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THE STRUCTURE OF THE ISOMERS OF METHYL 2,3-*O*-D-GLUCOPYRANOSYLIDENE-α-D-MANNOPYRANOSIDE HEXA-ACETATE

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ABSTRACT

The absolute configuration at the orthoester carbon atom of one of the two isomers of the title compound has been determined by X-ray analysis. Also, ^{1}H- and ^{13}C-n.m.r. data for the isomers are reported.

INTRODUCTION

We have reported[1,2] a new method for the synthesis of methyl 2,3-*O*-glycopyranosylidene-α-D-mannopyranosides, using trimethylsilyl trifluoromethanesulfonate as catalyst, and a series of analogues has been synthesised. However, the reaction usually gave an (*R,S*)-mixture at the orthoester carbon, with the isomers differing in the chemical shift (p.p.m.) of the signal of the orthoester carbon and optical rotation. We now describe the conversion of the isomers (**1a** and **1b**) of fully *O*-benzylated methyl 2,3-*O*-D-glucopyranosylidene-α-D-mannopyranoside into the corresponding hexa-acetates (**5a** and **5b**) and the determination of the absolute configuration of **5a** by X-ray analysis. The ^{1}H- and ^{13}C-n.m.r. data of **5a** and **5b** have also been obtained.

RESULTS AND DISCUSSION

Two isomers of methyl 4,6-di-*O*-benzyl-2,3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosylidene)-α-D-mannopyranoside[1] {**1a**, $[\alpha]_D$ +28° (chloroform), δ C-1′ 120.4; **1b**, $[\alpha]_D$ +10° (chloroform), δ C-1′ 119.0} were hydrogenolysed over Pd/C to give **2a** and **2b**, respectively. These isomers were also obtained from the methyl

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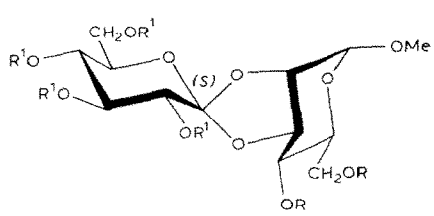
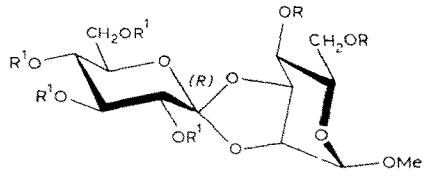


1a R = R' = Bzl
2a R = R' = H
3a R = Ac, R' = Bzl
4a R = H, R' = Bzl
5a R = R' = Ac



1b R = R' = Bzl
2b R = R' = H
3b R = Ac, R = Bzl
4b R = H, R' = Bzl
5b R = R' = Ac

4,6-di-*O*-acetyl-1,2-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosylidene)-α-D-mannopyranosides (**3a** and **3b**) *via* the *O*-deacetylation products **4a** and **4b**. Acetylation of **2a** and **2b** gave the crystalline title compounds, **5a** and **5b**, respectively.

X-Ray analysis. — The isomer **5a** was obtained as transparent prisms by slow concentration of a solution in ethyl acetate–hexane. The lattice constants and intensity data were obtained using a Nicolet P3/F four-circle diffractometer with graphite-monochromated CuKα radiation and a crystal having dimensions 0.38 × 0.28 × 0.20 mm. The space group was determined from systematic absences. The crystal data are listed in Table I. Of 2844 independent reflections measured within $2\theta < 150°$, 2620 had intensities greater than $3\sigma(|F_0|)$ and these were used for the structure analysis. No correction was made for absorption. The structure was solved by the direct method[3], and the structural parameters were refined by the full-matrix least-squares method[4]. All of the hydrogen atoms were located at the geometrically expected positions and excluded from the refinement. The weighting scheme used in the final stage was $W = 5.3766/[\sigma^2(F_0) + 0.000611\ (F_0)^2]$. Atomic scattering factors were taken from ref. 5. The final atomic* parameters are listed in Table II, and interatomic distances and angles are given in Table III. Both of the C–O bonds in the five-membered orthoester ring are slightly short[6,7], as was observed for the anomeric C–O bond in aldopyranosides[8]. Other bond distances and angles show the values common in carbohydrate derivatives, except for C-2′–C-1′ which is slightly short.

