

SYNTHESIS, CRYSTAL STRUCTURE, AND CONFORMATION OF 3-*O*-(6-*O*-ACETYL-2,3-ANHYDRO-4-DEOXY- α -L-*ribo*-HEXOPYRANOSYL)-1,2:5,6-DI-*O*-ISOPROPYLIDENE- α -D-GLUCOFURANOSE*

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ABSTRACT

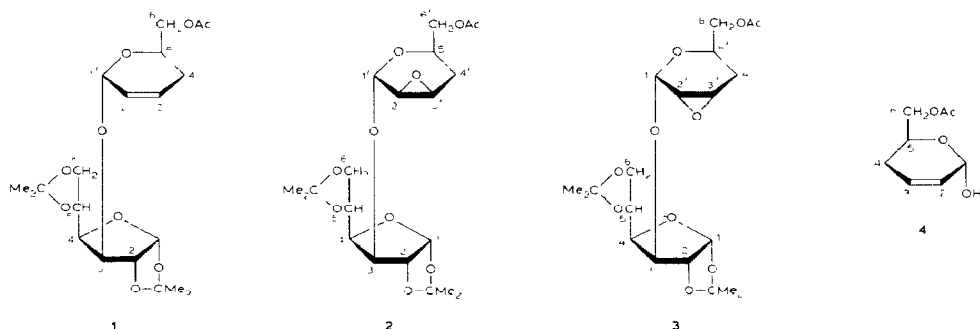
3-*O*-(6-*O*-Acetyl-2,3-anhydro-4-deoxy- α -L-*ribo*-hexopyranosyl)-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose has been synthesised and its monocrystal investigated by X-ray diffraction methods. The compound crystallises in the orthorhombic system, space group $P2_12_12_1$, with cell constants $a = 8.790(7)$, $b = 11.678(4)$, and $c = 21.457(10)$ Å. The intensity data were collected with a four-circle CAD-4 diffractometer. From a total of 1684 intensities, 1275 were of $I > 2\sigma_I$. The structure was solved by direct methods and refined by the full-matrix, least-squares procedure, resulting in R 0.057. The 4-deoxy-2,3-anhydropyranose ring is characterised by a sofa conformation (${}_5E$), the 1,2-*O*-isopropylidene ring has a hybrid conformation ($E + T$), and the 5,6-*O*-isopropylidene and the α -D-glucofuranose rings have twist (T) conformations. The ϕ and ψ torsion angles for the glycosidic linkage are $54(4)^\circ$ and $29(4)^\circ$, respectively.

INTRODUCTION

Sugar epoxides have been recently isolated from plant oligosaccharides¹, and they have been widely used as intermediates in the chemical modification of monosaccharides^{2,3} and in the synthesis of oligosaccharides^{4–7}.

A new approach⁸ to the synthesis of disaccharides involves cycloaddition of butyl glyoxalate to 3-*O*-(buta-1,3-dienyl)-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose, followed by epoxide formation and transformation. We have obtained epoxides by treatment of 3-*O*-(6-*O*-acetyl-2,3,4-trideoxy- α -L-*glycero*-hex-2-enopyranosyl)-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose⁹ (**1**) with *m*-chloroperbenzoic acid to give a mixture of the diastereoisomers 3-*O*-(6-*O*-acetyl-2,3-anhydro-4-deoxy- α -L-*lyxo*- (**2**) and -L-*ribo*-hexopyranosyl)-1,2:5,6-di-*O*-isop-

*Dedicated to Professor J. D. Dunitz (ETH, Zürich) on the occasion of his 60th birthday.



ropylidene- α -D-glucopyranose (**3**), the components of which were separable by silica gel chromatography.

Methyl 2,3-anhydro-4-deoxypyranosides exist in half-chair conformations^{2,10}. Although such factors as the Reeves' effect play an important role in the conformational equilibrium of these compounds, it was confirmed by ^1H -^{11–13} and ^{13}C -n.m.r.¹⁴ data that, in the most stable conformation, the MeO- and the 5-substituent adopt pseudo-axial and pseudo-equatorial positions, respectively. A similar conclusion was drawn by David *et al.*⁸ who assigned L^5H_0 conformations for the analogous *lyxo*- (**2**) and *ribo*-epoxides (**3**) on the basis of $J_{1,2}$ values of ~ 0 and 3.0 Hz, respectively.

