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Note

Preparation of methyl β-L-idoseptanoside and its derivatives [1]

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Synthesis of septanosides with the L-*ido* configuration may be achieved by inversion of configuration at C-5 of an appropriately substituted D-glucoseptanoside derivative. We have described [1] the preparation of methyl 3,4-*O*-isopropylidene-α-D-glucoseptanoside (**1a**) from methyl α-D-glucoseptanoside. Selective protection of the hydroxyl group on C-2 of **1a** would provide a suitably substituted derivative which could be converted into the L-*ido* derivative using an oxidation–reduction sequence or by nucleophilic displacement of an appropriate group. We describe here the selective benzoylation of **1a** and the preparation of methyl β-L-idoseptanoside derivatives by both oxidation–reduction and displacement of a sulfonyloxy group.

Benzoylation of **1a**.—Treatment of **1a** with benzoyl chloride in pyridine until all of the starting material had been consumed gave the dibenzoate **1b** [1] and a new product, **1c**, which appeared between **1a** and **1b** on thin-layer chromatography; **1c** was isolated by chromatography over silicic acid. Its IR spectrum had absorptions at 1720 and 3520 cm^{-1}, consistent with a monobenzoate structure. Analysis of the ^1H NMR spectrum allowed its identification as methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-glucoseptanoside (**1c**). The low-field doublet of doublets in the spectrum of **1c** corresponds to the similar multiplet assigned [1] to H-2 in the spectrum of **1b**. The yield of **1c** was 88%. Such a high yield of a monobenzoate is reminiscent of the preferential acylation of the C-2 hydroxy group in methyl 4,6-*O*-benzylidene-α-D-glucopyranoside [2,3]. We note also that the conformation of **1a** is probably the same as that of its derived diacetate [1]

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[1] Septanose Carbohydrates, Part 5. For Part 4, see ref. [1].

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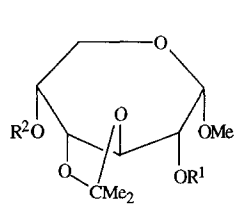
in which the C-5 acetoxy group is axially oriented. We would therefore expect the C-5 hydroxy group in **1a** to react slowly with acylating agents.

Oxidation of **1c**.—Treatment of **1c** with a catalytic quantity of ruthenium dioxide and sodium metaperiodate gave a single, crystalline, oxidation product, **2**. The IR spectrum showed carbonyl absorptions at 1735 (benzoate ester) and 1750 cm^{-1}. The ^1H NMR spectrum revealed the absence of a hydrogen on C-5 which confirms that the oxidation product is the 5-keto compound. Since the products of reduction of this ketone retained the D configuration at C-4 (see below), it follows that it is methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-*xylo*-hexoseptanosid-5-ulose (**2**).



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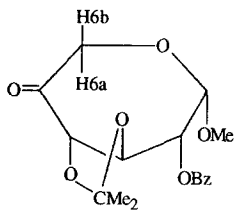
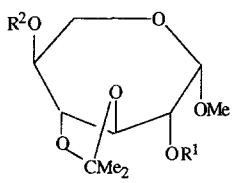
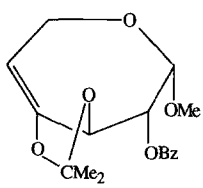


2

1a $R^1 = R^2 = H$
1b $R^1 = R^2 = Bz$
1c $R^1 = Bz$; $R^2 = H$
1d $R^1 = Bz$; $R^2 = Ts$





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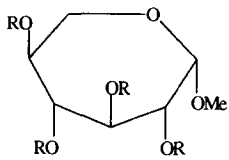


3a $R^1 = R^2 = H$
3b $R^1 = R^2 = Ac$
3c $R^1 = Bz$; $R^2 = H$
3d $R^1 = R^2 = Bz$
3e $R^1 = Bz$; $R^2 = Ac$

5a R = H
5b R = Ac
5c R = Bz

An indication of the solution-state conformation of **2** may be obtained from the proton–proton spin-coupling constants. The large magnitudes of $J_{2,3}$ and $J_{3,4}$, together with the stereochemical restrictions imposed by the *O*-isopropylidene group, restrict possible conformations to the segment $^{4,5}TC_{6,O}$, $^{1,2}C_5$, $^{5,6}TC_{3,4}$, $^4C_{O,1}$, $^{2,3}TC_{4,5}$, $^{6,O}C_3$, $^{3,4}TC_{1,2}$, $^2C_{5,6}$, $^{O,1}TC_{2,3}$, $^{4,5}C_1$, $^{1,2}TC_{6,O}$ of the pseudorotational continuum of chair and twist-chair conformations of the seven-membered ring [4]. Many of these conformations are considered unlikely in view of the large geminal coupling $J_{6a,6b}$ together with the absence of spin coupling between H-4 and H-6a. A geminal coupling of −18.6 Hz requires a ring conformation in which the H-6a–H-6b line is perpendicular to the C-4,C-5,C-6 plane, i.e., in which the C-5 carbonyl bond bisects the angle between the

C-6 geminal hydrogens [5]. This is not the case in the conformation $^{4,5}TC_{6,O}$ which has been proposed for the structurally related 1,2:3,4-di-*O*-isopropylidene-α-D-*xylo*-hexoseptanos-5-ulose for which values of −15.8 Hz ($J_{6a,6b}$) and 1.0 Hz ($J_{4,6b}$) were reported [6]. Similarly for the other conformations listed above, except for $^{2}C_{5,6}$. For this conformation, the C=O group bisects angle H-6a,C-6,H-6b, and we would not expect H-4 to be spin-coupled with H-6b. This conformation also accounts for the spin coupling between H-1 and H-6b, detected by a decoupling measurement, since they form a W-type arrangement. We note also that this conformation is favoured by the anomeric effect.

Reduction of **2**.—Addition of sodium borohydride to **2** in ethanol gave two products, **1c** and a new compound, identified as methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-β-L-idoseptanoside (**3c**) with **1c** being the major product. When **2** was added to an excess of borohydride in ethanol, **3c** was found to preponderate. Separation was effected with difficulty by chromatography over silicic acid. An IR spectrum of **3c** showed absorptions at 1710 (benzoate C=O) and 3500 cm^{-1} (OH). Hydrolysis of **3c** followed by reduction gave iditol (see below). In later preparations, it was found that the separation of the reduction products was more easily achieved by benzoylating the mixture to give the respective dibenzoates **1b** and **3d** which were readily separated by chromatography.