The ORTEP drawing[9] of **5a** shown in Fig. 1 also gives the thermal ellipsoids and the atomic notation. From the spatial relationship of the D-mannopyranoside and D-glucopyranosylidene moieties, the absolute configuration of the orthoester carbon atom of **5a** was determined to be (*S*). Therefore, the absolute configurations

*A complete list of atoms with thermal parameters and the list of observed and calculated structure-factors can be obtained from the author, or from Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/298/*Carbohydr. Res.*, 136 (1985) 1–11

TABLE I

CRYSTAL DATA FOR **5a**

$C_{25}H_{34}O_{17}$; mol. wt. 606.5; monoclinic $P2_1$

Lattice constants
a = 9.568(1) Å, b = 8.893(1) Å
c = 18.175(2) Å, β = 94.66(1)°
U = 1541.3(3) Å^3, Z = 2, D_x = 1.26 g.cm^{-3}
λ(CuKα) = 1.5418 Å, μ(CuKα) = 8.68 cm^{-1}

TABLE II

FRACTIONAL ATOMIC CO-ORDINATES AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS[a]

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
C-1′	0.4389(5)	0.8616(6)	0.2834(2)	3.84(10)
C-2′	0.4886(5)	0.8618(6)	0.2084(3)	4.07(10)
C-3′	0.3687(5)	0.8983(6)	0.1507(2)	3.86(10)
C-4′	0.2559(5)	0.7821(6)	0.1577(2)	3.96(10)
C-5′	0.2137(4)	0.7812(6)	0.2367(2)	3.68(10)
C-6′	0.1063(5)	0.6607(6)	0.2514(3)	4.30(10)
C-7′	0.7240(6)	0.9245(8)	0.1842(4)	6.50(11)
C-8′	0.8201(7)	1.0490(9)	0.1758(5)	8.32(11)
C-9′	0.4142(6)	1.0144(7)	0.0376(3)	6.04(11)
C-10′	0.4717(8)	0.9923(9)	−0.0358(4)	8.47(11)
C-11′	0.0982(6)	0.7333(7)	0.0525(3)	5.45(11)
C-12′	−0.0357(7)	0.7785(10)	0.0137(4)	8.13(11)
C-13′	0.1005(7)	0.4101(8)	0.2086(5)	7.36(11)
C-14′	0.1725(8)	0.2647(8)	0.1998(5)	8.48(11)
O-S1	0.5464(3)	0.8198(5)	0.3372(2)	4.01(9)
O-S2	0.3935(3)	1.0065(4)	0.3012(2)	3.53(8)
O-2′	0.5994(3)	0.9712(5)	0.2018(2)	4.84(9)
O-2′A	0.7494(5)	0.7949(7)	0.1736(4)	9.62(11)
O-3′	0.4177(4)	0.8904(5)	0.0776(2)	5.00(9)
O-3′A	0.3726(7)	1.1291(7)	0.0586(3)	9.68(11)
O-4′	0.1341(3)	0.8194(5)	0.1107(2)	4.66(9)
O-4′A	0.1693(6)	0.6258(7)	0.0372(3)	8.57(11)
O-5′	0.3335(3)	0.7537(4)	0.2875(2)	3.66(8)
O-6′	0.1656(4)	0.5166(5)	0.2408(3)	6.00(10)
O-6′A	−0.0137(7)	0.4418(9)	0.1647(5)	12.90(11)
C-1	0.6309(4)	0.9000(6)	0.4610(2)	3.86(10)
C-2	0.5802(4)	0.9494(6)	0.3834(3)	3.60(10)
C-3	0.4412(4)	1.0340(5)	0.3776(2)	3.42(10)
C-4	0.3384(4)	0.9734(5)	0.4295(2)	3.49(10)
C-5	0.4138(5)	0.9608(6)	0.5066(2)	3.79(10)
C-6	0.3181(6)	0.9036(7)	0.5626(3)	5.30(10)
C-7	0.7599(6)	1.0051(8)	0.5653(3)	6.14(11)
C-8	0.0962(5)	1.0301(7)	0.4157(4)	5.83(11)
C-9	−0.0102(6)	1.1539(8)	0.4148(4)	7.46(11)
C-10	0.3467(9)	0.8770(10)	0.6929(4)	9.41(11)
C-11	0.4150(9)	0.9099(9)	0.7628(4)	9.15(11)
O-1	0.6993(3)	1.0287(5)	0.4922(2)	4.37(9)
O-4	0.2252(3)	1.0815(5)	0.4299(2)	4.21(9)
O-4A	0.0703(5)	0.8986(7)	0.4090(4)	9.72(11)
O-5	0.5215(3)	0.8510(4)	0.5018(2)	3.93(9)
O-6	0.3932(5)	0.9159(6)	0.6345(2)	7.11(10)
O-6A	0.2329(8)	0.7927(11)	0.6882(4)	14.96(11)

