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Note

Conformation of 1,2-*O*-alkylidenehexopyranoses: tri-*O*-acetyl derivatives of D-allose and D-gulose

FELIX H. CANO, CONCHA FOCES-FOCES,
Departamento de Rayos X, Instituto de Química Física "Rocasolano", C.S.I.C., Serrano 119, 28006 Madrid (Spain)

JESUS JIMENEZ-BARBERO, MANUEL BERNABE, AND MANUEL MARTIN-LOMAS
Instituto de Química Orgánica, C.S.I.C., Juan de la Cierva 3, 28006 Madrid (Spain)
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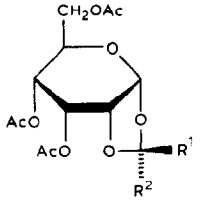
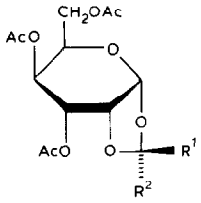
The conformation of the pyranoid ring of 1,2-*O*-alkylidenehexopyranoses has been investigated in the crystalline state and in solution[1–17]. The results indicate different conformations for 3,4,6-tri-*O*-acetyl-1,2-*O*-alkylidene-α-D-gluco- and -D-galacto-pyranose derivatives. Skew-boat ($^{o}S_{2}$) conformations have been assigned[17] to the pyranoid ring of 3,4,6-tri-*O*-acetyl-1,2-*O*-alkylidene-α-D-glucopyranoses in which the methyl or phenyl group at C-2 of the dioxolane ring (C-7 in the X-ray data) is *endo*, and distorted chair ($^{4}C_{1}$) conformations to the isomers having these groups *exo*. In contrast, the pyranoid rings of 3,4,6-tri-*O*-acetyl-1,2-*O*-alkylidene-α-D-galactopyranose derivatives have a distorted $^{4}C_{1}$ conformation that does not depend on the configuration at C-2 of the dioxolane ring[10,17].

In the solid state and in solution, the conformation of the pyranoid ring of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-ethylidene-α-D-allopyranose (**1**) is $^{o}S_{2}$ and is similar to that reported[10] for the *gluco* analogues. We now report on the crystal and molecular structure of 3,4,6-tri-*O*-acetyl-1,2-*O*-(*S*)-ethylidene-α-D-allopyranose (**2**), and the 300-MHz ^{1}H-n.m.r. spectra of **2**, 3,4,6-tri-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-



1 R^1 = H, R^2 = Me
2 R^1 = Me, R^2 = H
3 R^1 = CN, R^2 = Me



4 R^1 = O^{t}Bu, R^2 = Me
5 R^1 = CN, R^2 = Me
6 R^1 = H, R^2 = Me
7 R^1 = Me, R^2 = H

0008-6215/86/$ 03.50

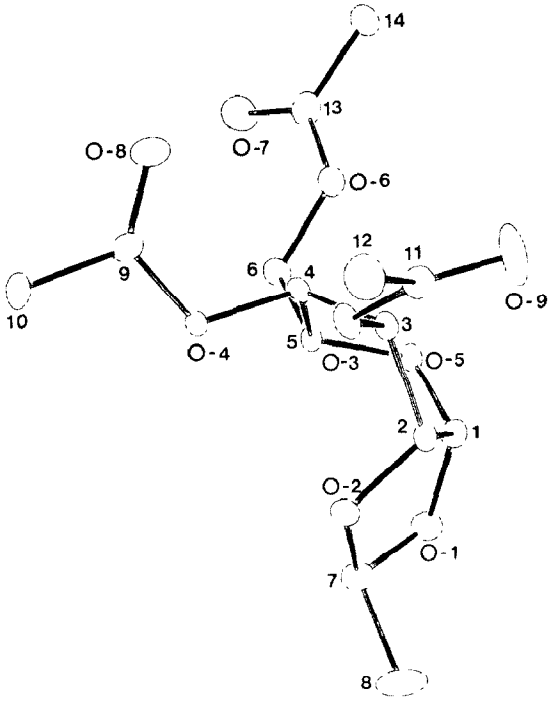


Fig. 1. ORTEP view of the structure of compound **2**, showing the atomic numbering