*Methyl 3,4-*O*-isopropylidene-β-*L*-idoseptanoside* (**3a**).—Debenzoylation of **3c** gave the crystalline diol, **3a**. Verification of the *ido* configuration of **3a** was achieved by the sequence acid hydrolysis, borohydride reduction, acetylation, and GLC analysis. A single product was obtained from **3a** showing the same retention time as that of iditol hexaacetate (10.9 min), well separated from the acetates of glucitol (9.0), and of galactitol (8.3) and altritol (7.4), which would have arisen from epimerization at C-4.

Acetylation of **3a** yielded the crystalline diacetate, **3b**, whose ^{1}H NMR spectrum was complicated by strong coupling [7] between H-3 and H-4. A similar effect was observed in the spectrum of **3d**. In contrast, a high-field spectrum of the acetate of **3c**, compound **3e**, was easily analyzed.

In the $^{4,5}TC_{6,O}$ conformation of derivatives of **1a**, O-5 is axially oriented and inversion of configuration at C-5 would give rise to a structure in which all of the oxygen atoms O-1 to O-5 are equatorial. In this structure, H-5 would be antiperiplanar to one of the C-6 protons, resulting in a large value for $J_{5,6a}$, or $J_{5,6b}$. However, values of 2.6 and 4.6 Hz were found for $J_{5,6a}$ and $J_{5,6b}$ for **3e**, implying a change in conformation upon inversion of configuration at C-5. Of the various possible conformations for **3e**, only $^{O,1}TC_{2,3}$ appears to account for the proton spin-coupling constants. As with the ketone **2**, this conformation is favoured by the anomeric effect and we note also that the C-5,O-5 bond is synclinal to the C-6,O-6 bond, an arrangement slightly more favourable [8] than that in which the C-5,O-5 bond is antiperiplanar to the C-6,O-6 bond, which would be the case for **3e** in the $^{4,5}TC_{6,O}$ conformation. The results of a single-crystal X-ray diffraction study of **3e**, which revealed the $^{O,1}TC_{2,3}$ conformation in the solid state, are presented in the accompanying paper [9].

Displacement reaction.—Treatment of methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-5-*O*-*p*-toluenesulfonyl-α-D-glucoseptanoside (**1d**) with lithium benzoate [10] in DMF gave **3d** in 50% yield, together with a new compound, methyl 2-*O*-benzoyl-5-deoxy-3,4-*O*-isopropylidene-β-L-*threo*-hex-4-enoseptanoside (**4**). The ^{1}H NMR spectrum was readily

Table 1
^{1}H NMR chemical shifts (ppm)

Compound	Solvent	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	OMe	CMe_2	OAc	Other
1b	$CDCl_3$	4.635	5.569	4.812	4.226	5.707	4.380	3.939	3.400	1.421, 1.273		
1c	$CDCl_3$	4.580	5.447	4.612	4.020	4.213	4.256	3.774	3.376	1.440 (2)		
1d	$CDCl_3$	4.539	5.427	4.557	4.009	5.016	4.344	3.787	3.357	1.343, 1.208		2.451 (Ar–Me)
2	$CDCl_3$	5.155	5.391	4.304	4.938		4.258 [a]	4.191 [a]	3.466	1.454, 1.474		
3b	$CDCl_3$	4.838	4.967	4.084	4.101	4.964	4.317	3.521	3.365	1.412, 1.409	2.147, 2.131	
3c	$CDCl_3$	4.711	5.406	4.170	3.91–4.00		4.349	3.469	3.376	1.420, 1.433		
3d	$CDCl_3$	5.036	5.280	4.350 [b]	4.382 [b]	5.307	4.513	3.717	3.384	1.444, 1.441		
3e	C_6D_6	4.836	5.504	4.348	4.244	5.179	4.137	3.349	2.890	1.276, 1.271	1.654	
4	C_6D_6	4.838	5.743	5.568		5.109	4.350	3.570	3.071	1.332, 1.180		
5b	$CDCl_3$	4.731	5.208	5.554	5.192	4.976	4.083	3.734	3.449		2.126, 2.049	
											2.078, 2.024	
5b	C_6D_6	4.675	5.601	5.981	5.544	5.083	3.877	3.625	2.988		1.673, 1.626	
											1.642, 1.612	
5c	$CDCl_3$	5.046	5.821	6.198	5.877	5.566	4.425	4.034	3.560			
6	$CDCl_3$	5.001	3.770	4.237	3.708	4.128	4.120	3.831	3.474	1.466, 1.428		
										1.454 (2)		
6	C_6D_6	5.005	3.694	4.562	3.674	4.296	4.116	3.651	3.125	1.397, 1.361		
										1.387, 1.312		
7b	Me_2CO-d_6	4.862	3.936	4.522	4.898	4.711	3.965	3.715	3.427	1.357, 1.347	2.074, 2.056	
8b	Me_2CO-d_6	4.756	4.868	5.242	3.984	4.225	4.072	3.637	3.489	1.337, 1.332	2.003, 2.002	

[a] Calculated as an AB system.
[b] Obtained by iterative analysis of H-2 to H-5, using the program PANIC (Bruker).

Table 2
^{1}H NMR coupling constants (Hz)

