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CRYSTAL AND MOLECULAR STRUCTURES OF 6-*O*-ACETYL-2,3,4-TRIDEOXY-α-DL-*glycero*-HEX-2-ENOPYRANOSE AND 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

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ABSTRACT

6-*O*-Acetyl-2,3,4-trideoxy-α-DL-*glycero*-hex-2-enopyranose (**1**) and 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 (**2**) have been investigated by X-ray diffraction methods. Compound **1** crystallises in the monoclinic system, space group $P2_1/a$, with cell constants $a = 21.123(5)$, $b = 4.439(2)$, $c = 10.085(2)$ Å, and $\beta = 110.22(2)°$. Compound **2** crystallises in the orthorhombic system, space group $P2_12_12_1$, with cell constants $a = 22.110(6)$, $b = 11.651(4)$, and $c = 8.658(3)$ Å. The intensity data were collected in a four-circle automatic diffractometer, with 1488 reflections for **1**, and 2151 for **2**. The structures were solved by direct methods. The atomic parameters were refined in an anisotropic mode by the full-matrix, least-squares procedure against 1065 and 1884 observed reflections for **1** and **2**, respectively, giving R = 0.046 for each compound. The 2-enopyranose rings in **1** and **2** adopt half-chair conformations (*H*), and that in **2** is markedly deformed. The 1,2-dioxolane ring in **2** has an envelope (*E*) conformation, whereas the 5,6-dioxolane ring is dynamically disordered and can be represented by a conformational hybrid (*E* + *P*). The α-D-glucofuranose ring in **2** has a twist conformation (*T*). The glycoside bond in **2** is characterized by ϕ and ψ torsion angles of 47(2)° and 32(2)°, respectively.

INTRODUCTION

Suitably functionalised derivatives of 5,6-dihydro-6-hydroxymethyl-2-methoxy-2*H*-pyran have been converted into racemic 4-deoxy-[1], 4,6-dideoxy-[2], and 3,6-dideoxy-hexopyranosides[3], amino sugars[2,4], isomeric hexopyranosides[5], and octoses[6]. 5,6-Dihydro-6-hydroxymethyl-2-methoxy-2*H*-pyran and its derivatives have been investigated[7,8] by ^{1}H- and ^{13}C-n.m.r. spectroscopy. Thus, 6(*R*)-hydroxy- and 6(*R*)-acetoxymethyl derivatives of 5,6-dihydro-2(*R*)-methoxy-2*H*-pyran adopt $^oH_5$ half-chair conformations in solution, whereas the 6(*R*),2(*S*) isomers

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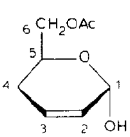

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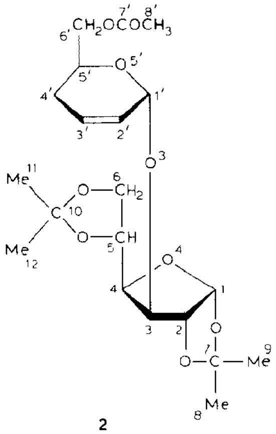

2

exist as a mixture of $^{o}H_5$ and $^{5}H_o$ conformers with the latter being slightly favoured.

The present X-ray investigation of 6-*O*-acetyl-2,3,4-trideoxy-α-DL-*glycero*-hex-2-enopyranose (**1**) supplements our previous investigations of unsaturated pyranoses and was stimulated because **1** can be used as a synthon for the asymmetric synthesis of disaccharides[9]. Thus, condensation of **1** with 1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose in the presence of a Lewis acid yields a separable mixture of two diastereoisomeric disaccharide derivatives. The comparison of their optical rotation data with those reported for disaccharides obtained by the cycloaddition of butadiene ethers of 1,2;5,6-*O*-isopropylidene-α-D-glucofuranose to butyl glyoxalate, with subsequent reduction of the carbobutoxy group[10], leads to the conclusion that the diastereoisomeric disaccharide derivatives are 3-*O*-(6-*O*-acetyl-2,3,4-trideoxy-α-L- and -α-D-*glycero*-hex-2-enopyranosyl)-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose. The diastereoisomer **2** was also subjected to X-ray investigations in order to compare the conformation of its 2*H*-pyran ring with that of **1**, to establish the conformations of the 1,3-dioxolane rings, and to determine the conformation of the glycoside bond.

EXPERIMENTAL

Well-shaped crystals of **1** and **2** were obtained from ether–acetone. Preliminary lattice constants and the space groups were established from the oscillation and Weissenberg photographs. The constants were refined during the intensity data collections.