It may be assumed that the 1,2:5,6-di-*O*-isopropylidene-D-glucopyranosyl substituent on C-1' has little or no effect on the conformation of the anhydropyranose ring. However, our X-ray crystal structure determinations of the unsaturated compounds **4** and **1** have shown⁹ that the half-chair (*H*) conformation characterising **4** is strongly deformed in **1**. In view of the conformational similarity of unsaturated methyl hex-2-enopyranosides and methyl 2,3-anhydrohexopyranosides¹⁴, it was of interest to determine the stereochemistry of epoxides **2** and **3**. Unexpectedly, **3**, chosen for X-ray study, was shown to adopt a deformed sofa (*E*) conformation of the pyranoid ring.

The stereoisomers **2** and **3** were separated by column chromatography and the latter, which crystallised from ether–acetone, was used for the X-ray investigation.

RESULTS AND DISCUSSION

The refined atomic coordinates for **3** are presented in Table I. Fig. 1 shows a projection of the molecular structure. Tables II and III contain the bond lengths and valence angles, respectively.

Conformation of the 2,3-anhydropyranose ring. — Positions 2 and 3 in the pyranoid ring of **3** are substituted by the epoxide ring. Table IV gives a comparison of bond lengths and angles involving the atoms C-2' and C-3' in **3** with those of the unsaturated rings of **1** and **4**. The valence angles at C-2' and C-3' resemble those in

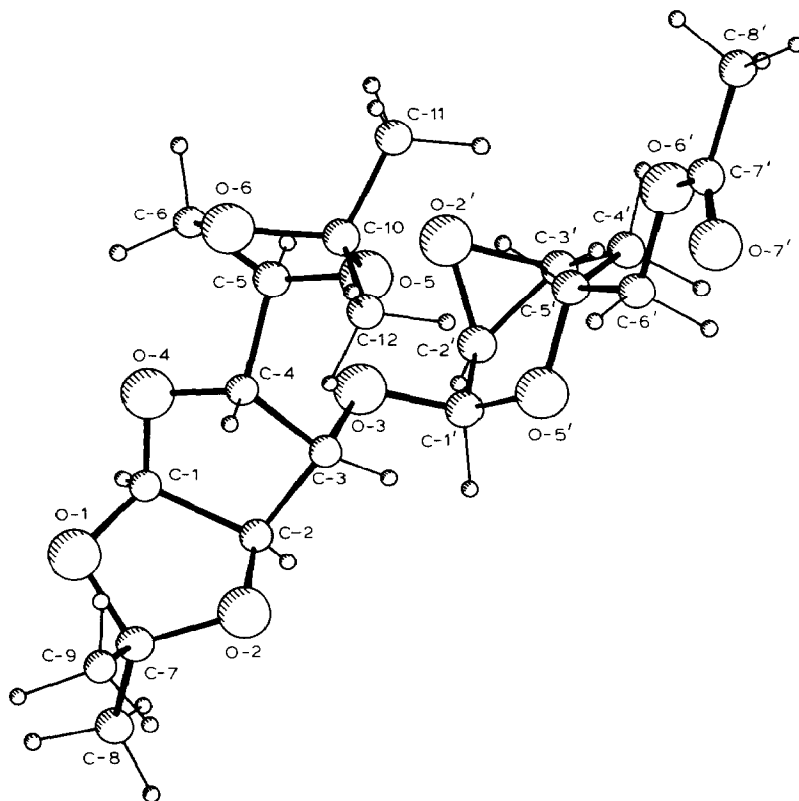


Fig. 1. Calculated projection of **3** oriented at optimal view.

unsaturated sugar rings ($\sim 120^\circ$), whereas the C-2'-C-3' bond adopts a length [1.446(12) Å in **3**] that is between those of single and double bonds. This well-known resemblance gives rise to the common assumption that the conformations of anhydropyranose rings cannot differ substantially from those of the unsaturated rings (half-chair).

