These are the same as for the corresponding hydroxyl group in the monohydrate except for the O-6′ group, which has the *gauche-trans* conformation in the monohydrate. The conformations of the O-1″ and O-6″ groups on the furanose residue are different from those observed in sucrose.

The hydrogen-bond distances and angles observed in the crystal structure are listed in Table VI. The weak hydrogen bonds which are a minor component of the three-center bond[15] are listed in the line below that of the major hydrogen bond components. All the three-center hydrogen bonds in the crystal have the same bonding pattern as shown in the schematic drawing in Fig. 2, where the minor component is the intramolecular hydrogen-bond formed between the oxygen atoms on the adjacent carbon atoms. Except for O-2′A, the acceptor atoms of the weak hydrogen bonds are the ring oxygen atoms or the glycosidic linkage oxygen atom.

† The interglycosidic oxygen atom between the glucose residues, conventionally designated O-4′, is here designated as O-1.

TABLE II

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

Atom	x	y	z	B_{eq} [a]	x	y	z	B_{eq} [a]
	Molecule A				Molecule B			
C-1	83369(8)	4561(2)	2542(3)	198(6)	57637(9)	5773(2)	2107(2)	204(6)
C-2	83074(9)	5584(2)	3157(2)	206(6)	61837(9)	5351(2)	1631(2)	217(7)
C-3	79269(9)	6201(2)	2712(2)	186(6)	65594(9)	6048(2)	1914(2)	206(6)
C-4	79907(8)	6355(2)	1433(2)	186(6)	64640(9)	7149(2)	1613(3)	216(7)
C-5	80210(9)	5307(2)	851(3)	204(6)	60247(9)	7482(2)	2041(2)	206(6)
C-6	80940(9)	5342(2)	−423(3)	281(8)	58910(9)	8513(2)	1609(3)	259(7)
O-1	79690(6)	3986(1)	2847(2)	183(4)	57788(6)	5726(1)	3323(2)	198(4)
O-2	82900(7)	5440(2)	4368(2)	278(5)	62552(7)	4326(2)	1964(2)	272(5)
O-3	79025(7)	7161(1)	3268(2)	247(5)	69428(6)	5726(2)	1337(2)	283(5)
O-4	76602(6)	6954(1)	910(2)	228(5)	67866(6)	7762(2)	2147(2)	300(5)
O-5	83678(6)	4730(1)	1348(2)	221(5)	56956(6)	6769(2)	1694(2)	210(5)
O-6	84447(7)	5969(2)	−761(2)	333(6)	58866(7)	8523(2)	383(2)	259(5)
C-1′	76428(9)	896(2)	2803(2)	187(6)	48814(8)	6109(2)	5942(2)	200(6)
C-2′	81169(9)	1144(2)	2957(2)	190(6)	47008(8)	6062(2)	4729(3)	200(6)
C-3′	81712(8)	2240(2)	3370(2)	184(6)	50092(9)	5592(2)	3881(2)	211(6)
C-4′	79754(9)	2940(2)	2484(2)	176(6)	54303(9)	6197(2)	3934(2)	185(6)
C-5′	75026(8)	2645(2)	2287(2)	187(6)	55935(9)	6316(2)	5167(2)	201(6)
C-6′	72874(9)	3202(2)	1321(3)	236(7)	59568(9)	7065(2)	5277(3)	258(7)
O-1′	74382(6)	969(1)	3888(2)	189(4)	49632(6)	5114(1)	6371(2)	209(5)
O-2′	83208(6)	484(1)	3761(2)	232(5)	43007(6)	5522(2)	4771(2)	230(5)
O-3′	86159(6)	2481(2)	3488(2)	253(5)	48180(6)	5672(2)	2770(2)	278(5)
O-5′	74656(6)	1584(1)	2002(2)	195(4)	52632(6)	6694(1)	5919(2)	217(5)
O-6′	75232(7)	3173(2)	272(2)	265(5)	58365(7)	8053(2)	4858(2)	303(5)
C-1″	73000(9)	−829(2)	4222(3)	224(7)	43173(9)	4649(2)	7372(3)	215(7)
C-2″	71103(8)	242(2)	4147(2)	185(6)	47932(9)	4888(2)	7480(2)	189(6)
C-3″	68946(9)	612(2)	5252(2)	193(6)	50655(9)	4024(2)	8020(2)	199(6)
C-4″	65588(9)	1358(2)	4816(2)	211(7)	54028(9)	4588(2)	8702(3)	224(7)
C-5″	64304(9)	895(2)	3650(3)	230(7)	51959(9)	5605(2)	8993(2)	220(7)
C-6″	63720(9)	1679(3)	2723(3)	259(7)	54995(9)	6489(3)	8845(3)	297(8)
O-1″	69829(7)	−1562(2)	4515(2)	280(5)	41130(6)	4535(2)	8464(2)	262(5)
O-2″	67812(6)	230(2)	3320(2)	215(5)	48323(6)	5716(1)	8246(2)	212(5)
O-3″	71793(6)	991(2)	6092(2)	230(5)	52618(6)	3345(2)	7244(2)	266(5)
O-4″	62130(7)	1436(2)	5612(2)	280(5)	55267(7)	4101(2)	9738(2)	327(6)
O-6″	63450(7)	1224(2)	1612(2)	295(5)	52951(8)	7411(2)	9159(2)	406(7)
	Water molecule							
O-W1	80956(7)	445(2)	5969(2)	313(6)				
O-W2	88078(8)	7219(2)	4816(3)	479(8)				
O-W3	85331(8)	8586(2)	2988(2)	299(5)				
O-W4	58017(8)	3262(2)	5283(2)	430(7)				
O-W5	52999(9)	2769(3)	3357(4)	810(10)				
O-W6	49852(9)	3894(2)	1376(2)	454(7)				

