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Septanose Carbohydrates. III* Oxidation–Reduction Products from 1,2:3,4-Di-*O*-isopropylidene-α-D-glucoseptanose: Preparation of L-Idose Derivatives

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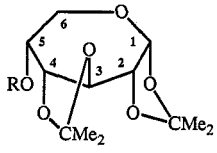
Abstract

Oxidation of 1,2:3,4-di-*O*-isopropylidene-α-D-glucoseptanose (1a) with dimethyl sulfoxide and acetic anhydride has yielded methylthiomethyl ether (1b), ketone (2), and a novel product (3). Reduction of (2) gave (1a) and its L-*ido* isomer (4a) which yielded the mono-*O*-isopropylidene compound (5a) on aqueous acid hydrolysis. Treatment of (5a) with acidified acetone gave (4a) and 1,2:4,5-di-*O*-isopropylidene-β-L-idoseptanose (7a). Reaction of (2) with methylmagnesium iodide yielded the two 5-*C*-methyl compounds (8) and (9). Hydrolysis of (8) and (9) gave 5-*C*-methyl-D-glucose (10) and 5-*C*-methyl-L-idose (11), respectively, as crystalline compounds which yielded crystalline pentaacetates on acetylation. Treatment of the *p*-toluenesulfonate (1c) with lithium benzoate in dimethylformamide gave the benzoate of (4a) and an elimination product (17). Reaction of (1c) with sodium methoxide in methanol yielded (17) and the isomeric elimination product (18).

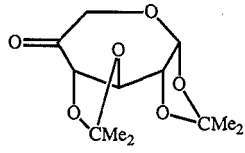
The isolation of 1,2:3,4-di-*O*-isopropylidene-α-D-glucoseptanose (1a) from the products of the reaction of D-glucose with acetone in the presence of sulfuric acid has been described.[1] We report here the conversion of (1a) into other septanose compounds by using oxidation–reduction sequences or displacement reactions on sulfonate ester derivatives of (1a).

Oxidation of (1a)

The action of dimethyl sulfoxide/acetic anhydride[2,3] on (1a) gave three major products: 1,2:3,4-di-*O*-isopropylidene-α-D-*xylo*-hexoseptanos-5-ulose (2)



(1a) R = H
(1b) R = CH_2SMe
(1c) R = Ts
(1d) R = Bz



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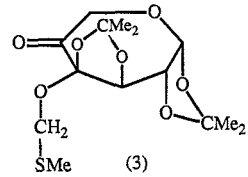

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* The article by Ng, C. J., and Stevens, J. D., in 'Methods in Carbohydrate Chemistry' (Eds R. L. Whistler and J. N. Bemiller) Vol. 7, p. 7 (Academic Press: New York 1976), is regarded as Part II in this series. For Part I, see ref. 1

[1] Stevens, J. D., *Aust. J. Chem.*, 1975, **28**, 525.
[2] Albright, J. D., and Goldman, L., *J. Am. Chem. Soc.*, 1967, **89**, 2416.
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Table 1. ^{1}H chemical shifts of 1,2-*O*-isopropylidenealdoseptanose compounds

Spectra were obtained at 300 MHz unless otherwise stated. Chemical shifts in ppm; first-order values unless otherwise stated

Cpd	Solvent	H1	H2	H3	H4	H5	H6$_a$	H6$_b$	*O*-Isopropylidene methyls				Other
(1b)	$CDCl_3$	5·051	4·197	4·548	3·832	4·244	4·169	3·508	1·593	1·454	1·447	1·387	4·872,[A,B] 4·845,[A,B] 2·177[C]
(1b)	C_6D_6	4·555	4·012	4·799	3·322	3·915	3·879	2·800	1·577	1·421	1·344	1·286	4·687,[A,B] 4·514,[A,B] 1·879[C]
(2)	C_6D_6	4·608	4·003	4·327	3·754		3·999	3·309	1·523	1·376	1·251	1·249	
(3)	$CDCl_3$	5·518	4·450	4·712			4·391[B]	4·237[B]	1·623	1·604	1·515	1·336	4·915,[A] 4·624,[A] 2·286[C]
(3)	C_6D_6	5·373	4·112	4·732			4·418	4·093	1·554	1·536	1·315	0·911	5·132,[A] 4·719,[A] 2·087[C]
(4a)	$CDCl_3$	5·115	4·207	4·005	3·638	3·908	4·184	3·232	1·561	1·457	1·457	1·390	2·748[D]
(4a)	C_6D_6	4·569	3·896	4·076	3·292	3·556	4·003	2·909	1·564	1·367	1·275	1·245	2·191[D]
(4b)	$CDCl_3$	5·111	4·229	4·089	3·799	5·053	4·234	3·169	1·567	1·450	1·439	1·399	2·100[E]
(4b)	C_6D_6	4·594	3·930	4·174	3·534	5·203	4·103	2·766	1·559	1·360	1·267	1·250	1·608[E]
(4c)	C_6D_6	4·680	4·017	4·243	3·675	5·450	4·241	2·871	1·579	1·347	1·291	1·226	
(4d)	$CDCl_3$	5·085	4·193	3·997	3·697	3·479	4·249	3·171	1·560	1·466	1·455	1·388	3·526[F]
(4d)	C_6D_6	4·569	3·901	4·096	3·503	3·142	3·980	2·902	1·586	1·382	1·330	1·259	3·295[F]
(4e)	$CDCl_3$	5·064	4·159	3·897	3·686	4·428	4·317	3·358	1·529	1·364	1·277	1·065	2·444[G]
(5a)	D_2O	5·338	4·239	3·708	3·476	3·658	4·093	3·348	1·544	1·411			
(5b)[I]	$C_6D_6/(CD_3)_2CO$[J]	5·415	4·379	5·405	5·224	5·080	4·108	3·427	1·471	1·312			1·980,[E] 1·970,[E] 1·948[E]
(5c)	C_6D_6	5·107	4·214	3·726	3·156	2·970	3·913	3·227	1·607	1·321			3·645,[F] 3·398,[F] 3·050[F]
(6)[K]	C_6D_6	5·174	4·889	3·575	3·612	3·100	3·788	3·680	1·487	1·454			3·402,[F] 3·144,[F] 2·966[F]
(7b)[L]	$CDCl_3$	5.11	4·12	5·37	3·62	3·88	4·28	3·35	1·59	1·39	1·39	1·36	2·13[E]
(8)	$CDCl_3$	5·084	4·210	4·424	3·579		3·987	3·300	1·589	1·462	1·462	1·393	1·212,[H] 2·285[D]
(8)	C_6D_6	4·584	4·024	4·668	3·081		3·760	2·675	1·606	1·380	1·313	1·273	0·898,[H] 1·893[D]
(9)	$CDCl_3$	5·149	4·211	3·937	3·692		3·825	3·294	1·563	1·458	1·453	1·390	1·412,[H] 2·407[D]
(9)	C_6D_6	4·637	3·939	4·048	3·425		3·679	3·022	1·547	1·387	1·270	1·249	1·206,[H] 1·822[D]
(17)[L]	C_6D_6	4·891	4·268	5·232		4·526	4·222	3·648	1·599	1·392	1·298	1·185	
(18)[K]	C_6D_6	4·935	4·005	4·349	4·181	4·969	5·961		1·586	1·357	1·322	1·222	

[A] OCH_2S. [B] Analysed as an AB system. [C] SMe. [D] OH. [E] Ac. [F] OMe. [G] ArMe. [H] C 5–Me. [I] 400 MHz. [J] 1:4. [K] 500 MHz. [L] 100 MHz.

in about 40% yield, the methylthiomethyl ether derivative (1b), and an unusual oxidation product, the sulfur-containing ketone (3). A more detailed study of the oxidation has revealed a large number of minor products which will be dealt with elsewhere.

In the ^{1}H n.m.r. spectrum of the crystalline ketone (2) (Tables 1 and 2) ($\nu_{C=O}$ 1740 cm^{-1}) the geminal hydrogen atoms on C6 give rise to an AB quartet, J_{gem} 15·8 Hz. The magnitude of this coupling constant is consistent[4,5] with a structure in which the C=O group lies between H6$_a$ and H6$_b$. This would be the case if there was no significant change in the conformation of the seven-membered ring on oxidation of (1a), and the similarity of the values of $J_{1,2}$, $J_{2,3}$ and $J_{3,4}$ for (1) and (2) (see Table 2) suggests that this is so. A significant feature of the ^{1}H n.m.r. spectrum of (2) is the four-bond coupling between H4 and H6$_b$. Similar axial–axial four-bond coupling appears to be a characteristic of six-membered-ring ketones.[6,7] The physical constants determined for ketone (2) agree with those reported earlier.[8]

Use of sodium metaperiodate and ruthenium dioxide (producing ruthenium tetraoxide)[9] gave yields of up to 67% of crystalline (2) from (1).