Crystal data for **1** ($C_8H_{12}O_4$, m.p. 84°): monoclinic, space group $P2_1/a$, $Z = 4$, $a = 21.123(5)$, $b = 4.439(2)$, $c = 10.085(2)$ Å, $\beta = 110.22(2)°$, $V = 887.25$ Å^3, $M_r = 172.18$, $F(000) = 368$, and $D_c = 1.29$ Mg.m^{-3}.

Crystal data for **2** ($C_{20}H_{30}O_9$, m.p. 93.5°): orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 22.110(6)$, $b = 11.651(4)$, $c = 8.658(3)$ Å, $V = 2230.33$ Å^3, $M_r = 414.44$, $F(000) = 888$, and $D_c = 1.23$ Mg.m^{-3}.

Measurement conditions common for **1** and **2**: STOE four-circle, single-crystal diffractometer controlled by a DEC-PDP15 minicomputer, CuKα radiation (λ = 1.54178 Å), scan mode $\omega/2\theta$, measurement range $2\theta_{max} = 129°$ at room temperature, and crystal stability controlled on two reflections at 25 reflection intervals.

For **1**, 1488 intensities (1065 of $I > 2\sigma_I$) were collected and, for **2**, 2151 intensities (1884 of $I > 2\sigma_I$).

The phase problem for both structures was solved by direct methods using the MULTAN program[11]. The structure of **1** was established unambiguously. For **2**, the electron density maxima representing the 5,6-*O*-isopropylidene ring indicated some disorder involving the remote atoms of the ring and the geminal methyl carbons.

The refinement of atomic positional and thermal parameters (initially isotropic and then anisotropic) was performed for **1** and **2** by the full-matrix, least-squares procedure (X-RAY 76 System[12], program CRYLSQ), using the atomic scattering factors implemented in the System.

For **1**, the refinement was accomplished by locating all positional H parameters from Fourier difference maps and adding them (as isotropic) for the last refinement step to the whole parameter set. The final reliability factors were R = 0.046 (R_w = 0.044, unit weights).

For **2**, all attempts to refine the disordered positions of the atoms of the 5,6-*O*-isopropylidene ring and geminal methyl carbons resulted in averaged positions with unusually high thermal-motion parameters, but giving a relatively reasonable geometry of the ring. Additional Fourier F_o as well as difference map computations led to the same results. Thus, the observed disorder cannot be treated as static at room temperature.

TABLE I

FRACTIONAL CO-ORDINATES ($\times 10^4$) AND EQUIVALENT, ISOTROPIC TEMPERATURE FACTORS ($\times$ 100) FOR **1**[a]

	x/a	y/b	z/c	U_{eq}[b]
C-1	5461(1)	653(7)	6965(3)	5.2(1)
C-2	5887(2)	579(9)	8486(3)	7.2(1)
C-3	6532(2)	19(10)	8939(3)	7.7(1)
C-4	6900(2)	−747(10)	7959(4)	6.9(1)
C-5	6407(1)	−1593(7)	6514(3)	4.8(1)
O-5	5865(1)	570(4)	6080(2)	4.6(1)
C-6	6735(1)	−1510(8)	5407(3)	5.9(1)
O-6	6285(1)	−2980(5)	4155(2)	6.0(1)
C-7	6424(1)	−2635(7)	2967(3)	6.2(1)
O-7	6891(1)	−1165(7)	2917(3)	9.6(1)
C-8	5939(2)	−4245(12)	1761(4)	8.4(2)
O-1	5016(1)	−1803(5)	6692(2)	5.5(1)
H(O-1)	4716(16)	−1580(80)	5869(34)	8(1)

[a] Estimated standard deviations in parentheses. [b] $U_{eq} = (U_1 \times U_2 \times U_3)^{1/3}$, where U_i are eigenvalues of the U_{ij} matrix.

TABLE II

FRACTIONAL CO-ORDINATES ($\times 10^4$) AND EQUIVALENT, ISOTROPIC TEMPERATURE FACTORS ($\times$ 100) FOR **2**[a]