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

Except for these weak hydrogen bonds, the erlose molecules have no intramolecular hydrogen-bonds, but the indirect intramolecular hydrogen-bonds are formed through the water molecules between the two hydroxyl groups in the same molecule (see Fig. 1). The O-W1 water molecule is located near the glycosidic

TABLE III

Fractional coordinates ($\times 10^3$) and isotropic B factors ($\times 10$) of H atoms

Atom	x	y	z	B (Å^2)	x	y	z	B (Å^2)
	Molecule A				Molecule B			
H-C1	860(1)	418(3)	278(3)	24	552(1)	536(3)	183(3)	24
H-C2	858(1)	599(3)	298(3)	25	615(1)	534(3)	78(3)	22
H-C3	764(1)	583(3)	285(3)	22	661(1)	602(3)	275(3)	28
H-C4	826(1)	674(3)	132(3)	23	646(1)	722(3)	76(3)	25
H-C5	774(1)	498(3)	95(3)	29	605(1)	752(3)	289(3)	31
H-C61	782(1)	560(3)	−77(4)	35	559(1)	867(3)	193(3)	29
H-C62	814(1)	460(3)	−68(3)	30	611(1)	904(3)	190(3)	32
H-C1′	760(1)	22(3)	249(3)	23	467(1)	645(3)	644(3)	24
H-C2′	826(1)	104(3)	221(3)	26	465(1)	676(3)	445(3)	28
H-C3′	803(1)	235(3)	410(3)	22	507(1)	486(3)	406(3)	25
H-C4′	813(1)	287(3)	177(3)	24	535(1)	687(3)	359(3)	29
H-C5′	735(1)	280(3)	304(3)	24	569(1)	562(3)	540(3)	22
H-C6′1	700(1)	288(3)	118(3)	30	605(1)	707(3)	612(3)	27
H-C6′2	727(1)	394(3)	152(3)	28	621(1)	681(3)	480(3)	27
H-C1″1	741(1)	−93(3)	349(3)	31	419(1)	524(3)	698(3)	31
H-C1″2	751(1)	−86(3)	488(3)	25	429(1)	399(3)	698(3)	30
H-C3″	676(1)	4(3)	566(3)	26	486(1)	360(3)	850(3)	32
H-C4″	667(1)	206(3)	471(3)	25	568(1)	467(3)	825(3)	29
H-C5″	615(1)	49(3)	376(3)	29	510(1)	561(3)	982(3)	26
H-C6″1	665(1)	208(3)	266(3)	26	575(1)	629(3)	935(3)	27
H-C6″2	608(1)	203(3)	296(4)	41	560(1)	653(3)	802(3)	33
H-O2	843(1)	593(4)	476(4)	41	633(1)	427(3)	271(4)	39
H-O3	776(1)	707(3)	397(4)	41	684(1)	548(4)	62(4)	41
H-O4	738(1)	677(4)	114(4)	51	680(1)	835(4)	184(4)	41
H-O6	866(1)	599(4)	−17(4)	51	581(1)	912(3)	13(4)	40
H-O2′	837(1)	−8(3)	334(4)	41	413(1)	574(3)	423(4)	41
H-O3′	872(1)	213(3)	403(4)	37	485(1)	501(4)	239(4)	41
H-O6′	767(1)	262(3)	20(4)	41	588(1)	854(3)	544(4)	39
H-O1″	684(1)	−177(4)	379(4)	51	413(1)	521(4)	871(4)	41
H-O3″	723(1)	163(3)	598(4)	39	506(1)	300(3)	688(4)	41
H-O4″	609(1)	203(4)	546(4)	51	574(1)	360(3)	978(4)	41
H-O6″	661(1)	76(3)	152(4)	51	543(1)	773(3)	966(4)	41
	Water molecule							
H-W11	779(1)	52(3)	601(4)	40				
H-W12	817(1)	47(4)	528(4)	51				
H-W21	623(2)	237(4)	45(5)	74				
H-W22	628(1)	238(3)	913(4)	40				
H-W31	671(1)	173(4)	806(4)	41				
H-W32	639(1)	143(4)	720(4)	51				
H-W41	566(1)	337(4)	599(4)	55				
H-W42	560(1)	312(3)	478(4)	54				
H-W51	535(1)	208(4)	309(4)	51				
H-W52	512(2)	313(4)	277(5)	74				
H-W61	510(1)	396(3)	83(4)	41				
H-W62	465(1)	371(4)	89(4)	51				

