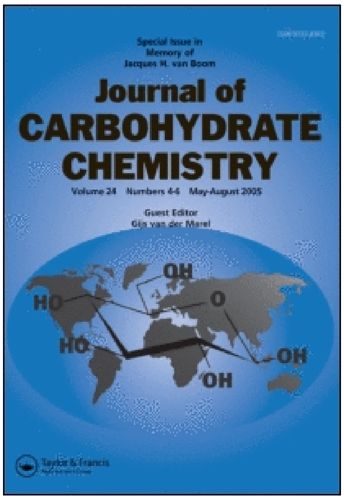

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The X-RAY Structure of 2,3,5-Tri-O-Acetyl-1, 6-Anhydro-α-D-Galactofuranose

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The X-RAY STRUCTURE OF 2,3,5-TRI-O-ACETYL-1,6-ANHYDRO-α-D-GALACTOFURANOSE[1]*

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ABSTRACT

The title compound 1 ($C_{12}H_{16}O_8$), $M_r = 288.25$, crystallizes in the monoclinic space group $P2_1$, with a = 808.8(4), b = 1003.0(5), c = 1762.0(1) pm, ß =101.53(4)°, V = 1400.5 x 10^6 pm^3, Z = 4 and two independent molecules in the asymmetric unit. The structure was solved by direct methods and refined to final residual values of R = 0.051 and R_w = 0.043 for 2159 reflections. The 1,3-dioxane rings of the anhydro bridges adopt chair conformations which are flattened in direction to half chairs (Puckering parameters Q = 60.4 (63.4) pm, Φ = 137.2 (138.2)°, Θ = 18.5 (17.7)°).

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* Dedicated to Professor George A. Jeffrey on the occasion of his 70th Birthday.

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The furanose rings are found in conformations which are intermediate between $^{O}E(D)$ and $^{O}T_1(D)$ and differ, therefore, to some extent from those found previously in other anhydrohexofuranoses (Puckering parameters: Q = 45.4 (44.6) pm, Φ = 9.7 (9.7)°).

INTRODUCTION

All eight hexoses can form inner glycosides of the 1,6-anhydro*furanose* type. Now, after our recent reported synthesis of 1,6-anhydro-α-L-idofuranose[2] at least one enantiomer of each of the diastereomers of this class of glycosans is known.

The chemistry of this group of compounds, however, is not as highly developed as that of the related 1,6-anhydrohexo*pyranoses*.[3]

We therefore made some efforts toward the development of this field of monosaccharide chemistry in the last few years,[1] including conformational studies which are of special interest in view of the general furanoid ring geometry.

In addition to 1,5-anhydrofuranoses[4] (and to a much lesser extent 3,6-anhydrofuranoses[5]) 1,6-anhydrofuranoses are relatively rigid simple systems in which the furanoid rings are fixed in a defined conformation in solution. Contrary to monocyclic furanoses, exhibiting high conformational flexibility through pseudorotation,[6] the former can give valuable basic data from stereochemical and spectroscopic (especially n.m.r.) investigations.

Disregarding derived dianhydrides only two X-ray structure analyses of 1,6-anhydrohexofuranoses have been reported so far: those of 1,6-anhydro-β-D-mannofuranose[7] and -α-L-gulofuranose.[8] Both structures are related insofar as their respective hydroxyl groups in positions 2 and 3 are in cis endo positions. In each compound the furanoid ring adopts an uncommon, almost ideal E_O conformation, leading us to the assumption that these and related systems would have the same geometry. To prove this, a study of other furanoid glycosans, especially some with a trans relationship of hydroxyl groups in positions 2 and 3 was indicated. As a first example we selected the title compound 1 because of its ready availability[9] and high crystallinity.