Table 2. ^{1}H–^{1}H coupling constants of 1,2-*O*-isopropylidenealdoseptanose derivatives

J in Hz; first-order values unless otherwise stated

Cpd	Solvent	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6_a}$	$J_{5,6_b}$	$J_{6_a,6_b}$	Other
(1b)	$CDCl_3$	3·94	7·16	9·71	2·24	1·64	1·67	13·89	11·68[A]
(1b)	C_6D_6	3·74	6·87	9·73	2·13	1·60	1·49	13·60	11·62[A]
(2)	C_6D_6	3·50	6·80	10·52				15·79	0·99[B]
(3)	$CDCl_3$	4·48	5·70					17·43	10·82,[A] 0·62[C]
(3)	C_6D_6	4·49	5·50					17·36	10·67,[A] 0·58[C]
(4a)	$CDCl_3$	3·93	7·22	9·60	9·13	5·90	10·45	12·65	3·00[D]
(4a)	C_6D_6	3·72	6·95	9·59	9·15	5·93	10·41	12·53	2·90[D]
(4b)	$CDCl_3$	3·94	7·33	9·51	9·68	6·00	10·46	12·54	
(4b)	C_6D_6	3·77	7·05	9·56	9·72	6·01	10·48	12·41	
(4c)	C_6D_6	3·78	7·08	9·58	9·70	6·05	10·44	12·45	
(4d)	$CDCl_3$	3·99	7·33	9·56	9·06	5·72	10·45	12·77	
(4d)	C_6D_6	3·78	7·07	9·61	9·02	5·91	10·44	12·60	
(4e)	$CDCl_3$	3·92	7·27	9·55	9·30	6·10	10·34	12·61	
(5a)	D_2O	4·01	7·64	9·94	8·97	5·78	10·52	12·70	
(5b)	$C_6D_6/(CD_3)_2CO$[M]	4·11	8·07	9·98	9·09	5·80	9·39	12·76	
(5c)	C_6D_6	4·12	8·02	8·09	6·46	4·93	6·03	12·91	0·37,[E] 0·60[B]
(6)	C_6D_6	6·54	8·42	0·82	6·07	3·61	0·76	13·21	0·80,[F] 0·61[E]
(7b)	$CDCl_3$	3·3	6·0	10·2	8·3	4·6	9·7	11·2	
(8)	$CDCl_3$	3·90	7·32	9·28				13·67	1·83[G]
(8)	C_6D_6	3·88	7·11	9·54				13·45	1·88[G]
(9)	$CDCl_3$	4·03	6·71	9·89				12·57	0·87[H]
(9)	C_6D_6	3·89	6·69	9·93				12·42	0·98[H]
(17)	C_6D_6	4·40	7·20			2·57	2·44	16·24	2·44,[F] 2·57,[I] 3·05[J]
(18)	C_6D_6	2·83	7·21	9·86	1·48	6·58			0·65,[K] 0·42,[C] 0·57,[L] 0·45,[F] 1·91[E]

[A] J_{OCH_2S}. [B] $J_{4,6_b}$. [C] $J_{1,6_a}$. [D] $J_{5,OH}$. [E] $J_{4,6_a}$. [F] $J_{3,5}$. [G] $J_{6_b,OH}$. [H] $J_{6_b,C5\text{-}Me}$. [I] $J_{3,6_a}$. [J] $J_{3,6_b}$. [K] $J_{1,4}$. [L] $J_{2,6}$. [M] 1:4.

[4] Pople, J. A., and Bothner-By, A. A., *J. Chem. Phys.*, 1965, **42**, 1339.
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[9] Butterworth, R. F., and Hanessian, S., *Synthesis*, 1971, 70.

Formation of the methylthiomethyl ether derivative (1b) is consistent with previous results of dimethyl sulfoxide/acetic anhydride oxidations of a variety of sugar derivatives and other alcohols.[3,10] Identification of this by-product followed from the characteristic ring proton absorptions in the ^{1}H n.m.r. spectrum and the presence of an absorption assigned to an SMe group at 2·18 ppm and an AB quartet, J_{AB} 11·7 Hz, assigned to the OCH_2S group. Similar values have been reported.[2,11,12]

The third dimethyl sulfoxide/acetic anhydride oxidation product was isolated as needle crystals, m.p. 115–116°. The combustion analysis and e.i. mass spectrum of this product indicated the formula $C_{14}H_{22}O_7S$, containing the group CH_2SMe (base peak *m/z* 60 due to $^+CH_2SMe$). This was supported by the presence of a methyl absorption at 2·29 ppm and an AB quartet, J_{AB} 10·8 Hz, in the ^{1}H n.m.r. spectrum. The methyl absorption may be compared with that of dimethyl sulfide (2·12 ppm) and dimethyl sulfoxide (2·62 ppm)[13] which effectively eliminates the possibility of a grouping $CH_2S(O)Me$ being present. Absorption at 1745 cm^{-1} in the infrared spectrum indicated the presence of a ketone group. The ^{1}H n.m.r. spectrum revealed the absence of hydrogen on C4 and C5 and the magnitude of $J_{1,2}$, $J_{2,3}$ and $J_{6_a,6_b}$ suggested the possibility that the conformation of the seven-membered ring is different to that of ketone (2), which would be consistent with a change of configuration at C4, resulting in the 3,4-*O*-isopropylidene ring being *cis*-fused. A four-bond coupling involving H1 and $H6_a$ could be accounted for if these hydrogens formed a W arrangement. Examination of a molecular model shows that a conformation[14] such as $B_{1,2,5}$ or $^{3,4,O}B$, or twist-boats derived from these by torsion about C1–C2 or C3–C4 respectively, would account for $J_{1,6_a}$. Other transformations (which will be reported in another paper in this series) carried out on (1a) resulted in the isolation of 5-*O*-acetyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactoseptanose which has been shown to adopt the conformation $^{1,2,5}B$ in the solid state.[15] It appeared curious, then, that this oxidation product should adopt a conformation in which the C1–C2 and the C3–C4 *O*-isopropylidene groups are both oriented (pseudo) axially on the seven-membered ring. We have verified the proposed structure of (3) and have found that it adopts the $^{3,4,O}B$ conformation in the solid state from an X-ray diffraction study.[16] More recent studies on the formation of (3), 1,2:3,4-di-*O*-isopropylidene-4-*C*-methylthiomethoxy-β-L-*arabino*-hexoseptanos-5-ulose, will be reported elsewhere. There appears to be no precedent for the formation of a compound such as (3) in dimethyl sulfoxide-based oxidations of carbohydrate derivatives.

Borohydride Reduction of (2)

Reduction of 1,2:3,4-di-*O*-isopropylidene-α-D-*xylo*-hexoseptanos-5-ulose (2) with sodium borohydride in ethanol solution gave two products, the D-*gluco*

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[11] James, K., Tatchell, A. R., and Ray, P. K., *J. Chem. Soc. C*, 1967, 2681.
[12] Pojer, P. M., and Angyal, S. J., *Aust. J. Chem.*, 1978, **31**, 1031.
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[14] Stoddart, J. E., 'Stereochemistry of Carbohydrates' pp. 102–4 (John Wiley: New York 1971).
[15] James, V. J., and Stevens, J. D., *Carbohydr. Res.*, 1980, **82**, 167.
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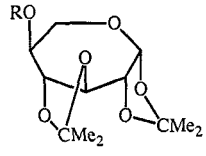
compound (1a) and its L-*ido* isomer (4a). The ratio of these two products was found to vary with the mode of addition of reagents. Slow addition of borohydride to a solution of the ketone gave a D-*gluco*/L-*ido* ratio of 1 : 1, whereas addition of the ketone to a large excess of borohydride resulted in a (1a)/(4a) ratio of 1 : 2·5. Initial separation of the isomers was effected by column chromatography with silicic acid to give (4a) as crystals, m.p. 162–163°. Subsequently it was found that whereas (1a) is very soluble in chloroform or ethyl acetate, (4a) has a remarkably low solubility in these solvents. This was made use of in a large-scale preparation in which (4a) was isolated by crystallization from an ethyl acetate solution of the reduction products. The L-*ido* isomer was characterized as the acetate (4b), benzoate (4c) and methyl ether (4d), all of which are crystalline.

That (4a) is a derivative of L-*idose* was verified by hydrolysis of (4a) to give a syrupy product whose ^{1}H n.m.r. spectrum in D_2O identified it as idose.[17] Use of sodium borodeuteride for the reduction of (2) gave the 5-D analogues of (1a) and (4a). Acid-catalysed hydrolysis of these compounds gave (5-D)-D-glucose and (5-D)-L-idose respectively.



(4a) R = H
(4b) R = Ac
(4c) R = Bz
(4d) R = Me
(4e) R = Ts

Conformation of 1,2:3,4-Di-*O*-isopropylidene-β-L-idoseptanose (4a)

Assignment of the ^{1}H n.m.r. spectrum of (4a) was possible at 300 MHz, and of the ^{1}H n.m.r. spectra of (4b) and (4c) at 100 MHz. Use of repeated spacings, supported by spin decoupling, allowed assignment of all the resonances due to ring hydrogens. Values for the chemical shifts and coupling constants of (4a) and its derivatives are included in Tables 1 and 2. A comparison of the coupling constants $J_{1,2}$, $J_{2,3}$ and $J_{3,4}$ of (4a) with those of (1a) indicates that the two isomers exist in solution in the same conformation. The solution-state conformation of (1a) has been discussed in detail.[1]

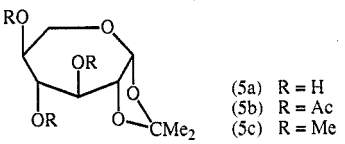
1,2-*O*-Isopropylidene-β-L-idoseptanose (5a)

Mild acid-catalysed hydrolysis of (4a) gave the monoacetal (5a). By allowing the hydrolysis to consume about 30% of (4a), formation of L-idose was kept to a minimum. The remaining diacetal (4a) was recovered and recycled. Crystallization of the hydrolysis product from methanol gave needle crystals, m.p. 165–166°, of 1,2-*O*-isopropylidene-β-L-idoseptanose (5a). Traces of L-idose, which impeded crystallization of (5a), were readily removed by passing a chloroform/methanol solution of the products down a small column of alumina.