[a] $B_{eq} = 8/3\ \pi^2\ \Sigma\Sigma U_{ij} a_i^* a_j^* a_i a_j$. Estimated standard deviations are given in parentheses.

TABLE III

SELECTED MOLECULAR PARAMETERS OF **5a**[a]

Bond	*Bond distance*	*Bond*	*Bond distance*
C-2′–C-1′	1.481(6)	C-13′–C-14′	1.480(10)
O-S1–C-1′	1.410(5)	O-6′–C-13′	1.252(8)
O-S2–C-1′	1.407(5)	O-6′A–C-13′	1.329(9)
O-5′–C-1′	1.398(5)	O-S1–C-2	1.446(5)
C-2′–C-3′	1 524(6)	O-S2–C-3	1.446(5)
O-2′–C-2′	1.452(6)	C-1–C-2	1.520(6)
C-3′–C-4′	1.507(6)	O-1–C-1	1.414(5)
O-3′–C-3′	1.446(5)	O-5–C-1	1.400(5)
C-4′–C-5′	1.524(6)	C-2–C-3	1.525(6)
O-4′–C-4′	1.427(5)	C-3–C-4	1.517(6)
C-5′–C-6′	1.523(7)	C-4–C-5	1.527(6)
O-5′–C-5′	1.432(5)	O-4–C-4	1.449(5)
O-6′–C-6′	1.421(7)	C-5–C-6	1.511(6)
C-7′–C-8′	1.455(9)	O-5–C-5	1.427(5)
O-2′–C-7′	1.326(6)	O-6–C-6	1.443(7)
O-2′A–C-7′	1.196(8)	O-1–C-7	1.423(6)
C-9′–C-10′	1.497(8)	C-8–C-9	1.498(8)
O-3′–C-9′	1.319(7)	O-4–C-8	1.322(6)
O-3′A–C-9′	1.170(7)	O-4A–C-8	1.199(8)
C-11′–C-12′	1.476(8)	C-10–C-11	1.411(11)
O-4′–C-11′	1.328(6)	O-6–C-10	1.233(8)
O-4′A–C-11′	1.219(7)	O-6A–C-10	1 241(10)

Bonds	*Bond angle*	*Bonds*	*Bond angle*
O-S1–C-1′–C-2′	111.6(3)	C-1′–O-S2–C-3	107.2(3)
O-S2–C-1′–C-2′	109.8(4)	C-2′–O-2′–C-7′	119.1(4)
O-S2–C-1′–O-S1	107.7(3)	C-3′–O-3′–C-9′	118 0(4)
O-5′–C-1′–C-2′	109.6(3)	C-4′–O-4′–C-11′	119.2(4)
O-5′–C-1′–O-S1	105.8(4)	C-1′–O-5′–C-5′	113.1(3)
O-5′–C-1′–O-S2	112.3(3)	C-6′–O-6′–C-13′	123.8(4)
C-1′–C-2′–C-3′	110.7(3)	O-1–C-1–C-2	103.9(4)
O-2′–C-2′–C-1′	111.6(4)	O-5–C-1–C-2	112.7(3)
O-2′–C-2′–C-3′	108.3(4)	O-1–C-1–O-5	112.4(4)
C-2′–C-3′–C-4′	107.4(4)	O-S1–C-2–C-1	110.4(4)
O-3′–C-3′–C-2′	109.8(3)	O-S1–C-2–C-3	101.6(3)
O-3′–C-3′–C-4′	109.4(3)	C-1–C-2–C-3	114.7(3)
C-3′–C-4′–C-5′	109.2(3)	O-S2–C-3–C-2	100.9(3)
O-4′–C-4′–C-3′	110.2(4)	O-S2–C-3–C-4	111.5(3)
O-4′–C-4′–C-5′	107.4(3)	C-2–C-3–C-4	112 8(3)
C-4′–C-5′–C-6′	113.7(4)	C-3–C-4–C-5	108.4(3)
C-4′–C-5′–O-5′	110.4(3)	O-4–C-4–C-3	106.8(3)
O-5′–C-5′–C-6′	106.5(4)	O-4–C-4–C-5	110.0(3)
O-6′–C-6′–C-5′	109.2(4)	C-4–C-5–C-6	112.1(4)
O-2′–C-7′–C-8′	112.0(6)	O-5–C-5–C-4	106.5(3)
O-2′A–C-7′–C-8′	125.3(6)	O-5–C-5–C-6	106.9(4)
O-2′A–C-7′–O-2′	122.6(6)	O-6–C-6–C-5	107.4(4)
O-3′–C-9′–C-10′	112.7(5)	O-4–C-8–C-9	111.8(5)
O-3′A–C-9′–C-10′	124.3(6)	O-4A–C-8–C-9	125.5(5)
O-3′A–C-9′–O-3′	122.9(5)	O-4A–C-8–O-4	122.6(5)
O-4′–C-11′–C-12′	112.6(5)	O-6–C-10–C-11	122.9(7)