RESULTS AND DISCUSSION

The crystal and molecular structure of compound 1 was determined by applying direct methods using programs MITHRIL[10] and SHELX.[11] Experimental data are shown in Table 1. The asymmetric unit is composed of two independent molecules of 1. Table 2 gives atomic coordinates for all atoms, including equivalent thermal parameters. The resulting three dimensional structure of one of the independent molecules is shown in Fig. 1. This is a SCHAKAL representation,[12] giving also the atom numbering scheme. Bond lengths and bond angles are summarized in Tables 3 and 4. For convenience in conformational discussions selected torsion angles are listed in Table 5 (The list of observed and calculated structure factors is available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 51554, the name of the authors, and the journal citation).

TABLE 1

Crystallographic Data for 1

Formula	$C_{12}H_{16}O_8$
Mol.wt.	288.25
M.p.	79-80°C
Space group	$P2_1$
Cell constants	
a	808.8(4) pm
b	1003.0(5) pm
c	1762.0(1) pm
$\alpha = \gamma$	90°
β	101.53(4)°
Volume	1400.5×10^6 pm^3
Z	4
F (000)	608
Density	1.37 g x cm^{-3}
λ (MoK_α)	70.9261 pm
μ (MoK_α)	0.75 cm^{-1}
Reflections measured	
($3^\circ \leqslant \Theta \leqslant 25^\circ$)	2626
Reflections with $F > 3\sigma(F)$	2159
Final residual factors	
R	0.051
R_w ($w_i = 1.619/[\sigma^2(F) + 0.00003 * F^2]$)	
Diffractometer	Hilger and Watts (Y290)

TABLE 2

Fractional Positional Parameters and Temperature-factors of all Atoms in 1 (e.s.d. in Parentheses); Values x 10^4 (x 10^3 for Hydrogen Atoms and U_{eq}).

Atom	x	y	z	U_{eq} or $U(A^2)$
Molecule I				
0-1	221(4)	6437(O)	1666(2)	57(4)
0-2	2439(4)	7563(6)	811(2)	46(4)
0-3	562(4)	6005(6)	-796(2)	53(4)
0-4	-391(4)	4813(6)	710(2)	49(4)
0-5	-3140(4)	7671(6)	137(2)	52(4)
0-7	4454(5)	6455(6)	1629(2)	62(5)
0-9	-1781(6)	6958(6)	-1470(2)	74(6)
0-11	-5127(5)	6162(6)	-338(2)	64(5)
C-1	863(7)	5586(7)	1172(3)	48(6)
C-2	1651(6)	6311(7)	563(3)	42(6)
C-3	161(6)	6551(7)	-98(3)	41(5)
C-4	-1261(6)	5754(7)	168(3)	44(6)
C-5	-2237(7)	6636(7)	619(3)	47(6)
C-6	-1029(7)	7333(8)	1257(3)	56(6)
C-7	3876(6)	7491(8)	1368(3)	45(6)
C-8	4596(7)	8839(8)	1554(3)	53(6)
C-9	-516(9)	6319(8)	-1459(3)	62(8)
C-10	40(10)	5785(11)	-2147(4)	105(11)
C-11	-4580(7)	7267(8)	-360(3)	53(7)
C-12	-5347(8)	8351(9)	-880(4)	77(8)
H-1	151(5)	504(6)	150(2)	57(15)
H-2	242(5)	577(5)	40(2)	38(13)
H-3	-6(5)	744(5)	-18(2)	36(12)
H-4	-198(5)	530(5)	-27(2)	43(13)
H-5	-301(6)	607(5)	82(2)	31(15)
H-61	-166(6)	774(5)	170(3)	69(16)

(continued)

