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CRYSTAL AND MOLECULAR STRUCTURES OF BENZYL 3-*O*-BENZOYL-4-*O*-BENZYL-2-*O*-(2,3,6-TRIDEOXY-α-L-*glycero*-HEX-2-ENOPYRANOSYL-4-ULOSE)-α-L-RHAMNOPYRANOSIDE

JANUSZ W. KRAJEWSKI, ZOFIA URBAŃCZYK-LIPKOWSKA, PRZEMYSLAW GLUZIŃSKI, ALEKSANDER ZAMOJSKI,
Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa (Poland)

AND KATARZYNA STADNICKA
Institute of Chemistry, Jagiellonian University, 30-060 Kraków (Poland)

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ABSTRACT

Benzyl 3-*O*-benzoyl-4-*O*-benzyl-2-*O*-(2,3,6-trideoxy-α-L-*glycero*-hex-2-enopyranosyl-4-ulose)-α-L-rhamnopyranoside has been investigated by X-ray diffraction methods. The crystals obtained from aqueous ethanol are orthorhombic, space group $P2_12_12_1$ with cell constants a = 10.775(2), b = 10.857(2), and c = 25.774(3) Å. A four-circle, automatic diffractometer was used for intensity-data collection. Out of 3370 reflection intensities, 2634 were of $I > 2\sigma_I$ and these were used for refinement. The structure was solved by direct methods, and the atomic parameters were then refined by the full-matrix, least-squares procedure. The unsaturated dihydropyranone ring adopts a deformed sofa conformation, whereas the rhamnopyranose ring adopts a chair conformation. The glycosidic linkage is characterised by torsion angles $\Phi 33(2)°$ and $\Psi -13(1)°$. A new classification for the conformations of glycosidic linkages is suggested.

INTRODUCTION

The recently synthesised disaccharide-precursor[1] benzyl 3-*O*-benzoyl-4-*O*-benzyl-2-*O*-(2,3,6-trideoxy-α-L-*glycero*-hex-2-enopyranosyl-4-ulose)-α-L-rhamnopyranoside (**1**) contains a disubstituted 5,6-dihydro-2*H*-pyran ring. Based on ^{1}H- and ^{13}C-n.m.r. data, Achmatowicz and Burzyńska[2] postulated the 1,2-diplanar (sofa) conformation for *trans*-6-methoxy-2-methyl-3,6-dihydro-2*H*-pyran-3-one. However, our X-ray diffraction studies[3] of the 4-*O*-substituted derivative **2** of benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside revealed that the 2-unsubstituted 6-alkoxy-3,6-dihydro-2*H*-pyran-3-one ring adopted a somewhat distorted, half-chair conformation. Since the n.m.r. data may be interpreted in terms of a half-chair or a sofa conformation, an X-ray structure determination was undertaken.

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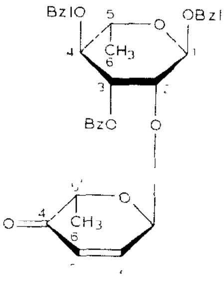

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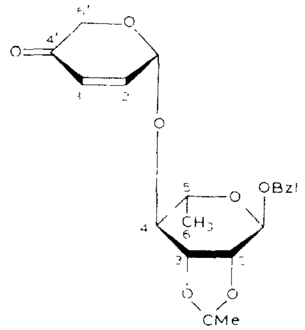

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EXPERIMENTAL

Compound **1** was obtained by $SnCl_4$-catalysed condensation of 1-*O*-acetyl-2,3,6-trideoxy-α,β-DL-*glycero*-hex-2-enopyranos-4-ulose with benzyl 3-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside. From the mixture of isomeric products, the LL-stereoisomer [m.p. 99–101° (from aqueous ethanol)] was isolated by chromatography[4], and a well-shaped crystal (0.20 × 0.27 × 0.32 mm) was chosen for the intensity collection.

Crystal data for **1** ($C_{33}H_{34}O_8$): orthorhombic, spacegroup $P2_12_12_1$, $Z = 4$, $a = 10.775(2)$ Å, $b = 10.857(2)$ Å, $c = 25.774(3)$ Å, $V = 3015.03$ Å^3, $M_r = 558.60$, $F(000) = 1184$, and $D_c = 1.23$ Mg.m^{-3}.