α-D-allopyranose (**3**), 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-(1-*tert*-butoxyethylidene)-α-D-gulopyranose (**4**), 3,4,6-tri-*O*-acetyl-1,2-*O*-(*S*)-(1-cyanoethylidene)-α-D-gulopyranose (**5**), 3,4,6-tri-*O*-acetyl-1,2-*O*-(*R*)-ethylidene-α-D-gulopyranose (**6**), and 3,4,6-tri-*O*-acetyl-1,2-*O*-(*S*)-ethylidene-α-D-gulopyranose (**7**). The calculated best ^3J values have been used in the general equation of Altona[18] in order to estimate the torsion angles.

Fig. 1 shows an ORTEP[19] representation of **2**. Final fractional co-ordinates for the non-hydrogen atoms are given in Table I. Table II shows the endocyclic torsion angles for **2** compared with those[10] for **1**. Table III shows the vicinal-proton torsion angles derived from the X-ray analysis.

Compound **2** is crystallographically pseudoisomorphic with **1**. The conformations of the pyranoid rings and the folding of the acetyl substituent chains in **1** and **2** are similar (see Fig. 1). Thus, the change in configuration at C-2 (C-7) in the dioxolane ring does not affect the conformation of the pyranoid ring nor the packing in the crystal. However, it does affect the conformation of the dioxolane ring, which is less puckered and flattened around the C-7–O-1 bond in **2**, so as to give a near-envelope at C-2, whereas for **1**, the conformation was a quasi-envelope at O-2, flattening the C-1–O-1 part of the ring.

The 300-MHz ^{1}H-n.m.r. spectra of the D-allopyranose derivatives **1**–**3**, the D-gulopyranose derivatives **4**–**6**, and a 1:1 mixture of **6** and **7** have been analysed

TABLE I

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C-1	0.0258(3)	0.2051(–)	−0.0613(4)	510(12)
O-1	−0.0234(3)	0.0725(7)	−0.1426(4)	721(11)
C-2	0.0963(3)	0.3035(7)	−0.1709(4)	508(12)
O-2	0.1203(3)	0.1809(7)	−0.2791(3)	632(10)
C-3	0.2065(3)	0.3695(7)	−0.0998(4)	448(11)
O-3	0.2778(3)	0.4590(6)	−0.2014(3)	553(9)
C-4	0.2814(3)	0.2326(7)	−0.0296(4)	414(10)
O-4	0.3620(2)	0.1598(6)	−0.1293(3)	455(7)
C-5	0.2061(3)	0.0877(7)	0.0249(4)	449(10)
O-5	0.0917(2)	0.1490(6)	0.0587(3)	504(8)
C-6	0.2555(4)	0.0082(7)	0.1594(5)	615(15)
O-6	0.2675(3)	0.1393(7)	0.2683(3)	683(10)
C-13	0.3291(5)	0.1068(9)	0.3885(5)	714(17)
O-7	0.3764(5)	−0.0255(9)	0.4096(5)	1183(21)
C-14	0.3387(7)	0.2550(12)	0.4863(6)	902(24)
O-8	0.5127(4)	0.2766(11)	−0.0111(7)	1379(26)
C-9	0.4762(3)	0.1891(9)	−0.1067(5)	644(15)
O-9	0.1999(4)	0.7011(7)	−0.1384(7)	1173(21)
C-10	0.5482(5)	0.1060(9)	−0.2152(7)	714(17)
C-11	0.2663(4)	0.6261(7)	−0.2078(5)	566(13)
C-12	0.3447(7)	0.7013(10)	−0.3151(9)	858(24)
C-7	0.0344(5)	0.0517(9)	−0.2734(6)	741(17)
C-8	−0.0507(9)	0.0673(19)	−0.3991(10)	1340(45)