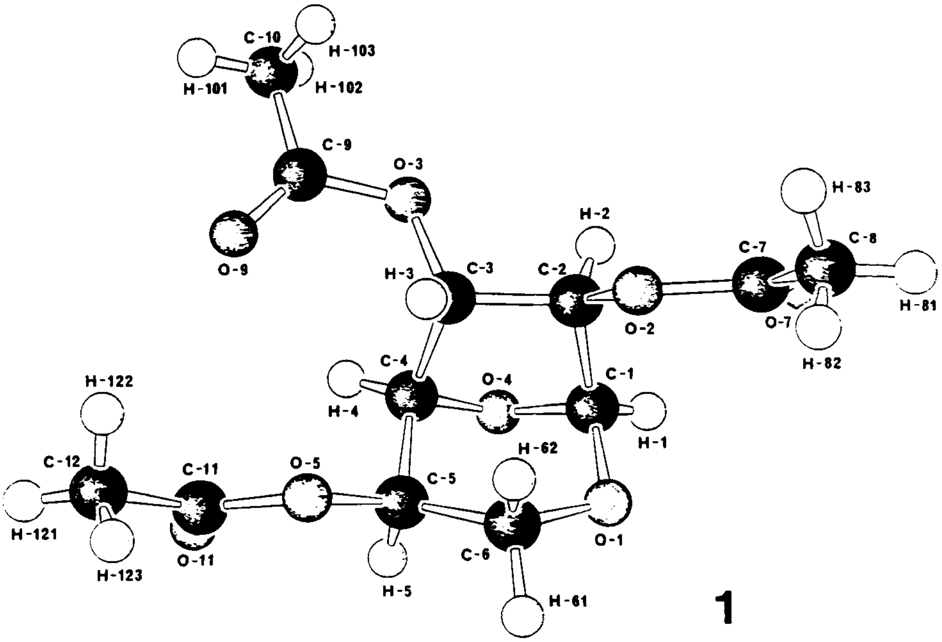
TABLE 2 (continued)

Atom	x	y	z	U_{eq} or $U(A^2)$
H-62	-55(5)	810(4)	105(2)	44(12)
H-81	554(5)	868(4)	199(2)	62(11)
H-82	399(6)	947(5)	175(3)	90(14)
H-83	494(7)	935(6)	112(3)	92(19)
H-101	-72(6)	611(5)	-257(2)	148(15)
H-102	33(5)	488(5)	-214(2)	143(14)
H-103	104(6)	627(5)	-209(3)	161(15)
H-121	-637(6)	808(5)	-122(2)	111(14)
H-121	-459(6)	858(6)	-119(3)	135(16)
H-123	-541(6)	903(5)	-57(3)	130(16)
Molecule II				
O-1	3574(5)	8631(5)	3196(2)	58(4)
O-2	6470(4)	7333(6)	4008(2)	56(4)
O-3	6142(4)	8827(6)	5653(2)	56(5)
O-4	3945(4)	10190(6)	4188(2)	52(4)
O-5	1514(4)	7399(6)	4707(2)	53(4)
O-7	7955(5)	8412(6)	3254(2)	65(5)
O-9	4333(6)	7930(7)	6320(2)	76(6)
O-11	230(5)	8945(7)	5308(2)	68(5)
C-1	4747(7)	9391(7)	3706(3)	51(6)
C-2	6002(6)	8582(7)	4286(3)	47(6)
C-3	5071(7)	8368(7)	4952(3)	44(5)
C-4	3515(6)	9233(7)	4719(3)	41(5)
C-5	2033(6)	8444(7)	4245(3)	45(5)
C-6	2628(7)	7724(8)	3589(3)	54(6)
C-7	7480(6)	7390(9)	3476(3)	52(7)
C-8	7858(8)	6020(8)	3228(4)	67(7)
C-9	5621(9)	8525(8)	6314(3)	59(7)

TABLE 2 (continued)