Of the 3370 intensities collected on a four-circle CAD-4 diffractometer (SLAF & BS, Kraków, Poland), using graphite-monochromated CuKα radiation and the $\omega/2\theta$ scan technique up to $2\theta_{max} = 150°$, 2634 had $I > \sigma_I$. No absorption correction was applied. The structure was solved by direct methods (program MULTAN [5]). The refinement of the atomic positional and anisotropic thermal parameters was performed using the X-RAY-70 System[6], by the full-matrix, least-squares procedure CRYLSQ. The atomic scattering factors were taken from the International Tables of X-ray Crystallography[7]. The positions of all hydrogen atoms were found from a difference-Fourier synthesis. The final refinement step involved all atomic parameters except the hydrogen temperature-factors (fixed as the B_{eq} of the adjacent atom + 1). The final R and R_w factors were 0.068 and 0.047 ($w = 1/\sigma_F^2$), respectively. The refined atomic co-ordinates are presented in Table I.

DISCUSSION

The three-dimensional structure of **1**, together with that of **2** reported earlier[3], is shown in the ORTEP diagram (Fig. 1). Tables II and III contain the bond lengths and valence angles, respectively. The values referring to the three phenyl rings (C–E) are omitted from the Tables; the mean values of bond lengths and angles are: for ring C, 1.367(10) Å and 120.0(6)°; for ring D, 1.360(8) Å and 120.0(4)°; and for ring E, 1.370(6) Å and 120.0(5)°.

TABLE I

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

Atom	x	y	z	B_{eq}[b]
C-1	5958(3)	−1194(3)	9151(1)	4.0(2)
C-2	7028(3)	−293(3)	9085(1)	3.7(2)
C-3	6540(3)	1018(3)	9019(1)	3.7(2)
C-4	5615(3)	1082(3)	8580(1)	3.8(2)
C-5	4567(4)	178(3)	8695(1)	4.4(2)
C-6	3632(4)	96(4)	8254(2)	5.9(2)
C-7	8878(4)	−1177(3)	8715(1)	4.3(2)
C-8	9650(4)	−938(4)	8240(2)	4.9(2)
C-9	9864(4)	−1790(5)	7894(2)	5.6(3)
C-10	9254(5)	−2980(5)	7930(2)	6.0(3)
C-11	8388(4)	−3176(4)	8391(2)	5.4(2)
C-12	8371(5)	−4484(4)	8573(2)	7.3(3)
C-13	4577(4)	−1827(4)	9827(2)	4.9(2)
C-14	5139(4)	−3060(4)	9950(2)	4.4(3)
C-15	4638(5)	−4128(5)	9735(2)	7.0(3)
C-16	5141(9)	−5273(6)	9868(3)	8.8(5)
C-17	6083(8)	−5318(9)	10217(4)	8.7(8)
C-18	6566(5)	−4318(8)	10414(3)	7.8(6)
C-19	6085(4)	−3160(5)	10294(2)	6.4(3)
C-20	8192(4)	2325(3)	9298(1)	4.0(2)
C-21	9408(4)	2846(3)	9143(1)	3.6(2)
C-22	10033(4)	3576(3)	9492(1)	4.4(2)
C-23	11198(4)	4027(4)	9378(2)	5.2(2)
C-24	11739(4)	3729(4)	8910(2)	5.6(2)
C-25	11117(4)	3007(4)	8558(2)	5.4(2)
C-26	9943(4)	2561(3)	8672(1)	4.5(2)
C-27	5408(5)	2982(4)	8114(2)	7.5(4)
C-28	4631(5)	4081(4)	8067(2)	4.6(3)
C-29	4870(4)	5148(5)	8355(2)	5.7(2)
C-30	4123(6)	6158(4)	8298(2)	6.4(3)
C-31	3155(5)	6129(5)	7978(2)	6.8(4)
C-32	2903(5)	5147(7)	7699(2)	7.0(3)
C-33	3620(6)	4125(5)	7731(2)	5.5(3)
O-1	5478(2)	−943(2)	9650(1)	4.3(1)
O-2	7709(2)	−603(2)	8623(1)	3.9(1)
O-3	7590(2)	1798(2)	8895(1)	4.3(1)
O-4	5066(2)	2279(2)	8558(1)	4.5(1)
O-5	5065(2)	−1049(2)	8755(1)	4.2(1)
O-6	9354(4)	−3760(3)	7597(1)	9.6(3)
O-7	8748(2)	−2426(2)	8825(1)	4.6(1)
O-8	7788(3)	2329(3)	9731(1)	5.9(2)

