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The crystal and molecular structure of the trisaccharide erlose as the monohydrate

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ABSTRACT

Erlose [*O*-β-D-fructofuranosyl-(1 → 2)-*O*-α-D-glucopyranosyl-(1 → 4)-α-D-glucopyranoside] monohydrate, $C_{18}H_{32}O_{16}\cdot H_2O$, $M_r = 522.45$, is orthorhombic, $P2_12_12_1$ with $a = 30.748$ (3), $b = 8.757$ (1), $c = 8.270$ (1) Å, and $Z = 4$. The structure was solved by direct methods, and refined to $R = 0.048$ for 1909 observed reflections. The torsion angles about the (1 → 2) and (1 → 4) glycosidic bonds are similar to those observed in other sucrose- and maltose-like oligosaccharides. The maltose moiety has an O-3′-H · · · O-2 intramolecular hydrogen-bond, but the sucrose moiety has no intramolecular hydrogen bonds. The hydrogen bonding in the crystal includes infinite and finite chains crosslinked by the water molecule.

INTRODUCTION

Erlose is a nonreducing trisaccharide receiving current attention, because of its sucrose-like taste and anticarious properties[1–3]. Hydrolysis of this sugar produces glucose and sucrose, and the structure includes sucrose and maltose moieties. Erlose was first isolated in small quantities from honey invertase digests of sucrose[4], but we recently have obtained it in large quantities as a very pure product by the transfer action of cyclodextrin glycosyltransferase in mixtures of starch and sucrose. This nonreducing sugar crystallizes in two hydrated forms, the mono- and tri-hydrates. Here we report the crystal structure of the monohydrate. The present study adds to the information concerning the stereochemistry of the α-(1 → 2) and (1 → 4) glycosidic bonding in oligosaccharides[5].

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TABLE I

Crystal and structure determination data for erlose monohydrate

Molecular formula	$C_{18}H_{32}O_{16}\cdot H_2O$	Crystal system	Orthorhombic
Molecular weight	522.45	Space group	$P2_12_12_1$
Cell dimension (Å)		Z	4
a	30.748 (3)	V (Å^3)	2226.8 (2)
b	8.757 (1)	D_x (g/cm^3)	1.558
c	8.270 (1)		
Crystal dimensions (mm)	0.3 × 0.3 × 0.25	Structure determination	MULTAN78
Measurement	Rigaku AFC-5RU	Refinement	Full-matrix least-squares
Radiation	Cu $K\alpha$ (λ = 1.54178 Å)	No. of reflections	1909
Max value of 2θ (°)	120	R	0.048
No. of reflections measured	1961	R_w	0.070
Range of h	0 → 34	Goodness of fit	1.5
k	0 → 9	Max shift/esd	0.01
l	0 → 9	$\Delta\rho_{max}$ (eÅ^{-3})	0.22

EXPERIMENTAL

Erlose monohydrate was crystallized as colorless prisms by slow evaporation of an MeOH solution. The crystal data and details of the intensity-data collection and structure determination are given in Table I. The data were not corrected for the absorption effect. The structure was solved with MULTAN78[6], and refined anisotropically for non-H atoms and isotropically for H atoms. The H atoms were located in the D-map. Atomic scattering factors used were obtained from International Tables for X-ray Crysallography[7]. All computations were performed with a FACOM M780 computer in the Data Processing Center of Kyoto University, using the programs KPPXRAY[8].

RESULTS AND DISCUSSION

The final atomic coordinates and thermal parameters are listed in Table II *. All of the bond distances and angles calculated with the atomic coordinates fall in the accepted range. Fig. 1 shows a view of the molecule with the atomic numbering scheme. Selected torsion angles about the covalent bonds are listed in Table III. The two pyranose rings have the same $^4C_1$ conformation, and the furanose ring is close to a $^3T_2$ (C-2*exo*) puckered conformation (ψ = 258.1 and q = 0.362 Å)[9].

(1 → 4)-Glycosidic linkage.—The C-1–O-1–C-4′ bond angle is 117.0(2)°, and the C–O bond distances are 1.402(4) Å and 1.440(4) Å, respectively. The bond angle is comparable with the 117° value observed in β-maltose monohydrate[11] and phenyl

* List of hydrogen atom coordinates, anisotropic thermal parameters, bond distances, bond angles and torsion 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/517/*Carbohydr. Res.*, 240 (1993) 39–45.

