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Note

X-Ray structure of methyl 3,6-anhydro-β-L-gulofuranoside

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In a previous study, we published five crystal structures of the eight possible isomers of methyl 3,6-anhydrohexofuranosides[1]. Of special interest was how the anomeric effect[2] could dominate the shape and pucker of otherwise highly flexible furanoid rings in these compounds. In accordance with previous ^{1}H-n.m.r. investigations in solution[3], the results showed that the conformations of the furanoid rings correspond to an almost quasi-axial orientation of the aglycon and that the driving force is the above-mentioned stereoelectronic effect. In all cases, the influence of the exo-anomeric effect was also observed[4].

Since the quality of the crystals of a sixth isomer, namely, the title compound **1**, was relatively poor, it was at first not possible to determine the crystal structure of this compound. Later[6], with the help of the computer programme SHELXS-84[5], the phase problem was solved by using direct methods and the least-squares method for refinement[1]. We now report the results of this structure determination.

Methyl 3,6-anhydro-β-L-gulofuranoside[3] (**1**) crystallises in the monoclinic space group $P2_1$ with two independent molecules in the asymmetric unit. Further crystallographic information is given in Table I.

The final positional and thermal parameters are listed in Table II. Bond lengths and bond angles are given in Tables III and IV. A SCHAKAL representation[7] of one of the independent molecules (I) is shown in Fig. 1, from which also the atom numbering scheme can be deduced*.

*Lists of observed and calculated structure amplitudes, atomic coordinates of the hydrogen atoms (calculated), and torsion angles are desposited 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/374/*Carbohydr. Res.*, 168 (1987) 115–119.

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TABLE I

CRYSTALLOGRAPHIC DATA FOR **1**

Formula	$C_7H_{12}O_5$
Mol. wt.	176.17
M.p. (degrees)	70–71
Space group	$P2_1$
Cell constants (pm)	
a	1233.4(30)
b	485.5(12)
c	1445.4(33)
β (degrees)	104.57(19)
Volume (pm^3)	837.69×10^6
Z	4
$F(000)$	376
Density (calc.) ($g \cdot cm^{-3}$)	1.40
λ (Mo$K\alpha$) (pm)	70.9261
μ (cm^{-1})	0.77
Crystal dimension (mm)	$0.4 \times 0.4 \times 0.3$
2θ range (degrees)	3–50
Reflections measured	1602
Reflections with $F_0 > 3\sigma(F_0)$	1025
Final residual factors	
R	0.111
R_w	0.083
Diffractometer	Syntex $P2_1$

Puckering parameters[8] for the furanose rings in the two independent molecules of **1** are $\phi = 11.1°$ (molecule I) and 9.1° (molecule II) with $Q = 0.34$ and 0.37 pm, respectively. These values correspond to the unusual conformational region ${}^{\circ}E \rightleftharpoons {}^{\circ}T_1$, which was already predicted[3] by the ^{1}H-n.m.r. experiments, and confirm that the anomeric effect[2] forces the aglycon into an almost quasi-axial position.

The torsion angles C-7–O-1–C-1–O-4 involving the aglycon are +62.8° (I) and +61.0° (II). Thus, the orientation of the aglycon also corresponds to the requirements of the exo-anomeric effect[4].

Puckering parameters[8] for the anhydro rings O-3–C-6–C-5–C-4–C-3 of the two independent molecules of **1** are $\phi = 239.1°$ (I), 240.5° (II) and $Q = 0.32$ (I), 0.38 (II). These values correspond to a C-6endo orientation of the anhydro rings. This conformation was also observed for four of the other five isomers[1].

As in all carbohydrates with free hydroxyl groups, the molecules I and II are interlinked in the crystal by a complicated pattern of hydrogen bonding. Only strong interactions with H···O distances <220 pm and O–H···O angles >153° are summarised in Table V. Besides these strong hydrogen-bonds, other weak interactions with distances <250 pm can be observed. Therefore, the classification of hydrogen bonding in **1** to different types, according to the rules of Jeffrey and Takagi[9], is given in the last column of Table V. For more details, see ref. 6 or refer to the deposited original data*.