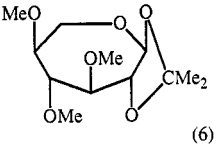
In contrast to the case of the triacetate of 1,2-*O*-isopropylidene-α-D-glucoseptanose, whose 60 MHz ^{1}H n.m.r. spectrum was easily analysed, the spectrum of (5b), by using a variety of solvents at 100 MHz, was not analysable by the first-order approximation. Satisfactory spectral dispersion was obtained

[17] Angyal, S. J., and Pickles, V. A., *Aust. J. Chem.*, 1972, **25**, 1695.

at 400 MHz and the chemical shifts and coupling constants are included in Tables 1 and 2. The latter values indicate that (4b) and (5b) have similar solution state conformations.



(5a) R = H
(5b) R = Ac
(5c) R = Me



(6)

1,2-*O*-Isopropylidene-3,4,5-tri-*O*-methyl-α-L-idoseptanose (6)

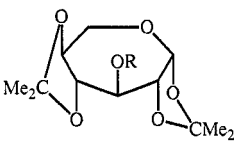
Although the geometrical requirements of *O*-isopropylidene groups inhibit the formation of *trans*-1,2-*O*-isopropylidene derivatives of both furanose and pyranose forms of aldoses,[18] the greater flexibility of the seven-membered ring could allow such derivatives of aldoseptanoses to be formed.

Methylation of (5a) with methyl iodide and silver oxide in dimethylformamide gave 1,2-*O*-isopropylidene-3,4,5-tri-*O*-methyl-β-L-idoseptanose (5c) as a liquid. Gas–liquid chromatography of the products formed by treatment of (5c) with acidified acetone indicated the presence of a new compound (A) in addition to (5c). Compound (A) was approximately 8% of the mixture. Column chromatography was used to separate the products. ^{1}H n.m.r. spectra of compound (A) are consistent with its formulation as 1,2-*O*-isopropylidene-3,4,5-tri-*O*-methyl-α-L-idoseptanose (6). In particular, a $J_{1,2}$ value of 6·5 Hz requires a *trans* arrangement of H1 and H2.

1,2:4,5-Di-*O*-isopropylidene-β-L-idoseptanose (7a)

Acetonation of (5a) under a variety of conditions gave a mixture of (4a) and another compound identified as 1,2:4,5-di-*O*-isopropylidene-β-L-idoseptanose (7a). Use of 0·1% sulfuric acid in acetone gave a product ratio falling from 1 : 11 after 20 min to 1 : 70 after 70 min for (7a)/(4a). Use of 2,2-dimethoxypropane and anhydrous copper sulfate gave a (7a)/(4a) ratio of 1 : 4·5 and this method was used for preparative-scale reactions. The two compounds could be separated by chromatography over neutral silicic acid, followed by crystallization of the enriched fractions. Use of acidic silicic acid was precluded by the isomerization of (7a) into (4a) during chromatography of this material.

The ^{1}H n.m.r. spectrum of acetate (7b) was readily analysed after assigning the doublet at 5·11 ppm, *J* 3·3 Hz, to H1. The data are listed in Tables 1 and 2.



(7a) R = H
(7b) R = Ac

[18] Clode, D. M., *Chem. Rev.*, 1979, **79**, 491.

Conformation of (7b)

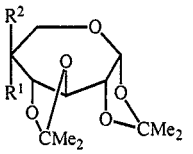
Disregarding the deviations of oxepan ring angles from the tetrahedral value, but making use of estimated torsional angles for twist-chairs *B* and *C* of oxepan,[19,20] we can derive dihedral angles between vicinal hydrogen atoms for the two twist-chair conformations of oxepan. Conformation $^{O,1}TC_{2,3}$ may be discarded as it cannot account for the large value of $J_{5,6_b}$. For the $^{3,4}TC_{1,2}$ conformation, reduction of the O1–O2 dihedral angle would be necessary in order to approach the optimum value for an *O*-isopropylidene ring (thought[21] to be 18–25°, with maximum value 30°). Such an angle reduction would also reduce the H2–H3 dihedral angle, which would account for the value of $J_{2,3}$; similar twisting about the C4–C5 bond in conformation $^{5,6}TC_{3,4}$ would be required to reduce the O4–O5 torsional angle, but this would result in an increase in the angle H5–H6_a, already too large to account for the value of $J_{5,6_a}$. Although conformation $^{4,5}TC_{6,O}$ provides a smaller O4–O5 torsion angle, still some reduction in this angle would be required for the 4,5-*O*-isopropylidene ring, again resulting in an increase in the H5–H6_a angle. From these considerations, compound (7b) probably exists in solution in the conformation $^{4,5}TC_{6,O}$, which is the same conformation adopted by the isomeric diacetal (4b).

1,2:3,4-Di-*O*-isopropylidene-5-*C*-methyl-α-D-gluco- and -β-L-ido-septanoses

Reaction of methylmagnesium iodide with ketone (2).—Ketone (2) reacted slowly with methylmagnesium iodide in a refluxing mixture of ether and benzene to give two products, identified (see below) as 1,2:3,4-di-*O*-isopropylidene-5-*C*-methyl-α-D-glucoseptanose (8) and 1,2:3,4-di-*O*-isopropylidene-5-*C*-methyl-β-L-idoseptanose (9). Identification of the two products as (8) and (9) was made on the basis of the similarity of spin coupling constants $J_{1,2}$, $J_{2,3}$ and $J_{3,4}$ of both isomers with the corresponding values for (1a), suggesting that all three compounds have the same conformation. Comparison of the geminal coupling constants $J_{6_a,6_b}$ for (8) and (9) with the corresponding values for (1a) and (4a), indicates that in (8) the oxygen atom on C5 is antiperiplanar to one of the C6 hydrogen atoms, resulting in a value of $J_{6_a,6_b}$ that is more negative than the value for $J_{6_a,6_b}$ in (9).[22,23] Also, H3 in (8) comes into resonance at lower field than H3 in (9), which is consistent with the known greater deshielding effect[24] of an axially opposed hydroxy group on a six-membered ring compared with the effect[25] of an axially opposed methyl group. Other n.m.r. evidence supports the assignments. As observed[1] in the ^{1}H n.m.r. spectrum of (1a) in $CDCl_3$, the hydroxylic hydrogen in (8) is spin coupled with H6_b (these hydrogens form a W arrangement when the hydroxylic hydrogen is antiperiplanar to C6), and in (9), H6_b is spin coupled

[19] Bocian, D. F., and Strauss, H. L., *J. Am. Chem. Soc.*, 1977, **99**, 2876.
[20] Strauss, H. L., personal communications to J.D.S., 1977.
[21] Altona, C., and van der Veek, A. P. M., *Tetrahedron*, 1968, **24**, 4377.
[22] Coxon, B., *Tetrahedron*, 1965, **21**, 3481.
[23] Hall, L. D., and Manville, J. F., *Can. J. Chem.*, 1967, **45**, 1299.
[24] Danneels, D., and Anteunis, M., *Tetrahedron Lett.*, 1975, 687.
[25] Danneels, D., and Anteunis, M., *Org. Magn. Reson.*, 1974, **6**, 617.

with the C 5 methyl hydrogens: similar long-range coupling of hydrogen atoms of axial methyl groups on six-membered rings is well documented.[26]



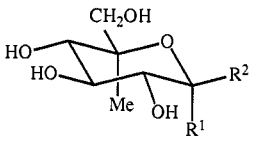
	R^1	R^2
(8)	OH	Me
(9)	Me	OH

5-*C*-Methyl-L-idose and 5-*C*-Methyl-D-glucose

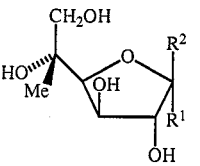
Aqueous hydrochloric acid hydrolysed (8) and (9) to give 5-*C*-methyl-D-glucose (10) and 5-*C*-methyl-L-idose (11) respectively, both isomers being obtained in crystalline form. The ^1H n.m.r. data for (10) and (11) are given in Tables 3 and 4. Each spectrum is dominated by the absorptions of the pyranose ring form in which C1–OH is equatorial [(10P$_\beta$) and (11P$_\alpha$)]. For these two species, the values of $J_{1,2}$, $J_{2,3}$ and $J_{3,4}$ are consistent with a normal chair conformation. In (11P), the CH_2OH group is axially oriented and, in keeping with this arrangement,[27] more vigorous acid treatment of (9) gave a high yield of the 1,6-anhydro compound, 1,6-anhydro-5-*C*-methyl-β-L-idopyranose (12a). The percentage composition of equilibrated D_2O solutions of (10) and (11) is as follows:

Compound	F_α	F_β	P_α	P_β
(10)	0·7	0·8	6·5	92·0
(11)	4·5	4·7	80·9	9·9

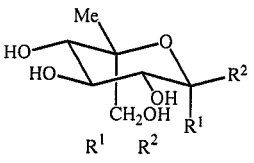
The furanose contribution for 5-*C*-methyl-D-glucose is significantly less than that for 5-*C*-methyl-L-idose. From the percentage of the pyranose forms of (10) and (11) in deuterium oxide solution, the free-energy differences between



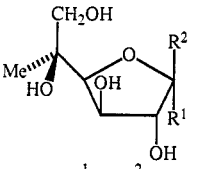
	R^1	R^2
(10P$_\alpha$)	OH	H
(10P$_\beta$)	H	OH



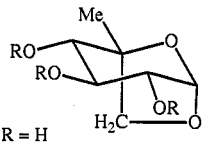
	R^1	R^2
(10F$_\alpha$)	OH	H
(10F$_\beta$)	H	OH



	R^1	R^2
(11P$_\alpha$)	H	OH
(11P$_\beta$)	OH	H



	R^1	R^2
(11F$_\alpha$)	H	OH
(11F$_\beta$)	OH	H



(12a) R = H
(12b) R = Ac

[26] Jackman, L. M., and Sternhell, S., 'Applications of Nuclear Magnetic Resonance in Organic Chemistry' 2nd Edn, p. 337 (Pergamon Press: Oxford 1969)
[27] Angyal, S. J., and Dawes, K., *Aust. J. Chem.*, 1968, **21**, 2747.

