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Crystal structures of rare disaccharides, α-D-glucopyranosyl β-D-psicofuranoside, and α-D-galactopyranosyl β-D-psicofuranoside

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ABSTRACT

The crystal structures of α-D-glucopyranosyl β-D-psicofuranoside and α-D-galactopyranosyl β-D-psicofuranoside were determined by a single-crystal X-ray diffraction analysis, refined to $R_1 = 0.0307$ and 0.0438, respectively. Both disaccharides have a similar molecular structure, in which psicofuranose rings adopt an intermediate form between ^4E and $^4T_3$. Unique molecular packing of the disaccharides was found in crystals, with the molecules forming a layered structure stacked along the *y*-axis.

D-Psicose is a C-3 epimer of D-fructose, and exists in small amounts in nature, belonging to the 'rare sugars'. In the past decade, a strategy for the bioproduction of D-psicose was developed by Granström and Izumori et al.,[1] and the physiological functions of D-psicose have been extensively investigated, such as the postprandial blood glucose suppressive effect.[2] D-Psicose possibly exists as linear, pyranose ring, and furanose ring forms (Fig. 1). Three-dimensional structures of D-psicose are helpful for understanding the mechanism of its physiological functions. Crystal structures of β-D-psicopyranose were reported, in which uncommon *trans–gauche* orientation of the hydroxymethyl group relative to the pyranose ring was observed.[3,4] Although D-psicose with a linear conformation and α-D-psicofuranose were found as substrates bound to L-rhamnose isomerase,[5] their precise structures could not be elucidated because of the limited resolution for protein crystallography. Structural information on crystal forms of D-psicose derivatives is also available,[6–13] but does not show the inherent structure of D-psicose due to the introduction of bulky substituent groups. Recently, dissacharides composed of a β-D-psicofuranose unit were successfully synthesized by the glycosylation reaction of monosaccharide acceptors with a D-psicofuranosyl benzyl phthalate derivative.[14] These non-reducing disaccharides are expected to have new biological activities, and to be useful in elucidating the precise structure of β-D-psicofuranose. We have determined the crystal structures of α-D-glucopyranosyl β-D-psicofuranoside (GlcPsi) and α-D-galactopyranosyl β-D-psicofuranoside (GalPsi, Fig. 1). The molecular features and intermolecular interactions in crystals of these disaccharides, and a structural comparison with α-D-glucopyranosyl β-D-fructofuranoside (sucrose, CCDC 634580)[15,16] are presented herein.

The molecular structure of GlcPsi and GalPsi is shown in Figure 2a and b, respectively. Geometrical parameters are listed in Table 1. All bond lengths and angles between non-hydrogen atoms are in the normal range, and the mean values are well consistent with those of sucrose (1.534 Å for C–C, 1.431 Å for C–O, 110.0° for X–C–X, and 113.5° for C–O–C). All torsion angles except those involving O4G are similar between GlcPsi and GalPsi, suggesting the three-dimensional structure of these molecules to be almost the same. The root mean square deviation of non-hydrogen atoms except O4G is 0.074 Å. The O6G atoms adopt a *gauche–trans* conformation, and O6G of GalPsi forms an intramolecular hydrogen bond with O6P. Another intramolecular hydrogen bond is found between O2G and O1P (Fig. 2 and Table 2), helping to fix the relative orientation of the pyranose and furanose rings. In sucrose, two intramolecular hydrogen bonds are found in O2G–O1F and O5G–O6F (Fig. 2c), and O6G adopts a *gauche–gauche* conformation to avoid an unusual short contact with O6F. Although this difference

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Abbreviations: GlcPsi, α-D-glucopyranosyl β-D-psicofuranoside; GalPsi, α-D-galactopyranosyl β-D-psicofuranoside.

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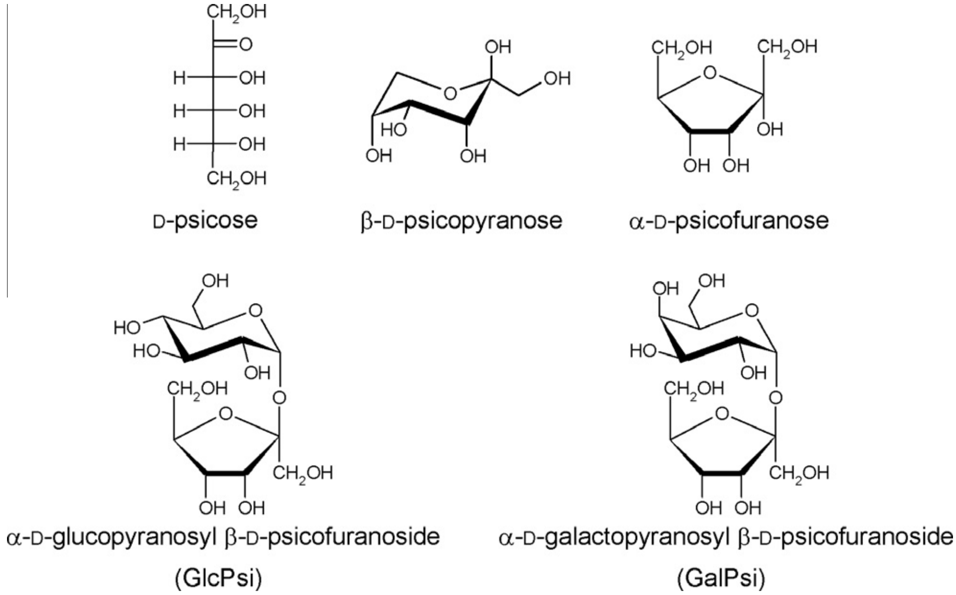

Figure 1. Chemical structure of D-psicose with a linear conformation, β-D-psicopyranose, α-D-psicofuranose, α-D-glucopyranosyl β-D-psicofuranoside (GlcPsi) and α-D-galactopyranosyl β-D-psicofuranoside (GalPsi).

in intramolecular hydrogen bonds between GlcPsi/GalPsi and sucrose seems to be due to the glycoside linkage between the pyranose and furanose rings, the glycoside linkage conformations are not so varied among GlcPsi, GalPsi, and sucrose; torsion angles of O5G–C1G–O1G–C2P/F and C1G–O1G–C2P/F–O5P/F are 115.4° and −52.1° (GlcPsi), 110.0° and −48.5° (GalPsi), and 108.4° and −44.3° (sucrose), respectively.