	x/a	y/b	z/c	U_{eq}[b]
C-1′	1123(2)	3638(4)	7995(5)	6.0(1)
C-2′	1285(2)	2392(4)	7929(6)	7.0(2)
C-3′	880(2)	1585(4)	7753(6)	7.8(2)
C-4′	213(2)	1845(4)	7701(6)	6.9(2)
C-5′	108(2)	3022(3)	8401(5)	5.6(1)
O-5′	506(1)	3845(2)	7673(3)	5.9(1)
C-6′	−513(2)	3548(4)	8152(6)	7.0(2)
O-6′	−945(1)	2796(2)	8931(4)	7.0(1)
C-7′	−1502(2)	3245(4)	9085(6)	7.4(2)
O-7′	−1641(1)	4161(3)	8578(5)	10.3(2)
C-8′	−1913(2)	2437(5)	9901(7)	9.5(2)
C-1	2205(2)	5646(4)	10902(5)	6.1(1)
C-2	1897(2)	5729(3)	9311(5)	5.5(1)
C-3	1265(2)	5259(3)	9627(4)	5.1(1)
C-4	1175(2)	5565(3)	11310(5)	5.5(1)
C-5	726(2)	4820(4)	12174(5)	6.7(2)
C-6	621(2)	5191(5)	13866(5)	9.4(1)
C-7	2365(2)	7445(4)	9837(6)	7.0(2)
C-8	2181(2)	8631(4)	10332(7)	10.5(2)
C-9	2925(2)	7463(5)	8844(6)	9.8(2)
C-10[c]	−273(2)	5235(6)	12644(7)	11.0(3)
C-11[c]	−610(5)	4115(12)	13012(13)	30.5(8)
C-12[c]	−668(5)	6123(13)	12122(12)	32.3(8)
O-1	2451(1)	6738(3)	11162(2)	8.1(1)
O-2	1871(1)	6929(2)	9025(3)	6.7(2)
O-3	1283(1)	4040(2)	9478(3)	5.4(1)
O-4	1762(1)	5392(2)	12000(3)	6.5(1)
O-5	152(1)	4973(3)	11486(3)	7.7(1)
O-6[c]	47(2)	5517(6)	13916(5)	18.4(3)
H-1′	1345(14)	4099(27)	7134(38)	4.9(9)
H-3	968(11)	5529(23)	9012(32)	3.3(7)

[a] Estimated standard deviations in parentheses. [b] $U_{eq} = (U_1 \times U_2 \times U_3)^{1/3}$, where U_i are eigenvalues of the U_{ij} matrix. [c] Atoms are dynamically disordered. The co-ordinates given are as refined for averaged positions. The large values of U_{eq} contain the components of the vibration amplitudes (see Fig. 2).

The last refinement step for **2** was performed as for **1**, but all methyl-H parameters were held invariant during the refinement. The final R value was 0.046 ($R_w = 0.041$, $w = \sin\theta/0.13 \leq 1$).

The refined positional parameters for the non-H atoms of **1** and **2**, together with their U_{eq} values, are given in Tables I and II, respectively*.

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*Additional data 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/269/*Carbohydr. Res.*, 125 (1984) 203–216.

DISCUSSION

The three-dimensional projections of single molecules of **1** and **2** are shown on ORTEP diagrams (Figs. 1 and 2, respectively). The bond lengths and valence angles are listed in Tables III and IV, respectively.

Conformations of the 2-enopyranose rings. — The dihydropyran ring in **1** adopts a near-ideal half-chair conformation $^{\circ}H_5$ as indicated by the asymmetry parameter $\Delta C_2 = 3.9(5)°$ as well as the deviations of O-5 and C-5 from the four-

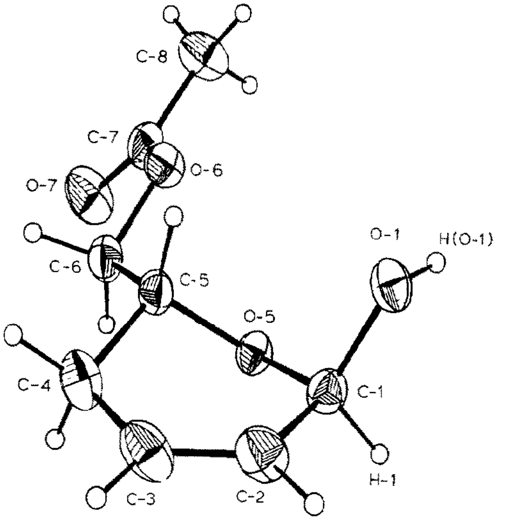

Fig. 1. The ORTEP diagram of **1**.

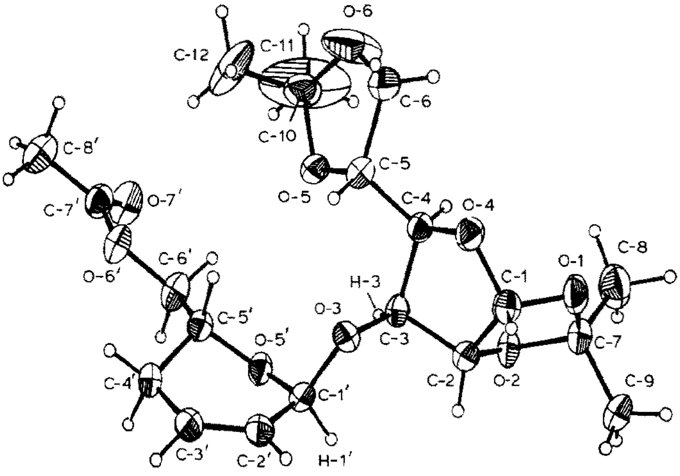

Fig. 2. The ORTEP diagram of **2**.

atom least-squares plane (Table V, column a). The inequality of these deviations (apart from their signs) reflects the deformation level.