Compound	Solvent	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	Others
1b	$CDCl_3$	3.82	7.69	9.62	2.54	2.04	3.20	14.20	0.45 ($J_{3,5}$)
1c	$CDCl_3$	3.83	7.99	9.64	2.47	2.65	3.32	13.18	
1d	$CDCl_3$	3.72	7.78	9.63	2.48	2.10	3.29	14.32	
2	$CDCl_3$	3.65	9.96	9.73				18.65	
3b	$CDCl_3$	4.47	9.18	9.61	7.66	4.83	2.79	14.33	
3c	$CDCl_3$	3.92	8.19	9.29	n.d.	5.48	6.78	13.00	
3d	$CDCl_3$	4.54	9.23 [a]	9.43 [a]	7.79 [a]	4.82	2.59	14.46	
3e	C_6D_6	4.40	9.28	9.47	7.73	4.92	3.03	14.20	
4	C_6D_6	3.00	9.63			4.17	6.85	14.68	0.65 ($J_{1,6a}$), 2.29 ($J_{3,5}$), 1.74 ($J_{3,6a}$), 0.89 ($J_{3,6b}$)
5b	$CDCl_3$	2.44	9.87	6.97	5.46	2.25	5.12	13.61	0.40 ($J_{1,3}$), 0.47 ($J_{1,6a}$), 0.69 ($J_{4,6b}$)
5b	C_6D_6	2.20	9.94	6.21	5.40	1.94	5.28	13.48	0.31 ($J_{1,3}$), 0.49 ($J_{1,6a}$), 0.76 ($J_{4,6b}$)
5c	$CDCl_3$	2.55	9.73	6.91	6.31	2.61	4.89	13.64	
6	$CDCl_3$	1.24	9.02	9.34	8.53	2.95	10.50	12.15	0.47 ($J_{1,3}$)
6	C_6D_6	1.16	9.00	9.18	8.77	2.62	9.95	11.72	
7b	Me_2CO-d_6	2.50	9.69	8.72	1.74	0.89	4.79	14.21	0.50 ($J_{1,3}$), 0.42 ($J_{1,5}$), 0.58 ($J_{1,6a}$), 1.14 ($J_{4,6b}$)
8b	Me_2CO-d_6	2.30	8.01	9.85	9.12	5.68	9.48	10.98	

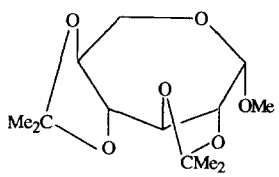
[a] Obtained by iterative analysis of H-2 to H-5, using the program PANIC (Bruker).

assigned: chemical shifts and coupling constants are included in Tables 1 and 2. The identity followed from the detailed analysis of the NMR spectrum, in particular, the absence of a signal due to H-4 and the presence of signals due to the geminal hydrogens on C-6, eliminating an isomeric structure with a C-5,C-6 double bond. Homoallylic coupling of H-3 with both H-6a and H-6b as well as allylic coupling of H-3 and H-5 and W-type four-bond coupling of H-1 and H-6a were detected. The conformation $^{4,5}C_1$ accounts for the various spin-coupling constants. In this conformation, the orientation of the C-1,O-1 bond with respect to the ring oxygen is similar to that found in α-pyranosides.

Methyl β-L-idoseptanoside (**5a**).—Hydrolysis of **3a** using dilute hydrochloric acid gave a single product (TLC) which failed to crystallize. Acetylation of the hydrolysis product gave a liquid tetraacetate and benzoylation gave a crystalline tetrabenzoate. Analysis of the ^{1}H NMR spectrum of the tetraacetate confirmed its identity as methyl 2,3,4,5-tetra-*O*-acetyl-β-L-idoseptanoside (**5b**). The hydrolysis product is thereby identified as methyl β-L-idoseptanoside (**5a**). As for the case of **3e**, proton spin-coupling constants for **5b** indicate that the most likely conformation is $^{O,1}TC_{2,3}$.

Benzoylation of **5a** yielded the crystalline tetrabenzoate, **5c**. Proton spin-coupling constants for **5c** are very similar to those of **5b**. We have subjected **5c** to a single-crystal X-ray diffration study in order to determine the solid-state conformation of this derivative. Details are included in the Experimental section (see Fig. 1 for the numbering scheme). In contrast to the solid-state conformation of the septanoside ring in **3e**, for **5c**, the ring is a twist-chair in which the pseudo-axis of symmetry passes through C-6,

i.e., the $^{3,4}TC_{1,2}$ conformation. In their detailed paper on the conformations of oxepane, Bocian and Strauss [11] showed that the energy difference between the two low-energy twist-chair conformations of oxepane, in which the pseudo-axis of symmetry passes through the carbon atom attached to oxygen and passes through the carbon once removed from oxygen (twist-chair *C* and twist-chair *B*, respectively), is only 0.05 kJ mol^{-1}. As the conformations $^{O,1}TC_{2,3}$ and $^{3,4}TC_{1,2}$ may be generated by twisting about the C-5,C-6 bond of the chair conformation $^{2}C_{5,6}$, the solution and solid-state conformations of **5c** are closely related and probably have very similar energies.



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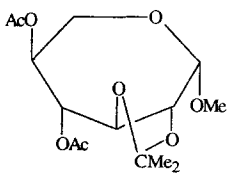

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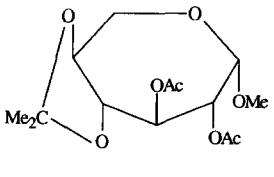

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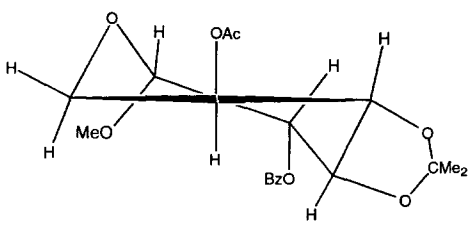
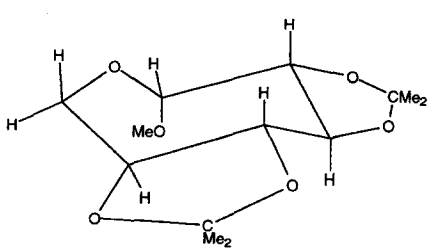
*Methyl 2,3:4,5-di-O-isopropylidene-β-*L*-idoseptanoside* (**6**).—Treatment of **3a** with acidified acetone gave the starting material as the major product (TLC) and the di-*O*-isopropylidene compound **6** as a minor product, appearing at high R_f, and mono-*O*-isopropylidene compounds appearing at an R_f slightly higher than that of **3a**. Using an acidified mixture of 2,2-dimethoxypropane and acetone, **6** was now the major product, with several new spots in TLC column chromatography of the reaction mixture gave crystalline **6** in 42% yield. Other components were identified as *O*-(2-methoxyisopropyl) derivatives of **3a** (see Experimental).