TABLE III *(continued)*

Bonds	*Bond angle*	*Bonds*	*Bond angle*
O-4′A–C-11′–C-12′	125.9(6)	O-6A–C-10–O-11	119.8(8)
O-4′A–C-11′–O-4′	121.4(5)	O-6A–C-10–O-6	116.9(8)
O-6′–C-13′–C-14′	119.5(6)	C-1–O-1–C-7	113.3(4)
O-6′A–C-13′–C-14′	119.2(7)	C-4–O-4–C-8	117.2(4)
O-6′A–C-13′–O-6′	118.3(7)	C-1–O-5–C-5	113.2(3)
C-2–O-S1–C-1′	108.0(3)	C-6–O-6–O-10	124.7(6)

[a]Bond lengths in Å, angles in degrees. Estimated standard deviations are given in parentheses.

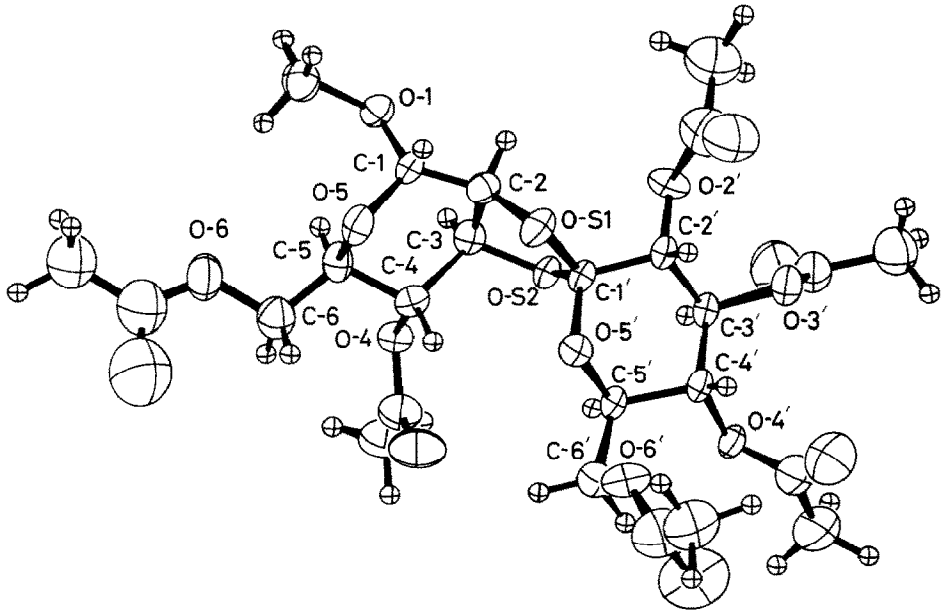


Fig. 1. Molecular model of compound **5a**.

of paired isomers of various reported derivatives[2] can now be assigned on the basis of the chemical shift of the resonance for the orthoester carbon atoms and the optical rotational values.

