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EPOXIDATION OF HIGHER SUGAR ALLYLIC ALCOHOLS*

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ABSTRACT

3-*O*-Benzyl-5-deoxy-5-*C*-[(*E*)-7-deoxy-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranos-7-ylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose (**1**) reacted with 3-chloroperoxybenzoic acid (MCPBA) to afford 5,6-anhydro-3-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*glycero*-α-D-*gluco*- (**2**) and -D-*glycero*-β-L-*ido*-hexo-1,4-furanose (**3**) in the ratio 19:81. The configurations of **2** and **3** were assigned on the basis of ^{1}H-n.m.r. data and chemical correlations. Treatment of **3** with benzyl alcohol–titanium tetra-isopropoxide afforded 3,6-di-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*glycero*-β-L-*ido*-hexo-1,4-furanose (**8**), which was converted into known 1,5-di-*O*-acetyl-2,3,4-tri-*O*-butylribitol (**10**). Epoxidation of **1** with *tert*-butyl hydroperoxide in the presence of $VO(acac)_2$ afforded **2** and **3** in the ratio 37:63. Epoxidation of 3-*O*-benzyl-6-*C*-[(*E*)-6-*O*-benzyl-7-deoxy-1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-heptopyranos-7-ylidene]-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**11**) with MCPBA afforded 6,7-anhydro-3-*O*-benzyl-7-*C*-(6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*threo*- (**12**) and -D-*threo*-α-D-*gluco*-hepto-1,4-furanose (**13**) in the ratio 21:79. The configurations of these epoxides were established on the basis of c.d. spectra. Epoxidation of **1** and **11** with MCPBA gave mainly the *syn*-epoxides (**3** and **13**) as predicted from the models of Sharpless and Teranishi.

INTRODUCTION

The most convenient route to higher carbon sugars involves the coupling of two monosaccharide moieties by the reaction of sugar-derived stabilized phosphoranes with sugar aldehydes[1,2] or by the addition of sugar vinyl anions to sugar aldehydes[2,3]. The former reaction afforded higher sugar enones that could be stereoselectively converted into the *desired* allylic alcohol[4,5]; the latter produced allylic alcohols directly (see Scheme 1) which are suitable starting materials for the

*These compounds are C_{12} and C_{13} sugar derivatives but, because of their resemblance to disaccharides and for easier comprehension, they are named as *x*-deoxy-*x*-(C-glycosyl)glycose derivatives.

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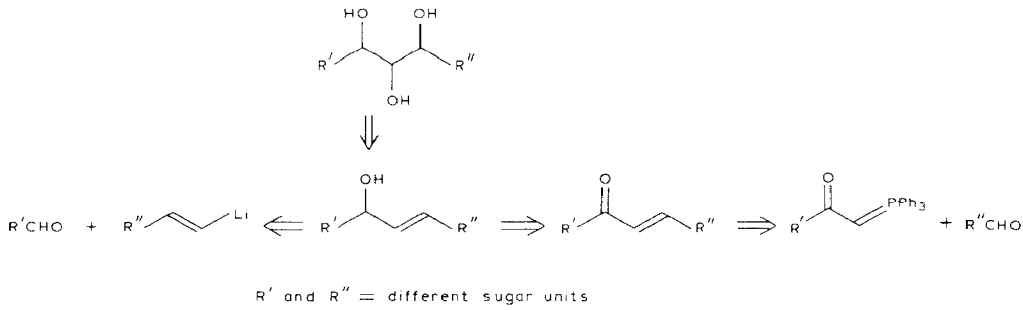
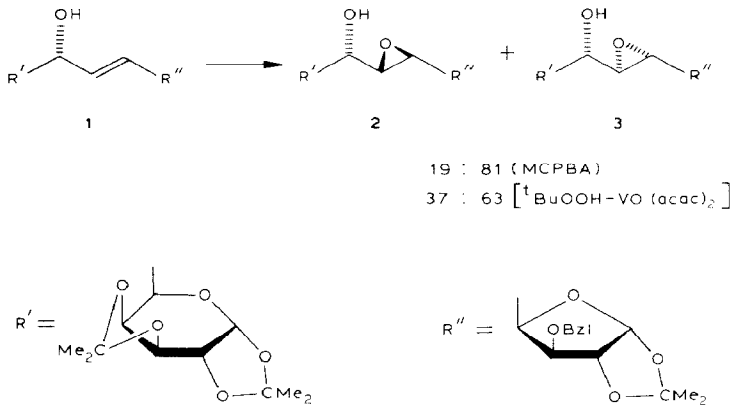


Scheme 1. A general method of the synthesis of higher sugars from simple monosaccharide sub-units.

preparation of higher carbon sugars. Osmylation[6] of these compounds follows Kishi's empirical rule for *cis*-hydroxylation and provides a route to higher sugars. The epoxidation of these molecule is now reported.