The dihydropyran ring in **2** deviates significantly from an ideal half-chair or sofa conformation. The calculation of the least-squares plane for C-C=C-C atoms indicates that the distance of C-5 from the plane is as much as 2.5 times larger than that of O-5.

Analysis of conformational calculations (Table V, column b) indicates that the 2,3-unsaturated 2*H*-pyran ring in **2** has a markedly distorted conformation of the half-chair towards the sofa ($H \rightarrow E$).

In 7-(methyl 2-acetamido-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranosid-4-yl)theophylline monohydrate[13] (**3**), the conformation of the 2,3-unsaturated ring (Table V, column c)* may be regarded as a typical hybrid $H + E$. This may be seen clearly in the diagram of puckering parameters (Fig. 3) where the point c lies halfway between H and E, and contradicts the assignment[13] of the ${}^{o}H_{5}$ conformation.

TABLE III

BOND DISTANCES (Å) FOR **1** AND **2**[a]

For **1**			
C-1–C-2	1.487(4)	C-1–O-1	1.404(4)
C-2–C-3	1.304(5)	C-5–C-6	1.504(5)
C-3–C-4	1.493(6)	C-6–O-6	1.447(3)
C-4–C-5	1.517(4)	O-6–C-7	1.338(4)
C-5–O-5	1.440(3)	C-7–O-7	1.197(4)
O-5–C-1	1.433(4)	C-7–C-8	1.476(5)
For **2**			
C-1–C-2	1.538(6)	C-10–C-12	1.428(14)
C-2–C-3	1.525(5)	C-10–O-5	1.407(6)
C-3–C-4	1.512(5)	O-5–C-5	1.412(5)
C-4–O-4	1.442(4)	C-3–O-3	1.426(4)
O-4–C-1	1.395(5)	O-3–C-1′	1.411(5)
C-1–O-1	1.402(5)	C-1′–C-2′	1.497(6)
O-1–C-7	1.425(6)	C-2′–C-3′	1.308(6)
C-7–C-8	1.502(7)	C-3′–C-4′	1.505(6)
C-7–C-9	1.507(6)	C-4′–C-5′	1.516(6)
C-7–O-2	1.432(5)	C-5′–O-5′	1.446(5)
O-2–C-2	1.421(5)	O-5′–C-1′	1.412(5)
C-4–C-5	1.516(6)	C-5′–C-6′	1.518(6)
C-5–C-6	1.543(7)	C-6′–O-6′	1.460(5)
C-6–O-6	1.326(7)	O-6′–C-7′	1.346(5)
O-6–C-10	1.348(7)	C-7′–O-7′	1.193(6)
C-10–C-11	1.535(15)	C-7′–C-8′	1.486(7)

[a] Estimated standard deviations in parentheses.

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*In Tables V, VII, VIII, and X, the numbering of atoms in rings has been unified to conform to the conventional rules.

TABLE IV

BOND ANGLES (°) FOR **1** AND **2**[a]