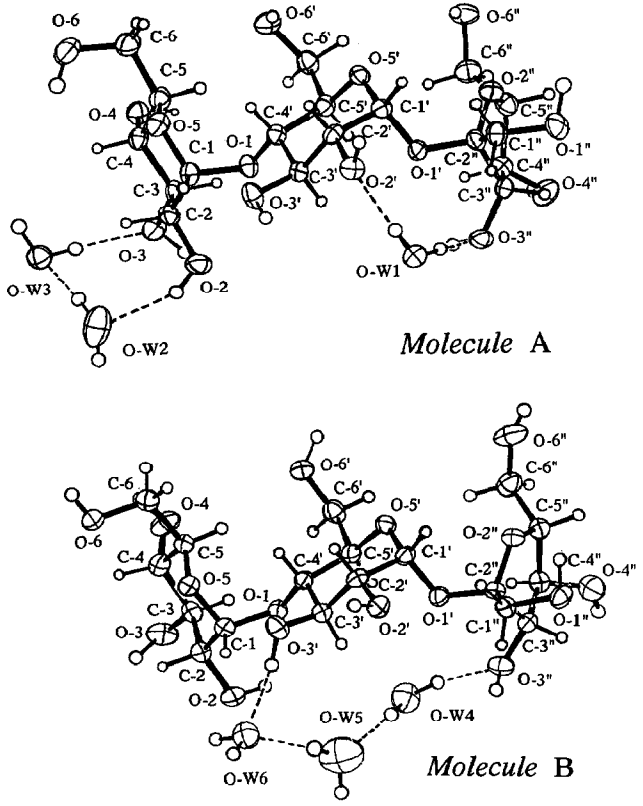

Fig. 1. View of the erlose molecules and the hydrogen-bonding water molecules with numbering scheme and thermal ellipsoids at 50% probability.

linkage O-1′ oxygen atom, and it forms the interresidue hydrogen bonds between the O-2′ hydroxyl group and O-3″ hydroxyl group in molecule A. The bridging water molecule acts as the double proton donor for the two interresidue hydrogen-bonds. The bridging pattern in the indirect intramolecular hydrogen bonds differs from those observed in other disaccharide hydrates[16–20]; the water molecules in methyl β-maltoside monohydrate[16] and sophorose monohydrate[17] act

TABLE IV

Cremer–Pople puckering parameters for glucopyranose and fructofuranose in erlose

	Glucopyranose				Fructofuranose	
	Q (Å)	Ψ (°)	Q (Å)	Ψ (°)	Q (Å)	Ψ (°)
Erlose·$3H_2O$						
molecule A	0.59	4.8	0.58	5.5	0.34	253
molecule B	0.54	6.6	0.55	4.9	0.28	250
Erlose·H_2O[3]	0.59	8.2	0.54	7.6	0.36	258

TABLE V

Selected bond distances (Å), bond angles (°), and torsion angles (°) for erlose trihydrate and other saccharides

