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CRYSTAL STRUCTURE OF DI-β-D-FRUCTOFURANOSE 2′, 1:2,3′-DIANHYDRIDE

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ABSTRACT

The crystals of di-β-D-fructofuranose 2′,1:2,3′-dianhydride are monoclinic, space group $P2_1$, with unit-cell dimensions a = 12.8557(14), b = 7.7266(7), c = 7.0322(9)Å, β = 97.395(10)°, z = 2. The structure was solved by the direct method, and refined to an R value of 0.046 and an Rw value of 0.048 for 2123 observed reflections. The conformations of the furanose rings are ^2E with P = 302.5° and τ_m = 39.4° for D-fructose 1, and $^3T_2$ with P = 145.7° and τ_m = 35.8° for D-fructose 2. The fused, 1,4-dioxane ring has a chair conformation with Cremer-Pople puckering parameters Q = 0.501 Å and θ = 8.1°.

INTRODUCTION

In studies on the hydrolysis of inulin by dilute sulfuric acid, Jackson and co-workers isolated three isomeric di-D-fructose anhydrides which they designated[1,2]

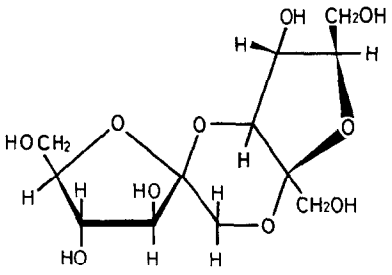

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TABLE I

CRYSTALLOGRAPHIC AND EXPERIMANTAL DATA

a (Å)	12.8557(14)
b (Å)	7.7266(7)
c (Å)	7.0322(9)
β(°)	97.395(10)
Space group	$P2_1$
Z (molecules/cell)	2
Volume (Å^3)	692.7
D_{cal} (mg/m^3)	1.56
Crystal size (mm)	0.4×0.4×0.5
Radiation	graphite-monochromated MoKα (λ = 0.7107 Å)
Reflections measured	2123
μ (cm^{-1})	1.47
Refinement on w(|F_o|-k|F_c|)^2,	where w = 1
R	0.046
R_w	0.048

TABLE II

POSITIONAL PARAMETERS (× 10^4 FOR NON-H ATOMS AND × 10^3 FOR H ATOMS)

Atom	x	y	z	B_{eq}	*Atom*	x	y	z	B_{iso}
O-1	2391(2)	7330(3)	5640(3)	2.2	HO-3	312(3)	189(7)	294(6)	2.2
O-2	969(2)	4347(3)	5199(3)	1.9	HO-6	28(3)	227(7)	931(6)	2.0
O-3	2809(2)	2587(4)	2260(3)	2.5	HC-11	284(3)	620(6)	327(6)	1.2
O-4	463(2)	1104(4)	1911(3)	2.9	HC-12	168(3)	674(6)	317(6)	1.4
O-6	226(2)	2649(4)	8295(3)	3.0	HC-3	147(3)	372(6)	185(6)	0.9
C-1	2229(2)	6225(4)	4001(4)	2.0	HC-4	155(3)	68(7)	413(6)	1.6
C-2	1961(2)	4395(4)	4548(4)	1.7	HC-5	−17(3)	270(6)	464(6)	1.3
C-3	1856(2)	3125(4)	2872(4)	1.9	HC-61	155(3)	184(6)	754(6)	1.0
C-4	1168(2)	1670(4)	3530(4)	2.0	HC-62	51(3)	42(6)	697(5)	1.0
C-5	606(2)	2552(4)	5092(4)	1.7	HO-4′	375(3)	405(6)	1115(6)	1.3
C-6	814(2)	1702(5)	7041(4)	2.0	HC-11′	242(4)	794(7)	947(7)	3.1
O-1′	3553(2)	9574(4)	8367(4)	3.3	HC-3′	231(3)	469(6)	849(5)	0.7
O-2′	4128(2)	6714(3)	6573(3)	2.4	HC-4′	407(3)	311(6)	843(6)	1.5
O-3′	2757(2)	3757(3)	5968(3)	1.7	HC-5′	529(3)	593(6)	851(6)	1.2
O-4′	4208(2)	4554(4)	10601(3)	2.4	HC-61′	473(3)	402(6)	502(6)	1.5
O-6′	6005(2)	5520(4)	5352(4)	3.6	HC-62′	566(4)	325(7)	692(7)	2.8
C-1′	3072(3)	7962(5)	8821(5)	2.9					
C-2′	3114(2)	6693(4)	7156(4)	2.0					
C-3′	2943(2)	4802(4)	7673(4)	1.8					
C-4′	4026(2)	4191(4)	8598(4)	1.9					
C-5′	4762(2)	5346(5)	7561(4)	2.2					
C-6′	5291(3)	4361(5)	6116(5)	2.8					

di-D-fructose anhydride I, II, and III. Di-D-fructose anhydride I and III were determined to be α-D-fructofuranose β-D-fructofuranose 2′,1:2,1′-dianhydride[3] and α-D-fructofuranose β-D-fructofuranose 2′,1:2,3′-dianhydride[4–6], respectively. For di-D-