TABLE II

EXPERIMENTAL TORSION ANGLES (°)[a] FOR THE PYRANOID AND DIOXOLANE RINGS

Angle	*Compound*	
	2	**1**
Pyranoid ring		
O-5–C-1–C-2–C-3	−20.6(5)	−19.6(5)
C-1–C-2–C-3–C-4	56.1(5)	55.1(5)
C-2–C-3–C-4–C-5	−30.8(5)	−30 7(5)
C-3–C-4–C-5–O-5	−27.3(5)	−27 5(5)
C-4–C-5–O-5–C-1	66.4(4)	66.6(5)
C-5–O-5–C-1–C-2	−40.0(5)	−40.8(5)
Dioxolane ring		
O-1–C-7–O-2–C-2	−14.0(6)	−38.8(5)
C-1–O-1–C-7–O-2	−2.7(6)	25.5(5)
C-2–C-1–O-1–C-7	16.9(5)	−2.9(5)
O-2–C-2–C-1–O-1	−24.4(4)	−20.4(5)
C-7–O-2–C-2–C-1	23.6(5)	35.9(5)

[a]E.s.d. values are given in parenthesis.

TABLE III

VICINAL-PROTON TORSION ANGLES (°)[a] DETERMINED BY THE X-RAY METHOD

Angle	*Compound*	
	2	**1**
H-1–C-1–C-2–H-2	−26(5)	−13(4)
H-2–C-2–C-3–H-3	62(5)	53(4)
H-3–C-3–C-4–H-4	−32(4)	−33(4)
H-4–C-4–C-5–H-5	−150(4)	−144(4)
H-5–C-5–C-6–H-6	60(4)	60(4)
H-5–C-5–C-6–H-6′	−63(5)	−67(4)

[a]E.s d values are given in parenthesis

TABLE IV

^{1}H-N M R SPECTRAL PARAMETERS FOR COMPOUNDS **1–7**

Parameter[a]	*Compound*[b]						
	1	**2**	**3**	**4**	**5**	**6**	**7**[c]
ν_1	5.167	5.262	5.847	5.608	4.941	5.582	5.65
ν_2	3.703	3.880	4.563	4.590	4.061	4.241	4.43
ν_3	5.111	5.225	5.176	5.162	5.135	5.143	5 15
ν_4	5 394	5.333	5.306	5.399	5.483	5 412	5.45
ν_5	4.312	4.148	4.032	4.327	4.240	4.472	4.31
ν_6	4.173	4.142	4.215	4.145	4.166	4.154	4 26
$\nu_{6'}$	4.135	4.132	4.176	4.145	4.085	4.154	4 26
$J_{1,2}$	5.5	4.9	5.4	5.1	5.2	5.4	4.7
$J_{1,3}$	−0.2	−0 1	−0.1	−0.1	0.2	0.1	
$J_{1,4}$	0.0	−0 4	−0.4	−0 1	−0.2	−0.1	
$J_{1,5}$	−0.7	−0.5	−0.4	−0.4	−0.5	−0 4	
$J_{1,6}$	−0.5	0 1	−0.1	0.1	−0.1	−0.1	
$J_{1,6'}$	0.0	−0.1	−0.1	0.0	−0.2	−0.1	
$J_{2,3}$	2.8	3.6	2.7	2.8	2.9	2.8	2.7
$J_{2,4}$	1.0	0.9	0.9	−0 1	−0.2	−0.2	
$J_{2,5}$	0.0	−0.2	−0 4	−0 1	−0.2	−0.2	
$J_{2,6}$	0.0	−0 1	0.0	0.0	−0.1	−0.1	
$J_{2,6'}$	0 0	−0.1	0.0	0.0	−0 1	−0.1	
$J_{3,4}$	6.3	5.4	6.2	6.7	6.4	6.6	6.6
$J_{3,5}$	0.0	−0.4	−0.3	−0.4	−0.2	−0.1	
$J_{3,6}$	0.0	−0.1	−0.1	0.0	−0.1	−0.1	
$J_{3,6'}$	0.0	−0.1	−0.1	0.0	−0.1	−0 1	
$J_{4,5}$	7.5	7 0	6 5	5.0	5.0	5.1	5.0
$J_{4,6}$	−0.2	−0.1	−0.1	−0.0	−0.1	−0.1	
$J_{4,6'}$	−0.5	−0.1	−0.1	−0.3	−0 2	−0.1	
$J_{5,6}$	3.2	3.3	3 5	6.4	6.2	6.3	5.6
$J_{5,6'}$	6.3	6.1	5.9	6.4	5.6	5.5	5.5
$J_{6,6'}$	−12.0	−11.5	−12.1	−11.9	−11.5	−11.4	−11 5