For **1**			
O-5–C-1–C-2	111.3(2)	O-5–C-5–C-6	106.2(2)
C-1–C-2–C-3	123.6(3)	C-4–C-5–C-6	111.5(3)
C-2–C-3–C-4	122.2(3)	C-5–C-6–O-6	107.7(2)
C-3–C-4–C-5	110.5(3)	C-6–O-6–C-7	116.7(2)
C-4–C-5–O-5	109.7(3)	O-6–C-7–O-7	122.6(3)
C-5–O-5–C-1	114.2(2)	O-6–C-7–C-8	112.2(3)
O-5–C-1–O-1	111.2(2)	C-8–C-7–O-7	125.2(4)
C-2–C-1–O-1	108.0(3)		
For **2**			
C-1–C-2–C-3	102.9(3)	O-5–C-10–C-11	106.7(6)
C-2–C-3–C-4	102.0(3)	O-5–C-10–C-12	109.9(6)
C-3–C-4–O-4	104.3(3)	O-6–C-10–O-5	106.6(4)
C-4–O-4–C-1	108.7(3)	C-10–O-5–C-5	109.1(3)
O-4–C-1–C-2	108.2(3)	O-5–C-5–C-6	103.3(3)
O-1–C-1–C-2	105.0(3)	C-2–C-3–O-3	108.4(3)
C-1–O-1–C-7	110.1(3)	C-4–C-3–O-3	108.9(3)
O-1–C-7–C-8	109.8(4)	C-3–O-3–C-1	113.9(3)
O-1–C-7–C-9	110.9(4)	O-3–C-1′–C-2′	107.3(3)
C-8–C-7–C-9	111.9(4)	O-3–C-1′–O-5′	111.4(3)
O-2–C-7–C-9	110.7(4)	C-1′–C-2′–C-3′	122.5(4)
O-2–C-7–C-8	108.6(3)	C-2′–C-3′–C-4′	122.0(4)
O-1–C-7–O-2	104.7(3)	C-3′–C-4′–C-5′	108.7(4)
C-7–O-2–C-2	107.3(3)	C-4′–C-5′–O-5′	109.4(3)
O-2–C-2–C-1	103.7(3)	C-5′–O-5′–C-1′	112.9(3)
C-3–C-4–C-5	115.2(3)	O-5′–C-1′–C-2′	112.9(3)
O-4–C-4–C-5	107.9(3)	C-4′–C-5′–C-6′	116.6(4)
C-4–C-5–C-6	113.9(4)	O-5′–C-5′–C-6′	102.8(3)
C-4–C-5–O-5	108.0(3)	C-5′–C-6′–O-6′	106.5(4)
C-5–C-6–O-6	104.8(4)	C-6′–O-6′–C-7′	114.3(3)
C-6–O-6–C-10	113.8(5)	O-6′–C-7′–O-7′	123.2(4)
O-6–C-10–C-11	107.0(6)	O-6′–C-7′–C-8′	111.1(4)
O-6–C-10–C-12	113.7(7)	O-7′–C-7′–C-8′	125.7(4)
C-12–C-10–C-11	112.6(7)		

[a] Estimated standard deviations in parentheses.

In the 2,3-unsaturated monosaccharides **4** and **5** reported earlier[14] (Table V, columns d and e), the 2*H*-pyran rings exist in a near-ideal half-chair conformation (*H*) close to that adopted by cyclohexene[15].

The AcO-6 groups in **1** and **2** are situated differently with respect to the rings; in **1**, the orientation is *trans-gauche*, whereas it is *gauche-trans* in **2**. The appropriate torsion angle values are given in Table VI. These differences may be caused by the interactions of the crystal lattice field.

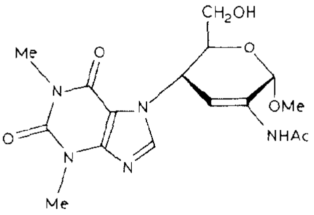
*Conformation of 1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranose.* — The α-D-glucofuranose ring in **2** is of interest from the point of view of conformations of saturated five-membered heterocycles. The results of the conformational calculations are presented in Table VII and illustrated in Fig. 4. The five-membered ring

TABLE V

CONFORMATION OF DIHYDROPYRAN RINGS

	1 (a)[a]	**2** (b)	**3** (c)	**4** (d)	**5** (e)
Atom deviations (Å) from least-squares planes (e.s.d. in parentheses)					
C-1	0.003(3)[b]	0.005(4)[b]	0.020(6)[b]	0.002(17)[b]	0.006(11)[b]
C-2	−0.011(4)[b]	−0.016(5)[b]	−0.035(6)[b]	−0.006(20)[b]	−0.012(10)[b]
C-3	0.014(4)[b]	0.016(5)[b]	0.035(6)[b]	0.005(17)[b]	0.014(11)[b]
C-4	−0.006(5)[b]	−0.007(5)[b]	−0.016(6)[b]	−0.002(17)[b]	−0.006(11)[b]
C-5	−0.430(3)	−0.530(4)	−0.572(6)	−0.390(17)	−0.448(9)
O-5	0.285(2)	0.217(3)	0.233(4)	0.315(8)	0.308(6)
Asymmetry parameters[16] (°) (e.s.d. in parentheses)					
ΔC_2	3.9(5)	10.9(6)	11.1(6)	1.2(2.2)	3.2(1.2)
ΔC_s	—	16.9(6)	19.8(6)	—	—
Puckering parameters[17] (see Fig. 3)					
Q (Å)	0.472	0.501	0.545	0.466	0.500
ϕ (°)	23.54	26.19	16.33	25.99	23.49
θ (°)	52.17	53.42	56.66	51.34	52.47
q_2 (Å)[c]	0.357	0.403	0.454	0.364	0.396
q_2 (Å)[d]	0.289	0.299	0.298	0.291	0.305
Conformation	*H*	*H* + *E*	*H* + *E*	*H*	*H*

[a] The letters in parentheses refer to the points on the puckering diagram (Fig. 3). The values for **3**–**5** are calculated from published data[13,14]. [b] Atoms defining the planes. [c] $q_2 = Q \sin\theta$. [d] $q_3 = Q \sin\theta$.