	Erlose·$3H_2O$ [a]		Erlose·H_2O[3]	Sucrose[10]	α-Maltose[11]	6′-Iodophenyl α-maltose[12]
	A	B				
Bond distance [b]						
C-1–O-5	1.410	1.407	1.415			
C-5–O-5	1.440	1.445	1.430			
C-1–O-1	1.417	1.417	1.402			
O-1–C-4′	1.435	1.437	1.440			
C-1′–O-5′	1.410	1.416	1.413			
C-5′–O-5′	1.435	1.439	1.444			
C-1′–O-1′	1.418	1.420	1.421			
O-1′–C-2″	1.430	1.426	1.428			
C-2″–O-2″	1.406	1.410	1.411			
C-5″–O-2″	1.450	1.436	1.449			
Bond angle [c]						
C-1–O-5–C-5	115	114	113			
O-1–C-1–O-5	108	109	111			
C-1–O-1–C-4′	115	117	117			
O-1′–C-1′–O-5′	112	111	110			
C-1′–O-5′–C-5′	116	115	114			
C-1′–O-1′–C-2″	118	116	117			
O-1′–C-2″–O-2″	113	112	113			
C-2″–O-2″–C-5″	111	112	111			
Torsion angle [c]						
α-(1 → 4) linkage						
O-5–C-1–O-1–C-4′	69	51	107		116	73
C-2–C-1–O-1–C-4′	−171	173	−131		−126	−164
C-1–O-1–C-4′–C-3′	90	74	108		122	84
C-1–O-1–C-4′–C-5′	−150	−164	−130		−118	−155
α-(1 → 2) linkage						
O-5′–C-1′–O-1′–C-2″	98	110	105	108		
C-2′–C-1′–O-1′–C-2″	−142	−130	−134	−129		
C-1′–O-1′–C-2″–O-2″	−56	−40	−61	−44		
C-1′–O-1′–C-2″–C-3″	−170	−155	−147	−160		
Primary alcohol groups						
O-5–C-5–C-6–O-6	−71	−65	−67		53	−58
C-4–C-5–C-6–O-6	51	58	54		176	66
O-5′–C-5′–C-6′–O-6′	−71	−65	74	−56	69	−64
C-4′–C-5′–C-6′–O-6′	51	58	167	64	−171	67
O-2″–C-2″–C-1″–O-1″	−58	−51	−61	171		
C-3″–C-2″–C-1″–O-1″	58	65	55	−72		
O-2″–C-5″–C-6″–O-6″	50	63	64	−70		
C-4″–C-5″–C-6″–O-6″	167	−178	−175	49		

[a] Present work. [b] Estimated standard deviations of the values for erlose·$3H_2O$ are < 0.004 Å. [c] Estimated standard deviations of the values for erlose·$3H_2O$ are < 0.3°.

as the acceptor only, and those in α,α-trehalose dihydrate[18,19] and α-melibiose monohydrate[20] act as the single donor and acceptor. In molecule A, the O-2 and O-3 hydroxyl groups on the same residue are also bonded through the O-W2 and

TABLE VI

Hydrogen-bond distances (Å) and angles (°)