[a]$\nu(\delta)$ and J(Hz). [b]**1**, **2**, and **5** in C_6D_6; **3**, **4**, **6**, and **7** in $CDCl_3$. [c]First-order analysis in a 1:1 mixture of **6** + **7**

TABLE V

VICINAL-PROTON TORSION ANGLES (°) AS DETERMINED FROM THE $J_{H,H}$ VALUES[19]

Angle	*Compound*						
	1	**2**	**3**	**4**	**5**	**6**	**7**
H-1–C-1–C-2–H-2	−14	−20	−15	−18	−17	−15	−23
H-2–C-2–C-3–H-3	56	50	57	56	55	56	57
H-3–C-3–C-4–H-4	−28	−36	−29	−155	−152	−153	−153
H-4–C-4–C-5–H-5	−150	−146	−139	−26	−26	−25	−26

iteratively, and the best computed data are given in Table IV.

In the D-allopyranose derivatives, the ^3J values for **2** and **3** are similar to those[10] for **1**. Both **2** and **3** have a large and positive $J_{2,4}$ value which has been taken to indicate an average skew conformation of the pyranoid ring. This conformation must be similar to that determined in the solid state for **1** and **2**. Therefore, the average conformation of the pyranoid ring, both in the solid state and in solution, is not influenced by the configuration at C-2 of the dioxolane ring.

The vicinal H,H torsion angles calculated using the empirical generalisation of the Karplus equation proposed by Altona[18] are presented in Table V. Care should be taken when comparing the torsion angles estimated from n.m.r. data with those determined by X-ray analysis, but a reasonable agreement was found for **1** and **2**. In the D-gulopyranose derivatives, the computed ^3J values for **4–6** and those observed from the first-order analysis of the spectrum for **7** are indicative of a major skew-boat conformation of the pyranoid ring in each compound. Inspection of molecular models indicates that the value of $\phi_{3,4}$ could be used to distinguish between the $^4C_1$ and $^0S_2$ conformations. Although the torsion angles determined from vicinal couplings are only approximate, the general equation of Altona[18] accounts for a quasi-*trans* axial–axial arrangement of H-3,4 as expected for an $^0S_2$ conformation. If the conformation of the pyranoid ring had been $^4C_1$, $\phi_{3,4}$ should be in the range 50–60° and these angles could not account for the observed $J_{3,4}$ value of ~6.5 Hz.

N.O.e. experiments provide additional evidence of a major $^0S_2$ conformation of the pyranoid rings for **3–6** in solution. Thus, irradiation of the signal of the *endo*-methyl group of **3** and **6** induced increases of 7 and 6%, respectively, of the signal assigned to H-5, as previously reported[10] for **1**.

Thus, it is concluded that the pyranoid rings of the 3,4,6-tri-*O*-acetyl derivatives of 1,2-*O*-alkylidene-α-D-allopyranose (**1–3**) and 1,2-*O*-alkylidene-α-D-gulopyranose (**4–7**) adopt skew conformations and are not influenced by the configuration at C-2 (C-7) of the dioxolane ring.