Consideration of the torsion angles calculated for the ring under discussion in **3** (Table V) allows the conclusion that fusion of pyranoid and oxirane rings generates strain in the former. This results in the formation of a five-atom plane in the 2,3-anhydropyranose moiety of **3** (Table VI) which is characteristic for the sofa conformation. The values of the torsion angles for the C-1'-C-2' and C-2'-C-3' bonds are close to zero and the remaining signs of torsion angles from the sequence 00 - + - +, thus defining the sofa $_5E$ conformation. This is corroborated by the calculation of the puckering parameters¹⁶ ϕ and q_2 , which place the conformation of the pyranose ring under discussion on the puckering diagram¹⁶ in the proximity of the sofa point (Fig. 2). The corresponding data for dihydropyran rings in **1** and **4**, listed for comparison, indicate the conformations $H + E$ and 0H_5 , respectively. It is concluded that the conformation of the 2,3-epoxypyranose ring in **3** in the crystalline state differs qualitatively from that of 2,3-dihydropyran.

TABLE I

ATOMIC CO-ORDINATES ($\times 10^4$) AND EQUIVALENT, ISOTROPIC TEMPERATURE FACTORS (\AA^2)^a

Atom	x	y	z	B_{eq}^b
C-1	7045(11)	1739(7)	206(4)	4.1(2)
C-2	8541(9)	1698(7)	568(3)	3.6(2)
C-3	8138(9)	2247(6)	1181(3)	3.1(2)
C-4	6459(10)	1947(7)	1238(3)	3.9(2)
C-5	5532(10)	2750(8)	1657(4)	4.3(2)
C-6	3889(13)	2400(11)	1710(5)	6.4(3)
C-7	8115(11)	-118(7)	172(4)	4.7(3)
C-8	9122(15)	-228(12)	-387(4)	6.5(4)
C-9	7518(14)	-1220(9)	416(5)	6.3(3)
C-10	4988(12)	2098(9)	2650(4)	5.0(3)
C-11	4434(30)	2903(18)	3123(10)	10.9(1.6)
C-12	5589(29)	997(16)	2912(7)	10.8(8)
C-1'	9615(9)	3951(6)	1334(3)	3.2(2)
C-2'	9544(11)	5188(7)	1143(4)	3.9(2)
C-3'	9548(13)	6048(7)	1608(4)	4.5(3)
C-4'	9566(10)	5743(7)	2284(4)	4.0(2)
C-5'	8953(9)	4542(6)	2368(4)	3.3(2)
C-6'	9151(11)	4020(7)	3002(4)	4.0(2)
C-7'	8066(12)	4176(8)	4000(4)	4.7(3)
C-8'	7176(15)	4909(10)	4441(5)	6.7(4)
O-1	6821(9)	600(5)	2(3)	5.0(3)
O-2	8841(7)	511(5)	657(2)	4.3(2)
O-3	8247(6)	3463(4)	1120(2)	3.5(1)
O-4	5895(6)	2051(5)	614(2)	4.4(2)
O-5	6098(7)	2649(6)	2274(3)	4.9(2)
O-6	3814(10)	1753(11)	2236(5)	8.5(4)
O-2'	8172(8)	5797(5)	1278(2)	4.7(2)
O-5'	9809(7)	3774(4)	1967(2)	3.8(1)
O-6'	8291(7)	4679(5)	3447(2)	4.2(2)
O-7'	8561(10)	3257(6)	4125(3)	6.3(3)

^aEstimated standard deviations in parentheses. ^b $B_{eq} = 8\pi^2(U_1 \times U_2 \times U_3)^{1/3}$.

Conformation of the 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose system. — Tables VII and VIII present the results and conclusions of conformational calculations (asymmetry parameters and least-squares planes) performed for various 1,2- and/or 5,6-*O*-isopropylidene- α -D-glucofuranose derivatives, including **3**, as well as using the literature data for **1**, **5–9**, and **10**. The conformational assignments indicate a significant mobility. For the glucofuranose ring, there is a *T* (twist) assignment in five compounds and an *E* (envelope) assignment in three compounds; no hybrids were found for this ring. However, hybrids are found (among “pure” conformations) for three compounds containing a 1,2-*O*-isopropylidene ring, thus indicating an even greater mobility than for the glucofuranose ring.