The X-ray analysis of a derivative of destomycin A disclosed[6] destomic acid-1,5-lactone to be linked with the (*R*) configuration to the *cis*-2,3-diol function of the D-talopyranose moiety in the $B_{1,4}$ conformation. However, the D-mannopyranose moiety in **5a** exists in the $^4C_1$(D) conformation. The intracyclic torsional angles in Table IV indicate that the D-mannopyranose ring is flattened at C-2 and C-3, whereas the D-glucopyranosylidene ring adopts a perfect $^4C_1$(D) conformation. The intracyclic torsional angles of the five-membered ring, and the equation of the plane and the deviation of each atom from the plane shown in Table V indicate an envelope conformation in which C-3, instead of O-3 of the D-talopyranose ring for destomycin A[6], deviated significantly from the average plane of the other four

TABLE IV

SELECTED TORSIONAL ANGLES (°)

C-1–C-2–C-3–C-4	−37.0	O-S1–C-2–C-3-O-S2	−37.1
C-2–C-3–C-4–C-5	49.7	C-2–C-3–O-S2-C-1′	34.0
C-3–C-4–C-5–O-5	−64.4	C-3–O-S2–C-1′–O-S1	−17.9
C-4–C-5–O-5–C-1	69.9	C-2–O-S1–C-1′–O-S2	−7.6
C-5–O-5–C-1–C-2	−56.3	C-1′–O-S1–C-2–C-3	28.0
O-5–C-1–C-2–C-3	38.5	C-4–C-5–C-6–O-6	−172.1
C-1′–C-2′–C-3′–C-4′	−58.2	O-5–C-5–C-6–O-6	71.6
C-2′–C-3′–C-4′–C-5′	55.8	C-4′–C-5′–C-6′–O-6′	62.9
C-3′–C-4′–C-5′–O-5′	−56.8	O-5′–C-5′–C-6′–O-6′	−58.9
C-4′–C-5′–O-5′–C-1′	59.6		
C-5′–O-5′–C-1′–C-2′	−60.6		
C-3′–C-2′–C-1′–O-5′	59.8		

TABLE V

LEAST-SQUARES PLANE AND DEVIATIONS (Å) OF ATOMS FROM THE PLANE
$-0.6958x - 0.3545y + 0.6247z + 2.099 = 0.0$[a]

C-1′	−0.040	C-2	−0.024
O-S1	0.040	C-3[b]	0.563
O-S2	0.025		

[a]x, y, and z refer to crystallographic axes *a*, *b*, and *c**, respectively [b]Atom not included in the least-squares calculation.

atoms. It is clear from the data in Table IV that the relationships of the C-6–O-6 and C-6′–O-6′ bonds to the C-5–C-6, O-5–C-6 and C-5′–C-6′, O-5′–C-6′ bonds are *trans-gauche* and *gauche-gauche*, respectively.

The crystal structure of **5a** viewed along the *a* axis is shown in Fig. 2.

N.m.r. spectroscopy. — Signals in the 500-MHz ^{1}H-n.m.r. spectra of **5a** and **5b** could be easily assigned (Table VI), and the coupling constants indicate that the D-glucopyranosylidene and D-mannopyranoside rings exist in typical and flattened $^4C_1$(D) conformations, respectively (Fig. 1). The dihedral angles calculated using modified Karplus equations[10–12], and shown in Table VII, indicate that the D-mannopyranoside ring of **5a** is slightly more flattened in solution than in the solid state, due to more-flexible molecular motions, and that the tendency is slightly larger in **5b** than in **5a**. Dreiding models suggest that the C-2 side of the D-glucopyranosylidene ring in the (*R*)-isomer is slightly crowded by the D-mannopyranoside ring and its substituents. Thus, the chemical shifts of the signals for H-4 of the (*S*)-isomer (**5a**) and H-2 of the (*R*)-isomer (**5b**) reflect the shielding effect. It is characteristic that the resonances of H-6 and H-6′ of the (*R*)-isomer appeared as a doublet.