EXPERIMENTAL

General methods. — Melting points were measured in capillary tubes and are uncorrected. T.l.c. was performed on Silica Gel GF_{254} (Merck) with detection by charring with sulfuric acid. Column flash chromatography was performed on Merck silica gel (230–400 mesh). Optical rotations were determined with a Perkin–Elmer 141 polarimeter.

3,4,6-Tri-O-acetyl-1,2-O-[(R)- and (S)-ethylidene]-α-D-allopyranose (**1** *and* **2**). — Flash chromatography (hexane–ethyl acetate, 4:1) of the mixture of diastereoisomers prepared[23] from crude penta-*O*-acetyl-β-D-allopyranose, with subsequent crystallisation from 2-propanol, gave **1**, m.p. 111–113°, $[\alpha]_D^{20}$ +33° (*c* 0.5, chloroform) {lit.[23] m.p. 108–112°, $[\alpha]_D^{20}$ +35° (chloroform)}, and **2**, m.p. 108–112°, $[\alpha]_D^{20}$ +26° (*c* 0.5, chloroform).

Anal. Calc. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found (for **2**): C, 50.70; H, 6.12.

3,4,6-Tri-O-acetyl-1,2-O-(S)-(1-cyanoethylidene)-α-D-allopyranose (**3**). — A solution of crude tetra-*O*-acetyl-α-D-allopyranosyl bromide [prepared from penta-*O*-acetyl-β-D-allopyranose (1.95 g, 5 mmol) by conventional treatment with HBr–HOAc–Ac_2O] in dry acetonitrile (15 mL) was treated[24] with potassium cyanide (1.63 g, 25 mmol) and tetrabutylammonium bromide (750 mg, 2.5 mmol) for 24 h. The mixture was then diluted with chloroform (100 mL), washed with water (5 × 50 mL), passed through a bed of silica gel, and concentrated. Flash chromatography (hexane–ethyl acetate, 4:1) of the residue gave **3** (1.12 g, 63%), m.p. 169–170° (from ethanol), $[\alpha]_D^{20}$ +3° (*c* 2, chloroform).

Anal. Calc. for $C_{15}H_{19}NO_9$: C, 50.42; H, 5.37; N, 3.92. Found: C, 50.51; H, 5.72; N, 3.80.

3,4,6-Tri-O-acetyl-1,2-O-(R)-(1-tert-butoxyethylidene)-α-D-gulopyranose (**4**). — A solution of crude tetra-*O*-acetyl-α-D-gulopyranosyl bromide [prepared from penta-*O*-acetyl-β-D-gulopyranose[25] (1.47 g, 3.75 mmol) by conventional treatment with HBr–HOAc–Ac_2O] in dry nitromethane (15 mL) was stirred with *tert*-butyl alcohol (0.9 g, 12.5 mmol) and 2,4,6-trimethylpyridine (0.6 g, 5 mmol) at room temperature for 24 h. Benzene (20 mL) was added, and the mixture was filtered and concentrated. Column chromatography (hexane–ethyl acetate, 4:1) of the residue afforded **4** (700 mg, 46%) as a syrup, $[\alpha]_D^{20}$ +29° (*c* 0.5, chloroform).

Anal. Calc. for $C_{18}H_{28}O_{10}$: C, 53.46; H, 6.98. Found: C, 53.21; H, 7.13.

3,4,6-Tri-O-acetyl-1,2-O-(S)-(1-cyanoethylidene)-α-D-gulopyranose (**5**). — Crude tetra-*O*-acetyl-α-D-gulopyranosyl bromide [prepared from penta-*O*-acetyl-β-D-gulopyranose (0.97 g, 2.5 mmol) by conventional treatment with HBr–HOAc–Ac_2O] was treated as described for the allopyranosyl analogue, to yield **5** (380 mg, 38%), $[\alpha]_D^{20}$ +29° (*c* 0.5, chloroform).