The fused-ring system of 1,2-*O*-isopropylidene- α -D-glucofuranose appears in four conformational combinations: (*T*, *E* + *T*), (*E*, *T*), (*T*, *E*), and (*E*, *T* + *E*) (the first symbol refers to the glucofuranose ring). The interconformational energy

TABLE II

BOND DISTANCES (Å)^a

C-1-C-2	1.527(12)	C-10-O-5	1.420(12)
C-2-C-3	1.506(10)	O-5-C-5	1.420(10)
C-3-C-4	1.522(12)	C-3-O-3	1.429(8)
C-4-O-4	1.433(9)	O-3-C-1'	1.408(10)
O-4-C-1	1.386(10)	C-1'-C-2'	1.503(11)
C-1-O-1	1.414(10)	C-2'-C-3'	1.446(12)
O-1-C-7	1.459(12)	C-2'-O-2'	1.429(11)
C-7-C-8	1.496(14)	O-2'-C-3'	1.441(12)
C-7-C-9	1.485(14)	C-3'-C-4'	1.505(12)
C-7-O-2	1.425(11)	C-4'-C-5'	1.513(11)
O-2-C-2	1.424(9)	C-5'-O-5'	1.452(9)
C-4-C-5	1.534(12)	O-5'-C-1'	1.385(8)
C-5-C-6	1.504(11)	C-5'-C-6'	1.501(11)
C-6-O-6	1.359(16)	C-6'-O-6'	1.441(10)
O-6-C-10	1.420(14)	O-6'-C-7'	1.338(10)
C-10-C-11	1.465(24)	C-7'-O-7'	1.188(12)
C-10-C-12	1.500(22)	C-7'-C-8'	1.497(15)

^aEstimated standard deviations in parentheses.

TABLE III

BOND ANGLES (DEGREES)^a

C-1-C-2-C-3	103.2(6)	O-5-C-10-O-6	105.8(7)
C-2-C-3-C-4	101.5(6)	C-5-O-5-C-10	109.0(7)
C-3-C-4-O-4	103.9(6)	O-5-C-5-C-6	104.1(7)
C-4-O-4-C-1	108.4(6)	C-2-C-3-O-3	109.2(6)
O-4-C-1-C-2	108.4(6)	C-4-C-3-O-3	107.5(6)
O-1-C-1-C-2	104.3(7)	C-3-O-3-C-1'	115.4(6)
C-1-O-1-C-7	110.8(7)	O-3-C-1'-C-2'	105.3(6)
O-1-C-7-C-8	108.1(8)	O-3-C-1'-O-5'	111.4(6)
O-1-C-7-C-9	108.1(8)	C-1'-C-2'-C-3'	120.5(7)
C-8-C-7-C-9	114.7(9)	C-1'-C-2'-O-2'	117.2(7)
O-2-C-7-C-8	111.4(8)	C-2'-O-2'-C-3'	60.5(6)
O-2-C-7-C-9	110.3(7)	O-2'-C-2'-C-3'	60.2(6)
O-1-C-7-O-2	103.7(7)	C-2'-C-3'-O-2'	59.4(6)
C-2-O-2-C-7	108.6(6)	O-2'-C-3'-C-4'	114.9(8)
O-2-C-2-C-1	105.0(6)	C-2'-C-3'-C-4'	118.3(7)
C-3-C-4-C-5	114.9(7)	C-3'-C-4'-C-5'	110.9(7)
O-4-C-4-C-5	108.2(7)	C-4'-C-5'-O-5'	108.5(6)
C-4-C-5-C-6	112.9(8)	C-5'-O-5'-C-1'	115.2(6)
C-4-C-5-O-5	108.1(7)	O-5'-C-1'-C-2'	114.6(6)
C-5-C-6-O-6	105.1(9)	C-4'-C-5'-C-6'	116.3(6)
C-6-O-6-C-10	109.0(1.0)	O-5'-C-5'-C-6'	103.1(6)
O-6-C-10-C-11	112.0(1.3)	C-5'-C-6'-O-6'	108.9(6)
O-6-C-10-C-12	104.3(1.1)	C-6'-O-6'-C-7'	115.4(6)
C-11-C-10-C-12	114.1(1.2)	O-6'-C-7'-O-7'	122.9(8)
O-5-C-10-C-11	109.3(1.2)	O-6'-C-7'-C-8'	112.7(8)
O-5-C-10-C-12	111.0(1.2)	C-8'-C-7'-O-7'	124.4(8)

^aEstimated standard deviations in parentheses.