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

TABLE II

BOND DISTANCES (Å)[a]

C-1–C-2	1.522(5)	C-9–C-10	1.452(7)
C-2–C-3	1.527(5)	C-10–C-11	1.526(7)
C-3–C-4	1.509(5)	C-11–O-7	1.438(5)
C-4–C-5	1.528(5)	O-7–C-7	1.393(5)
C-5–O-5	1.440(4)	C-10–O-6	1.210(6)
O-5–C-1	1.411(4)	C-11–C-12	1.496(6)
C-5–C-6	1.521(5)	C-3–O-3	1.449(4)
C-1–O-1	1.413(4)	O-3–C-20	1.351(4)
O-1–C-13	1.439(5)	C-20–O-8	1.199(5)
C-13–C-14	1.503(6)	C-20–C-21	1.481(5)
C-2–O-2	1.438(4)	C-4–O-4	1.429(4)
O-2–C-7	1.425(4)	O-4–C-27	1.423(6)
C-7–C-8	1.503(4)	C-27–C-28	1.463(7)
C-8–C-9	1.303(6)		

[a]Estimated standard deviations in parentheses

TABLE III

BOND ANGLES (DEGREES)[a]

O-5–C-1–C-2	111.3(3)	C-11–O-7–C-7	114.8(3)
C-1–C-2–C-3	110.5(3)	C-9–C-10–O-6	122.6(4)
C-2–C-3–C-4	110.7(3)	C-11–C-10–O-6	120.5(4)
C-3–C-4–C-5	108.3(3)	O-7–C-11–C-12	107.2(4)
C-4–C-5–O-5	109.9(3)	C-10–C-11–C-12	112.6(4)
C-5–O-5–C-1	115.8(3)	C-2–C-3–O-3	107.5(3)
C-2–C-1–O-1	104.8(3)	C-4–C-3–O-3	108.9(3)
O-5–C-1–O-1	112.8(3)	C-3–O-3–C-20	117.0(3)
C-1–O-1–C-13	114.0(3)	O-3–C-20–O-8	122.9(4)
O-1–C-13–C-14	112.9(3)	O-3–C-20–C-21	112.3(3)
C-13–C-14–C-15	120.1(4)	O-8–C-20–C-21	124.8(4)
C-13–C-14–C-19	120.8(4)	C-20–C-21–C-22	118.5(3)
C-1–C-2–O-2	109.2(3)	C-20–C-21–C-26	121.3(3)
C-3–C-2–O-2	107.5(3)	C-3–C-4–O-4	110.3(3)
C-2–O-2–C-7	114.6(2)	C-5–C-4–O-4	106.8(3)
O-2–C-7–C-8	106.2(3)	C-4–O-4–C-27	114.4(3)
O-2–C-7–O-7	111.7(3)	O-4–C-27–C-28	110.9(4)
O-7–C-7–C-8	112.9(3)	C-27–C-28–C-29	121.6(4)
C-7–C-8–C-9	122.1(4)	C-27–C-28–C-33	121.9(4)
C-8–C-9–C-10	120.6(4)	C-4–C-5–C-6	112.4(3)
C-9–C-10–C-11	116.7(4)	O-5–C-5–C-6	106.1(3)
C-10–C-11–O-7	111.3(3)		

[a]Estimated standard deviations in parentheses.