TABLE III

BOND LENGTHS[a] AND ANGLES[a]

Atoms	*Length* (Å)	*Atoms*	*Length* (Å)
C-1–O-1	1.428	C-1′–O-1′	1.444
C-2–O-3′	1.422	C-2′–O-1	1.410
C-2–O-2	1.411	C-2′–O-2′	1.416
C-3–O-3	1.412	C-3′–O-3′	1.440
C-4–O-4	1.430	C-4′–O-4′	1.425
C-5–O-2	1.462	C-5′–O-2′	1.456
C-6–O-6	1.434	C-6′–O-6′	1.435
C-1–C-2	1.517	C-1′–C-2′	1.534
C-2–C-3	1.526	C-2′–C-3′	1.529
C-3–C-4	1.539	C-3′–C-4′	1.534
C-4–C-5	1.548	C-4′–C-5′	1.549
C-5–C-6	1.512	C-5′–C-6′	1.501
	Angle (°)		*Angle* (°)
O-1–C-1–C-2	111.5	O-1′–C-1′–C-2′	108.9
C-1–C-2–C-3	113.8	C-1′–C-2′–C-3′	114.2
C-1–C-2–O-2	110.6	C-1′–C-2′–O-2′	109.8
C-1–C-2–O-3′	109.6	C-1′–C-2′–O-1	105.6
O-2–C-2–O-3′	111.2	O-2′–C-2′–O-1	108.6
C-3–C-2–O-3′	107.7	C-3′–C-2′–O-1	114.3
C-3–C-2–O-2	103.9	C-3′–C-2′–O-2′	104.2
C-2–C-3–C-4	103.6	C-2′–C-3′–C-4′	104.1
C-2–C-3–O-3	115.5	C-2′–C-3′–O-3′	110.6
C-4–C-3–O-3	115.6	C-4′–C-3′–O-3′	103.1
C-3–C-4–C-5	103.3	C-3′–C-4′–C-5′	101.5
C-3–C-4–O-4	108.3	C-3′–C-4′–O-4′	112.6
C-5–C-4–O-4	113.2	C-5′–C-4′–O-4′	108.6
C-4–C-5–C-6	114.1	C-4′–C-5′–C-6′	112.6
C-4–C-5–O-2	106.3	C-4′–C-5′–O-2′	107.8
C-6–C-5–O-2	110.3	C-6′–C-5′–O-2′	108.6
C-5–C-6–O-6	106.9	C-5′–C-6′–O-6′	107.7
C-2–O-2–C-5	107.7	C-2′–O-2′–C-5′	109.4
C-1–O-1–C-2′	114.5	C-2 –O-3′–C-3′	114.7

[a] The e.s.d. values for the bond lengths and angles are in the ranges of 0.005-0.006 Å and 0.3-0.4°, respectively.

fructose anhydride II, McDonald and Turcotte[7] preferred di-D-fructose 2′,1:2,4′-dianhydride, whereas Wolfrom *et al.*[8] suggested an anomer of anhydride III, but the structure was not determined. This crystal-structure determination shows that di-D-fructose anhydride II is di-β-D-fructofuranose 2′,1:2,3′-dianhydride.

EXPERIMENTAL

Di-D-fructose anhydride II was prepared by acid hydrolysis of inulin, using the procedure described by Jackson and McDonald[2]. The product was recrystallized several times from ethanol; m.p. 200°, $[\alpha]_D^{20} + 14.2°$ (*c* 1.01, H_2O). *Anal.* Calc. for

TABLE IV

SELECTED CONFORMATIONAL ANGLES[a]