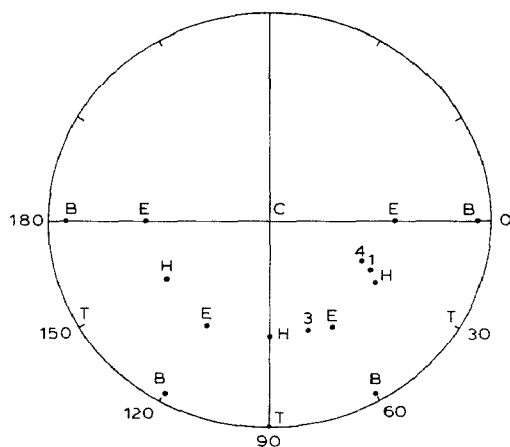
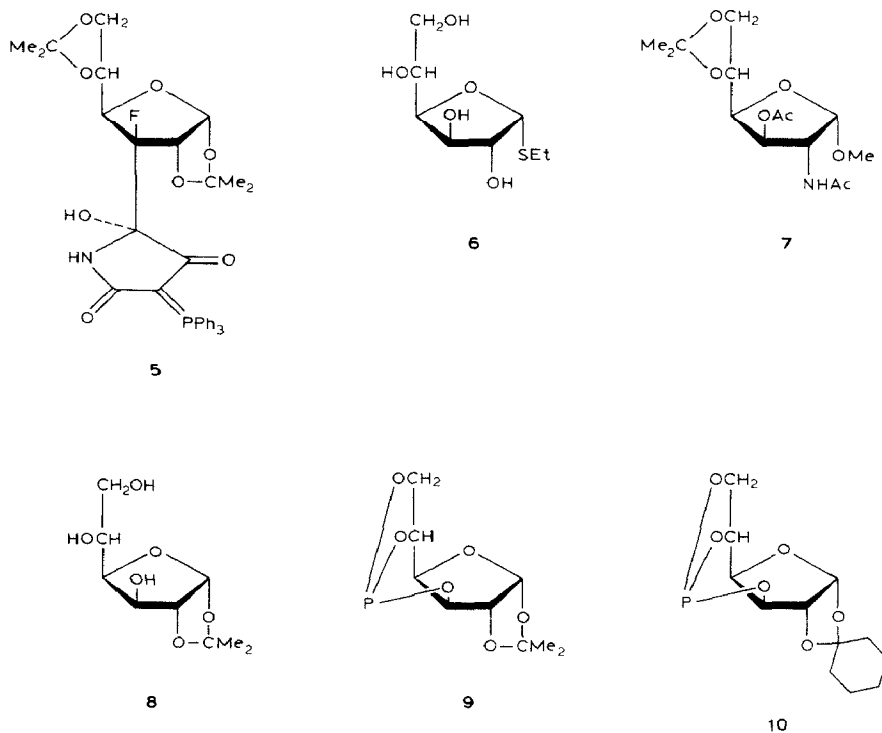


Fig. 2. The diagram of puckering parameters, according to Cremer and Pople¹⁶, for the dihydropyran rings in 1 and 4 and for the pyranose ring in 3. The numbered points refer to the compounds, and capital letters denote the ideal conformations of various types.

TABLE IV

COMPARISON OF BOND LENGTH (Å)^a AND ANGLES (DEGREES)^a FOR C-2' AND C-3' ATOMS IN EPOXYPYRANOSE AND DIHYDROPYRAN RINGS

	1	3	4
C-1'-C-2' (Å)	1.497(6)	1.503(11)	1.487(4)
C-2'-C-3' (Å)	1.308(6)	1.446(12)	1.304(5)
C-3'-C-4' (Å)	1.505(6)	1.505(12)	1.493(6)
C-1'-C-2'-C-3' (°)	122.5(4)	120.5(7)	123.6(3)
C-2'-C-3'-C-4' (°)	122.0(4)	118.3(7)	122.2(3)

^aEstimated standard deviations in parentheses.