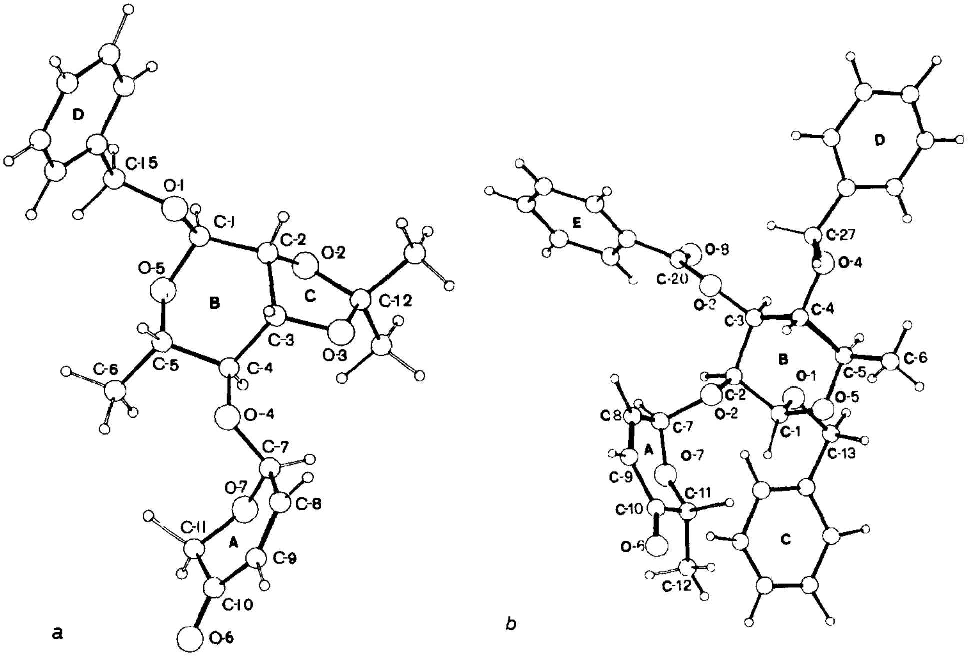


Fig. 1. ORTEP diagrams for (*a*) **2** and (*b*) **1**.

Conformation of the glycoside linkage. — This conformation was analysed on the basis of the characteristic Φ and Ψ torsion angles and on calculations of the appropriate three-atom planes. The torsion angles Φ and Ψ for **1** are defined[8] as H-1′–C-1′–O-2–C-2 and H-2–C-2–O-2–C-1′, respectively. Table IV shows the geometry and the torsion angles for the glycoside linkages of **1** and **2** compared with those[9,10] of some other disaccharides. The results of theoretical studies[11] for cellobiose are also included.

Compounds **1** and **2** have different conformations, as shown by the values of Φ and Ψ. In **1**, H-1′ and H-2 are on the same side of the plane defined by C-1′–O-2–C-2, and the distance between H-1′ and H-2 in **1** is rather short [2.09(4) Å]. In **2**, H-1′ and H-4 are situated nearly symmetrically with respect to the plane defined by C-1′–O-4–C-4 (Φ and Ψ are positive), and the distance is 2.41(8) Å. The largest H–H distance [2.62(1) Å] is found in linkage B of erythromycin A, and the corresponding dihedral angle is 85.5°.

The conformations of the glycosidic linkages for **3** and **4** (ring 2) (Table IV) correspond to those for **1** and **2**.

For the favoured conformer of cellobiose[11] (**5**), H′ is significantly twisted out of the C–O–C′ plane, whereas H lies in that plane (Φ and Ψ are 51° and 0°, respectively).

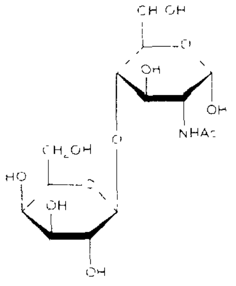
From the above examples, the conclusion may be drawn that glycosidic linkages in disaccharides may adopt three conformations: (*a*) H and H′ lie on the same side of the C–O–C′ plane, and the signs of Φ and Ψ are opposite; (*b*) H and

TABLE IV

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

	1	**2**	**3**[a]	**4**[b] *Ring 1*	*Ring 2*	**5**[c]	
C′–O–C(°)	114.5(2)[d]	113.2(4)	116.4(5)	114.6(6)	112.8(6)	113.4	114.4
C′–O (Å)	1.425(5)	1.415(9)	1.400(8)	1.401(10)	1.390(8)	—	—
C–O (Å)	1.439(4)	1.451(6)	1.447(8)	1.434(8)	1.454(9)	—	—
H′–H (Å)	2.09(4)	2.41(8)	2.24(8)	2.62(1)	2.29(1)	2.29	2.16
Torsion angles (°)							
Φ	33(2)	29(4)	44(4)	54(1)	49(1)	51	−10
Ψ	−13(1)	26(2)	−38(4)	37(1)	16(1)	0	−29
Deviations (Å) from C′–O–C plane							
H′	−0.55(3)	0.43(6)	−0.63(6)	0.75(1)	0.80(1)	—	—
H	−0.23(2)	−0.44(4)	−0.51(6)	−0.65(1)	−0.29(1)	—	—

[a]Calculated from the data[9] for *N*-acetyl-lactosamine [4-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-α-D-glucopyranose]. [b]Calculated from the data[10] for erythromycin A [c]β-Cellobiose[11] [d]Figures in parentheses are e.s.d. values.