Anal. Calc. for $C_{15}H_{19}NO_9$: C, 50.42; H, 5.37; N, 3.92. Found: C, 50.32; H, 5.24; N, 3.71.

3,4,6-Tri-O-acetyl-1,2-O-[(R)- and (S)-ethylidene]-α-D-gulopyranose (**6** *and* **7**). — A solution of crude tetra-*O*-acetyl-α-D-gulopyranosyl bromide [prepared

TABLE VI

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE FOR COMPOUND **2**

Crystal data	
Formula	$C_{14}H_{20}O_9$
Crystal habit	Transparent, colourless, prismatic
Crystal size (mm)	0.10× 0.17 × 0.37
Symmetry	Monoclinic, $P2_1$
Unit-cell determination	Least squares fit from 86 reflections up to $\theta = 45$ (CuKα)
Unit-cell dimensions (Å)	11.4581(2), 7.9222(1), 9.2491(1), 91.422(2)
Packing: V (Å^3), Z	839.31(2), 2
D (g.cm^{-3}), M, F(000)	1.311, 331.30, 350
Experimental data	
Radiation and technique	CuKα. Four-circle PW 1100 Philips diffractometer
Monochromator	Graphite oriented
Collection mode (w/2θ)	θ <65
Total independent data	1539
Observed data	1412 (4$\sigma(I)$)
Stability	Two reflections every 90 min; no variation
Solution and refinement	X-Ray 76 System[20]. Vax 11/750
Solution	Multan 80[21]
Refinement mode	Least squares on F's. Observed reflections only. Full matrix
Final shift/error	0.12
Parameters:	
no. of variables	287
degrees of freedom	1125
ratio of freedom	4.9
Weighting scheme	Empirical to give no trends in $\langle w \Delta^2 \rangle$ vs. $\langle \lvert F_o \rvert \rangle$ or $\langle \sin \theta/\lambda \rangle$
Max. thermal factors (Å^2)	U22(08) = 0.215(7)
Final ΔF peaks	0.29
Final R, R_w	0.044, 0.050
Atomic factors	International Tables for X-Ray Crystallography[22]

from penta-*O*-acetyl-β-D-gulopyranose (0.97 g, 2.5 mmol) by conventional treatment with HBr–HOAc–Ac_2O] in acetonitrile (10 mL) was stirred[26] with sodium borohydride (150 mg, 3.8 mmol) and tetrabutylammonium iodide (500 mg, 1.2 mmol) at room temperature for 24 h. The mixture was diluted with chloroform (100 mL), washed with water (3 × 100 mL), filtered through cotton, and concentrated to dryness. Flash chromatography (hexane–ethyl acetate, 4:1) of the residue gave **6** (300 mg, 39%) as a syrup, $[\alpha]_D^{20}$ +63° (*c* 0.5, chloroform).

Anal. Calc. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.47; H, 6.35.

Eluted second was a 1:1 (^{1}H-n.m.r. data) mixture (90 mg, 12%) of **6** and **7**, $[\alpha]_D^{20}$ +42° (*c* 0.5, chloroform).

Anal. Found: C, 50.52; H, 6.26.

X-Ray data. — Crystal and experimental data and refinement parameters are given in Table VI.

^{1}H-N.m.r. spectroscopy. — The 300-MHz spectra (internal Me_4Si) were recorded for solutions in $CDCl_3$ (for **3, 4, 6,** and **6** + **7**) or C_6D_6 (**1, 2,** and **5**) with a

Varian XL-300 spectrometer. Analyses were performed by an ASPECT 2000 data system using a PANIC programme. The experimental and calculated spectra from the resulting best values matched satisfactorily.

Supplementary material. — Bond distances and bond angles, thermal parameters, hydrogen co-ordinates, and structure factor tables have been 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/323/*Carbohydr. Res.*, 145 (1986) 319–327.

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