Atom	x	y	z	U_{eq} or $U(A^2)$
C-10	6839(9)	9009(10)	7005(4)	88(9)
C-11	640(7)	7805(9)	5250(3)	54(7)
C-12	319(9)	6698(8)	5747(4)	82(8)
H-1	521(5)	990(5)	337(2)	52(13)
H-2	700(4)	913(4)	450(2)	34(10)
H-3	488(5)	754(4)	502(2)	39(11)
H-4	327(5)	968(4)	519(2)	29(10)
H-5	107(5)	909(5)	404(2)	25(13)
H-61	169(6)	747(6)	320(3)	63(17)
H-62	325(5)	699(4)	382(2)	34(12)
H-81	839(6)	621(5)	278(3)	107(15)
H-82	696(6)	551(5)	294(3)	117(17)
H-83	845(6)	544(5)	360(3)	124(14)
H-101	668(6)	848(6)	748(3)	154(17)
H-102	676(5)	992(5)	707(2)	131(14)
H-103	780(6)	880(6)	694(3)	151(16)
H-121	-26(7)	707(6)	610(3)	137(18)
H-122	130(6)	642(5)	606(3)	103(16)
H-123	-12(6)	595(5)	546(3)	141(17)

Despite some differences in the individual bond lengths and angles, the overall geometry of molecules I and II is quite similar. In both molecules the six membered 1,3-dioxane ring (O-1/C-1/O-4/C-4/C-5/C-6) adopts a slightly distorted chair conformation. Puckering parameters following the definition of Cremer



1

FIG. 1 A SCHAKAL[12] drawing of molecule I of the title compound 1 showing atom numbering.

and Pople[13] are Q = 60.4 (63.4) pm, Φ =137.2 (138.2)° and Θ=18.5 (17.7)°. Thus, in both molecules this ring is flattened at C-6 in direction to a halfboat (envelope) conformation. This corresponds to analogous conformations in the 1,6-anhydro-manno- and -gulo-hexofuranoses.[7,8]

The described[15] boat conformation of this ring in 1, already found to be incorrect by a careful reevaluation of n.m.r. results,[16,17] therefore has no justification.

Of special interest is the conformation of the furanoid ring O-4/C-1/C-2/C-3/C-4. Puckering

T A B L E 3

Atomic Distances (pm) in 2,3,5-Tri-*O*-acetyl-1,6-anhydro- -*D*-galactofuranose (**1**) (e.s.d. in Parentheses).

	Molecule I	Molecule II
C-1 - C-2	153.6(9)	152.3(8)
C-2 - C-3	151.8(7)	153.0(8)
C-3 - C-4	154.9(8)	151.6(8)
C-4 - C-5	151.2(9)	153.6(8)
C-5 - C-6	150.6(8)	152.0(9)
C-7 - C-8	148.3(11)	149.2(11)
C-9 - C-10	147.7(11)	148.6(9)
C-11- C-12	147.6(10)	146.9(11)
C-1 - O-1	139.3(7)	139.5(7)
C-1 - O-4	140.1(7)	141.6(8)
C-2 - O-2	143.6(8)	142.4(9)
C-3 - O-3	144.1(7)	143.5(6)
C-4 - O-4	142.4(7)	143.2(8)
C-5 - O-5	144.4(8)	144.1(8)
C-6 - O-1	143.5(7)	145.1(8)
C-7 - O-2	136.5(5)	136.3(7)
C-7 - O-7	119.2(10)	118.8(10)
C-9 - O-3	134.7(7)	135.1(8)
C-9 - O-9	120.4(9)	120.3(9)
C-11- O-5	137.1(7)	136.1(8)
C-11- O-11	119.7(10)	120.0(11)
C-1 - H-1	88.4(46)	92.2(45)
C-2 - H-2	91.4(45)	98.4(35)
C-3 - H-3	91.2(45)	85.4(45)
C-4 - H-4	98.4(39)	99.8(37)
C-5 - H-5	95.8(49)	102.5(42)
C-6 - H-61	109.3(50)	59.6(46)
C-6 - H-62	97.2(43)	94.0(41)

(continued)

TABLE 3 (continued)