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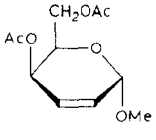

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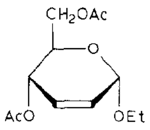

5

of α-D-glucofuranose has a slightly distorted $^3T_4$ conformation. The distances of C-3 and C-4 from the three-atom plane through the remaining atoms are similar. Their deviation values are 0.311(4) and −0.280(4) Å, respectively. The asymmetry parameter ΔC_2 also indicates a small distortion of the *T* conformation.

The 1,2-dioxolane ring has a distorted envelope conformation (*E*→*T*). On the other hand, the 5,6-dioxolane ring* may be regarded as a conformational hybrid of the planar and envelope form (*E* + *P*), as indicated by the torsion angles (see Table VIII) being <15°; the deviation of C-10 from the four-atom least-squares plane through the remaining atoms is approximately half that of the deviation of O-2 in the 1,2-dioxolane ring. The value of the puckering parameter q is

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*The conformation of the 5,6-dioxolane ring discussed is based on the intermediate positions of dynamically disordered O-6 and C-10.

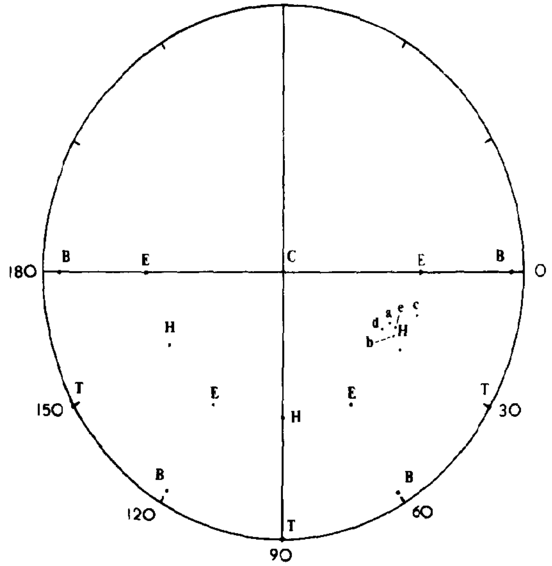


Fig. 3. The diagram of puckering parameters for dihydropyran rings. Capital letters denote the ideal conformations of different types. For small letters, see text.

TABLE VI

COMPARISON OF SOME TORSIONAL ANGLES (°) FOR THE DIHYDROPYRAN RINGS IN **1** AND **2**[a]

	1	2
C-1–C-2–C-3–C-4	−3.0(7)	−3.8(8)
C-2–C-3–C-4–C-5	−15.3(6)	−18.7(7)
C-3–C-4–C-5–O-5	46.2(4)	51.5(5)
C-4–C-5–O-5–C-1	−63.5(3)	−66.1(4)
C-5–O-5–C-1–C-2	44.0(3)	41.8(5)
O-5–C-1–C-2–C-3	10.3(5)	−6.8(7)
C-4–C-5–C-6–O-6	167.2(3)	63.4(5)
O-5–C-5–C-6–O-6	−73.3(3)	−177.0(3)

[a] Estimated standard deviations in parentheses.

also half that of the 1,2-dioxolane envelope. The above results indicate a marked flattening of the 5,6-dioxolane ring and may be regarded as evidence for a conformational hybrid.

In order to compare the conformations of five-membered rings, calculations were also performed for the diastereoisomeric furanose, using the data reported by Einstein and Slessor[18]. The ring of the β-D-idofuranose derivative **6** has an almost ideal envelope (${}^4E$) conformation. The asymmetry parameter [calculated from the ring torsion angles (see Tables VII and VIII)], the deviation of C-4 from the four-atom least-squares plane, as well as the puckering parameters are close to those of an ideal envelope conformation. The 1,2-dioxolane ring in this case may be re-