Table 3. ^{1}H chemical shifts of 5-*C*-methylaldohexose compounds

Spectra were obtained at 500 MHz. Chemical shifts in ppm; first-order values unless otherwise stated; n.d. denotes not detected

Cpd	Solvent	H1	H2	H3	H4	H6$_a$	H6$_b$	C5–Me	Acetate methyls				
(10P$_\alpha$)	D_2O[A]	5·279	3·532	3·922	3·618	3·520[B]	3·460[B]	1·269					
(10P$_\beta$)	D_2O[A]	4·812	3·214	3·674	3·568	3·579[B]	3·548[B]	1·180					
(10F$_\alpha$)	D_2O[A]	5·538	4·102	4·383	4·117	n.d.	n.d.	n.d.					
(10F$_\beta$)	D_2O[A]	5·226	4·096	4·283	4·083	n.d.	n.d.	n.d.					
(11P$_\alpha$)	D_2O[A]	4·889	3·247	3·700	3·451	3·919	3·606	1·310					
(11P$_\beta$)	D_2O[A]	5·220	3·570	3·944	3·482	3·960	3·595	1·293					
(11F$_\alpha$)	D_2O[A]	5·246	4·092	4·300	4·106	n.d.	n.d.	n.d.					
(11F$_\beta$)	D_2O[A]	5·560	4·096	4·394	4·123	n.d.	n.d.	n.d.					
(12a)	D_2O	5·338	3·548	3·526	3·491	4·061	3·416	1·435					
(12b)	$CDCl_3$[C]	5·434	4·880	5·299	5·058	4·233	3·440	1·368	2·080	2·064	2·010		
(12b)	C_6D_6[C]	5·485	5·100	5·625	5·213	3·982	3·083	1·013	1·742	1·645	1·610		
(13)	$CDCl_3$	5·960	5·110	5·376	5·306	4·067	3·888	1·428	2·108	2·107	2·039	2·026	2·013
(13)	C_6D_6	6·212	5·449	5·631	5·574	4·060	3·859	1·066	1·699	1·681	1·678	1·577	1·537
(14)	$CDCl_3$	6·374	5·136	5·612	5·320	3·921[B]	3·903[B]	1·436	2·144	2·119	2·041	2·036	2·020
(15)	$CDCl_3$	6·061	5·114	5·570	5·156	4·700	4·000	1·283	2·204	2·100	2·049	2·040	2·004
(15)	C_6D_6	6·494	5·463	5·916	5·320	4·709	3·993	1·070	1·931	1·697	1·668	1·588	1·559
(16)	$CDCl_3$	6·312	5·119	5·584	5·148	4·520	4·217	1·301	2·107	2·093	2·069	2·027	2·020

[A] 310 K. [B] Calculated as an AB system. [C] Shifts of H3 and H4 refined by analysis of H1 to H4 as a four-spin system by using the Brüker program PANIC.

the pyranose α- and β-anomers are calculated as 6·86 kJ for (10) and 5·48 kJ for (11).

We have verified the configuration assignments for (8) and (9) by an X-ray study[28] on a crystal of (11P$_\alpha$). This study confirmed that the pyranose ring is only slightly distorted (flattened in the region C4–C5–O5) from the average ring structure exhibited by β-D-glucopyranose compounds. With OH at C1 equatorial, an axial CH_2OH group on C5 causes only minor distortion of the ring.

The vicinal spin coupling constants of the ring hydrogens agree well with those of the α- and β-pyranose forms of D-glucose (included in Table 4) taking into account the effect[29] of the axial Me or CH_2OH group on C5, which results in $J_{3,4}$ being larger for (10P) and (11P) than for D-glucopyranose. We note small differences in our values of the vicinal proton coupling constants for α- and β-glucose compared with those reported earlier.[30]

^{13}C n.m.r. data for compounds (10) and (11) are presented in the Experimental. The chemical shifts of C1 and C3 for (10P$_\beta$) and (11P$_\alpha$) show the expected upfield shifts, compared with those of β-glucopyranose,[31] resulting from the axial group on C5. C4 in each of the pyranose isomers of (11) is at lower field than those of (10), in keeping with the relative shifts of C4 in glucose and 6-deoxyglucose.[31] It had been observed earlier[32] that an axial hydroxy

Table 4. ^{1}H–^{1}H coupling constants of 5-*C*-methylaldohexose compounds

J in Hz; first-order values unless otherwise stated; n.d. denotes not determined

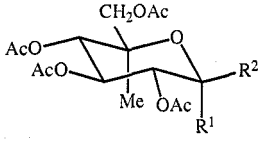
Compound	Solvent	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{6a,6b}$	Other
(10P$_\alpha$)	D_2O[A]	4·10	9·80	9·76	12·02	0·50[C]
(10P$_\beta$)	D_2O[A]	8·10	9·29	9·70	12·07	
(10F$_\alpha$)	D_2O[A]	3·99	2·53	4·04	n.d.	
(10F$_\beta$	D_2O[A]	0·80	1·38	3·98	n.d.	
(11P$_\alpha$)	D_2O[A]	8·10	9·47	9·91	12·56	0·80[D]
(11P$_\beta$)	D_2O[A]	4·12	9·77	9·77	12·06	0·69,[D] 0·46[C]
(11F$_\alpha$)	D_2O[A]	1·08	1·53	3·85	n.d.	0·61[C]
(11F$_\beta$)	D_2O[A]	3·83	2·24	3·75	n.d.	0·65[C]
α-D-Glucopyranose	D_2O	3·79	9·83	9·14	12·40	0·52[C]
β-D-Glucopyranose	D_2O	7·96	9·30	9·00	12·26	
(12a)	D_2O	1·67	8·30	8·70	8·11	1·60[E]
(12b)	$CDCl_3$	1·85	8·42	8·56	7·95	1·56[E]
(12b)	C_6D_6	1·86	8·44	8·51	7·93	1·59[E]
(13)	$CDCl_3$	8·15	9·42[B]	9·93	12·10	
(13)	C_6D_6	8·14	9·30[B]	9·92	12·10	
(14)	$CDCl_3$	4·14	10·40	10·18	12·14	0·49[C]
(15)	$CDCl_3$	7·87	9·25	9·87	12·62	0·34[D]
(15)	C_6D_6	7·87	9·17	9·81	12·63	0·44[D]
(16)	$CDCl_3$	4·06	10·24	10·06	12·00	0·70,[D] 0·48,[C] 0·34[F]

[A] 310 K. [B] $J_{2,3}$ adjusted to give good agreement of experimental and computed line frequencies by using the Brüker program PANIC. [C] $J_{1,3}$. [D] $J_{6a,Me}$. [E] $J_{4,6b}$. [F] $J_{1,6b}$.

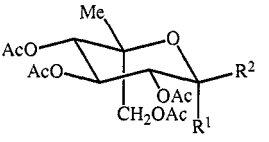
[28] Craig, D. C., and Stevens, J. D., *Aust. J. Chem.*, 1990, **43**, 2087.
[29] Altona, C., and Haasnoot, C. A. G., *Org. Magn. Reson.*, 1980, **13**, 417.
[30] Curalto, W., Neuringer, L. J., Ruben, D., and Haberkorn, R., *Carbohydr. Res.*, 1983, **112**, 297.
[31] Bock, K., and Pedersen, C., *Adv. Carbohydr. Chem. Biochem.*, 1983, **41**, 27.
[32] Grover, S. H., and Stothers, J. B., *Cand. J. Chem.*, 1974, **52**, 870.

group on a cyclohexane-type ring causes a downfield shift of the carbon atom of a syn-axial methyl group. Similar downfield shifts are observed for the axial C 5 methyl group in ($10P_\alpha$) compared with that of ($10P_\beta$) and for the axial C 5 hydroxymethyl group in ($11P_\beta$) compared with that of ($11P_\alpha$). For the furanose forms of (11), the nearly identical chemical shifts of H 2 precluded the assignment of C 2 by one-bond ^{13}C–^1H correlation. Assignment was achieved by using the indirect J-spectrum procedure[33] and these results were used to assign C 2 in ($10F_\alpha$) and ($10F_\beta$) by analogy. The relative chemical shifts of C 1–C 4 in the furanose forms are consistent with the values obtained for the L-idofuranose anomers.[31]

Acetylation of ($10P_\beta$) and ($11P_\alpha$) yielded the corresponding crystalline pentaacetates (13) and (15) respectively. Treatment of (13) with $ZnCl_2$ and acetic anhydride[34] gave a mixture of (13) and its C 1 isomer (14) which was resolved by liquid chromatography, and similar treatment of (15) gave a mixture of (15) and (16). The ^1H n.m.r. parameters for these acetates, included in Tables 3 and 4, are consistent with regular pyranose chair conformations.