D–H···A	Code [a]	D···A	D–H	H···A	∠D–H···A
O-2A–H-O2A···O-W2	i	2.884(4)	0.90(5)	2.06(5)	151(5)
O-3A–H-O3A···O-6′A	iii	2.718(3)	0.94(4)	1.78(4)	177(4)
O-4A–H-O4A···O-3B	i	2.800(3)	0.94(4)	1.94(4)	149(4)
O-6A–H-O6A···O-W4	ii	2.830(3)	0.96(4)	2.01(4)	141(4)
···O-5A	i	2.954(3)		2.58(5)	103(3)
O-2′A–H-O2′A···O-W3	v	2.727(3)	0.90(4)	1.87(4)	159(4)
O-3′A–H-O3′A···O-6B	iii	3.000(3)	0.84(4)	2.17(4)	166(3)
···O-2′A	i	2.793(3)		2.51(4)	92(3)
O-6′A–H-O6′A···O-1″A	iv	2.758(4)	0.86(4)	1.93(4)	160(5)
···O-5′A	i	2.903(3)		2.58(4)	103(3)
O-1″A–H-O1″A···O-4B	v	2.958(3)	0.99(4)	2.01(5)	158(4)
O-3″A–H-O3″A···O-4A	iii	2.749(3)	0.86(4)	1.89(4)	174(4)
O-4″A–H-O4″A···O-W4	i	2.742(4)	0.88(5)	1.86(4)	174(5)
O-6″A–H-O6″A···O-W1	iv	2.896(4)	1.03(3)	1.94(4)	154(4)
···O-2″A	i	2.738(3)		2.27(5)	106(3)
O-2B–H-O2B···O-6A	iii	2.833(3)	0.90(5)	1.94(4)	172(4)
···O-1B	i	2.841(3)		2.67(4)	92(2)
O-3B–H-O3B···O-2A	ii	2.848(3)	0.95(5)	1.93(5)	161(5)
O-4B–H-O4B···O-W1	ii	2.746(4)	0.85(5)	1.90(5)	170(5)
O-6B–H-O6B···O-2′B	vi	2.691(4)	0.87(4)	1.87(4)	155(5)
O-2′B–H-O2′B···O-6″A	vi	2.736(3)	0.87(4)	1.88(4)	164(4)
O-3′B–H-O3′B···O-W6	i	2.850(4)	0.98(4)	1.89(5)	168(4)
O-6′B–H-O6′B···O-1″B	vii	2.759(4)	0.94(4)	1.82(4)	172(5)
O-1″B–H-O1″B···O-4″A	vii	2.898(4)	0.93(5)	2.09(5)	145(5)
···O-2″B	i	2.736(3)		2.35(3)	105(3)
O-3″B–H-O3″B···O-6″B	viii	2.679(3)	0.88(4)	1.81(4)	167(4)
O-4″B–H-O4″B···O-W2	iii	2.703(4)	0.94(4)	1.77(3)	172(4)
O-6″B–H-O6″B···O-6B	ix	2.748(3)	0.83(4)	1.95(4)	160(4)
O-W1–H-W11···O-3″A	i	2.947(3)	0.96(4)	2.00(3)	168(3)
O-W1–H-W12···O-2′A	i	2.664(3)	0.84(5)	1.83(5)	178(5)
O-W2–H-W21···O-6″A	iii	2.960(4)	0.92(6)	2.05(6)	168(5)
O-W2–H-W22···O-W3	i	2.910(4)	0.99(4)	1.93(4)	170(5)
O-W3–H-W31···O-3A	i	2.731(3)	0.87(4)	1.91(4)	158(4)
O-W3–H-W32···O-4″A	ii	2.876(3)	0.95(4)	1.93(5)	178(5)
O-W4–H-W41···O-3″B	i	2.837(3)	0.94(4)	1.92(4)	165(4)
O-W4–H-W42···O-W5	i	2.810(5)	0.88(4)	1.96(4)	163(5)
O-W5–H-W51···O-3′B	x	3.068(5)	0.97(5)	2.16(5)	155(5)
O-W5–H-W52···O-W6	i	3.012(5)	1.00(6)	2.03(6)	166(5)
O-W6–H-W61···O-6′B	x	2.912(4)	0.98(4)	1.95(4)	166(5)
O-W6–H-W62···O-4″B	xi	2.753(3)	0.90(4)	1.85(4)	178(4)

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

O-W3 water pair with the hydrogen-bonding sequence O-2 → O-W2 → O-W3 → O-3. The intraresidue hydrogen bonding is stabilized in the six-membered cyclic structure. Similar five-membered cyclic structures were observed in *p*-nitrophenyl maltohexaose triiodide complex[21]. In molecule B, the three water molecules,

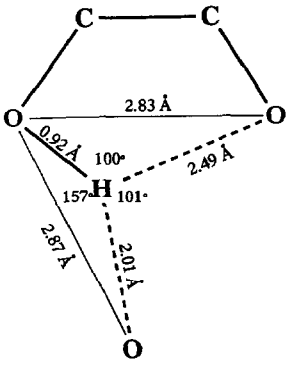

Fig. 2. Schematic drawing of the three-center hydrogen bond with the average distances and angles.

O-W4–O-W5–O-W6, bridge between the O-3′ hydroxyl group and the O-3″ hydroxyl group with the hydrogen-bonding sequence O-3′ → O-W6 ← O-W5 ← O-W4 → O-3″. Similar clusters of the water molecules were found in oligosaccharide crystals that include large numbers of hydrate water molecules, such as raffinose pentahydrate[22]. The crystal structure has a complex hydrogen-bonding network shown in schematic representation, except for the weak hydrogen-bonds, in Fig. 3. All hydroxyl groups participate in the intermolecular hydrogen-bonds. Each hydroxyl group acts as the single donor and acceptor in the cooperative hydrogen-bonding chains, except O-3′A and O-2B that act as a donor only, and O-6″A and O-6B that accept two hydrogen bonds. The water molecule forms four hydrogen bonds, except for the O-W5 molecule, which forms three hydrogen bonds. The water molecules crosslink the infinite and finite hydrogen-bond chains as commonly observed in other carbohydrate crystals[22,23]. A closed loop consisting of the three water molecules and two hydroxyl groups is formed in the nets. Such a hydrogen-bonding system, including the three-center bonds, well satisfies the rules governing hydrogen bonding of the carbohydrate crystals, as proposed by Jeffrey and Mitra[24]: it maximizes the hydrogen-bond energy by including as many oxygen