$^{O,1}TC_{2,3}$ Conformation of **3e**



$^{6,O}C_3$ Conformation of **6**

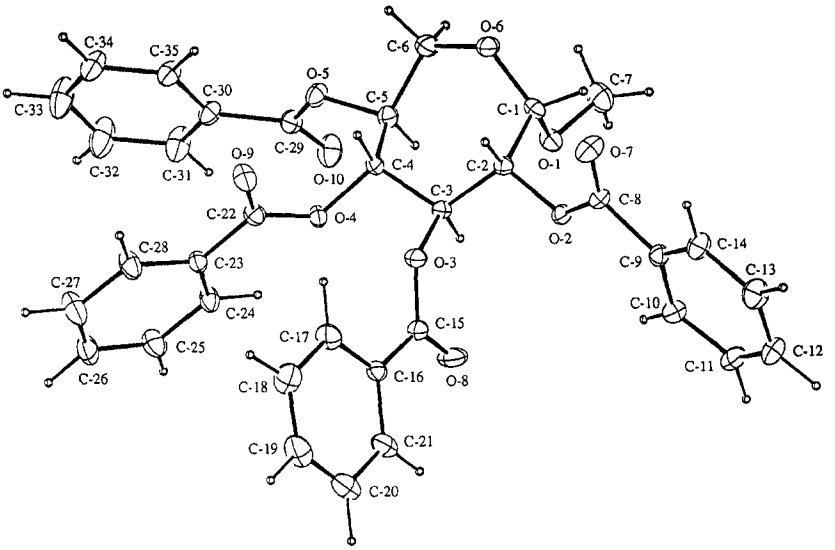
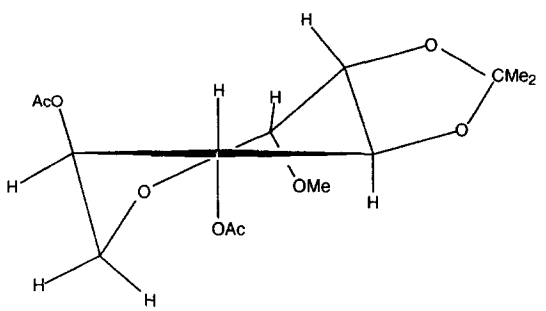
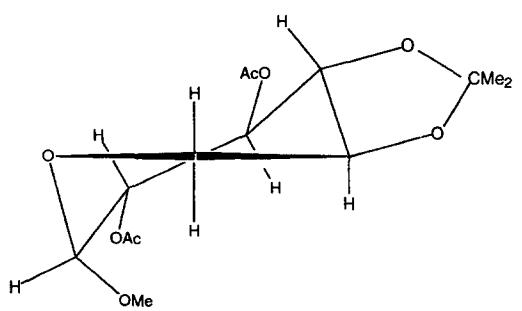


Fig. 1. ORTEP plot of **5c**, showing atomic notation and thermal ellipsoids.



$^{1,2}TC_{6,O}$ Conformation of **7b**



$^{3,4}TC_{1,2}$ Conformation of **8b**

Compound **6** showed no absorption in the 3-μm region of the IR spectrum and its EI mass spectrum showed a peak at m/z 259, corresponding to the loss of CH_3 from a di-*O*-isopropylidene derivative of **5a**. Identification as methyl 2,3:4,5-di-*O*-isopropylidene-β-L-idoseptanoside (**6**) followed from the analysis of its ^{1}H NMR spectrum.

Possible conformations of **6** were selected by considering the geometric requirements for the fusion of two adjacent trans five-membered rings on the septanoside ring. The following conformations satisfy that requirement: $^2C_{5,6}$, $^{3,4}TC_{1,2}$, $^{6,O}C_3$, $^{2,3}TC_{4,5}$, $^4C_{O,1}$, $^{5,6}TC_{3,4}$, and $^{1,2}C_5$. The small magnitude of $J_{1,2}$ suggests that the H-1,H-2 dihedral angle is close to 90°: this is the case for conformations $^{6,O}C_3$ and $^{2,3}TC_{4,5}$. Of these, the $^{6,O}C_3$ conformation more readily accounts for the magnitudes of $J_{5,6a}$ and $J_{5,6b}$.

*Methyl 2,3- and 4,5-*O*-isopropylidene-β-*L*-idoseptanosides* (**7a** *and* **8a**).—Analysis of the products from the reaction of **3a** with acidified acetone by GLC on an acetylated sample gave 3% of **6**, 75% of **3b**, and 22% for a single peak assigned as the acetate of a mono-*O*-isopropylidene compound (LAC column). Using the ECNSS-M column, the latter appeared as two peaks, representing 7 and 15% of the reaction mixture. The two components co-eluted on column chromatography. Analysis of the ^{1}H NMR spectrum of the derived acetates confirmed the presence of two mono-*O*-isopropylidene diacetates in the ratio ca. 1:2. The major component, with H-4 and H-5 appearing at low field, is identified as methyl 4,5-di-*O*-acetyl-2,3-*O*-isopropylidene-β-L-idoseptanoside (**7b**) and the minor component, with H-2 and H-3 appearing at low field, is identified as methyl 2,3-di-*O*-acetyl-4,5-*O*-isopropylidene-β-L-idoseptanoside (**8b**).

Conformation of **7b**.—Possible conformations of **7b** are restricted by the presence of the trans-fused *O*-isopropylidene group to the segment of the pseudorotational continuum of chair and twist-chair forms $^OC_{3,4}$ to $^{1,2}C_5$. Of these conformations, only $^{1,2}TC_{6,O}$ accounts for the small magnitudes of $J_{4,5}$ and $J_{5,6a}$ which require H-4 dihedral angles close to 90°. We note that this conformation was deduced for the related D-*gluco* compound, methyl 4,5-di-*O*-acetyl-2,3-*O*-isopropylidene-α-D-glucoseptanoside [1]. For both isomers, the close to W arrangement of H-4 and H-6a gives rise to a ^4J coupling. Also, H-1 is long-range coupled to H-3 and H-6b and also shows ^5J coupling to H-5. This arrangement of H-1 and H-5 in the $^{1,2}TC_{6,O}$ conformation of **7** is similar to that of equatorial H-1 and equatorial H-5 in pyranose compounds — such hydrogens are also spin-coupled [12–14].

Conformation of **8b**.—The magnitude of $J_{5,6b}$ for **8b** indicates that H-5 is antiperiplanar to H-6b. Conformations $^4C_{5,6}$ through $^{6,O}C_3$ to $^{3,4}C_O$ in the pseudorotational continuum of chair and twist-chair forms satisfy this requirement. All but $^{3,4}TC_{1,2}$ are effectively eliminated by the magnitudes of $J_{2,3}$, $J_{5,6a}$, and $J_{1,2}$. This conformation is favoured by the anomeric effect.

1. Experimental

General methods.—See ref. [1].

*Methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-glucoseptanoside* (**1c**).—A solution of methyl 3,4-*O*-isopropylidene-α-D-glucoseptanoside (**1a**, 825 mg) in pyridine (10 mL)

was cooled in ice–water and stirred while 20% (v/v) benzoyl chloride in pyridine (2.9 mL) was added dropwise. After 30 min, TLC in 1:4 EtOAc–benzene showed no **1a** at R_f 0.05 but two products at R_f 0.2 and 0.6. The product at R_f 0.6 corresponded to the dibenzoate **1b** [1]. Water (40 mL) was added and additions of solid $NaHCO_3$ were made until effervescence ceased. The mixture was extracted with $CHCl_3$ (1 × 50, 2 × 10 mL) and each extract was washed with 1.5 M H_2SO_4 (2 × 50 mL) and saturated aq $NaHCO_3$ (25 mL). The extracts were combined, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was dissolved in warm EtOAc and seeded after the addition of light petroleum to yield the title compound (**1c**, 520 mg). A second crystallization yielded a further 190 mg (total 710 mg).

The mother liquors were dissolved in benzene and chromatographed on silicic acid (5 g) packed in 1:4 EtOAc–light petroleum; **1b** (134 mg) was eluted with the same solvent, and 1:1 EtOAc–petroleum eluted **1c**. The yield of **1c** from the chromatography was 310 mg and the total yield was 1.02 g (88%).

Recrystallization of **1c** from EtOAc–light petroleum or EtOH initially gave needles, mp 78–80 °C, but subsequent recrystallizations from EtOAc–light petroleum or benzene–light petroleum gave plates; mp 124 °C; $[\alpha]_D^{23}$ +59.8° (*c* 0.9, $CHCl_3$); IR 1720 (C=O), 3520 cm^{-1} (OH). Anal. Calcd for $C_{17}H_{22}O_7$: C, 60.3; H, 6.6. Found: C, 60.6; H, 6.6.

Methyl 2-O-benzoyl-3,4-O-isopropylidene-5-O-p-toluenesulfonyl-α-D-glucoseptanoside (**1d**).—Methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-glucoseptanoside (**1c**, 500 mg) was treated with *p*-toluenesulfonyl chloride (750 mg) in pyridine (2.0 mL). After 24 h, TLC in 1:1 EtOAc–benzene showed a single product at R_f 0.65 and no **1c** at R_f 0.4. Ice–water (10 mL) was added and the mixture was extracted with $CHCl_3$ (1 × 10, 1 × 5 mL), with each extract being washed successively with 1.5 M H_2SO_4 (10 mL) and saturated aq $NaHCO_3$ (10 mL). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue crystallized on standing to give **1d** (706 mg, 97%).

Recrystallization of **1d** from benzene–light petroleum gave needles which melted at ca. 130 °C, then resolidified to give stout needles; mp 164–165 °C; $[\alpha]_D^{22}$ +49.2° (*c* 1.0, $CHCl_3$); IR 1725 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{28}O_9S$: C, 58.5; H, 5.7. Found: C, 58.7; H, 5.7.

Methyl 2-O-benzoyl-3,4-O-isopropylidene-α-D-xylo-hexoseptanosid-5-ulose (**2**).—The monobenzoate **1c** (3.0 g) was dissolved in ethanol-free $CHCl_3$ (30 mL) and the solution was stirred vigorously with RuO_2 (100 mg) while aliquots of aq 2.5% $NaIO_4$ (20 mL) and Na_2CO_3 (0.1 g) were added at hourly intervals. The reaction was monitored by TLC in 1:4 EtOAc–benzene and six aliquots of $NaIO_4$ (1.6 equiv) were required to give complete conversion of **1c** at R_f 0.2 into **2** at R_f 0.5. Propan-2-ol (2 mL) was added and the mixture was stirred for a further 30 min. The $CHCl_3$ layer was separated and the aqueous layer was washed with $CHCl_3$ (2 × 25 mL). The combined $CHCl_3$ extracts were evaporated under reduced pressure and **2** crystallized on standing (2.83 g, 95%). Recrystallization of **2** from EtOH or EtOAc–light petroleum gave needles; mp 115–116 °C; $[\alpha]_D^{22}$ +126.8° (*c* 1.4, $CHCl_3$); IR 1735 (ester C=O), 1750 cm^{-1} (ketone C=O). Anal. Calcd for $C_{17}H_{20}O_7$: C, 60.7; H, 6.0. Found: C, 60.8; H, 5.8.

Methyl 2-O-benzoyl-3,4-O-isopropylidene-β-L-idoseptanoside (**3c**).—The ketone **2** (2.8 g) was added to a stirred solution of $NaBH_4$ (0.48 g) in EtOH (30 mL). After 5 min, TLC in 1:1 EtOAc–benzene showed the absence of ketone (R_f 0.75), and the presence of **3c** (R_f 0.5) and the *gluco* isomer **1c** (R_f 0.4). Acetone (5 mL) was added and the solution was deionized with Amberlite IRC-50(H^+) resin and evaporated under reduced pressure. Methanol was evaporated from the residue to remove boric acid. The residue was dissolved in benzene and chromatographed on silicic acid (50 g) packed in 2:3 ether–light petroleum. The separation was not completely successful with **3c** (0.55 g), **1c** (0.96 g) and a mixture (1.3 g) being obtained. Further chromatography of the mixture yielded **3c** (0.44 g) and **1c** (0.60 g). Total yield of **3c** was 0.99 g (35%).

It was later found that the separation of the *gluco* and *ido* isomers was easier after conversion into the respective dibenzoates **3d** and **1b**. Chromatography on silicic acid packed in 1:4 EtOAc–light petroleum separates **3d** and **1b** easily.

The ratio of the D-*gluco* and L-*ido* alcohols after reduction was estimated by GLC of the mixture after successive debenzoylation and acetylation. Only the corresponding 3,4-monoacetal diacetates were detected and the ratio was 55:45, favouring the L-*ido* derivative.

Recrystallization of **3c** from EtOAc–light petroleum gave prisms; mp 125 °C; $[\alpha]_D^{22}$ +90.0° (*c* 1.4, $CHCl_3$); IR 1710 (C=O), 3500 cm^{-1} (OH). Anal. Calcd for $C_{17}H_{22}O_7$: C, 60.3; H, 6.6. Found: C, 60.2; H, 6.6.