TABLE V

SOME TORSIONAL ANGLES (DEGREES)^a FOR 3

<i>α-D-Glucofuranose ring</i>		<i>5,6-O-Isopropylidene ring</i>	
O-4-C-1-C-2-C-3	-11.0(8)	C-5-C-6-O-6-C-10	27.2(1.2)
C-1-C-2-C-3-C-4	29.3(7)	C-6-O-6-C-10-O-5	-21.7(1.2)
C-2-C-3-C-4-O-4	-38.2(7)	O-6-C-10-O-5-C-5	6.4(1.0)
C-3-C-4-O-4-C-1	32.9(8)	C-10-O-5-C-5-C-6	9.3(1.0)
C-4-O-4-C-1-C-2	-13.7(8)	O-5-C-5-C-6-O-6	-22.3(1.1)
<i>1,2-O-Isopropylidene ring</i>		<i>2,3-Anhydropyranose ring</i>	
C-1-O-1-C-7-O-2	19.5(8)	O-5'-C-1'-C-2'-C-3'	-5.1(1.2)
O-1-C-7-O-2-C-2	-28.0(8)	C-1'-C-2'-C-3'-C-4'	-2.3(1.4)
C-7-O-2-C-2-C-1	25.9(8)	C-2'-C-3'-C-4'-C-5'	-22.8(1.2)
O-2-C-2-C-1-O-1	-13.0(8)	C-3'-C-4'-C-5'-O-5'	54.4(9)
C-2-C-1-O-1-C-7	-4.1(8)	C-4'-C-5'-O-5'-C-1'	-66.2(8)
		C-5'-O-5'-C-1'-C-2'	40.1(9)

^aEstimated standard deviations in parentheses.

barriers in these systems are low and the conformations may be affected seriously by substituents. Thus, in **1** and **3**, which have similar 3-substituents with the same conformation of glycosidic linkage, the conformation assignments for the 1,2-*O*-isopropylidene- α -D-glucofuranose system are the same (*T*, *E* + *T*). The bulky 3-substituent in **5** changes the conformation to *E*, *T*.

Some light may be thrown on the problem of conformational mobility in the 1,2-*O*-isopropylidene- α -D-glucofuranose system by the results of a series of MM computations¹⁷. The model of the system was **8**, in which the conformation *T*, *E* was assigned. The free minimisation of strain energy (without any restrictions) performed for this model led to a "pure" *E*, *E* conformation. On the other hand, if the conformation of the glucofuranose moiety was restricted to *T*, the strain-energy minimisation resulted in a change of the 1,2-*O*-isopropylidene conformation, also to *T*, *i.e.*, the conformation system became "pure" *T*, *T*. When the minimisation process was continued with the restriction removed, the *T*, *T* conformation was converted again into *E*, *E*. The differences in strain-energy levels in this cycle of

TABLE VI

RING CONFORMATIONS OF EPOXYPYRANOSES IN **3**, AND DIHYDROPYRAN IN **1** AND **4**

Atom	1	3	4
<i>Atom deviations (\AA)^a from least-squares planes</i>			
C-1'	0.005(1) ^b	-0.05(1) ^b	0.003(3) ^b
C-2'	-0.016(5) ^b	0.02(1) ^b	-0.011(4) ^b
C-3'	0.016(5) ^b	0.05(1) ^b	0.014(4) ^b
C-4'	-0.007(5) ^b	-0.05(1) ^b	-0.006(5) ^b
C-5'	-0.530(4)	-0.70(1)	-0.430(3)
O-5'	0.217(3)	0.02(1) ^b	0.285(2)
<i>Asymmetry parameters¹⁵ (degrees)^a</i>			
ΔC_5	16.9(6)	13(1)	—
ΔC_2	10.9(6)	16(1)	3.9(5)
<i>Puckering parameters¹⁶ (see Fig. 2)</i>			
Q (\AA)	0.50	0.50	0.47
ϕ ($^\circ$)	26.2	70.5	23.5
θ ($^\circ$)	53.4	54.1	52.2
q_2 (\AA) ^c	0.40	0.41	0.36
Conformation	⁰ H ₅	₅ E	⁰ H ₅

^aEstimated standard deviations in parentheses. ^bAtoms defining the planes. ^c $q_2 = Q \cdot \sin \theta$

TABLE VII

CONFORMATIONAL ASSIGNMENTS FOR 1,2:5,6-DI-*O*-ISOPROPYLIDENE- α -D-GLUCOFURANOSE RINGS

Compound	α -D-Glucofuranose	1,2- <i>O</i> -Isopropylidene	5,6- <i>O</i> -Isopropylidene
1 ⁹	<i>T</i>	<i>E</i> + <i>T</i>	<i>E</i> + <i>P</i>
3	<i>T</i>	<i>E</i> + <i>T</i>	<i>T</i>
5 ¹⁸	<i>E</i>	<i>T</i>	<i>E</i>
6 ¹⁹	<i>T</i>	—	—
7 ²⁰	<i>E</i>	—	<i>T</i>
8 ²¹	<i>T</i>	<i>E</i>	—
9 ²²	<i>E</i>	<i>T</i> + <i>E</i>	—
10 ²²	<i>T</i>	<i>E</i> ^a	—

^a1,2-*O*-Cyclohexylidene.

minimisations were within 2.2 kcal/mol. Thus, the energy barriers between the various conformations in this ring system are small, and the rings can adopt either *T* or *E* conformations (including the intermediate hybrids) depending on the influence of other factors.