TABLE II

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

Atom	x	y	z	B_{eq} [a]
C-1	2861 (1)	1733 (4)	4088 (5)	2.30 (11)
C-2	2476 (1)	1514 (4)	2933 (5)	2.52 (11)
C-3	2122 (1)	2656 (4)	3229 (5)	2.48 (11)
C-4	1999 (1)	2631 (4)	5014 (5)	2.61 (11)
C-5	2408 (1)	2984 (4)	5997 (5)	2.39 (11)
C-6	2329 (1)	3127 (5)	7785 (5)	3.30 (12)
O-1	3084 (1)	3074 (3)	3678 (3)	2.20 (9)
O-2	2640 (1)	1597 (4)	1325 (3)	3.80 (10)
O-3	1757 (1)	2283 (3)	2231 (4)	3.16 (10)
O-4	1669 (1)	3713 (3)	5307 (4)	3.60 (10)
O-5	2716 (1)	1791 (3)	5711 (3)	2.59 (10)
O-6	2116 (1)	1866 (4)	8483 (3)	3.42 (10)
C-1′	4312 (1)	4636 (4)	2517 (4)	1.94 (10)
C-2′	4130 (1)	3374 (4)	1422 (4)	1.97 (10)
C-3′	3652 (1)	3099 (4)	1714 (4)	1.85 (10)
C-4′	3549 (1)	2965 (4)	3509 (4)	1.98 (10)
C-5′	3754 (1)	4228 (4)	4501 (4)	1.87 (10)
C-6′	3712 (1)	3941 (5)	6297 (5)	2.91 (10)
O-1′	4137 (1)	6088 (3)	2112 (3)	2.13 (9)
O-2′	4205 (1)	3737 (3)	−223 (3)	2.48 (10)
O-3′	3525 (1)	1715 (3)	899 (3)	2.43 (9)
O-5′	4214 (1)	4287 (3)	4145 (3)	1.89 (8)
O-6′	3819 (1)	5294 (3)	7167 (3)	3.01 (10)
C-1″	4610 (1)	7360 (4)	279 (4)	2.42 (10)
C-2″	4439 (1)	323 (4)	2004 (4)	1.97 (10)
C-3″	4209 (1)	8775 (4)	2541 (4)	2.14 (10)
C-4″	4265 (1)	8765 (4)	4379 (4)	2.37 (10)
C-5″	4715 (1)	8072 (4)	4539 (4)	2.02 (10)
C-6″	4780 (1)	7124 (4)	6051 (4)	2.41 (11)
O-1″	4891 (1)	8613 (3)	−25 (3)	2.79 (10)
O-3″	3764 (1)	8825 (3)	2035 (3)	2.77 (10)
O-4″	4237 (1)	265 (3)	4997 (4)	3.39 (10)
O-5″	4790 (1)	7179 (3)	3089 (3)	2.07 (9)
O-6″	5215 (1)	6611 (3)	6225 (3)	2.82 (10)
O-W	3858 (1)	10017 (5)	8009 (5)	5.52 (13)

[a] $B_{eq} = 4/3\Sigma_i\Sigma_j b_{ij} a_i a_j$

α-maltoside[14], and 118° in β-maltose monohydrate[12] and methyl-β-maltoside[13] by neutron studies; it deviates from 120° in α-maltose[10] and 113° in 4-iodophenyl α-maltoside[14]. The torsion angles of the (1 → 4)-glycosidic linkage for six maltose-type disaccharides are given in Table III. In comparison with these results, erlose is in best agreement with phenyl α-maltoside. The torsion angles about the primary alcohol groups in Table III indicate that the primary alcohol group in the nonprimed residue has a −*sc* (*gauche–gauche*) conformation, while one in the primed residue has a +*sc* (*gauche–trans*) conformation. The combination of these primary alcohol conformations differs from that observed in α-maltose, whereas it is the same as that found in phenyl α-maltoside. An intramolecular hydrogen-bond

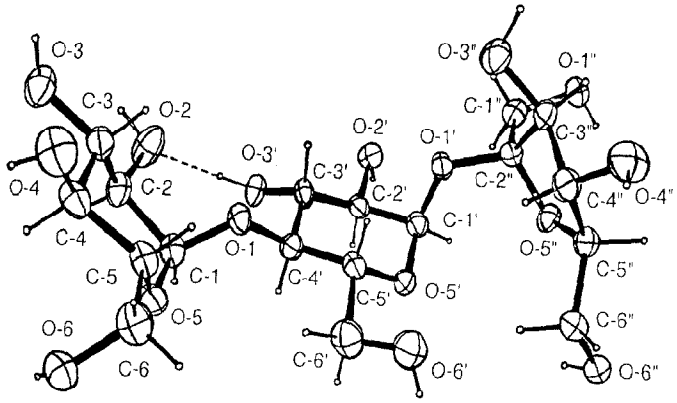

Fig. 1. View of the erlose molecule with numbering scheme and thermal ellipsoids at 50% probability.

is formed between the O-2 and O-3′ hydroxyl oxygen atoms, in which the proton of the O-3′ hydroxyl group is involved (see Table IV). The hydrogen bonding is the same to the other maltose-type sugars except for β-maltose monohydrate, in which the O-2 hydroxyl group is the proton donor for the intramolecular hydrogen bond.