TABLE II

FRACTIONAL POSITIONAL PARAMETERS AND TEMPERATURE FACTORS OF CARBON AND OXYGEN ATOMS IN 1[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Molecule I									
O-1	867(6)	6489(0)	8673(5)	47(2)	87(2)	76(2)	−9(2)	−4(2)	−12(2)
O-2	3538(6)	9293(14)	8664(5)	70(2)	51(2)	55(2)	25(2)	−3(2)	−12(2)
O-3	4412(5)	6796(15)	10308(5)	32(2)	73(2)	67(2)	−3(2)	7(2)	7(2)
O-4	1933(5)	8894(15)	10024(5)	36(2)	66(2)	77(2)	8(2)	10(2)	9(2)
O-5	3642(6)	5082(14)	12003(5)	54(2)	48(2)	64(2)	6(2)	−8(2)	−8(2)
C-1	1737(8)	8512(17)	9023(7)	52(2)	49(2)	36(2)	2(2)	−1(2)	3(2)
C-2	2816(8)	7229(17)	8850(8)	36(2)	67(2)	83(2)	25(2)	0(2)	−12(2)
C-3	3316(7)	5687(16)	9830(7)	28(2)	43(2)	63(2)	−10(2)	2(2)	−19(2)
C-4	2571(7)	6492(16)	10473(7)	41(2)	47(2)	44(2)	25(2)	22(2)	14(2)
C-5	3345(7)	7507(17)	11444(7)	27(2)	67(2)	40(2)	19(2)	−14(2)	−18(2)
C-6	4344(8)	8511(17)	11080(7)	55(2)	49(2)	52(2)	−4(2)	5(2)	9(2)
C-7	−195(8)	7282(19)	8805(8)	28(2)	193(2)	104(2)	8(2)	29(2)	3(2)
Molecule II									
O-1′	8149(6)	8046(0)	3359(5)	58(2)	126(2)	64(2)	−31(2)	24(2)	−24(2)
O-2′	5508(5)	5637(14)	3580(5)	45(2)	64(2)	76(2)	−6(2)	2(2)	−22(2)
O-3′	5864(5)	8088(14)	5245(5)	37(2)	72(2)	63(2)	16(2)	11(2)	2(2)
O-4′	8012(5)	5725(14)	4734(5)	53(2)	72(2)	62(2)	14(2)	4(2)	16(2)
O-5′	7849(6)	9743(14)	6780(5)	63(2)	67(2)	68(2)	−19(2)	−10(2)	−4(2)
C-1′	7512(8)	6245(17)	3732(7)	40(2)	138(2)	50(2)	−1(2)	7(2)	−29(2)
C-2′	6392(8)	7629(16)	3715(7)	46(2)	48(2)	60(2)	−21(2)	−14(2)	−5(2)
C-3′	6615(8)	9022(16)	4689(7)	43(2)	37(2)	57(2)	17(2)	2(2)	23(2)
C-4′	7800(8)	8078(16)	5226(7)	43(2)	53(2)	66(2)	−13(2)	−9(2)	28(2)
C-5′	7658(8)	7338(17)	6228(7)	56(2)	99(2)	39(2)	−10(2)	−4(2)	12(2)
C-6′	6474(8)	6257(16)	5996(7)	44(2)	42(2)	79(2)	35(2)	−7(2)	−20(2)
C-7′	9263(8)	7090(18)	3403(8)	50(2)	201(2)	74(2)	−55(2)	27(2)	−27(2)

[a]Values × 10^4 (U_{ij} × 10^3). E.s.d. in parentheses.