The ^{13}C-n.m.r. signals of **5a** and **5b** were assigned as shown in Table VIII on the basis of their splittings and by selective ring-proton decoupling, and those of

TABLE VI

^{1}H-N M R PARAMETERS OF METHYL 2,3-*O*-D-GLUCOPYRANOSYLIDENE-α-D-MANNOPYRANOSIDE DERIVATIVES

Compound	*Chemical shifts (δ) and coupling constants (Hz)*[a]												
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5}$)	*H-5* ($J_{5,6a}$)	*H-6a* ($J_{5,6b}$)	*H-6b* ($J_{6a,6b}$)	*H-2'* ($J_{2',3'}$)	*H-3'* ($J_{3',4'}$)	*H-4'* ($J_{4',5'}$)	*H-5'* ($J_{5',6'a}$)	*H-6'* ($J_{5',6'b}$)	*H-6'b* ($J_{6'a,6'b}$)
3a	4.95s	4.18d	4.33dd	5.47dd	3.7–3.9m	4.23dd	4.06dd			3.6–4.0m			
	(0)	(6.1)	(7.7)	(10.6)	(5.4)	(2.5)	(12.2)						
3b	5.04s	4.36d	4.55t	5.04dd	3.8–3.9m	4.05d				3.6–4.0m			
	(0)	(6.5)	(6.4)	(10.3)	(3.9)								
5a	5.00s	4.10d	4.46dd	5.40dd	3.82ddd	4.25dd	4.11dd	5.26d	5.31t	5.24t	4.16ddd	4.35dd	4.25dd
	(0)	(6.0)	(7.4)	(10.7)	(5.4)	(2.0)	(12.1)	(10.1)	(9.4)	(10.1)	(3.4)	(2.0)	(12.8)
5b	5.07s	4.33d	4.46t	4.92dd	3.81dt	4.13d		5.34d	5.36t	5.17t	3.99ddd	4.19dd	4.07dd
	(0)	(6.4)	(6.4)	(11.1)	(3.8)			(9.4)	(9.4)	(9.4)	(3.8)	(2.2)	(12.4)

[a]Other protons: **3a**, δ 3.36 (s, OMe), 2.02 (s, 2 Ac), 4.80 and 4.90, 4.77 and 4.83, 4.53 and 4.79, 4.46 and 4.71 (4 ABq, each 2 H, *J* 11.5, 11.5, 10.7, and 12.2 Hz, 4 CH_2Ph); **3b**, 3.37 (s, OMe), 2.03 and 1.92 (2 s, each 3 H, 2 Ac), 5.13 and 4.76, 4.87 and 4.76, 4.81 and 4.49, 4.60 and 4.46 (4 ABq, each 2 H, *J* 11.2, 11.0, 10.7, and 12.0 Hz, 4 CH_2Ph); **5a**, 3.39 (s, OMe), 2.07, 2.07, 2.05, 2.05, 2.01 and 1.99 (6 s, each 3 H, 6 Ac); **5b**, 3.43 (s, OMe), 2.20, 2.08, 2.07, 2.05, 2.03, and 2.00 (6 s, each 3 H, 6 Ac).

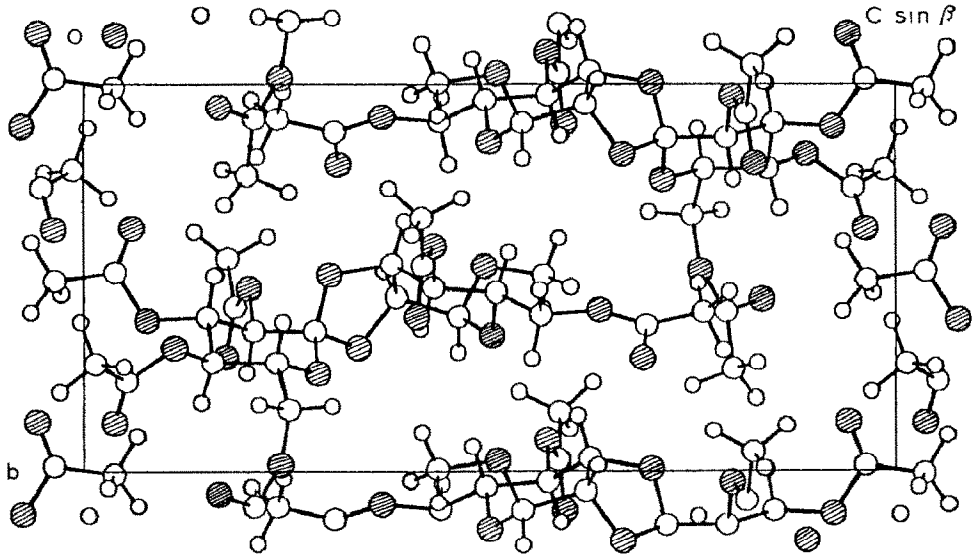


Fig. 2. Projection of the crystal structure along the *a* axis. Shaded atoms are oxygens.