TABLE III

Selected torsion angles (°) for erlose monohydrate and other saccharides

(1 → 4) Linkage	Erlose	α-Maltose	β-Maltose · H_2O	Methyl β-maltoside	Phenyl α-maltoside	4-Iodophenyl α-maltoside
O-5–C-1–O-1–C-4′	107	116	122	110	109	73
C-2–C-1–O-1–C-4′	−131	−126	−117	−128	−129	−164
C-1–O-1–C-4′–C-3′	108	122	132	129	102	84
C-1–O-1–C-4′–C-5′	−130	−118	−108	−109	−139	−155

(1 → 2) Linkage	Erlose	Sucrose	Melezitose form I	Melezitose form II	Raffinose	Planteose	1-Kestose	Stachyose
O-5′–C-1′–O-1′–C-2″	105	108	100	109	82	109	85	110
C-2′–C-1′–O-1′–C-2″	−134	−129	−142	−129	−158	−131	−153	−132
C-1′–O-1′–C-2″–O-5″	−61	−44	−31	−43	11	−27	−66	−50
C-1′–O-1′–C-2″–C-3″	−147	−160	−142	−128	−105	−142	177	−165

Primary alcohol groups	Erlose	Sucrose	α-Maltose	Phenyl α-maltoside
C-4–C-5–C-6–O-6	−67		53	−60
C-4–C-5–C-6–O-6	54		176	62
O-5′–C-5′–C-6′–O-6′	74	−56	69	72
C-4′–C-5′–C-6′–O-6′	167	64	−171	−170
O-5″–C-2″–C-1″–O-1″	−61	171		
C-3″–C-2″–C-1″–O-1″	55	−72		
O-5″–C-5″–C-6″–O-6″	64	−70		
C-4″–C-5″–C-6″–O-6″	−175	49		

TABLE IV

Hydrogen bond distances (Å) and angles (°)

D–H···A	Code [a]	D···A	D–H	H···A	∠D–H···A
O-2–H-O2···O-6	i	2.859 (4)	0.90 (4)	2.03 (5)	154 (3)
O-3–H-O3···O-6′	ii	2.764 (4)	1.05 (5)	1.72 (5)	175 (3)
O-4–H-O4···O-1′	iii	2.897 (4)	0.86 (5)	2.15 (5)	145 (4)
O-6–H-O6···O-3″	iii	3.020 (4)	0.98 (5)	2.12 (5)	151 (3)
O-2′–H-O2′···O-6″	iv	2.707 (4)	0.95 (5)	1.78 (5)	166 (4)
O-3′–H-O3′···O-2		2.746 (3)	0.92 (3)	1.83 (3)	173 (2)
O-6′–H-O6′···O-2′	v	2.815 (4)	0.74 (6)	2.12 (6)	157 (6)
O-1″–H-O1″···O-5′	vi	2.907 (3)	0.88 (6)	2.10 (6)	152 (5)
O-3″–H-O3″···O-3′	vii	2.797 (4)	0.90 (6)	1.90 (6)	171 (3)
O-4″–H-O4″···O-W		2.758 (5)	0.86 (6)	1.92 (6)	166 (4)
O-6″–H-O6″···O-1″	iv	2.826 (4)	0.88 (7)	2.00 (7)	157 (4)
O-W–H-WA···O-3′	iii	2.995 (5)	0.86 (6)	2.20 (6)	157 (4)
O-W–H-WB···O-3	viii	2.836 (5)	0.84 (6)	2.00 (6)	163 (4)
Weak hydrogen bond					
O-2–H-O2···O-5	ix	3.203 (4)	0.90 (4)	2.96 (5)	98 (3)