TABLE VII

RING CONFORMATIONS IN **2** AND **6**

2						**6**[a]					
1,2-Dioxolane		*Furanose*		*5,6-Dioxolane*		*1,2-Dioxolane*		*Furanose*		*5,6-Dioxolane*	
Atom deviations (Å) from least-squares planes (e.s.d. in parentheses)											
C-1	0.032(5)[b]	C-3	0.311(4)	O-6	0.011(7)[b]	C-1	0.030(7)[b]	C-3	−0.005(7)[b]	O-6	−0.037(6)[b]
C-2	−0.018(4)[b]	C-2	0.000(4)[b]	C-6	−0.011(6)[b]	C-2	−0.021(6)[b]	C-2	0.006(6)[b]	C-6	0.176(10)[b]
O-2	−0.425(2)	C-1	0.000(5)[b]	C-5	0.007(5)[b]	O-2	0.010(5)[b]	C-1	−0.007(6)[b]	C-5	−0.175(10)[b]
C-7	0.023(5)[b]	O-4	0.000(2)[b]	O-5	−0.003(4)[b]	C-7	−0.469(7)	O-4	0.003(5)[b]	O-5	0.037(6)[b]
O-1	−0.013(3)[b]	C-4	−0.280(4)	C-10	−0.205(4)	O-1	−0.010(5)[b]	C-4	0.569(7)	C-10	0.325(10)
Asymmetry parameters[16] *(°) (e.s.d. in parentheses)*											
ΔC_2	8.0(4)		2.9(4)		5.0(7)						6.8(9)
ΔC_s	5.8(4)				2.8(7)		4.9(6)		0.9(6)		7.8(9)
Puckering parameters[17]											
q (Å)	0.279		0.359		0.136		0.304		0.376		0.314
ϕ (°)	79.0		89.7		174.6		100.9		104.7		59.3
Conformation	*E* + *T*		*T*		*E* + *P*		*E*		*E*		*E* + *T*

[a] Values calculated from published data[18] [b] Atoms defining the planes.

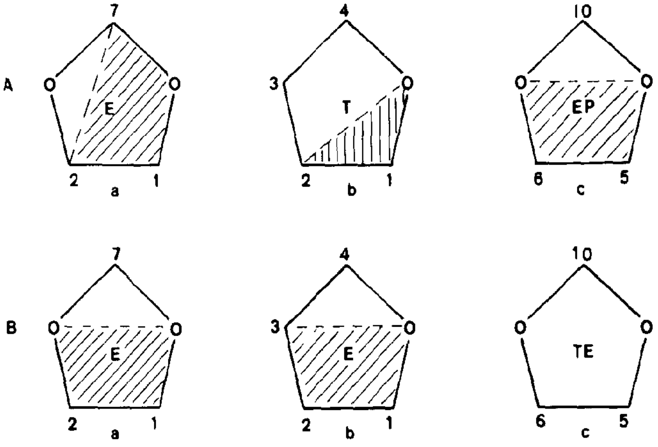


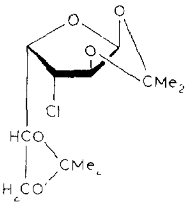
Fig. 4. Conformation of five-membered hetero rings. A, for **2**: (a) 1,2-dioxolane, (b) α-D-glucofuranose, and (c) 5,6-dioxolane rings. B, for **6**: (a) 1,2-dioxolane, (b) β-D-idofuranose, and (c) 5,6-dioxolane rings.

TABLE VIII

COMPARISON OF SOME TORSION ANGLES (°) IN **2** AND **6**[a]

	2	**6**
Furanose ring		
O-4–C-1–C-2–C-3	−10.8(4)	1.2(6)
C-1–C-2–C-3–C-4	28.9(4)	−23.7(6)
C-2–C-3–C-4–O-4	−37.6(3)	38.3(6)
C-3–C-4–O-4–C-1	32.2(4)	−39.6(6)
C-4–O-4–C-1–C-2	−13.1(4)	23.9(7)
1,2-Dioxolane ring		
O-1–C-1–C-2–O-2	−14.2(4)	4.0(7)
C-1–C-2–O-2–C-7	27.9(4)	−23.3(6)
C-2–O-2–C-7–O-1	−31.2(4)	34.1(6)
O-2–C-7–O-1–C-1	21.7(4)	−31.5(6)
C-7–O-1–C-1–C-2	−4.6(4)	16.8(7)
5,6-Dioxolane ring		
O-5–C-5–C-6–O-6	1.7(6)	25.1(8)
C-5–C-6–O-6–C-10	11.4(7)	−34.1(8)
C-6–O-6–C-10–O-5	−16.6(8)	30.9(9)
O-6–C-10–O-5–C-5	14.6(7)	−14.5(9)
C-10–O-5–C-5–C-6	−7.9(5)	−6.8(9)
Other angles		
O-4–C-1–C-2–O-2	104.1(4)	−113.1(5)
C-3–C-2–C-1–O-1	−129.2(3)	118.3(6)
C-6–C-5–C-4–O-4	66.9(4)	173.5(6)
C-6–C-5–C-4–C-3	−177.2(4)	55.3(9)
O-4–C-4–C-5–O-5	−179.1(3)	−70.2(9)
C-3–C-4–C-5–O-5	−63.1(5)	171.5(6)

[a] Estimated standard deviations in parentheses.