TABLE VII

COMPARISON OF DIHEDRAL ANGLES (°) FOR VICINAL RING-PROTONS[a]

Compound	*Calculation method*	*Vicinal protons*						
		1,2	*2,3*	*3,4*	*4,5*	*2',3'*	*3',4'*	*4',5'*
5a	a[10]	79.5	31	150	(180)	(180)	(180)	(180)
	b[11]	80	35	150	(180)	175	165	175
	c[12]	(90)	33	158	(180)	173.5	174	(180)
	d[b]	81 5	37	169.7	175.6	178.2	175.8	176.8
5b	a[10]	79.5	28	147	(180)	(180)	(180)	(180)
	b[11]	80	32	143	(180)	165	165	165
	c[12]	(90)	29.5	152	(180)	167.5	174	168

[a]Angles in parentheses are those from scaled-out *J* values for the equations. [b]From X-ray data.

other compounds by reference to the data for α-D-mannopyranoside[13–17] and α,β-D-glucopyranoside derivatives[17–20].

Except for the substituent and solvent effects, the difference in the chemical shift between (*R*)- and (*S*)-isomers is due to the shielding effect of neighboring atoms in the crowded area C-2,3,4,1',2', in addition to those caused by the conformational difference of the central five-membered ring. Actually, a larger difference was observed in the chemical shift of the signals of these carbons. It is characteristic that C-2,3,1',2' of the (*S*)-isomer are more shielded than the corresponding carbon atoms of the (*R*)-isomer.

TABLE VIII

^{13}C CHEMICAL SHIFT (p.p.m.) DATA FOR RING-CARBON ATOMS OF **2–5**[a,b]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*OMe*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*
2a	98.30	79.70	80.68	70.43[c]	68.57	61.79	56.08	121.3	73.74	76.63	71.11[c]	75.45	61.79
2b	98.15	75.89	79.89	70.48[c]	69.06	61.69	56.08	120.0	71.69[c]	75.89	70.57[c]	75.75	61.69
3a	97.69	78.29	81.27	68.54	65.78	62.47	54.94	120.8	76.88	83.55	77.26	73.79	68.00
3b	97.85	77.75	78.73	70.27	65.34	62.85	54.89	119.3	74.60	83.87	76.67	73.20	68.60
4a	97.74	79.91	81.11	69.30	68.38	62.42	54.94	120.2	77.91	83.60	78.45	73.79	69.14
4b	97.42	79.16	79.48	69.62	68.59	62.69	54.89	119.0	74.66	83.92	77.86	73.20	68.59
5a	97.31	77.48	79.05	70.29	65.51	62.09	55.10	119.1	68.11	72.00	67.46	71.09	61.17
5b	97.23	75.01	77.15	69.11	65.21	62.38	55.07	117.7	67.55	72.23	67.94	70.33	61.51

[a]Data for carbon atoms in acetyl and benzyl groups are omitted. [b]A solution of **2** in D_2O was used, and solutions in $CDCl_3$ for **3–5**. [c]Assignments may be interchanged.

EXPERIMENTAL

General methods. — All melting points are uncorrected. The solutions were concentrated under diminished pressure at ≯50° (bath). Optical rotations were measured with a Carl Zeiss LEP-Al polarimeter. I.r. spectra were recorded with a JASCO Model A-102 spectrometer. ^{1}H-N.m.r. spectra were recorded with a JEOL PS-100 spectrometer or Bruker AM-500 spectrometer, for solutions in $CDCl_3$ (internal Me_4Si) unless otherwise stated. ^{13}C-N.m.r. spectra were recorded with a JEOL FX-90 spectrometer for solutions in $CDCl_3$ unless otherwise stated. Chromatography was performed on Wakogel C-200, flash chromatography on Wakogel C-300, and preparative t.l.c. on silica gel 60 (Merck).