TABLE III

ATOMIC DISTANCES (pm) IN 1[a]

Bond	*Molecule I*	*Molecule II*
C-1–C-2	154.5(15)	153.0(14)
C-2–C-3	158.2(14)	152.3(14)
C-3–C-4	151.4(15)	154.1(12)
C-4–C-5	156.5(12)	154.4(15)
C-5–C-6	153.6(15)	150.8(14)
C-1–O-1	144.9(10)	137.3(12)
C-1–O-4	141.8(12)	144.7(12)
C-2–O-2	141.0(12)	143.3(11)
C-3–O-3	145.8(10)	144.3(13)
C-4–O-4	146.4(11)	140.4(12)
C-5–O-5	142.3(11)	140.1(11)
C-6–O-3	141.2(13)	145.7(11)
C-7–O-1	142.4(13)	143.6(13)

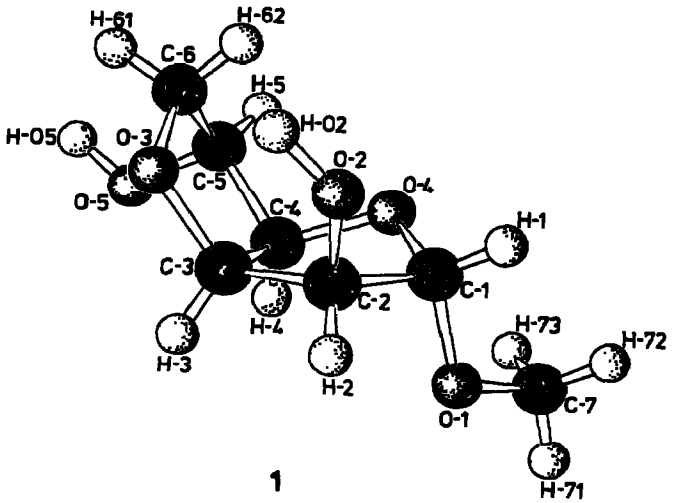
[a]E.s.d. in parentheses.

TABLE IV

BOND ANGLES (DEGREES) IN 1[a]

Angle	*Molecule I*	*Molecule II*
C-1–O-1–C-7	113.3(5)	114.4(5)
C-3–O-3–C-6	111.1(7)	108.9(7)
C-1–O-4–C-4	106.4(7)	106.1(7)
O-1–C-1–O-4	111.4(7)	111.2(7)
O-1–C-1–C-2	105.2(6)	108.5(6)
O-4–C-1–C-2	106.6(8)	104.4(8)
O-2–C-2–C-1	110.8(7)	111.0(7)
O-2–C-2–C-3	112.6(8)	112.3(8)
C-1–C-2–C-3	101.8(8)	103.2(8)
O-3–C-3–C-2	110.8(7)	112.5(7)
O-3–C-3–C-4	105.5(7)	106.6(7)
C-2–C-3–C-4	104.3(7)	105.2(7)
O-4–C-4–C-3	105.9(7)	105.1(7)
O-4–C-4–C-5	106.6(6)	111.4(7)
C-3–C-4–C-5	107.7(8)	103.0(8)
O-5–C-5–C-4	105.1(7)	107.4(7)
O-5–C-5–C-6	110.0(7)	115.6(8)
C-4–C-5–C-6	98.8(7)	101.8(8)
O-3–C-6–C-5	107.2(7)	104.0(7)

[a]E.s.d. in parentheses.



1

Fig. 1. A SCHAKAL[7] drawing of molecule I of methyl 3,6-anhydro-β-L-gulofuranoside (1) showing atom numbering. Corresponding atoms in molecule II of 1 are primed.

TABLE V

ANGLES AND DISTANCES IN HYDROGEN BONDS OBSERVED IN 1

Molecule	*Hydrogen bond*	*Distance O–H (pm)*	*Distance H···O (pm)*	*Angle O–H···O (°)*	*Type*[a]
I	O-2–H-O2···O-3[a]	100.0	191.1	157.6	IVB
I	O-5–H-O5···O-2′	98.6	183.5	172.2	IA
II	O-2′–H-O2′···O-3′[a]	93.5	202.9	170.4	IVA
II	O-5′–H-O5′···O-5[a]	100.0	187.8	163.5	IB

[a]Oxygen atoms in symmetry-related molecules.

Despite the relatively poor quality of the crystals, the results obtained seem to be significant and accord with the observations reported for the other five related isomers[1].

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