Treatment of **3c** with benzoyl chloride in pyridine yielded the dibenzoate **3d** which crystallized as stout needles from benzene; mp 182–183 °C; $[\alpha]_D^{22}$ +137.3° (*c* 1.3, $CHCl_3$); IR 1715, 1730 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{26}O_8$: C, 65.2; H, 5.9. Found: C, 65.2; H, 6.1.

Treatment of **3c** with Ac_2O and pyridine gave the 5-*O*-acetyl derivative **3e** which crystallized as needles from EtOH; mp 182–183 °C; $[\alpha]_D^{21}$ +141.2° (*c* 0.8, $CHCl_3$); IR 1710 (OBz), 1740 cm^{-1} (OAc). Anal. Calcd for $C_{19}H_{24}O_8$: C, 60.0; H, 6.4. Found: C, 59.7; H, 6.3.

Methyl 3,4-O-isopropylidene-β-L-idoseptanoside (**3a**).—Methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-β-L-idoseptanoside (**3c**, 600 mg) was dissolved in 0.01 M methanolic NaOMe (20 mL) and the solution was heated under reflux. After 6 h, TLC in 1:1 EtOAc–benzene, using HF_{254} silica gel, showed that debenzoylation was complete. Water (10 mL) was added, and the solution was treated with Amberlite IRC-50(H^+) resin and evaporated under reduced pressure. The crystalline residue contained methyl benzoate which was removed by chromatography on silicic acid. Methyl benzoate was eluted by EtOAc and **3a** was eluted with 1:4 EtOH–EtOAc The yield of **3a** was 400 mg (96.5%). Recrystallization of **3a** from EtOAc gave prisms; mp 162 °C; $[\alpha]_D^{22}$ +76.5° (*c* 1.1, H_2O); IR 3450, 3510 (OH); *m/z* 219 (M − 15). Anal. Calcd for $C_{10}H_{18}O_6$: C, 51.3; H, 7.7. Found: C, 51.6; H, 7.9.

Treatment of **3a** with Ac_2O–pyridine gave the diacetate **3b**. Recrystallization of **3b** from benzene–light petroleum gave needles; mp 75–76 °C; $[\alpha]_D^{22}$ +137.9° (*c* 0.8, $CHCl_3$); IR 1735, 1750 cm^{-1} (C=O); *m/z* 303 (M − 15). Anal. Calcd for $C_{14}H_{22}O_8$: C, 52.8; H, 7.0 Found: C, 53.0; H, 7.0.

A sample (6 mg) of **3a** was converted into the corresponding hexitol hexaacetate, identified as iditol hexaacetate using GLC.

Sulfonate displacement of methyl 2-O-*benzoyl-3,4*-O-*isopropylidene-5*-O-p-*toluenesulfonyl-α*-D-*glucoseptanoside* (**1d**).—Compound **1d** (400 mg) and LiOBz (0.8 g) were dissolved in hot DMF (4.0 mL) and the solution was stirred at 120 °C. After 8 h, TLC in 1:4 EtOAc–light petroleum showed only a trace of starting material (R_f 0.05), and two products at R_f 0.3 and 0.4. The product at R_f 0.3 corresponded to methyl 2,5-di-*O*-benzoyl-3,4-*O*-isopropylidene-β-L-idoseptanoside (**3d**). The solution was poured into saturated aq $NaHCO_3$ (50 mL) and extracted with $CHCl_3$ (1 × 20, 2 × 10 mL), each extract being washed with water (5 × 50 mL) to remove DMF. The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dissolved in benzene and chromatographed on silicic acid (12 g) packed in 1:19 EtOAc–light petroleum. The product of R_f 0.4 (94 mg), eluted with 1:9 EtOAc–light petroleum, was obtained as a colourless syrup, identified by ^{1}H NMR as the elimination product, methyl 2-*O*-benzoyl-5-deoxy-3,4-*O*-isopropylidene-β-L-*threo*-hex-4-enoseptanoside (**4**). Elution with the same solvent, evaporation, and recrystallization from benzene–light petroleum yielded **3d** (188 mg, 50%), mp 182–183 °C, identical to the authentic sample.

Methyl β-L-*idoseptanoside* (**5a**).—Methyl 3,4-*O*-isopropylidene-β-L-idoseptanoside (**3a**, 50 mg) was dissolved in 0.05 M HCl (10 mL). After 30 h at 20 °C, TLC in 1:1 acetone–EtOAc showed some **3a** at R_f 0.5 and a single product at R_f 0.25. The solution was neutralized with Amberlite IRA-400 (HCO_3^-) resin and evaporated under reduced pressure. Ethanol–benzene was similarly evaporated from the residue to remove water. The residue was chromatographed on silicic acid (10 g) packed in 1:1 EtOAc–light petroleum. Starting material (87 mg) was eluted with EtOAc, and the title compound (342 mg, 83.5%) with 1:4 EtOH–EtOAc. Compound **5a**, a viscous syrup, did not crystallize.

Treatment of **5a** with Ac_2O–pyridine gave the tetraacetate **5b** which was purified by silicic acid chromatography. The syrupy **5b** was distilled using a short-path distillation apparatus (120 °C bath, 0.1 mm Hg); $[\alpha]_D^{22}$ +118.1° (*c* 0.8, $CHCl_3$); IR 1755 cm^{-1} (C=O). Anal. Calcd for $C_{15}H_{22}O_{10}$: C, 49.7; H, 6.1. Found: C, 49.6; H, 6.1.

Treatment of **5a** with benzoyl chloride in pyridine yielded a crystalline tetrabenzoate, **5c**. Recrystallization of **5c** from MeOH gave needles; mp 129–130 °C; $[\alpha]_D^{22}$ +120.4° (*c* 1.6, $CHCl_3$); IR 1740 (br) cm^{-1} (C=O). Anal. Calcd for $C_{35}H_{30}O_{10}$: C, 68.8; H, 5.0. Found: C, 68.9; H, 4.8.