	R^1	R^2
(13)	H	OAc
(14)	OAc	H



	R^1	R^2
(15)	H	OAc
(16)	OAc	H

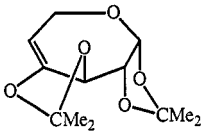
Furanose derivatives of (10) and (11) and the 3-*O*-benzyl analogues of (12b) and (13) have been reported earlier.[35]

Nucleophilic displacement of sulfonyloxy groups by using alkali metal salts of carboxylic acids in dimethylformamide is a well proven procedure[36] for inversion of configuration of secondary alcohols. Treatment of the *p*-toluenesulfonate (1c), derived from (1a), with lithium benzoate in dimethylformamide produced two compounds. One was identified as the benzoate (4c) and the other, which travelled much faster than (4c) on silica gel thin-layer chromatograms, has been identified as the product of elimination, 5-deoxy-1,2:3,4-di-*O*-isopropylidene-*β*-L-*threo*-hex-4-enoseptanose (17). In an attempt to obtain (17) in higher yield, (1c) was treated with sodium methoxide in methanol. Analysis of the reaction products by g.l.c. showed that two products had been formed, (17) and another 'olefin' identified as 5-deoxy-1,2:3,4-*O*-isopropylidene-*α*-D-*xylo*-hex-5-enoseptanose (18). It was expected that formation of (18) would be favoured by use of a more hindered base: this proved to be the case. Treatment of (1c) with potassium t-butoxide in t-butyl alcohol gave (17) and (18) in the ratio 1 : 2. Separation of (17) and (18) by liquid chromatography or crystallization proved to be unsatisfactory. Pure samples were obtained by preparative g.l.c. The structures of (17) and (18) were deduced from the ^1H n.m.r. spectra (see Tables 1 and 2).

[33] Morris, G. A., *J. Magn. Reson.*, 1981, **44**, 277.
[34] Wolfrom, M. L., and Thompson, A., in 'Methods in Carbohydrate Chemistry' (Eds R. W. Whistler and M. L. Wolfrom) Vol. 2, p. 211 (Academic Press: New York 1963).
[35] Funabashi, M., Sato, H., and Yoshimura, J., *Bull. Chem. Soc. Jpn*, 1976, **49**, 788.
[36] Baker, B. R., in 'Methods in Carbohydrate Chemistry' (Eds R. L. Whistler and M. L. Wolfrom) Vol. 2, p. 441 (Academic Press: New York 1963).

The facile elimination of the tosyloxy group in (1c) is a result of the *trans* coplanar arrangement of the 'axial' hydrogen atoms on C4 and C6 and the 'axial' oxygen atom on C5.

Treatment of the tosylate (4e) with lithium benzoate in dimethylformamide gave the D-*gluco* benzoate (1d) as the major product together with a trace of the elimination product (17). The success of this displacement reaction suggests the possibility of using (4e) for the preparation of other D-glucose derivatives in which the oxygen function on C5 is replaced by other elements.



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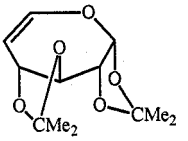

(18)

Experimental

General

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. Infrared spectra were recorded by using paraffin mulls and a Perkin–Elmer 580 instrument. ^1H n.m.r. spectra were recorded by using a Jeol FX-100 (at 100 MHz), a Bruker CXP-300 (300 MHz), a Bruker AM-400 (400 MHz) or a Bruker AM-500 (500 MHz) spectrometer. Tetramethylsilane was used as internal reference for organic solvents, and chemical shifts are reported in ppm from $SiMe_4$. Digital resolution in the transformed spectrum was generally *c.* 0·06 Hz. Acetone was used as internal reference for D_2O solutions, and chemical shifts are in ppm from sodium 3-(trimethylsilyl)(D_4)propionate, the shift of acetone being taken as 2·234 ppm. ^{13}C n.m.r. spectra were recorded at 125 MHz by using composite pulse decoupling (WALTZ-16) for proton-decoupled spectra, standard Bruker ^1H–^{13}C correlation programs for the correlation spectra, and the program of Morris[16] for the indirect J-spectrum. Shifts are relative to internal dioxan at 67·40 ppm with acetone (31·07 ppm) as the internal reference material.

Electron-impact mass spectra were recorded by using an AEI-MS12 single-focusing mass spectrometer and the high-resolution spectra were obtained by using a peak timing technique[37] on an AEI-MS902 spectrometer with a Chem-Spec c.i. source with hydrogen as reagent gas.

Optical rotations were determined by using a Bendix NPL Automatic polarimeter, model 143C or a Perkin–Elmer 141 polarimeter.

Solvents

Ether refers to diethyl ether, light petroleum is the fraction distilling at 60–80°, and ethanol refers to 95% ethanol unless otherwise stated. Dimethylformamide and dimethyl sulfoxide were distilled from calcium hydride and stored over 4A molecular sieves.

Chromatography

Column chromatography was generally carried out with columns packed so that the height-to-diameter ratio was approximately 10 : 1, slight pressure being applied to speed elution. Unless otherwise stated, silicic acid refers to Mallinckrodt A.R. silicic acid, 100 mesh. Gas–liquid chromatography (g.l.c.) was carried out by using a custom-built instrument fitted with glass-lined insert and flame ionization detector and a glass column packed with 3% DEGA (Analabs, stabilized) on Chromosorb W.H.P. (100–120 mesh).

[37] Brophy, J. J., Nelson, D., Goldsack, R. J., Lidgard, R. O., and Melley, D. P., *Lab. Pract.*, 1979, 615.

Acetylation Procedure

The standard procedure for acetylations involved treatment of the hydroxylic compound with a 1 : 1 mixture of acetic anhydride and pyridine. After removing volatiles on a Büchi evaporator, the residue was dissolved in ethanol and this solution was kept at room temperatue for *c.* 30 min in order to destroy remaining acetic anhydride. After evaporation of the ethanol solution, a chloroform solution of the residue was shaken with 1 M sulfuric acid followed by saturated sodium bicarbonate solution, filtered through a short bed of silicic acid and evaporated.

Oxidation of 1,2:3,4-Di-O-isopropylidene-α-D-glucoseptanose (1a)

(A) *By using dimethylsulfoxide/acetic anhydride.*—To a mixture of dimethyl sulfoxide (50 ml) and acetic anhydride (30 ml) was added (1a) (5·00 g). After 7 days at room temperature (*c.* 25°), the mixture was evaporated at 0·5 mm to give a residue of oil and crystals. A solution of the products in diethyl ether (25 ml) was added to a column of silicic acid (Mallinckrodt CC4, 100–200 mesh, 100 g), packed in ether/light petroleum (1 : 1) which was developed with ether/light petroleum (1 : 1), collecting 25-ml fractions. Fractions 8–12 contained a mixture of compounds (see below for further chromatography). Elution with ethyl acetate/light petroleum (1 : 1) gave 2·89 g (58%) of crude *1,2:3,4-di-O-isopropylidene-α-D-xylo-hexoseptanos-5-ulose* (2). Crystallization of crude (2) from benzene/light petroleum gave colourless needles (1·32 g), m.p. 137–140°, $[\alpha]_D^{18}$ −119·1° (*c*, 1·4 in $CHCl_3$) (Found: C, 55·8; H, 7·2. $C_{12}H_{18}O_6$ requires C, 55·8; H, 7·0%) ν_{max} 1740 cm^{-1}.

Chromatography of the mixture in fractions 8–12 (2·50 g) in ether/light petroleum (1 : 3) over silica gel (Merck 7736, 40 g), collecting 10-ml fractions, and changing the eluent to ether/light petroleum (1 : 2) after fraction 10 was collected, gave fractions 18–21 showing a single spot on t.l.c. Crystallization of the residue (0·50 g) from these fractions from benzene/light petroleum gave needles of *1,2:3,4-di-O-isopropylidene-4-C-methylthiomethoxy-β-L-arabino-hexoseptanos-5-ulose*, m.p. 117–118° $[\alpha]_D^{25}$ −51·0° (*c*, 1·5 in $CHCl_3$) (Found: C, 50·4; H, 6·6. $C_{14}H_{22}O_7S$ requires C, 50·3; H, 6·6%). ν_{max} 1745 cm^{-1}. E.i. *m/z* 319 (M−15), 60 (100%, $^+CH_2SMe$). Evaporation of fractions 27–37 gave a colourless oil (1·00 g) which crystallized on standing. Crystallization from benzene/light petroleum gave colourless needles of *1,2:3,4-di-O-isopropylidene-5-O-methylthiomethyl-α-D-glucoseptanose*, m.p. 78–80°, $[\alpha]_D$ 8·2° (*c*, 1·6 in $CHCl_3$) (Found: C, 52·8; H, 8·0. $C_{14}H_{24}O_6S$ requires C, 52·5; H, 7·6%).

(B) *By using ruthenium dioxide and sodium metaperiodate.*—A mixture of (1a) (6·00 g), sodium metaperiodate (11·0 g), sodium carbonate (6·0 g) and ruthenium dioxide (Engelhard, 0·500 g) was stirred vigorously in water (60 ml) and chloroform (ethanol-free, 60 ml) for 2 h. After addition of propan-2-ol (2 ml), stirring was continued for 0·5 h. After removal of ruthenium dioxide by filtration and addition of 60 ml of water to the filtrate, the aqueous layer was extracted with chloroform (2×30 ml). Evaporation of the dried ($MgSO_4$) chloroform extracts gave a crystalline residue which was recrystallized from benzene/light petroleum to give 3·13 g of (2). A further 0·89 g of ketone was obtained from the mother liquors, giving a total of 4·02 g (67%).

2,4-Dinitrophenylhydrazone of (2)

To (2) (71 mg) in methanol (2·5 ml) was added 2,4-dinitrophenylhydrazine (80 mg) and 2 drops of 2 M sodium methoxide in methanol. The solution was refluxed for 4·5 h. Evaporation of the reaction mixture left a residue which was chromatographed on silicic acid (3 g). Elution with benzene gave the 2,4-dinitrophenylhydrazone of acetone (50 mg), m.p. 125–126°, no depression admixture with acetone 2,4-dinitrophenylhydrazone; i.r. spectrum identical to that of acetone 2,4-dinitrophenylhydrazone.

Elution with ethyl acetate/benzene (1 : 19) gave the *2,4-dinitrophenylhydrazone* of (2) which crystallized from methanol/water as yellow plates, m.p. 230–231°, $[\alpha]_D^{21}$ 79·2° (*c*, 0·53 in $CHCl_3$) (Found: C, 49·2; H, 5·0. $C_{18}H_{22}N_4O_9$ requires C, 49·3; H, 5·1%).