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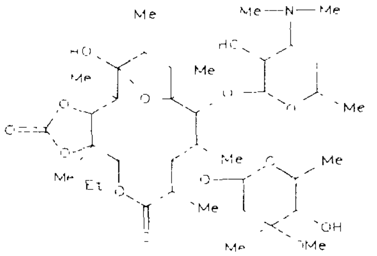

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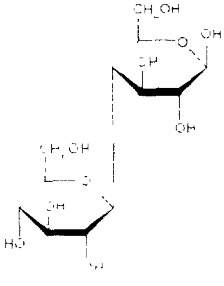

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H′ are on opposite sides of the C–O–C′ plane (Ψ and Φ have the same sign); and (*c*) either H or H′ lies (approximately) in the C–O–C′ plane.

Conformation of the dihydropyranone ring. — Although the conformation of the ulose ring (A) in **2** (Fig. 1*a*) has been established[3] as ${}^{0}H_{5}$, the extent of deformation has not been determined. It was stated, based on least-squares calculation of the plane defined by C–C=C–C, that the deviation of C-11 therefrom could be twice that of O-7 (Fig. 2*a*). This may be interpreted as a tendency for the four-atom plane to transform into the five-atom plane that is characteristic of the sofa-type conformation (*E*) (Fig. 2*b*). In this way, the ulose ring in **2** may be regarded as a half-chair (*H*) deformed towards the sofa (*E*).

In **1**, the ulose ring is additionally substituted by the pseudo-equatorial methyl group (C-12) (Fig. 1*b*). Its pseudo-equatorial position is proved by the torsion angle of 147.7(4)° for C-9–C-10–C-11–C-12. As may be seen from Table V, five atoms of the ulose ring form a "good" least-squares plane (all ring atoms ex-

TABLE V

CONFORMATION OF DIHYDROPYRANONE RINGS

Atom deviations (Å) from least-squares planes (e.s.d. in parentheses)					
Atom	*(a)* **1**	*(b)* **2**	*Atom*	*(c) A*[a]	*(d) B*[a]
C-7	0.033(4)[b]	0.089(7)[b]	C-1	0.030(4)[b]	−0.020(4)[b]
C-8	−0.043(4)[b]	−0.019(7)[b]	C-2	−0.030(4)[b]	0.020(4)[b]
C-9	0.019(5)[b]	0.019(7)[b]	C-3	0.018(5)[b]	−0.010(4)[b]
C-10	0.015(5)[b]	−0.086(7)[b]	C-4	0.212(5)	−0.351(4)
C-11	−0.024(5)[b]	−0.239(7)	C-5	−0.422(5)	0.309(5)
O-7	0.560(3)	0.401(5)	C-6	−0.018(5)[b]	0.015(5)[b]
Asymmetry parameters[12] (°) *(e.s.d. in parentheses)*					
ΔC_2	—	7.9(9)		10.4(6)	2.4(5)
ΔC_s	6.5(5)	—		13.8(6)	—
Puckering parameters[13] *(see Fig. 3)*					
Q(Å)	0.418	0.425		0.420	0.428
Φ(°)	20.48	27.96		40.73	28.47
θ(°)	58.05	54.33		56.88	54.19
q_2(Å)[c]	0.355	0.345		0.352	0.347
q_3(Å)[d]	0.221	0.248		0.229	0.250
Conformation	*E*	*H*		*H*+*E*	*H*

[a]Cyclohexenone rings calculated from the data reported by Klinga *et al.*[14]. [b]Atoms defining the planes. [c]$q_2 = Q \times \sin\theta$. [d]$q_3 = Q \times \cos\theta$.