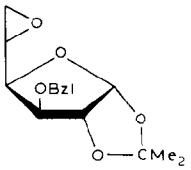
RESULTS AND DISCUSSION

The readily available compound selected for study was 3-*O*-benzyl-5-deoxy-5-*C*-[(*E*)-7-deoxy-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranos-7-ylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose[4] (**1**). Reaction of **1** with 3-chloroperoxybenzoic acid (MCPBA) afforded the diastereoisomeric epoxyalcohols 5,6-anhydro-3-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*glycero*-α-D-*gluco*- (**2**) and -D-*glycero*-β-L-*ido*-hexo-1,4-furanose (**3**) in the ratio 19:81.



The configurations of **2** and **3** were deduced from their ^{1}H-n.m.r. spectra which showed significant differences. The resonance of H-12 (see Table II for numbering) in **3** was shifted ~0.1 p.p.m. to *lower* field and that of H-10 was shifted

~0.1 p.p.m. to *higher* field compared to the corresponding resonances in **2** (see Table II). Significant differences were also observed in the $J_{8,9}$ values (5.2 Hz for **3**, 7.3 Hz for **2**). By comparing these data with the $J_{4,5}$ (5.6 and 7.6 Hz, respectively), δ H-1 (5.93 and 5.83 p.p.m., respectively), and δ H-3 (3.85 and 3.93 p.p.m., respectively) values for 5,6-anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-ido- (**4**)[7] and -α-D-gluco-furanose (**5**)[8], the L-*ido* and D-*gluco* configurations were assigned to **3** and **2**, respectively.



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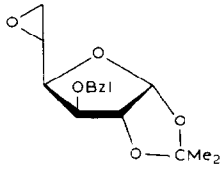

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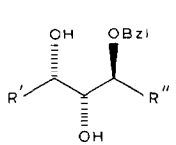
In seeking to establish the configurations of **2** and **3** by chemical correlations, **3** was treated with benzyl alcohol in the presence of titanium tetra-isopropoxide. This method is claimed to be highly regioselective, with nucleophilic attack on the oxirane ring in α-epoxy alcohols occurring almost exclusively at the position β to the hydroxyl group[9], and, hence, should afford the vicinal diol **6** which can be converted into 3,5-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[10] (**7**). How-



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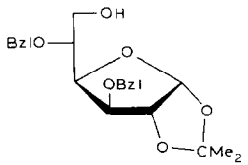

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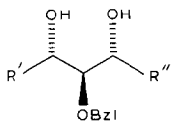

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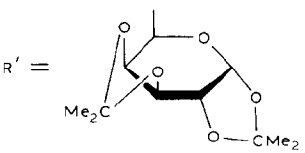
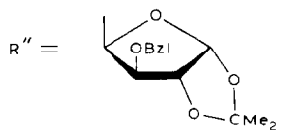
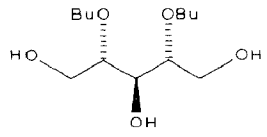




ever, the attack of the nucleophile on **3** occurred at the position α to the hydroxyl group, to afford, in low yield, 3,6-di-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*glycero*-β-L-*ido*-hexo-1,4-furanose (**8**). The configuration of **8** was established by its conversion into known[11] 1,5-di-*O*-acetyl-2,3,4-tri-*O*-butylribitol (**10**). *O*-Butylation of **8** followed by hydrogenolysis of the benzyl groups and hydrolysis of the isopropylidene groups gave a polyol which was oxidised with periodate; the product was reduced with

sodium borohydride to afford the triol **9**, which was converted in a few steps into **10**. This result indicated that **8** had the L-*glycero*-β-L-*ido* configuration and, hence, that **3** had the D-*glycero*-β-L-*ido* configuration. These results accorded with those base on ^{1}H-n.m.r. data.



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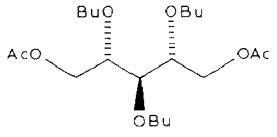