Reduction of 1,2:3,4-Di-O-isopropylidene-α-D-xylo-hexoseptanos-5-ulose

(A) To a stirred solution of (2) (130 mg) in ethanol (2 ml) was added sodium borohydride (10 mg). After 15 min, ion-exchange resin (Amberlite IRC-50, H^+ form) was added and the mixture stirred until neutral (pH paper). After filtration, the solution was evaporated and the solvent was evaporated 3 times from solutions of the residue in methanol. An ethanol solution of the products was used for g.l.c. analysis [170°, retention times: (4a) 12·6 min, (1a) 17·8 min], (1a)/(4a) 1 : 1.

(B) To a stirred solution of $NaBH_4$ (25 mg) in ethanol (1 ml) was added (2) (50 mg). After 15 min, excess hydride was destroyed by the addition of acetone, and the mixture was processed as in (A), (1a)/(4a) 1 : 1·85.

(C) To a stirred solution of sodium borohydride (1·00 g) in ethanol (30 ml) cooled to 10°, was added in portions a solution of (2) (2·00 g) in ethanol (12 ml). The reaction mixture was stirred for 0·5 h at 15° and for 1 h at 25°. After the addition of acetone (4 ml) and water (10 ml), the reaction mixture was concentrated (Büchi evaporator) and a mixture of the residue in water was extracted with chloroform (30 ml, 1×15 ml). Each extract was washed, by using the same water (10 ml) for each, and passed down a short bed of silica gel. Evaporation of the eluates gave 2·01 g of residue. Chromatography of the products by using silica gel [Merck 7736, 120 g packed in ether/benzene (1 : 1), in a 3·8 cm i.d. column], collecting 50-ml fractions eluted with ether/benzene (1 : 1), gave (4a) (1·32 g) in fractions 11–15, and (1a) (0·66 g) in fractions 18–24. Crystallization of (4a) from ethyl acetate (10 ml) gave *1,2:3,4-di-O-isopropylidene-β-L-idoseptanose* (0·85 g), m.p. 179–180°, $[\alpha]_D^{22}$ −20·4° (*c*, 1·2 in $CHCl_3$) (Found: C, 55·5; H, 7·8. $C_{12}H_{20}O_6$ requires C, 55·4; H, 7·7%). A second crop of (4a) (0·35 g), m.p. 178·5–179°, was obtained (EtOAc, 2 ml), giving 1·10 g (55%) of purified (4a). Crystallization of the residue in fractions 18–24 from benzene/light petroleum gave (1a), m.p. 145–146°.

(D) Sodium borohydride reduction of (2) was carried out as in (C). After the addition of acetone to destroy excess borohydride, water (14 ml) was added to the residue left on evaporation of the reaction mixture, whereupon crystallization occurred. The crystalline product was collected, washed with water (2×2 ml) and air dried. Crystallization of the crude product (1·01 g) from ethyl acetate (a small amount of insoluble material was removed by filtration) gave (4a) (0·58 g), m.p. 178–179° [a trace of (1a) in this product was detected by g.l.c.].

(E) Sodium borodeuteride (0·20 g) was added to a solution of (2) (2·58 g) in ethanol (50 ml) cooled in an ice-water bath. After 2 h, the reaction mixture was neutralized by adding ion-exchange resin (Amberlite IRC-50). Evaporation of the filtered mixture gave a residue from which methanol was evaporated three times. Chromatography of the products over silica gel (Merck 7734, 100 g) in ether/benzene (1 : 1), gave (5-D)-(4a) (0·90 g), a mixture of the two products (0·64 g), and (5-D)-(1a) (1·07 g).

Hydrolysis of (5-D)-(1a) and (5-D)-(4a)

After a solutiom of (5-D)-(1a) (357 mg) in 0·1 M HCl (3 ml) had been kept at 60° for 43 h, the hydrolysate was neutralized by using ion-exchange resin (Amberlite IRA-400, HCO_3^-), filtered and evaporated. An aqueous ethanol solution of the residue was seeded with D-glucose to give (5-D)-D-glucose (102 mg), m.p. 143–145°, its identity being verified by the ^1H n.m.r. spectrum of a D_2O solution.

To a solution of (5-D)-(4a) (52 mg) in water (3 ml, warming required to effect solution) was added 1 M HCl (0·33 ml). After the mixture had been kept at 40° for 21 h, t.l.c. (silica plate, 1 : 9 absolute ethanol/ethyl acetate) showed hydrolysis was complete. Neutralization of the reaction mixture with Amberlite IR-4B resin was followed by freeze drying to give syrupy (5-D)-L-idose, the identity of which was confirmed by comparison of its ^1H n.m.r. spectrum of a D_2O solution with that of L-idose. Similar treatment of (4a) yielded syrupy L-idose.

Derivatives of 1,2:3,4-Di-O-isopropylidene-β-L-idoseptanose

(A) Acetylation of (4a) by using the standard procedure gave *5-O-acetyl-1,2:3,4-di-O-isopropylidene-β-L-idoseptanose* as colourless prisms, m.p. 163–164° (benzene/light petroleum),

$[\alpha]_D^{22}$ 4·9° (*c*, 1·2 in $CHCl_3$) (Found: C, 55·9; H, 7·3. $C_{14}H_{22}O_7$ requires C, 55·6; H, 7·3%).

(B) Benzoyl chloride (0·15 ml) was added to a solution of (4a) (0·090 g) in pyridine (1 ml). After the solution had stood for 1·5 h at room temperature, chloroform and saturated sodium bicarbonate solution were added and the chloroform extract was washed successively with 2 M hydrochloric acid and saturated sodium bicarbonate solution, dried over $MgSO_4$ and evaporated. Chromatography of the residue on silicic acid, eluting with ether/light petroleum (1 : 3), gave *5-O-benzoyl-1,2:3,4-di-O-isopropylidene-β-L-idoseptanose* as colourless plates, m.p. 155–156° (light petroleum), $[\alpha]_D^{26}$ 37·6° (*c*, 0·95 in $CHCl_3$) (Found: C, 62·9; H, 6·7. $C_{19}H_{24}O_7$ requires C, 62·6; H, 6·6%).

(C) Silver oxide (0·5 g) was added to a refluxing solution of (4a) (0·21 g) in methyl iodide (3·5 ml). After 1·5 h, silver salts were filtered from the cooled reaction mixture and washed with chloroform. Evaporation of solvents left a residue which crystallized from light petroleum (40–60°) to give prisms (0·13 g). Recrystallization from light petroleum (40–60°) gave *1,2:3,4-di-O-isopropylidene-5-O-methyl-β-L-idoseptanose* as prisms, m.p. 63–65°, $[\alpha]_D^{20}$ −27·2° (*c*, 1·1 in $CHCl_3$). A sample was short-path distilled at 0·2 mm, 100° bath (Found: C, 57·2; H, 8·0. $C_{13}H_{22}O_6$ requires C, 57·0; H, 8·1%).

(D) A solution of (4a) (0·50 g) and *p*-toluenesulfonyl chloride (0·75 g) in anhydrous pyridine (5 ml) was kept at 30° for 20 h. After addition of a few drops of water to hydrolyse excess reagent, the reaction mixture was shaken with water and chloroform, the chloroform solution was washed successively with 2 M sulfuric acid and saturated sodium bicarbonate solution and filtered through silicic acid (2 g). Evaporation of solvent left a gum which crystallized after several days. Crystallization from benzene/light petroleum gave *1,2:3,4-di-O-isopropylidene-5-O-p-toluenesulfonyl-β-L-idoseptanose* as needles, m.p. 109–110°, $[\alpha]_D$ 15·8 (*c*, 1·47 in $CHCl_3$) (Found: C, 55·3; H, 6·5. $C_{19}H_{26}O_8S$ requires C, 55·1; H, 6·3%).

1,2-O-Isopropylidene-β-L-idoseptanose (5a)

To a solution of (4a) (11·20 g) in water (660 ml) was added 1 M hydrochloric acid (13 ml). After the mixture had stood at 22° for 36 h, ion-exchange resin (Amberlite IRA-400, HCO_3^-, *c.* 20 g) was added and the mixture stirred until neutral. Extraction of the filtered solution with chloroform (4×100 ml) gave (4a) (8·85 g) from the organic extracts. After dissolving the recovered starting material in water (500 ml), 1 M hydrochloric acid (10 ml) was added and the mixture kept at 23° for 36 h. Workup as above gave 3·47 g of (4a). The combined aqueous solutions were freeze dried and the residue yielded crystals from methanol. Concentration of the mother liquors gave more crystals, a total of 4·42 g (68% based on unrecovered starting material) from 5 crops. Recrystallization from methanol gave *1,2-O-isopropylidene-β-L-idoseptanose* as plates, m.p. 165–166°, $[\alpha]_D^{24}$ −13·4° (*c*, 0·85 in H_2O) (Found: C, 49·1; H, 7·3. $C_9H_{16}O_6$ requires C, 49·1; H, 7·3%).

Acetylation of (5a) with acetic anhydride and pyridine gave, after the usual workup, *3,4,5-tri-O-acetyl-1,2-O-isopropylidene-β-L-idoseptanose* (5b) as plates, m.p. 138–139° (methanol/water), $[\alpha]_D^{22}$ 35·7° (*c*, 1·1 in $CHCl_3$). A sample was short-path distilled at 2 mm, bath 125° (Found: C, 52·0; H, 6·5. $C_{15}H_{22}O_9$ requires C, 52·0; H, 6·4%).