Atoms	*Angle (°)*	*Atoms*	*Angle (°)*
(a) D-Fructose 1		C-1′-C-2′-C-3′-O-3′	166.9
C-5-O-2-C-2-C-3	39.0	O-3′-C-3′-C-4′-O-4′	−158.2
O-2-C-2-C-3-C-4	−37.1	O-4′-C-4′-C-5′-C-6′	134.6
C-2-C-3-C-4-C-5	21.2		
C-3-C-4-C-5-O-2	1.0	O-1 -C-1 -C-2 -O-2	67.6
C-4-C-5-O-2-C-2	−25.2	O-1 -C-1 -C-2 -C-3	−175.9
(b) D-Fructose 2		O-1′-C-1′-C-2′-C-3′	162.5
C-5′-O-2′-C-2′-C-3′	−28.8	O-1′-C-1′-C-2′-O-2′	45.8
O-2′-C-2′-C-3′-C-4′	36.8	O-1′-C-1′-C-2′-O-1	−71.1
C-2′-C-3′-C-4′-C-5′	−29.6		
C-3′-C-4′-C-5′-O-2′	13.2	O-6 -C-6 -C-5 -C-4	−178.9
C-4′-C-5′-O-2′-C-2′	9.8	O-6 -C-6 -C-5 -O-2	61.6
(c) 1,4-Dioxane ring		O-6′-C-6′-C-5′-C-4′	−175.9
O-3′-C-3′-C-2′-O-1	45.1	O-6′-C-6′-C-5′-O-2′	64.8
C-3′-C-2′-O-1 -C-1	−47.4		
C-2′-O-1 -C-1 -C-2	52.1	C-1 -O-1 -C-2′-O-2′	68.5
O-1 -C-1 -C-2 -O-3′	−55.3	C-1 -O-1 -C-2′-C-1′	−173.8
C-1 -C-2 -O-3′-C-3′	56.7		
C-2 -O-3′-C-3′-C-2′	−51.2	C-3′-O-3′-C-2 -O-2	−65.9
		C-3′-O-3′-C-2 -C-3	−179.1
(d) Other interesting angles			
C-1 -C-2-C-3-O-3	75.2		
O-3′-C-2-C-3-O-3	−46.5		
O-3 -C-3-C-4-O-4	−91.2		
O-4 -C-4-C-5-C-6	122.3		

[a] The torsion angel *A*-1-*A*-2-*A*-3-*A*-4 is viewed along *A*-2-*A*-3, with clockwise rotation of *A*-1 taken to be positive. The e.s.d. is ~0.5°.

$C_{12}H_{20}O_{10}$: C, 44.45; H, 6.22. Found: C, 44.35; H, 6.25. Crystals were grown from 90% ethanol solution at room temperature. The crystallographic and experimental data are given in Table I. Data collection was made on a RIGAKU AFC-5FOS automated diffractometer. The cell dimensions were refined from setting angles of 20 reflections in the 2θ range 31–37°. Intensities were measured by the mixed $\theta - 2\theta$ scanning mode up to $2\theta = 60°$. The structure was solved by direct methods[9] and were refined by a block-diagonal least-squares program with anisotropic temperature factors for carbon and oxygen atoms. Sixteen H atoms out of twenty were located from difference synthesis, and refined with isotropic temperature factors. The four H atoms not revealed were not included in the computation. Final atomic parameters are given in Table II*. Bond lengths and angles and selected confor-

* Tables of the anisotropic thermal parameters for non-hydrogen atoms, the least-squares best planes, and the observed and calculated structure factors are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition. P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/393 *Carbohydr. Res, 177* (1988) 13–20.

mational angles are given in Table III and IV, respectively.

DISCUSSION

Di-D-fructose anhydride II is di-β-D-fructofuranose 2′,1:2,3′-dianhydride, which is an anomer of di-D-fructose anhydride III (α-D-fructofuranose β-D-fructofuranose 2′,1:2,3′-dianhydride)[4–6]. The molecular conformation, with the atomic notation, is shown in Fig. 1.

The furanose rings of the D-fructose moieties have the ^2E conformation (C-2-endo) with pseudorotation phase angle and maximum torsion angle[11] of P = 302.5° and τ_m = 39.4° for D-fructose 1 (see Fig. 2a), and the $^3T_2$ conformation (C-3-endo C-2-exo), with P = 145.7° and τ_m = 35.8° for D-fructose 2 (see Fig. 2b). These conformations are compared with those found for the D-fructose moieties of the other compounds (see Table V). The ring conformation of D-fructose 2 is similar to that found in D-fructose 1 of 1-kestose [*O*-β-D-fructofuranosyl-(2→1)-β-D-fructofuranosyl α-D-glucopyranoside[17]], and, in these ring conformations, the conformational angle of O-1–C-2′–C-3′–O-3′ for D-fructose 2 of anhydride II and the corresponding angle for D-fructose 1 of 1-kestose are 45.1 and 22.0°, respectively, whereas the corresponding values in the other β-D-fructose are in the range of −11 to −46.5° (see Table V).