Methyl 2,3:4,5-di-O-*isopropylidene-β*-L-*idoseptanoside* (**6**).—Methyl 3,4-*O*-isopropylidene-β-L-idoseptanoside (**3a**, 500 mg) was stirred with 9:1 2,2-dimethoxypropane–acetone (10 mL) containing 0.1% H_2SO_4 (v/v). As there was still undissolved **3a** after 1 h at room temperature, acetone (5 mL) containing 0.1% H_2SO_4 (v/v) was added. After a further 2.5 h, TLC in 1:1 EtOAc–benzene showed the presence of five products apart from **3a** at R_f 0.05. These were **6** at R_f 0.75, **A** at R_f 0.65, **B** at R_f 0.4, **C** at R_f 0.35, and monoacetals at R_f 0.1; **6** and the monoacetals are also present when **3a** is treated with acidified acetone. The identification of the monoacetals appears in the following section.

The reaction mixture was neutralized with pyridine (0.1 mL) and evaporated under reduced pressure. The residue was dissolved in benzene and chromatographed on silicic acid (30 g) packed in 1:9 ether–light petroleum. The least polar compound (258 mg) was eluted with the same solvent and identified as methyl 2,3:4,5-di-*O*-isopropylidene-

β-L-idoseptanoside (**6**). The yield of **6** from **3c** was 44%. Elution with 1:1 EtOAc–light petroleum gave a mixture of **B** and **C** (110 mg), and elution with EtOAc gave a mixture (115 mg) of monoacetals and **3a**.

Recrystallization of the diacetal **6** from light petroleum (bp 30–40 °C) gave a sample, pure by GLC (LAC column); mp 90 °C; $[\alpha]_D^{23}$ +106.8° (*c* 0.8, $CHCl_3$); no IR absorption in the hydroxyl region; *m/z* 259 (M − 15). Anal. Calcd for $C_{13}H_{22}O_6$: C, 56.9; H, 8.1. Found: C, 57.2; H, 8.1.

Treatment of the mixture of **B** and **C** (8 mg) with 0.05 M HCl (0.2 mL) and 1,4-dioxane (0.1 mL) for 8 h at 22 °C gave **3a** as judged by TLC. The solution was neutralized with pyridine, evaporated, and acetylated; GLC of the acetylation mixture gave only the diacetate of **3a**, thus verifying the TLC results. Components **B** and **C** are tentatively identified as the 2- and 5-*O*-(2-methoxyisopropyl) derivatives of methyl 3,4-*O*-isopropylidene-β-L-idoseptanoside. NMR data: ^1H (60 MHz), 1.40–1.50 (2 × CMe_2), 2.85 (s, OH), 3.24 (2 × OMe), 3.50–4.60 (7 H).

Component **A** was not eluted during silicic acid chromatography and may be methyl 3,4-*O*-isopropylidene-2,5-di-*O*-(2-methoxyisopropyl)-β-L-idoseptanoside, being exceptionally acid-labile.

*Treatment of methyl 3,4-*O*-isopropylidene-β-L-idoseptanoside* (**3a**) *with acidified acetone.*—The title compound (185 mg) was dissolved in acetone (5 mL) containing 0.01% H_2SO_4 (v/v). After 24 h at room temperature, TLC in 1:9 acetone–EtOAc showed **3a** at R_f 0.4 and other monoacetals at R_f 0.5. TLC in 1:1 EtOAc–benzene also showed the presence of **6** as a minor product (R_f 0.75). An acetylated sample of the reaction mixture was analyzed using GLC (LAC column) and was shown to contain diacetal **6** (3%) with 3.5-min retention time (150 °C column temperature), 3,4-monoacetal diacetate **3b** (75%) with 4.2-min retention time (180 °C), and presumably the diacetates of other monoacetals (22%) with 2.8-min retention time (180 °C). Using the ECNSS-M column at 175 °C, the unidentified peak was separated into two components with retention times of 6.8 min (7%) and 8.0 min (15%).

The reaction mixture was neutralized with pyridine (0.1 mL) and evaporated under reduced pressure. The residue was recrystallized from EtOAc (1 mL) to give **3a** (60 mg). The mother liquor was chromatographed on silicic acid (15 g) packed in EtOAc to give, after a trace amount of diacetal **6**, the monoacetals (55 mg) and more of **3a** (70 mg). The monoacetals were treated with Ac_2O–pyridine and, from the NMR data (Tables 1 and 2), the mixture of products was found to be methyl 4,5-di-*O*-acetyl-2,3-*O*-isopropylidene-β-L-idoseptanoside (**7b**) and the isomeric 4,5 monoacetal diacetate **8b**, with **7b** being the major component.

Crystal data.—Suitable needle crystals of **5c** were obtained from an EtOH solution: $C_{35}H_{30}O_{10}$, *M* 610.6; orthorhombic, space group $P2_12_12_1$; $a = 10.7921(5)$, $b = 17.1620(11)$, $c = 17.2368(8)$ Å; $V = 3192.5(3)$ Å^3; $D_c = 1.27$ g cm^{-3}, $Z = 4$; $\mu_{Cu} = 7.38$ cm^{-1}; crystal size 0.15 × 0.17 × 0.36 mm; $2\theta_{max} = 140°$; min. and max. transmission factors 0.82 and 0.90. The number of reflexions was 2222 considered observed out of 3399 unique data. Final residuals *R* and R_w were 0.054 and 0.079 for the observed data.

Structure determination.—Reflexion data were measured with an Enraf–Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using nickel-filtered copper radiation (λ

Table 3
Non-hydrogen atomic parameters [with estimated standard deviations (esds) in parentheses]