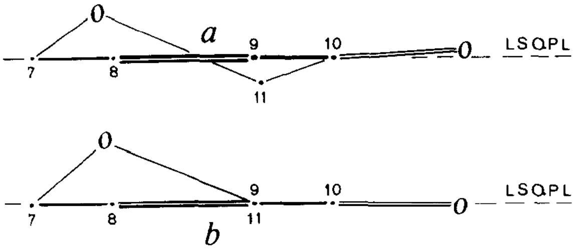

Fig. 2. The dihydropyranone rings in (*a*) **2** and (*b*) **1**.

cept O-7). However, the asymmetry parameter, ΔC_s 6.5(5)°, indicates a considerable deviation from the ideal sofa (*E*) conformation. The calculated puckering-parameters for this ulose ring, represented by the point (a) on the puckering diagram (Fig. 3), corroborates the assignment of the sofa conformation (*E*) deformed towards the half-chair conformation (*H*). It partly confirms the preference of ulose rings for sofa conformations, suggested[2] on the basis of ^{1}H-n.m.r. data. In the ulose rings, there are three contiguous sp^2-hybridised carbons which enable the five-atom plane to exist, thus making possible the sofa conformation. However, this was not sufficient in the case of **2**. It is not clear whether the influence of the crystal-lattice field or the interaction of the methyl and carbonyl groups may be responsible for these differences in ulose-ring conformations.

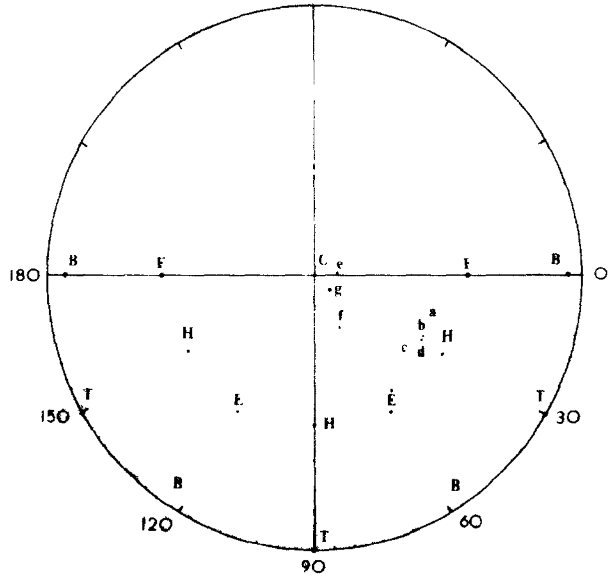

Fig. 3. Diagram of puckering parameters for the dihydropyranone and rhamnopyranose rings in **1** and **2**. The small letters refer to columns in Tables V and VI.

TABLE VI

CONFORMATION OF RHAMNOPYRANOSE RING

Atom deviations (Å) from least-squares planes (e.s.d. in parentheses)			
Atom	*(e)* **1**	*(f)* **2**	*(g)* **5**[a]
C-1	0.605(4)	0 541(5)	0 632(2)
C-2	0.006(3)[b]	0.081(5)[b]	0.003(2)[b]
C-3	−0.005(4)[b]	−0.078(5)[b]	−0.003(2)[b]
C-4	−0.704(4)	−0.637(5)	−0.722(2)
C-5	0.006(4)[b]	0.083(5)[b]	0.003(2)[b]
O-5	−0.006(2)[b]	−0.086(6)[b]	−0.001(1)[b]
Asymmetry parameters[12] (°) (e.s.d in parentheses)			
ΔC_2	4.9(4)	5.4(6)	3 8(1)
ΔC_s	3.5(4)	18.3(6)	2.6(1)
Puckering parameters[13] *(see Fig. 3)*			
Q (Å)	0.560	0.536	0.581
Φ(°)	357.55	64.21	50.00
θ(°)	174.12	162.35	174 61
q_2 (Å)[c]	0.057	0.162	0 054
q_3 (Å)[d]	−0 557	−0.511	−0 578
Conformation	$^1C_4$	$^1C_4$	$^1C_4$

[a] Calculated from the data for α-L-rhamnopyranose monohydrate[15] [b] Atoms defining the planes [c] $q_2 = Q \times \sin\theta$ [d] $q_3 = Q \times \cos\theta$

The X-ray diffraction studies[14] of bis(2-hydroxy-4,4,6,6-tetramethyl-1-cyclohexen-3-one)selenide enable the conformations of both cyclohexenone rings (Table V, column c and d) to be calculated for modelling purposes. The results may be regarded as proof that identical substitution of the rings does not imply the same conformation, since one ring is a typical half-chair conformation (*H*), and the other is a hybrid of (*H*) and (*E*) conformations.