The 1,4-dioxane ring is fused to the furanose ring of D-fructose 2, and connects with the ring of D-fructose 1 at the anomeric carbon atom (C-2) in a spiro arrangement (see Fig. 1). The dioxane ring has a chair conformation, with Cremer–

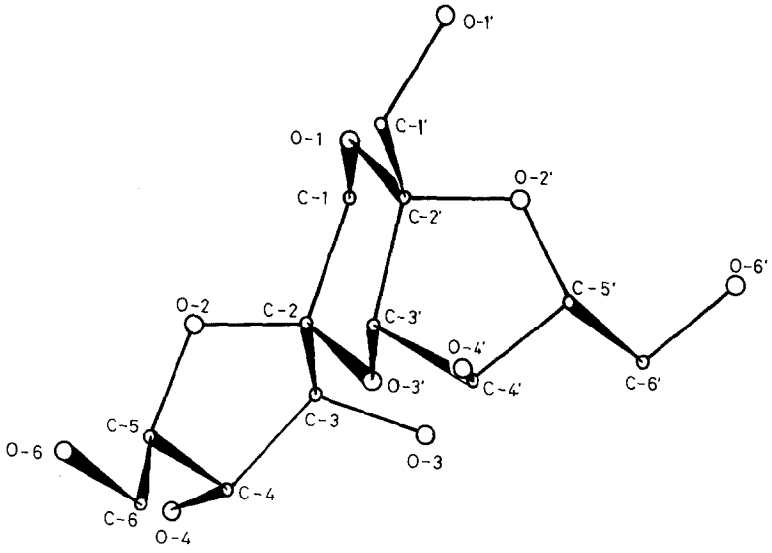

Fig. 1. A perspective view of the molecule of di-D-fructose anhydride II, with the atomic numbering.

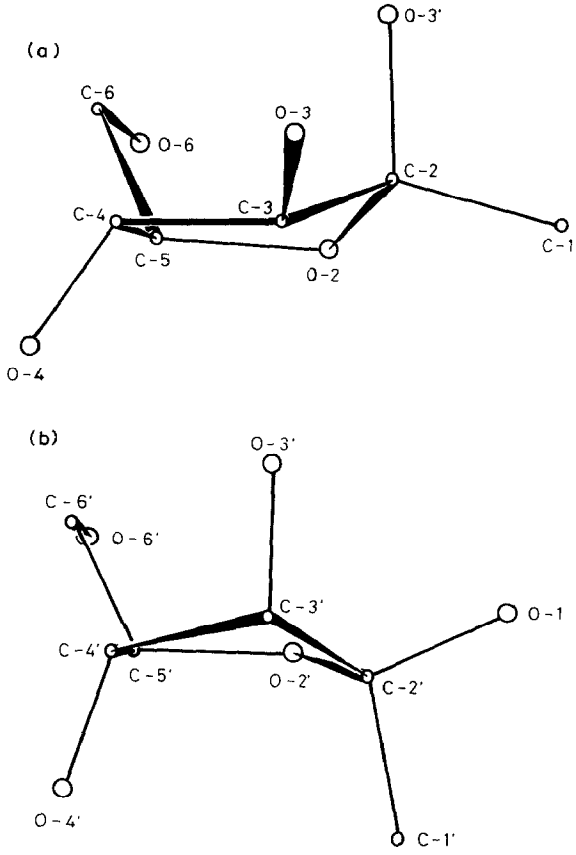

Fig. 2. Comparison of conformations of the two β-D-fructose moieties, showing puckering. [(a) D-fructose 1, and (b) D-fructose 2.].

Pople puckering parameters[10] of $Q = 0.501$ Å, $\theta = 8.1°$, and $\phi = 117.4°$. The ring conformation is significantly different from that found[6] in anhydride III, which is a skew conformation with $Q = 0.673$ Å, $\theta = 85.5°$, and $\phi = 18.3°$.