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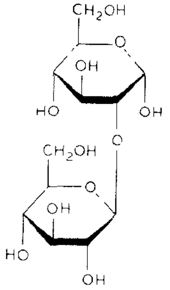

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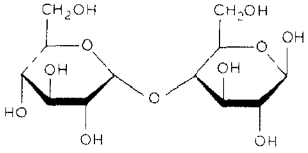

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garded as a slightly deformed envelope, whereas the 5,6-dioxolane ring is a hybrid of $E + T$ conformations. The calculated asymmetry parameters[19] for this last ring, ΔC_2 and ΔC_s (Table VII), indicate the possible existence of a two-fold axis and a plane of symmetry.

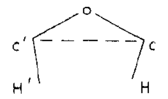
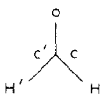
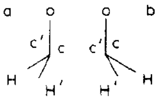
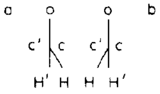
Thus, **2** and **6** differ significantly, in that the conformations of the furanose rings are *T* and *E*, respectively, the 1,2-dioxolane rings are both *E* (but of different deformation levels), and the 5,6-dioxolane rings are $E + P$ and $E + T$, respectively.

Conformation of the glycosidic bond. — This conformation in **2** may be described by the torsion angles ϕ and ψ, the values of which are similar and positive (Table IX). We have suggested[20] a classification of glycoside bond types, the principles of which are based on the positions of H-C_x and H-C′ relative to the C_x–O–C′ plane of the glycoside bond. Table IX shows three alternative conformations as projections along C_x–C′ and a vertical projection. The projections are correlated with the signs of ϕ and ψ angles for each type.

As may be seen from the glycoside link projections for **2** (Fig. 5), the bond may be assigned to the first type.

TABLE IX

CLASSIFICATION OF CONFORMATION POSSIBILITIES FOR GLYCOSIDIC BONDS

	Signs of angles ϕ and	ψ		
I	(+) or (−)	(+) (−)	a b	
II	(+) or (−)	(−) (+)	a b	
III	(0) or (+)	(+) (0)	a b	

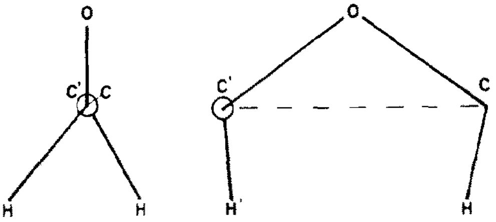


Fig. 5. Conformation of the glycosidic bonds in 2.

TABLE X

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

	2	7	8
Distances and valence angles (e.s.d. in parentheses)			
C'-O-C (°)	114.0(3)	113.7(4)	117.9(2)
C'-O (Å)	1.412(5)	1.402(8)	1.414(4)
C-O (Å)	1.425(4)	1.441(8)	1.419(4)
H'-H (Å)	2.48(4)	2.15(7)	2.072(7)
Torsion angles (°) (e.s.d. in parentheses)			
ϕ	47(2)	40(4)	4.8(5)
ψ	32(2)	−17(4)	13.3(4)
Atom deviations (Å) from C'-O-C plane (e.s.d. in parentheses)			
H'	−0.72(2)	−0.62(5)	−0.086(6)
H	0.42(2)	−0.25(5)	0.236(4)

The classification may be illustrated with α-sophorose[21] (**7**) and β-maltose hydrate[22] (**8**) (Table X). The glycoside bond of **7** is assigned as type IIa (the ϕ and ψ are + and −, respectively), whereas that in **8** is type I (both signs positive).

The values of ϕ and ψ for known structures of oligosaccharides lie mostly within the limits of ±60°. The exceptions involve additional intra- and intermolecular interactions which cause the sugar rings to rotate. Similarly, the distances between both glycoside H atoms are mostly within the range of 2.1–2.6 Å. These distances, which may sometimes be larger than 2.6 Å, are unlikely to be reduced much below 2.0 Å because of the van der Waals interactions. This distance in **8** (2.072 Å) seems to be near to the lower limit.

The intermolecular hydrogen bridge in **1**. — A strong, potential, intermolecular hydrogen-bonding was found in the crystal structure of **1**, namely, HO-1 · · · O-5'* (symmetry of acceptor 1 − x, − y, 1 − z). This causes a second, symmetrical hydrogen bond, linking the same enantiomeric pair of molecules into a dimer. The characteristic distances and angles are to be: O-1 · · · O-5'* 2.825(2) Å, H(O-1) · · · O-5'* 1.975(3) Å, O-1 · · · H(O-1)* 0.85(3) Å, and O-1–H(O-1) · · · O-5'* 171(4)°.

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