The puckering of a sugar ring is generally represented by Cremer–Pople parameters,[17] as listed in Table 1. The relatively large amplitude (q) and polar angle (θ) close to 0.0° of the glycopyranose rings of GlcPsi (0.573 Å, 5.4°) and galactopyranose ring of GalPsi (0.573 Å, 4.8°) suggest that pyranose rings adopt an ideal chair (C) form of $^4C_1$. Pseudorotation angles (ϕ) of psicofuranose rings are 278° (GlcPsi) and 281° (GalPsi), indicating that these five-membered rings are puckered in the intermediate form between ^4E (288°) and $^4T_3$ (270°). The angle of the fructofuranose ring of sucrose is 264.5°, being the intermediate form between $^4T_3$ (270°) and E_3 (252°).[15] This deviation of ϕ between psicofuranose and fructofuranose rings is caused by the different configurations of C3P and C3F in furanose rings. The C4P atoms of GlcPsi/GalPsi move above the furanose ring to avoid steric hinderance between O3P and O4P at the same side of the furanose plane. The ring puckering of a furanose ring affects the positions of O6P and O6F. The O6P of GlcPsi/GalPsi is far from O5G, while the O6F of sucrose is close enough to O5G to form a hydrogen bond. Therefore, the formation of an intramolecular hydrogen bond by O6P/O6F is thought

Table 1
Geometrical and Cremer–Pople parameters for GlcPsi and GalPsi

Mean bond distances (Å)	GlcPsi	GalPsi
C–C	1.518(9)	1.51(1)
C–O	1.420(1)	1.43(1)

Mean bond angles (°)	GlcPsi	GalPsi
X–C–X (X = C or O)	109(4)	109(4)
C–O–C	114(5)	113(5)

Glycoside linkage torsion angles (°)				GlcPsi	GalPsi
O5G	C1G	O1G	C2P	115.4(2)	110.0(6)
C1G	O1G	C2P	O5P	−52.1(3)	−48.5(8)
Hydroxymethyl group torsion angles (°)					
O5G	C5G	C6G	O6G	64.6(3)	58.5(8)
O5P	C5P	C6P	O6P	−62.5(3)	−66.4(9)
O1P	C1P	C2P	O5P	176.5(2)	172.4(6)

Cremer–Pople parameters

Pyranose ring			Furanose ring		
	GlcPsi	GalPsi		GlcPsi	GalPsi
q (Å)	0.573(3)	0.574(7)	q (Å)	0.435(3)	0.438(8)
θ (°)	5.0(3)	4.7(7)	ϕ (°)	278.0(3)	281.1(9)
ϕ (°)	115(3)	151(9)			

Table 2
Geometry of hydrogen bonds of GlcPsi and GalPsi

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry code
GlcPsi					
Intramolecular hydrogen bond					
O1P–H···O2G	0.82	1.95	2.724(3)	158	
O3G–H···O2G	0.82	2.53	2.839(3)	104	
Intermolecular hydrogen bond					
O–H···O					
O2G–H···O6G	0.82	1.90	2.670(3)	155	$x, y, z-1$
O3G–H···O6P	0.82	2.09	2.861(3)	158	$x-1, y, z-1$
O4G–H···O3P	0.82	2.33	3.048(3)	147	$-x+1, y-1/2, -z+1$
O4G–H···O5G	0.82	2.40	2.807(3)	111	$x-1, y, z$
O6G–H···O4P	0.82	1.92	2.719(3)	164	$-x+2, y-1/2, -z+2$
O3P–H···O3G	0.82	1.86	2.648(3)	162	$-x+1, y+1/2, -z+1$
O4P–H···O1P	0.82	1.88	2.697(3)	171	$x, y, z+1$
O6P–H···O4G	0.82	2.32	3.090(3)	157	$x+1, y, z$
C–H···O					
C2G–H···O6G	0.98	2.57	3.097(3)	114	$x, y, z-1$
GalPsi					
Intramolecular hydrogen bond					
O1P–H···O2G	0.82	1.94	2.731(8)	162	
O6P–H···O6G	0.82	2.52	2.922(9)	112	
Intermolecular hydrogen bond					
O–H···O					
O2G–H···O6G	0.82	1.93	2.705(8)	157	$x, y, z-1$
O3G–H···O6P	0.82	2.07	2.804(8)	149	$x-1, y, z-1$
O4G–H···O1P	0.82	2.11	2.922(8)	172	$-x+1, y-1/2, -z+1$
O6G–H···O3P	0.82	2.35	3.035(7)	142	$-x+2, y-1/2, -z+2$
O6G–H···O4P	0.82	2.20	2.906(8)	144	$-x+2, y-1/2, -z+2$
O3P–H···O3G	0.82	1.82	2.624(7)	168	$-x+1, y+1/2, -z+1$
O4P–H···O1P	0.82	1.98	2.780(8)	164	$x, y, z+1$
C–H···O					
C1G–H···O3G	0.98	2.53	3.414(10)	150	$-x+1, y+1/2, -z+1$