The orientations of the C-1 atom about the endocyclic O-1–C-2′ bond are *gauche*$^-$, *gauche*$^+$, and *trans* to the C-3′, O-2′ and C-1′ atoms, respectively (see Table IV). These orientations are very similar to those found[6] in anhydride III [C-1–O-1–C-2′–C-3′ = −46.5°, C-1–O-1–C-2′–O-2′ = 70.2°, and C-1–O-1–C-2′–C-1′ = −173.7°]. The orientations of C-3′ about O-3′–C-2 are *gauche*$^+$, *gauche*$^-$, and *trans* to C-1, O-2, and C-3, respectively (see Table IV). These orientations are very reasonable. In anhydride III, the orientation of C-3′ about O-3′–C-2 [C-3′–O-3′–C-2–C-1 = −35.7°, C-3′–O-3′–C-2–O-2 = 85.3°, and C-3′–O-3′–C-2–C-3 = −160.7°][6] deviates by about 20 to 25° out of the ideal *gauche* and *trans* positions. The difference between anhydride II and III (ref. 6) in the orientation of C-3′ about O-3′–C-2 may be caused by the fact that the D-fructose 1 moieties of anhydrides II

TABLE V

COMPARISON AMONG THE RING CONFORMATIONS OF D-FRUCTOFURANOSE MOIETIES

Compounds		P (°)	τ_m (°)	ν^a (°)	References
Anhydride II					This paper
fructose 1	^2E	302.5	39.4	−46.5	
fructose 2	$^3T_2$	145.7	35.8	45.1	
Anhydride III					6
fructose 1[b]	$^4T_3$	8.5	40.4	89.8	
fructose 2	E_5	50.6	26.8	−11.0	
Sucrose	E_3	344.8	35.4	−39.2	12
Isomaltulose	E_3	348.6	34.2	−36.3	13
Raffinose	$^4T_3$	4.5	38.8	−32.5	14
Planteose	$^4T_3$	354.5	39.1	−39.6	15
Melezitose					
form I	$^4T_3$	6.2	38.4	−27.9	16
form II	E_3	339.6	38.6	−39.6	17
1-Kestose					18
fructose 1	^3E	168.5	29.9	22.0	
fructose 2	E_3	342.3	42.1	−44.5	
6-Kestose					19
fructose 1	$^4T_3$	2.3	42.6	−39.1	
fructose 2	E_3	340.7	35.3	−34.6	
Fructose 6-PO_3K_2	$^2T_3$	330.9	36.8	−42.3	20
Fructose 1,6-diPO_3Na_3	E_3	343.3	37.6	−40.2	21

[a] The conformational angle of O-3′-C-2-C-3 O-3 for the fructose 1 of anhydride II and the corresponding ones for the other fructofuranosyl moieties. [b] α-D-Fructofuranosyl moiety.

and III have β and α configurations, respectively.

The mean plane of the furanose ring of D-fructose 2 makes an angle of 62° to the mean planes of both the furanose ring of D-fructose 1 and the dioxane ring. This value is smaller than the corresponding ones of 71 and 82° found[6] in anhydride III. The angle of 82° between the mean planes of the furanose ring of D-fructose 1 and the dioxane ring is remarkably larger than that of 27° found[6] in anhydride III.

The C–C and C–O bonds (see Table III) are in the range 1.501–1.549 and 1.410–1.452 Å, respectively, which agree well with the values found in the other oligosaccharides (1.49–1.55 Å for C–C and 1.39–1.46 Å for C–O). The bond lengths of O-2–C-2 and O-2′–C-2′ are observed to be significantly shorter than those of O-2–C-5 and O-2′–C-5′, respectively (see Table III). The shortening of O-2–C-2 and O-2′–C-2′ may be effected by the anomeric disproportionation reported by Rohrer[15].

The intermolecular O···O hydrogen bonds are listed in Table VI. The molecules are connected by two endless, hydrogen-bond chains; one is ···O-4···O-6···O-4··· around a two-fold screw axis parallel to b. The other is ···O-3···O-6′···O-1′···O-4′···O-3··· around the two-fold screw axis parallel to b.

TABLE VI

HYDROGEN-BOND DISTANCES

Hydrogen bonds	*Symmetry operation*[a]	*O···O (Å)*
O-3–HO-3···O-6′	$(1-x, -1/2+y, 1-z)$	2.652
O-4.....O-6	$(-x, -1/2+y, 1-z)$	2.810
O-6–HO-6···O-4	$(x, y, 1+z)$	2.790
O-1′.....O-4′	$(1-x, 1/2+y, 2-z)$	2.876
O-4′–HO-4′···O-3	$(x, y, 1+z)$	2.729
O-6′.....O-1′	$(1-x, -1/2+y, 1-z)$	2.843

[a] The symmetry operation was performed on the acceptor oxygen atoms. The e.s.d. values for O···O are 0.005–0.007 Å.

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