After stirring a mixture of (5a) (0·20 g), methyl iodide (2·5 ml), silver oxide (2·5 g) and dimethylformamide (4 ml) for 8 h at 22°, benzene (10 ml) was added and solids were removed by filtration, and washed with benzene. After washing the benzene solution with 1% aqueous KCN and with 2 portions of water, evaporation gave a colourless syrup (0·23 g), purified by chromatography on silicic acid by using ether/light petroleum (1 : 4). Short-path distillation of this product (10^{-2} mm, bath 120°) gave *1,2-O-isopropylidene-3,4,5-tri-O-methyl-β-L-idoseptanose* (5c), $[\alpha]_D^{22}$ 31·0° (*c*, 2·0 in $CHCl_3$) (Found: C, 55·1; H, 8·7. $C_{12}H_{22}O_6$ requires C, 55·0, H, 8·5%).

1,2-O-Isopropylidene-3,4,5-tri-O-methyl-α-L-idoseptanose (6)

After keeping a solution of (5a) (5 mg) in acetone containing 1% sulfuric acid (0·1 ml) at 22° for 5 h, excess aqueous ammonia was added and the mixture was analysed by g.l.c. at 125°. The starting material (92%) had a retention time of 7·5 min, and a second component (8%) had a retention time of 11·5 min.

A solution of trimethyl ether (5c) (640 mg) in a mixture of acetone (20 ml) and sulfuric acid (0·2 ml) was kept at 25° for 4 h. After addition of a slight excess of 15 M aqueous ammonia, the mixture was filtered and evaporated. Water was removed from the residue by threefold evaporation of ethanol/benzene solutions. Chromatography of the residue on silica gel (Merck, Kieselgel 60H, 7736, 80 g, 29 by 330 mm), eluting with ether/light petroleum (1 : 2) and collecting 20-ml fractions, gave (5c) (467 mg) in fractions 31–41, and in fractions 48–58 *1,2-O-isopropylidene-3,4,5-tri-O-methyl-α-L-idoseptanose* (40 mg) as an oil, $[\alpha]_D^{22}$ −16·4° (*c*, 4 in C_6H_6).

1,2:4,5-Di-O-isopropylidene-β-L-idoseptanose (7a)

Small-scale experiments were carried out to determine satisfactory conditions for the preparation of (7a) from (5a). G.l.c. retention times at 160° were 5 min for (4a) and 4 min for (7a). The following ratios of (7a) to (4a) were observed at the time that (5a) could not be detected by t.l.c.: (A) by using acetone containing 0·1% sulfuric acid (1 : 1); (B) by using dimethylformamide containing 2,2-dimethoxypropane and 0·1% sulfuric acid (1 : 5·3); (C) by using 2,2-dimethoxypropane and anhydrous copper sulfate (1 : 4·5); (D) by using acetone and anhydrous copper sulfate (1 : 7·1). In case (A), the proportion of (4a) increased rapidly.

A suspension of anhydrous copper sulfate (1 g) and (5a) (0·395 g) in 2,2-dimethoxypropane (10 ml) was stirred for 45 min at 22°. The residue left on evaporation of the filtered reaction mixture was chromatographed on silicic acid (Mallinckrodt CC-7, 20 g) by using ether/light petroleum. Early fractions rich in (7a) were rechromatographed as before to give 38 mg of material containing only a small amount of (4a). Crystallization from benzene/light petroleum gave 27 mg which recrystallized to give *1,2:4,5-di-O-isopropylidene-β-L-idoseptanose*, m.p. 157–159° (benzene/light petroleum), $[\alpha]_D^{20}$ −2·3° (*c*, 1·0 in $CHCl_3$) (Found: C, 55·6; H, 7·6. $C_{12}H_{20}O_6$ requires C, 55·4; H, 7·7%).

Acetylation of (7a) with acetic anhydride and pyridine gave, after the usual workup, *3-O-acetyl-1,2:4,5-di-O-isopropylidene-β-L-idoseptanose* as needles, m.p. 121–122° (benzene), $[\alpha]_D^{22}$ 34·1° (*c*, 0·4 in $CHCl_3$) (Found: C, 55·8; H, 7·3. $C_{14}H_{22}O_7$ requires C, 55·6; H, 7·3%).

1,2:3,4-Di-O-isopropylidene-5-C-methyl-α-D-glucoseptanose (8) and 1,2:3,4-Di-O-isopropylidene-5-C-methyl-β-L-idoseptanose (9)

To a refluxing solution of methylmagnesium iodide, prepared from methyl iodide (10·6 ml) and magnesium turnings (4 g) in diethyl ether (100 ml), was added ketone (2) (5·00 g) in benzene [50 ml; solution dried by refluxing (2) in benzene by using a Dean–Stark head] over 40 min. After 3 h at reflux, 10% aqueous ammonium chloride (150 ml) was added, initially in small portions. The separated ether phase was washed with water, dried ($MgSO_4$), filtered through a short bed of silica gel and evaporated. Chloroform extracts (2×50 ml) of the aqueous solution and washings were dried ($MgSO_4$), filtered through silicic acid and evaporated. A solution of the products in benzene/light petroleum gave *1,2:3,4-di-O-isopropylidene-5-C-methyl-β-L-idoseptanose* (9) as needles (0·52 g), m.p. 188–189°, $[\alpha]_D^{23}$ −20·4° (*c*, 1·2 in $CHCl_3$) (Found: C, 56·8; H, 8·1. $C_{13}H_{22}O_6$ requires C, 56·9; H, 8·1%).

Evaporation of the filtrates gave 4·2 g of residue which was chromatographed on basic alumina (250 g, Woelm, for thin-layer chromatography), collecting 50-ml fractions. Eluent was ethyl acetate/light petroleum (3 : 17), changed to 1 : 3 after fraction 16, 1 : 2 after fraction 31, and 1 : 1 after fraction 39, by using g.l.c. to monitor elution; retention time for (8) 5·2 min, for (9) 4·6 min. Fractions 7–32 contained only one compound. Crystallization of this material from benzene/light petroleum gave needle crystals (2·74 g), and the filtrate yielded 0·30 g of crystalline residue. Recrystallization of the needle crystals gave *1,2:3,4-di-O-isopropylidene-5-C-methyl-α-D-glucoseptanose* (8) as needles, m.p. 100–101° (benzene/light petroleum), $[\alpha]_D^{23}$ 43·6° (*c*, 1·9 in $CHCl_3$) (Found: C, 57·1; H, 8·1. $C_{13}H_{22}O_6$ requires C, 56·9; H, 8·1%). Fractions 37–54 gave the L-*ido* isomer (9) (0·33 g). Total yields: (8) 57%, (9) 16%.

5-C-Methyl-D-glucose

A solution of (8) (1·00 g) in 0·1 M hydrochloric acid (10 ml) was kept at 60° for 6 h. T.l.c. (silica gel, ethanol/ethyl acetate, 1 : 9) showed a trace of high R_F material (mono-*O*-isopropylidene derivative) after 5 h. Freeze drying the neutralized (Amberlite IRA-400, CO_3^- resin) hydrolysate gave a colourless residue which gave crystals (0·52 g) from ethanol. Recrystallization gave *5-C-methyl-D-glucose* as stout needles, m.p. 147–150° (ethanol), $[\alpha]_D^{22}$ −24·5° (6 min), −21·4° (equil., 60 min) (*c*, 1·02 in H_2O) (Found: C, 43·3; H, 7·5. $C_7H_{14}O_6$ requires C, 43·3; H, 7·3%). ^{13}C n.m.r. (D_2O, 300 K) P_α: 93·93, C1; 79·59, C5; 72·66, C2; 71·78, C4; 69·95, C3; 67·13, C6; 19·27, Me. P_β: 92·62, C1; 78·12, C5; 75·29, C2; 73·49, C3; 71·49, C4; 66·99, C6; 14·43, Me. F_α: 97·04, C1; 80·82, C4; 77·38, C3; 77·00, C2; 75·18 or 75·07, C5; 21·76 or 22·00, Me. F_β: 102·55, C1; 84·26, C4; 81·45, C2; 76·19, C3; 75·07 or 75·18, C5; 22·00 or 21·76, Me.

5-C-Methyl-L-idose

To a solution of (9) (880 mg) in a mixture of acetone (10 ml) and water (40 ml) was added 1 M hydrochloric acid (4·4 ml). After the mixture had been kept at 30° for 24 h, t.l.c. (EtOH/EtOAc, 1 : 9; silica) showed the presence of (9), a spot at intermediate R_F (0·6) (probably mono-*O*-isopropylidene compound) and an intense low R_F (0·24) spot. Some of the acetone solvent (6 g) was evaporated (Büchi evaporator, 30° bath) from the reaction mixture, and the solution was kept at 30° for a further 48 h. Freeze drying the neutralized (Amberlite IR-4B resin) hydrolysate gave a colourless residue. After filtering a solution of the residue in absolute ethanol (4 ml) through Kieselguhr to remove small amounts of flocculent material, the filtrate was concentrated to *c.* 2 ml and seeded with crystals obtained from a previous preparation in which the syrupy sugar had spontaneously crystallized. After some crystallization had taken place, a mixture of absolute ethanol/ethyl acetate (1 : 2), was added. After further crystallization, the crystals were collected and washed with ethyl acetate/ethanol to give *5-C-methyl-L-idose* (2 crops, 261 mg, 46%), m.p. 106–110°, $[\alpha]_D$ −27·1° (6 min), −22·2° (equil., 60 min) (*c*, 2·07 in H_2O) (Found, 41·6; H, 7·4. $C_7H_{14}O_6.\frac{1}{2}H_2O$ requires C, 41·4; H, 7·4%). ^{13}C n.m.r. (D_2O, 300 K) P_α: 92·55, C1; 78·48, C5; 77·20, C4; 75·91, C2; 73·07, C3; 60·61, C6; 22·92, Me. P_β: 93·06, C1; 80·02, C5; 77·62, C4; 72·50, C2; 69·88, C3; 65·01, C6; 23·96, Me. F_α: 103·06, C1; 83·13, C4; 81·27, C2; 76·57, C3; 74·88 or 74·74, C5; 67·38 or 67·28, C6; 20·77 or 20·51, Me. F_β: 97·54, C1; 79·92, C4; 77·65, C3; 76·81, C2; 74·74 or 74·88, C5; 67·28 or 67·38, C6; 20·51 or 20·77, Me.