Methyl 4,6-di-O-acetyl-2,3-O-[(1S)-2,3,4,6-tetra-O-benzyl-D-glucopyranosylidene]-α-D-mannopyranoside (**3a**) *and its (1R)-isomer* (**3b**). — Condensation of 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone and methyl 4,6-di-*O*-acetyl-2,3-di-*O*-(trimethylsilyl)-α-D-mannopyranoside in the presence of trimethylsilyl trifluoromethanesulfonate, under conditions previously reported[2], afforded 77.4% of a mixture of **3a** and **3b**. Flash chromatography (3:1 hexane–ether) of the mixture gave syrupy **3a** (51.5%), $[\alpha]_D$ +29.5° (*c* 1.3, chloroform); ν_{max}^{NaCl} 1742 cm^{-1} (ester); and **3b** (18.7%), $[\alpha]_D$ +27.7° (*c* 1, chloroform); ν_{max}^{NaCl} 1750 cm^{-1} (ester).

Anal. Calc. for $C_{45}H_{50}O_{13}$: C, 67.66; H, 6.31. Found: **3a** C, 67.25; H, 6.29; **3b** C, 67.16; H, 6.42.

Deacetylation of **3a** *and* **3b**. — A solution of **3a** or **3b** (1 mmol) in methanolic 10–25mM sodium methoxide (30 mL) was stirred at room temperature overnight, neutralised with acetic acid, and concentrated. The product (**4a** or **4b**) was purified by column chromatography (1:1 hexane–ethyl acetate).

Methyl 2,3-*O*-[(1*S*)-2,3,4,6-tetra-*O*-benzyl-D-glucopyranosylidene]-α-D-mannopyranoside (**4a**, 70.4%) had m.p. 108–111.5° (from ethanol–hexane), $[\alpha]_D$ +29.7° (*c* 1.1, chloroform). The (1*R*)-isomer **4b** was obtained as a syrup (69.5%), $[\alpha]_D$ +6.5° (*c* 1.8, chloroform).

Anal. Calc. for $C_{41}H_{46}O_{11}$: C, 68.89; H, 6.49. Found: **4a** C, 68.77; H, 6.66; **4b** C, 69.01; H, 6.60.

Hydrogenation of **1a** *and* **1b**. — A suspension of **1a** or **1b** (1 mmol) and 10% Pd/C (600–700 mg) in methanol (~100 mL) and acetic acid (0.5–3%) was hydrogenated at atmospheric pressure until the theoretical amount of hydrogen was absorbed (3–6 days), a small amount of water (3–5 mL) being added after 5–8 h. The mixture was then filtered, and passed through a column of Amberlite IRA-400 (HO^-) resin which was washed with water and methanol. The combined effluent was concentrated to 10 mL at <30° and then freeze-dried.

Methyl 2,3-*O*-[(1*S*)-D-glucopyranosylidene]-α-D-mannopyranoside (**2a**, 98.7%) had m.p. 165–170° (dec.), $[\alpha]_D$ +54° (*c* 3.4, water). The (1*R*)-isomer (**2b**, 88.1%) had m.p. 160–170° (dec.), $[\alpha]_D$ +41.6° (*c* 2, water).

Anal. Calc. for $C_{13}H_{22}O_{11}$: C, 44.07; H, 6.26. Found: **2a** C, 44.63; H, 6.20; **2b** C, 44.51; H, 6.39.

Acetylation of **2a** *and* **2b**. — Conventional treatment of **2b** (86 mg, 0.24 mmol) with pyridine (1 mL) and acetic anhydride (0.28 mL) at 0° gave syrupy methyl 4,6-di-*O*-acetyl-2,3-*O*-[(1*R*)-2,3,4,6-tetra-*O*-acetyl-D-glucopyranosylidene]-α-D-mannopyranoside (**5b**; 126 mg, 85.5%), which, after purification by column chromatography (3:17 acetone–hexane), had m.p. 68–70°, $[\alpha]_D$ +28° (*c* 8.2, chloroform); ν_{max}^{KBr} 1740 cm^{-1} (ester).

Similar acetylation of **2a** gave the (1*S*)-isomer **5a** (84.7%), m.p. 236–238° (from ethyl acetate–hexane), $[\alpha]_D$ +40°, (*c* 2.1, chloroform); ν_{max}^{KBr} 1740 cm^{-1} (ester).

Anal. Calc. for $C_{25}H_{34}O_{17}$: C, 49.51; H, 5.65. Found: **5b** C, 49.24; H, 5.77; **5a** C, 49.77; H, 5.38.

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