Conformations of rhamnopyranose rings. — The results of conformational calculations for the rhamnopyranose rings (*B*) in **1** and **2**, and, for comparison, those for α-L-rhamnopyranose monohydrate[15], are noted in Table VI.

The rhamnopyranose ring in **1** (Table VI, e), despite four bulky substituents, is not markedly distorted. The deviation from the ideal-chair conformation is similar to that of α-L-rhamnopyranose (Table VI, g).

There is marked distortion of the rhamnopyranose ring in **2**, caused by fusion with the dioxolane ring[3]. The effect on parameters of the above-mentioned distortion is represented by the point (f) in Fig. 3.

Conformations of the O-*benzoyl and* O-*benzyl groups.* — The conformations of the *O*-benzyl groups were investigated in comparison with the known conformations of benzyl alcohol and its ethers. Based on ^{1}H-n.m.r. data, Ito and Hirota[16] stated that there are four variants of conformation, as shown in the Newman projections in Fig. 4. Consideration of the corresponding Newman projections for the *O*-benzyl groups in **1** and **2** (Fig. 5) leads to the conclusion that the group having phenyl ring C in **1** may be characterised by the conformation that approximates to variant *d* (Fig. 4). On the other hand, the *O*-benzyl groups (D) in both disaccharides conform to variant *a*.

The BzO-3 group in **1** is situated sterically in such a manner that C-20 is *anti* with respect to C-4, and *gauche* to C-2, of the rhamnopyranose ring [the torsion angles C-4–C-3–O-3–C-20 and C-2–C-3–O-3–C-20 are 149.5(3)° and −90.3(3)°, re-

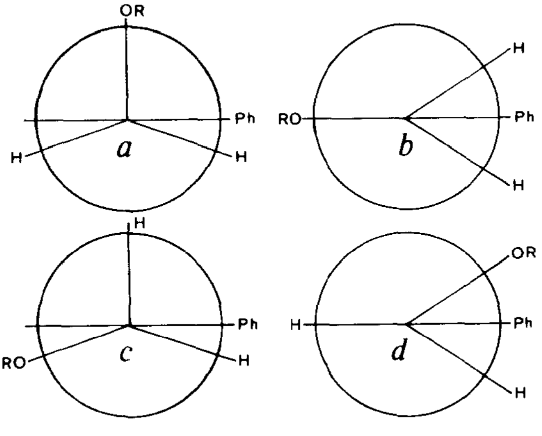

Fig. 4. Various conformations for *O*-benzyl groups.

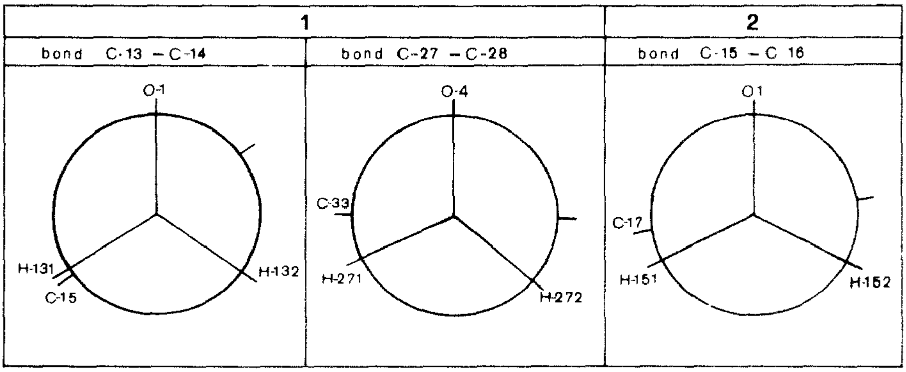

Fig. 5 The conformations of *O*-benzyl groups in **1** and **2**.

spectively]. The plane formed by O-3, C-20, and O-8 of the benzoyl fragment is twisted with respect to the least-squares planes (*a*) of the phenyl ring E by 13.5(2)° and (*b*) of the rhamnopyranose ring (through C-2, C-3, C-5, and O-5) by 91.7(2)°.

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