The 5,6-*O*-isopropylidene ring in **3** has a *T* (twist) conformation. The same assignment applies to **7**, but, in **5**, an *E* (envelope) conformation is assigned. In **1**, the assignment is *E* + *P* (flattened envelope), but it may result from the dynamic disorder of O-6. Thus, some mobility of the conformation for the 5,6-*O*-isopropylidene ring should also be assumed.

TABLE VIII

RING CONFORMATIONS IN **1** AND **3**

1				3							
<i>1,2-O-Isopropylidene</i>		<i>α-D-Glucofuranose</i>		<i>5,6-O-Isopropylidene</i>		<i>1,2-O-Isopropylidene</i>		<i>α-D-Glucofuranose</i>		<i>5,6-O-Isopropylidene</i>	
<i>Atom deviations (Å)^a from least-squares planes</i>											
C-1	0.032(5) ^b	C-1	0.000 ^b	C-5	0.007(5) ^b	C-1	0.02(1) ^b	C-1	0.00 ^b	C-5	0.00 ^b
O-1	−0.013(3) ^b	C-2	0.000 ^b	O-5	−0.003(4) ^b	O-1	0.02(1) ^b	C-2	0.00 ^b	O-5	0.00 ^b
C-7	0.023(5) ^b	C-3	0.311(4)	C-10	−0.205(4)	C-7	0.02(1) ^b	C-3	−0.28(1)	C-10	0.00 ^b
O-2	−0.425(2)	C-4	−0.280(4)	O-6	0.011(7) ^b	O-2	−0.38(1)	C-4	0.32(1)	O-6	−0.15(1)
C-2	−0.018(4) ^b	O-4	0.000 ^b	C-6	0.011(6) ^b	C-2	0.01(1) ^b	O-4	0.00 ^b	C-6	0.24(1)
<i>Asymmetry parameters¹⁵ (degrees)^a</i>											
ΔC _s	5.8(4)	—		2.8(7)		4.9(7)		—		—	
ΔC ₂	8.0(4)	2.9(4)		5.0(7)		7.7(7)		3.2(8)		2.2(1.1)	
<i>Conformation</i>											
<i>O₂E + T</i>		<i>³T₄</i>		<i>₁₀E + P^c</i>		<i>O₂E + T</i>		<i>⁴T₃</i>		<i>⁶T_{O6}</i>	

^aEstimated standard deviations in parentheses. ^bAtoms defining the planes. ^cP, planar conformation.

TABLE IX

GEOMETRY AND CONFORMATION OF GLYCOSIDIC BONDS (H'–C'–O–C–H)

	1	3
<i>Distances and bond angles^a</i>		
C'–O–C (°)	114.0(3)	115.4(6)
C'–O (Å)	1.412(5)	1.408(10)
C–O (Å)	1.425(4)	1.429(8)
H'–H (Å)	2.48(4)	2.6(1)
<i>Torsion angles (°)^a</i>		
φ	47(2)	54(4)
ψ	32(2)	29(4)
<i>Deviations (Å)^a from C'–O–C plane</i>		
H'	−0.72(2)	−0.83(7)
H	0.42(2)	0.47(7)

^aEstimated standard deviations in parentheses.

Neither the available literature data nor the present investigations permit conclusions to be made about the mutual dependence of conformations in the saccharide ring system discussed above.

Conformation of the glycosidic linkage. — The conformation of the glycosidic linkage in **3** may be assigned to the type I⁹; H and H' of the linkage are placed unsymmetrically on both sides of the C'–O–C plane. This conformation is close to that observed in **1** (Table IX); the values of ϕ and ψ , as well as the values of hydrogen deviations from the C'–O–C plane, are the same in **1** and **3**, within their double standard deviations.