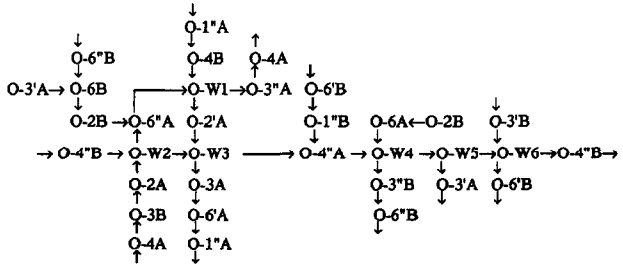

Fig. 3. Schematic diagram of the hydrogen-bonding scheme in erlose trihydrate. The minor components of three-center bonds are omitted.

atoms as possible, and maximizes the cooperativity by forming many hydrogen-bond chains.

REFERENCES

1 T. Yamada, S. Kimura, and K. Igarashi, *Caries Res.*, 14 (1980) 239–247.
2 S. Kitahata, S. Yoshikawa, S. Okada, K. Takeuchi, S. Imai, T. Nishikawa, and S. Arai, *J. Jpn. Soc. Starch Sci.*, 28 (1981) 142–149.
3 T. Taga, E. Inagaki, Y. Fujimori, and S. Nakamura, *Carbohydr. Res.*, 240 (1993) 39–45.
4 G.A. Jeffrey, *Acta Crystallogr., Sect. B*, 46 (1990) 89–103.
5 P. Main, S.E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M.M. Woolfson, MULTAN88 system, Universities of York, UK, and Louvain, Belgium, 1987.
6 T. Debaerdemaeker, C. Tate, and M.M. Woolfson, *Acta Crystallogr., Sect. A*, 44 (1988) 353–357.
7 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.
8 T. Taga, T. Higashi, and H. Iizuka, KPPXRAY system, Kyoto University, Japan, 1985.
9 D. Cremer and J.A. Pople, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
10 G.M. Brown and H. Levy, *Acta Crystallogr., Sect. B*, 29 (1973) 790–808.
11 F. Takusagawa and R.A. Jacobson, *Acta Crystallogr., Sect. B*, 34 (1978) 213–218.
12 T. Tanaka, N. Tanaka, T. Ashida, and M. Kakudo, *Acta Crystallogr., Sect. B*, 32 (1976) 155–160.
13 L. Tvaroska and S. Perez, *Carbohydr. Res.*, 149 (1986) 389–410.
14 G.M. Lipkind, V.E. Verovsky, and N.K. Kochetkov, *Carbohydr. Res.*, 133 (1984) 1–13.
15 R. Taylor, O. Kennard, and W. Versichel, *J. Am. Chem. Soc.*, 106 (1984) 244–248.
16 S.S.C. Chu and G.A. Jeffrey, *Acta Crystallogr.*, 23 (1967) 1038–1049.
17 P.J. Ohanessian, F. Longchambon, and F. Arene, *Acta Crystallogr., Sect. B*, 34 (1978) 3666–3671.
18 G.M. Brown, D.C. Rohrer, B. Berking, C.A. Beevers, R.O. Gould, and R. Simpson, *Acta Crystallogr., Sect. B*, 28 (1972) 3145–3158.
19 T. Taga, M. Senma, and K. Osaki, *Acta Crystallogr., Sect. B*, 28 (1978) 3258–3263.
20 J.A. Kanters, G. Roelofseon, H.M. Doesburg, and T. Koops, *Acta Crystallogr., Sect. B*, 32 (1976) 2830–2837.
21 W. Hinrichs and W. Saenger, *J. Am. Chem. Soc.*, 112 (1990) 2789–2796.
22 H.M. Berman, *Acta Crystallogr., Sect. B*, 26 (1970) 290–299.
22 G.A. Jeffrey and M. Saenger, *Hydrogen Bonding in Biological Structures*, Springer Verlag, Berlin, 1991.
23 G.A. Jeffrey and J. Mitra, *Acta Crystallogr., Sect. B*, 39 (1983) 469–480.