	x	y	z	B_{eq} [a]
O-1	0.4625(4)	0.2058(2)	0.6713(2)	5.9(1)
O-2	0.5192(3)	0.3539(2)	0.7398(2)	4.7(1)
O-3	0.5440(3)	0.4342(2)	0.6029(2)	5.1(1)
O-4	0.5292(3)	0.3628(2)	0.4659(2)	4.8(1)
O-5	0.5967(4)	0.2217(3)	0.4350(2)	6.0(1)
O-6	0.6716(4)	0.1966(3)	0.6377(2)	6.2(1)
O-7	0.6934(4)	0.3617(3)	0.8074(3)	7.4(2)
O-8	0.3418(4)	0.4575(3)	0.6129(4)	8.6(2)
O-9	0.7110(4)	0.4159(3)	0.4335(3)	7.5(2)
O-10	0.4045(5)	0.1866(4)	0.4015(3)	8.5(2)
C-1	0.5826(5)	0.2328(3)	0.6847(3)	5.0(2)
C-2	0.5848(5)	0.3198(3)	0.6760(3)	4.8(2)
C-3	0.5254(5)	0.3505(3)	0.6035(3)	4.5(1)
C-4	0.5864(5)	0.3199(3)	0.5292(3)	4.6(1)
C-5	0.5648(6)	0.2348(4)	0.5147(3)	5.4(2)
C-6	0.6479(7)	0.1801(4)	0.5586(4)	6.8(2)
C-7	0.4385(9)	0.1290(5)	0.6990(5)	9.3(2)
C-8	0.5896(5)	0.3737(3)	0.8026(3)	4.7(2)
C-9	0.5113(6)	0.4107(3)	0.8654(3)	5.2(2)
C-10	0.3860(6)	0.4174(4)	0.8609(4)	6.5(2)
C-11	0.3222(7)	0.4466(6)	0.9240(5)	9.1(3)
C-12	0.3800(9)	0.4714(5)	0.9880(5)	8.4(3)
C-13	0.5093(10)	0.4666(5)	0.9919(4)	9.0(3)
C-14	0.5736(7)	0.4355(4)	0.9305(4)	6.7(2)
C-15	0.4458(6)	0.4808(4)	0.6007(3)	5.3(2)
C-16	0.4801(6)	0.5629(3)	0.5847(3)	5.2(2)
C-17	0.5964(8)	0.5833(4)	0.5588(4)	7.2(2)
C-18	0.6213(9)	0.6612(6)	0.5401(5)	9.2(3)
C-19	0.5335(12)	0.7152(5)	0.5524(5)	9.3(3)
C-20	0.4197(10)	0.6974(5)	0.5789(5)	8.5(3)
C-21	0.3939(7)	0.6210(4)	0.5950(4)	7.2(2)
C-22	0.6011(6)	0.4046(3)	0.4201(3)	5.3(2)
C-23	0.5368(6)	0.4363(3)	0.3518(3)	5.1(2)
C-24	0.4151(5)	0.4176(4)	0.3362(3)	6.1(2)
C-25	0.3576(7)	0.4477(5)	0.2705(4)	7.9(3)
C-26	0.4203(10)	0.4959(6)	0.2210(4)	9.2(3)
C-27	0.5428(9)	0.5105(6)	0.2344(5)	9.8(3)
C-28	0.6023(7)	0.4813(5)	0.3002(5)	7.9(2)
C-29	0.5064(6)	0.2064(4)	0.3837(4)	5.5(1)
C-30	0.5480(6)	0.2184(4)	0.3020(3)	5.9(1)
C-31	0.4613(7)	0.2122(6)	0.2464(4)	9.8(3)
C-32	0.4953(8)	0.2226(9)	0.1691(4)	12.7(5)
C-33	0.6153(9)	0.2384(8)	0.1518(4)	11.7(4)
C-34	0.7038(6)	0.2448(6)	0.2064(4)	8.5(3)
C-35	0.6681(5)	0.2343(5)	0.2838(3)	6.4(2)

[a] B_{eq} (Å^2) is the isotropic equivalent of the anisotropic temperature factor.

Table 4
Selected bond lengths (Å), angles (°), and torsional angles (°) [a]

C-1–C-2	1.501(8)	O-6–C-1–C-2	111.9(5)	O-6–C-1–C-2–C-3	76.7(6)
C-2–C-3	1.500(7)	C-1–C-2–C-3	115.3(5)	C-1–C-2–C-3–C-4	−59.8(6)
C-3–C-4	1.533(7)	C-2–C-3–C-4	113.1(4)	C-2–C-3–C-4–C-5	69.3(6)
C-4–C-5	1.499(9)	C-3–C-4–C-5	114.0(5)	C-3–C-4–C-5–C-6	−81.2(6)
C-5–C-6	1.502(8)	C-4–C-5–C-6	115.6(5)	C-4–C-5–C-6–O-6	42.7(8)
C-6–O-6	1.416(7)	C-5–C-6–O-6	117.9(5)	C-5–C-6–O-6–C-1	32.1(9)
O-6–C-1	1.403(7)	C-6–O-6–C-1	121.4(5)	C-6–O-6–C-1–C-2	−83.5(7)
C-1–O-1	1.396(7)	O-6–C-1–O-1	113.1(5)	C-6–O-6–C-1–O-1	40.2(7)
O-1–C-7	1.427(8)	C-2–C-1–O-1	109.1(5)	C-3–C-2–C-1–O-1	−49.2(6)
C-2–O-2	1.432(6)	C-1–O-1–C-7	114.8(5)	O-6–C-1–O-1–C-7	72.1(7)
C-3–O-3	1.450(7)	C-1–C-2–O-2	108.8(4)	C-2–C-1–O-1–C-7	−162.7(5)
C-4–O-4	1.453(6)	C-3–C-2–O-2	106.6(4)	O-6–C-1–C-2–O-2	−163.7(4)
C-5–O-5	1.434(6)	C-2–C-3–O-3	107.2(5)	C-4–C-3–C-2–O-2	179.4(4)
		C-4–C-3–O-3	106.0(4)	C-1–C-2–C-3–O-3	−176.2(5)
		C-3–C-4–O-4	105.7(4)	C-5–C-4–C-3–O-3	−173.6(4)
		C-5–C-4–O-4	107.6(4)	C-2–C-3–C-4–O-4	−172.7(5)
		C-4–C-5–O-5	106.0(4)	C-6–C-5–C-4–O-4	161.9(5)
		C-6–C-5–O-5	104.0(5)	C-3–C-4–C-5–O-5	164.3(4)
				O-6–C-6–C-5–O-5	158.4(6)

[a] Esds in parentheses.

1.5418 Å). Data were corrected for absorption using the method of de Meulenaer and Tompa [15]. Reflexions with $I > 3\sigma(I)$ were considered observed. The structure was determined by direct phasing and Fourier methods. Hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full-matrix least squares. Reflexion weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography [16]. Structure solution was by MULTAN-80 [17] and refinement used BLOCKLS, a local version of ORFLS [18]. ORTEP-II [19] running on a Macintosh IIcx was used for the structural diagram, and an IBM 3090 computer was used for calculations.

The structure and atom numbering scheme is shown in Fig. 1. Atomic parameters are given in Table 3, and selected bond lengths, angles, and torsional angles are given in Table 4. Tables of all atom and thermal parameters, interatomic distances, angles and torsional angles, and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre [3].

[3] Data may be obtained from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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