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

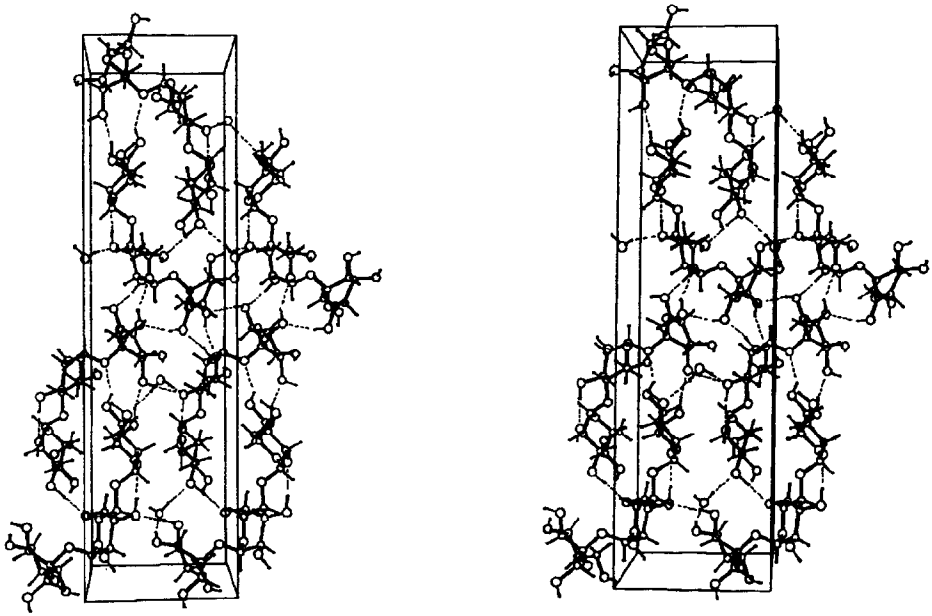

Fig. 2. Stereoscopic view of the molecular packing of erlose monohydrate along the *c*-axis. Dotted lines indicate hydrogen bonds.

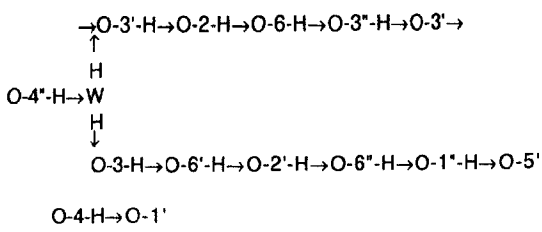

Fig. 3. Hydrogen-bonding system in erlose monohydrate crystal.

(1 → 2)-Glycosidic linkage.—The C-1′–O-1′–C-2″ bond angle is 116.5 (2)°, and the C–O bond distances are 1.421(4) Å and 1.428(4) Å, respectively. The bond angle may be compared with that of 114.30(8)° observed in sucrose by a neutron-diffraction study[15]. The torsion angles of the (1 → 2)-linkage for eight oligosaccharides are given in Table III. Comparison of these results leads to the conclusion that there is no special similarity between erlose and the other oligosaccharides. The intramolecular hydrogen-bonds bridging (1 → 2)-linked glucose and fructose residues observed in sucrose are not present in erlose. In other sucrose-like oligosaccharides, an intramolecular hydrogen-bond has been found in melezitose (form II)[18] and stachyose[23,24], but not in melezitose (form I)[16,17], raffinose[19], planteose[20], 1-kestose[21], and 6-kestose[22]. The hydrogen-bond formation relates to the orientation of the primary alcohol groups in the furanose residue. As the torsion angles in Table III indicate, erlose has a *gauche–gauche* conformation for the O-1″ group and a *gauche–trans* conformation for the O-6″ group, whereas the sucrose forming the intramolecular hydrogen-bonds has a *trans–gauche* conformation for the O-1″ group and a *gauche–gauche* conformation for the O-6″ group.

Hydrogen bonding.—A stereoscopic drawing of the crystal structure, viewed along the *c*-axis, is shown in Fig. 2. The hydrogen bonds formed in the structure are listed in Table IV. All of the hydroxyl groups participate in the hydrogen bonds. Each hydroxyl group, except for O-3′, O-4, and O-4″, forms two hydrogen bonds. The O-3′ hydroxyl group forms three hydrogen bonds, while the O-4 and O-4″ hydroxyl groups form only one hydrogen bond, acting as a proton donor. The glycosidic linkage atom (O-1′) and the ring oxygen atom (O-5′) accept one hydrogen bond. The ring oxygen atom (O-5) forms a very weak hydrogen bond as the minor component of three-center bonds[25]. The hydrogen-bonding scheme in the crystal structure, except for the weak hydrogen bond, consists of infinite and finite chains crosslinked into a net by the water molecule, with a separate O-4′-H · · · O-1′ bond, as shown in Fig. 3.

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