C-8 - H-81	97.8(34)	99.2(53)
C-8 - H-82	90.7(49)	94.8(48)
C-8 - H-83	100.9(59)	93.1(45)
C-10- H-101	92.9(42)	101.6(51)
C-10- H-102	93.9(51)	92.2(53)
C-10- H-103	93.3(50)	83.2(53)
C-12- H-121	95.4(42)	92.7(59)
C-12- H-122	92.8(54)	91.8(46)
C-12- H-123	88.6(51)	93.5(51)

TABLE 4

Bond Angles (degrees) in 1 (e.s.d. in Parentheses)

	Molecule I	Molecule II
C-1 - O-1 - C-6	112.5(4)	113.0(5)
C-2 - O-2 - C-7	115.8(6)	115.9(6)
C-3 - O-3 - C-9	115.7(5)	115.6(5)
C-1 - O-4 - C-4	103.1(5)	102.3(5)
C-5 - O-5 - C-11	115.4(6)	115.5(6)
O-1 - C-1 - O-4	112.7(5)	111.1(5)
O-4 - C-1 - H-1	107.5(36)	111.9(30)
O-4 - C-1 - C-2	102.1(5)	102.9(5)
O-1 - C-1 - H-1	102.9(28)	101.4(24)
O-1 - C-1 - C-2	114.0(5)	114.7(6)
C-2 - C-1 - H-1	117.9(30)	115.3(26)
O-2 - C-2 - C-1	114.9(5)	115.2(5)
C-1 - C-2 - H-2	109.9(29)	110.2(23)
C-1 - C-2 - C-3	103.5(5)	103.0(5)
O-2 - C-2 - H-2	109.2(27)	111.3(22)
O-2 - C-2 - C-3	109.4(5)	110.2(6)
C-3 - C-2 - H-2	109.7(26)	106.4(19)

TABLE 4 (continued)

O-3 - C-3 - C-2	108.3(5)	108.0(5)
C-2 - C-3 - H-3	111.9(26)	111.8(29)
C-2 - C-3 - C-4	102.1(5)	102.8(5)
O-3 - C-3 - H-4	107.8(24)	106.7(28)
O-3 - C-3 - C-4	111.8(5)	112.0(5)
C-4 - C-3 - H-3	114.7(27)	115.3(29)
O-4 - C-4 - C-3	104.3(5)	105.3(5)
C-3 - C-4 - H-4	111.0(23)	108.7(20)
C-3 - C-4 - C-5	110.8(5)	111.6(5)
O-4 - C-4 - H-4	110.9(27)	111.1(22)
O-4 - C-4 - C-5	106.0(5)	104.8(4)
C-5 - C-4 - H-4	113.3(25)	114.9(22)
O-5 - C-5 - C-4	111.5(5)	110.6(5)
C-4 - C-5 - H-5	106.9(30)	108.9(26)
C-4 - C-5 - C-6	109.6(5)	109.1(5)
O-5 - C-5 - H-5	110.7(28)	112.2(25)
O-5 - C-5 - C-6	106.4(6)	104.8(6)
C-6 - C-5 - H-5	111.9(26)	111.2(23)
O-1 - C-6 - C-5	111.8(5)	110.0(6)
C-5 - C-6 - H-62	109.6(22)	106.1(23)
C-5 - C-6 - H-61	112.6(26)	110.8(32)
O-1 - C-6 - H-62	113.1(24)	114.1(25)
O-1 - C-6 - H-61	104.7(24)	104.0(30)
H-61- C-6 - H-62	104.8(37)	112.0(43)
O-2 - C-7 - O-7	122.4(6)	122.7(6)
O-7 - C-7 - C-8	127.1(6)	126.9(6)
O-2 - C-7 - C-8	110.5(5)	110.4(6)
C-7 - C-8 - H-83	116.9(32)	118.1(29)
C-7 - C-8 - H-82	120.4(30)	118.2(32)
C-7 - C-8 - H-81	103.3(25)	101.6(30)
H-82- C-8 - H-83	100.3(44)	106.2(43)
H-81- C-8 - H-82	112.8(40)	116.1(41)

(continued)

TABLE 4 (continued)