1,6-Anhydro-5-C-methyl-β-L-idopyranose (12a)

A solution of (9) (267 mg) in 0·1 M hydrochloric acid (5 ml) was kept at 80° for 50 h. The residue left on evaporation of the neutralized [Amberlite IRA-400 (HCO_3^-) resin] hydrolysate was dissolved in ethanol, benzene added and the mixture evaporated. Chromatography of the products over silica gel by using absolute ethanol/ethyl acetate (1 : 19), gave 140 mg of crystalline product which yielded *1,6-anhydro-5-C-methyl-β-L-idopyranose* (90 mg) (ethyl acetate), m.p. 131–132°, $[\alpha]_D$ 101·0° (*c*, 1·46 in H_2O) (Found: C, 47·6, H, 6·8. $C_7H_{12}O_5$ requires C, 47·7; H, 6·9%).

Concentration of the filtrate from crystallization of (12a) gave a residue which was acetylated (Ac_2O/pyridine) in the usual manner to give the crystalline peracetate. Recrystallization from aqueous ethanol gave *2,3,4-tri-O-acetyl-1,6-anhydro-5-C-methyl-β-L-idopyranose* as needles, m.p. 70–71°, $[\alpha]_D$ 110·9° (*c*, 1·08 in $CHCl_3$) (Found: C, 51·8; H, 5·9. $C_{13}H_{18}O_8$ requires C, 51·7; H, 6·0%).

Pentaacetates of 5-C-Methyl-D-glucose

Small-scale acetylation of (10) with acetic anhydride and pyridine at 0°, with g.l.c. analysis, showed only one product. Finely ground (10) (386 mg) was added to a stirred mixture of acetic anhydride (6 ml) and pyridine (3 ml) at 0°. After 1 h the reaction mixture was allowed to warm to and kept at 22° for 24 h. After the usual workup, the product was dissolved in a mixture

of acetic acid and acetic anhydride (1 : 1, 5 ml), and anhydrous $ZnCl_2$ (*c.* 100 mg) was added. After the mixture had been heated at 100° for 45 min, a chloroform solution of the residue left on evaporation was washed with water and saturated sodium bicarbonate solution. The residue left on evaporation of the solvent was chromatographed over silica gel (Merck 7736, 100 g) by using ether/benzene (1 : 3), collecting 25-ml fractions. The single product (282 mg) in fractions 19–24 crystallized from ethanol to give *1,2,3,4,6-penta*-O-*acetyl-5*-C-*methyl-β*-D-*glucopyranose* (13) as very fine needles, m.p. 130–131°, $[\alpha]_D$ −23·9° (*c*, 1·24 in $CHCl_3$) (Found: C, 50·5; H, 6·2. $C_{17}H_{24}O_{11}$ requires C, 50·5; H, 6·0%), g.l.c. (200°) R_t 9·7 min. Fractions 25–36 contained only the second product (274 mg) which crystallized from benzene/light petroleum. Recrystallization give *1,2,3,4,6-penta*-O-*acetyl-5*-C-*methyl-α*-D-*glucopyranose* (14) as prisms (benzene/light petroleum), m.p. 135–136°, $[\alpha]_D$ 72·2° (*c*, 1·54 in $CHCl_3$) (Found: C, 50·5; H, 6·2. $C_{17}H_{24}O_{11}$ requires C, 50·5; H, 6·0%), g.l.c. (200°) R_t 11·7 min. From a ^1H n.m.r. spectrum ($CDCl_3$ solution, 16 s relaxation delay, 90° pulse) of the products obtained by $ZnCl_2$-catalysed isomerization, the ratio of (13) to (14) was 1 : 1·08.

Pentaacetates of 5-C-*Methyl*-L-*idose*

A mixture prepared by adding finely ground (11) (60 mg) to pyridine/acetic anhydride (2 ml, 1 : 1) at 0° was kept at 0° for 24 h. After the usual workup, the crystalline product was crystallized from ethanol to give prisms (68 mg), m.p. 112–114°. Recrystallization from ethanol/water gave *1,2,3,4,6-penta*-O-*acetyl-5*-C-*methyl-α*-L-*idopyranose* (15), m.p. 112–113°, $[\alpha]_D$ −15·4° (*c*, 1·045 in $CHCl_3$) (Found: C, 50·4; H, 5·9. $C_{17}H_{24}O_{11}$ requires C, 50·5; H, 6·0%), g.l.c. (200°) R_t 7·4 min.

Treatment of (15) (20 mg) with $ZnCl_2$ in acetic anhydride/acetic acid (2 : 1) at 100° for 45 min, with workup as described for preparation of (13) and (14), gave two products, g.l.c. (200°) R_t 7·4, 9·8 min, identified by ^1H n.m.r. as (15) and (16) in the ratio 1 : 1·13.

Treatment of 1,2:3,4-Di-O-*isopropylidene-5*-O-p-*toluenesulfonyl-α*-D-*glucoseptanose (1c) with Lithium Benzoate in Dimethylformamide*

A stirred mixture of (1c) (1·00 g), lithium benzoate (1·00 g) and dimethylformamide (20 ml, dried over P_2O_5) was kept at 123–125° for 40 h. The cooled, diluted (water, 80 ml) reaction mixture was extracted with ethyl acetate/light petroleum (1 : 1, 50 ml, 25 ml). The extracts were shaken with water (2×40 ml) and saturated sodium bicarbonate solution, and filtered through a small bed of silica gel. Treatment of the residue left on evaporation of the solvents with ethyl acetate (3 ml) and light petroleum (6 ml), gave plate crystals (0·28 g) identified as (1c) by t.l.c. Chromatography of the remainder of the products by using silica gel (Merck, 7736, 30 g) and ethyl acetate/light petroleum (1 : 6) as developing solvent, collecting 10-ml fractions, gave from fractions 13–15 olefin (17) (255 mg. 62% on unrecovered tosylate), m.p. 64–65° (40–60° light petroleum), g.l.c. (140°) R_t 8·0 min. Fractions 21–26 contained benzoate (4c) (91 mg, 15% on unrecovered tosylate), m.p. 154–155° (benzene/light petroleum). G.l.c. analysis of the reaction products showed the presence of a small amount of (18), ratio (17)/(18) 24 : 1.

Treatment of Tosylate (1c) with Sodium Methoxide in Methanol

A solution of (1c) (350 mg) in anhydrous methanol (5 ml) and 2 M sodium methoxide in methanol (5 ml) was kept at 70° (stoppered flask) for 50 h. The residue left on evaporation of the reaction mixture was shaken with water (8 ml) and benzene/light petroleum (1 : 1, 10 ml). The organic layer was washed with water (4 times), added to a short column of silica gel (Mallinckrodt CC7) and the olefins were eluted with 5% ethyl acetate in benzene. Preparative g.l.c. gave two products. Material eluted first was collected as colourless needles (16 mg) of *5-deoxy-1,2:3,4-di*-O-*isopropylidene-α*-D-xylo-*hex-5-enoseptanose* (18), m.p. 144–145°, $[\alpha]_D^{22}$ −16·9° (*c*, 0·62 in CH_3OH) (Found: $M^{+\bullet}$, 242·1142. $C_{12}H_{18}O_5$ requires $M^{+\bullet}$, 242·1154), g.l.c. (140°) R_t 6·0 min. The material eluted second was collected as colourless plates (55 mg) of *5-deoxy-1,2:3,4-di*-O-*isopropylidene-β*-L-threo-*hex-4-enoseptanose* (17), m.p. 62–63°, $[\alpha]_D^{22}$ −33·8° (*c*, 0·925 in CH_3OH) (Found: $M^{+\bullet}$, 242·1156, $C_{12}H_{18}O_5$ requires $M^{+\bullet}$, 242·1154),

g.l.c. (140°) R_t 8·0 min. G.l.c. analysis of the reaction products gave the ratio of (17) to (18) as 3 : 1.

Treatment of Tosylate (1c) with Potassium t-Butoxide in t-Butyl Alcohol

A mixture of potassium t-butoxide (200 mg, MSA Research Corporation), tosylate (1c) (100 mg) and t-butyl alcohol (3 ml) was stirred for 48 h at 80°. The residue left on evaporation of solvent was shaken with water (4 ml) and ethyl acetate/light petroleum (1 : 1, 6 ml). After washing the organic layer once with water, g.l.c. analysis gave the ration of (17) to (18) as 1 : 2.

Treatment of Tosylate (4e) with Lithium Benzoate in Dimethylformamide

A mixture of (4e) (0·040 g), lithium benzoate (0·100 g) and dimethylformamide (1 ml) was kept at 140° for 24 h. The cooled reaction mixture was shaken with water (15 ml) and chloroform (5 ml), and the chloroform extract was washed with water (15 ml), filtered through a short bed of silicic acid, and evaporated. A ^{1}H n.m.r. spectrum of the products showed that the major product is the *gluco* benzoate (1d), with the 4,5-ene (17) as a minor product. A solution of the products in a few drops of ethanol gave prisms, m.p. 153–154° [reported[1] for (1d), 154–155°].

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