EXPERIMENTAL

General. — ¹H-N.m.r. spectra were recorded with a JEOL JNM-4H-100 spectrometer for solutions in CDCl₃ (internal Me₄Si). Optical rotations were measured at ~20°. T.l.c. was conducted on silica gel GF₂₅₄ (Merck) and column chromatography on silica gel (230–400 mesh, Merck).

*Epoxidation of 3-O-(6-O-acetyl-2,3,4-trideoxy- α -L-glycero-hex-2-enopyranosyl)-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (**1**).* — A solution of **1** (0.207 g, 0.5 mmol) in dichloromethane (1 mL) was stirred with an excess of freshly purified *m*-chloroperbenzoic acid (0.25 g) in dichloromethane (4 mL) overnight at room temperature. Monitoring by t.l.c. (hexane–ether–methanol, 50:48:2) then showed complete disappearance of **1**. The solution was cooled to 0°, filtered, washed with saturated aqueous sodium hydrogencarbonate, and concentrated, and the oily residue was subjected to column chromatography (hexane–ether, 7:3) to give, first, 3-O-(6-O-acetyl-2,3-anhydro-4-deoxy- α -L-lyxo-hexopyranosyl)-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (**2**; 0.113 g, 52.5%), m.p. 107–109°, [α]_D –51° (c 1, chloroform). ¹H-N.m.r. data: δ 1.95 (m, 2 H, $J_{3',4'}$ 6.5, $J_{4',5'}$ 2.6 Hz, H-4',4''), 2.12 (s, 3 H, OAc), 3.0 (d, 1 H, $J_{2',3'}$ 3.6 Hz, H-2'), 3.43 (m, 1 H, H-3'), 4.5 (d, 1 H, H-5'), 4.61 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 5.23 (s, 1 H, H-1'), and 5.97 (d, 1 H, H-1).

Anal. Calc. for C₂₀H₃₀O₁₀: C, 55.80; H, 7.03. Found: C, 55.45; H, 7.01.

Eluted second was 3-O-(6-O-acetyl-2,3-anhydro-4-deoxy- α -L-ribo-hexopyranosyl)-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (**3**; 0.88 g, 40.9%), m.p. 94–94.5°, [α]_D –49° (c 0.9, chloroform). ¹H-N.m.r. data: δ 1.8–2.0 (m, 2 H, H-4',4''), 2.15 (s, 3 H, OAc), 3.32 (t, 1 H, $J_{1',2'}$ 3, $J_{2',3'}$ 4 Hz, H-2'), 4.42–3.97 (m, 7 H, H-3,4,5,6,6',6'), 4.55 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-2), 5.2 (d, 1 H, H-1'), and 5.97 (d, 1 H, H-1).

Anal. Found: C, 55.95; H, 7.43.

X-Ray diffraction investigations. — Colourless crystals of **3** were obtained from ether–acetone solution. A CAD-4 diffractometer was used with stability controlled on two reflections at 25 reflection intervals at room temperature. Lattice parameters were refined against 20 reflections. Crystal data: C₂₀H₃₀O₁₀. M_r = 430.44, orthorhombic, space group P2₁2₁2₁; Z = 4, a = 8.790(7), b = 11.678(4), c

= 21.457(10) Å, $V = 2202.6 \text{ Å}^3$, $F(000) = 920$, $D_x = 1.30 \text{ Mg.m}^{-3}$, $\mu(\text{MoK}\alpha) = 0.65 \text{ mm}^{-1}$. Of the 1684 intensities collected on a four-circle CAD-4 diffractometer [Laboratory of Organic Chemistry, Federal Institute of Technology (ETH), Zürich, Switzerland], using graphite-monochromated MoK α radiation and a $\omega/2\theta$ scan technique up to $2\theta_{\text{max}} 50^\circ$, 1275 had $I > 2\sigma_I$. No absorption correction was applied. The structure was solved by direct methods (MULTAN 80²³). The refinement of the atomic positional and anisotropic thermal parameters was performed using the X-RAY 70 System²⁴ and the full-matrix, least-squares procedure. The atomic scattering factors were taken from the International Tables for X-ray Crystallography²⁵. The positions of hydrogen atoms were found from difference Fourier maps. The final refinement involved all atomic parameters except the hydrogen temperature factors (fixed as the B_{eq} of the adjacent atom + 1). The final R factor was 0.057 (unit weights) at the average shift/error value of 0.09.

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