H-81 - C-8 - H-82	102.6(36)	94.4(41)
O-3 - C-9 - O-9	122.7(6)	122.6(6)
O-9 - C-9 - C-10	125.3(7)	126.1(7)
O-3 - C-9 - C-10	112.1(7)	111.3(6)
C-9 - C-10- H-103	96.6(13)	106.6(34)
C-9 - C-10- H-102	117.0(27)	111.9(28)
C-9 - C-10- H-101	106.0(31)	109.3(31)
H-102- C-10- H-103	107.4(42)	110.9(47)
H-101- C-10- H-103	109.1(44)	105.0(46)
H-101- C-10- H-102	118.4(42)	112.8(41)
O-5 - C-11- O-11	121.7(6)	122.4(6)
O-11 - C-11- C-12	126.2(7)	125.8(7)
O-5 - C-11- C-12	112.2(6)	111.8(6)
C-11 - C-12- H-123	104.5(30)	111.8(29)
C-11 - C-12- H-122	107.6(33)	111.0(34)
C-11 - C-12- H-121	112.2(29)	105.4(38)
H-122- C-12- H-123	107.6(47)	105.9(47)
H-121- C-12- H-123	117.1(43)	120.4(48)
H-121- C-12- H-122	107.6(40)	101.9(44)

TABLE 5

Selected Torsion Angles (degrees) in 1 (Values for the Molecule II in Parentheses)

C-7 - O-2 - C-2 - H-2	-55.4(-54.9)
C-9 - O-3 - C-3 - H-3	-48.6(-49.9)
C-11- O-5 - C-5 - H-5	-42.6(-47.5)
H-1 - C-1 - C-2 - H-2	35.3(43.1)
O-2 - C-2 - C-3 - O-3	111.4(110.7)
H-2 - C-2 - C-3 - H-3	-127.2(-127.2)
H-3 - C-3 - C-4 - H-4	97.6(97.4)
H-4 - C-4 - C-5 - H-5	61.0(63.6)
H-5 - C-5 - C-6 - H-62	-160.6(-163.2)
H-5 - C-5 - C-6 - H-61	-44.4(-41.4)

parameters[13] are Q = 45.4 (44.6) pm and Φ = 9.7 (9.7)°. The overall ring puckering, for which the value of Q is a measure, is of the same magnitude as in the manno and gulo compounds investigated (46.4 and 47.2 pm, respectively).[14] The phase angle Φ of 9.7° corresponds to a conformation, almost exactly intermediate between ^{O}E and $^{O}T_1$. This was unexpected, in as much as in the other structures investigated almost ideal envelope conformations with oxygen out of plane have been found (Φ = 179.9 and 178.2°).[14] Because of the repulsion between the cis-2,3-hydroxyl groups in the manno and gulo derivatives, respectively, a deviation from an ideal E_O (or ^{O}E) conformation would have been more plausible. The observed conformation of the furanoid ring in 1 is nevertheless still of the expected kind differing considerably from that preferentially adopted by other furanoid systems. It is worth mentioning that, by bridging the 1,6-anhydrohexofuranose system, its furanoid ring can be forced into conformations, very different from the usual E_O (or ^{O}E) conformation of the parent compounds. X-ray structure analyses have been performed of 2,3,5-O-orthoacetyl-1,6-anhydro-α-L-gulofuranose,[18] 1,6:3,5-dianhydro-α-L-gulofuranose,[8] 2-O-Acetyl-1,6:3,5-dianhydro-α-L-idofuranose[19] and 1,6:2,5-dianhydro-α-L-gulofuranose.[14]

The orientation of the acetoxy groups in 1 is as usually observed arranging the carbonyl oxygen ideally parallel to the C-H-bond of the carbon atom bearing the substituent[20]. The values of the first three torsion angles in Table 5 (42° up to 55°) nevertheless differ considerably from 0°. They are, however, in the range observed in other sugar acetates.[20]

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