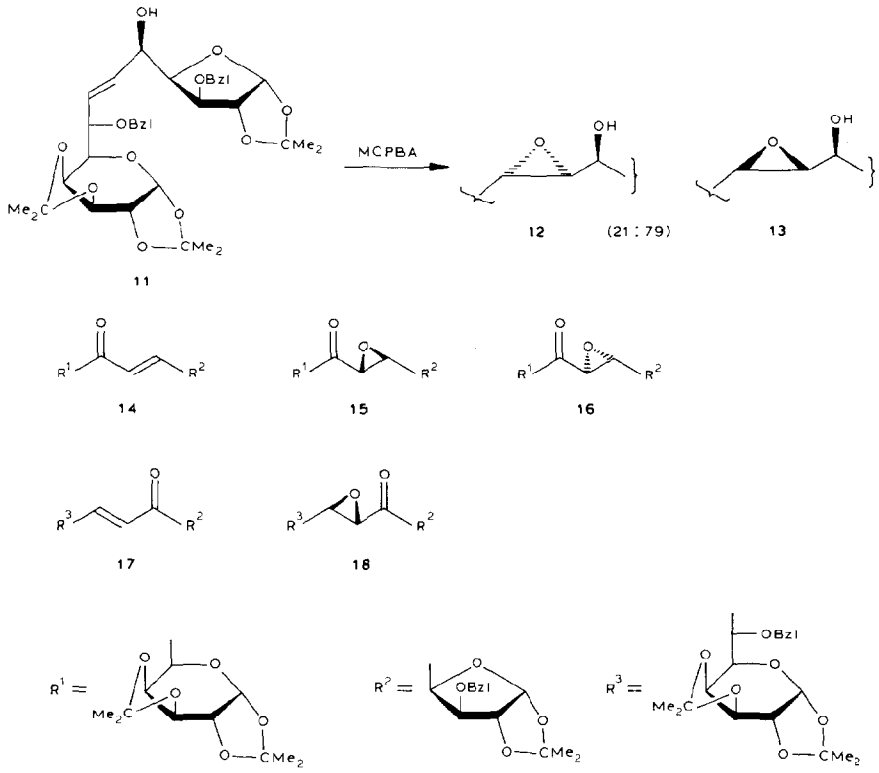
10 (*ribo*)

Oxidation of the double bond in allylic alcohols with *tert*-butyl hydroperoxide (tBHP) in the presence of vanadium catalyst should afford[11,12] the *opposite (anti)* epoxyalcohol. However, epoxidation of **1** with tBHP in the presence of $VO(acac_2)$ afforded the epoxide **3** as the main product; the amount of the stereoisomer **2** was significantly increased (the ratio of **2:3** was 37:63; *cf.* 19:81 on epoxidation with MCPBA).

The Sharpless method produces enantiomerically pure epoxyalcohols by oxidation of optically inactive allylic alcohols with tBHP in the presence of titanium tetra-isopropoxide and either diethyl D- or L-tartrate[14]. A disadvantage of this approach is the sensitivity of the steric course of the reaction to the pre-existing chiral centres[14]. However, when this method was applied to **1**, a low yield of the epoxides **2** and **3** was obtained in a ratio that was *almost identical*, regardless of the configuration of the diethyl tartrate used as catalyst, with that obtained using MCPBA and there were many side products. The influence of the chiral centres in **1** was much more important therefore than the influence of the chiral catalyst. The low yield in the Sharpless epoxidation of **1** may be connected with both steric effects and complexation of titanium ion to different oxygen atoms in **1**.

3-*O*-Benzyl-6-*C*-[(*E*)-6-*O*-benzyl-7-deoxy-1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-heptopyranos-7-ylidene]-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose[3] (**11**) reacted with MCPBA to afford 6,7-anhydro-3-*O*-benzyl-7-*C*-(6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*threo*- (**12**) and -D-*threo*-α-D-*gluco*-hepto-1,4-furanose (**13**) in the ratio 21:79.

The configuration of the major stereoisomer **13** was assigned on the basis of the c.d. spectra of the epoxyketones **15, 16,** and **18** obtained by Swern oxidation[15] of the respective epoxyalcohols **2, 3,** and **13**. In these compounds, the carbonyl chromophore is attached to two chiral units, namely, the sugar derivative and the oxirane ring, of which the former induced the *negative* Cotton effect, as could be assigned from c.d. spectra of enones **14** and **17** (see Table I). The data in Table I show that the Cotton effect becomes *less* negative for **16** and **18** (obtained from the major epoxyalcohols **3** and **13**, respectively) and *more* negative for **15** (obtained from the minor isomer **2**), suggesting that the oxirane ring in the major isomers **16**



and **18** (and in **3** and **13**) should have the *same* configuration. The *syn* configuration was assigned to **3**, and consequently the major stereoisomer (**13**) from epoxidation of **11** must also have the *syn* configuration.

Thus, oxidation of higher sugar allylic alcohols with MCPBA involved good stereoselectivity (~4:1) and gave mainly the *syn*-epoxyalcohols as predicted from

TABLE I

C.D. SPECTRAL DATA FOR **14–18**

Compound	λ_{max}	$\bar{\nu}$ [*kK*]	$\Delta\varepsilon$
14	339.8	29.4	−0.451
	332.2	30.1	−0.451
15	307.4	32.5	−0.632
	266.2	37.6	+0.068
16	322.6	31.0	−0.216
	291.2	34.3	+0.357
17	343.4	29.1	−0.056
	298.3	33.5	+0.013
18	296.2	33.8	+0.787

the models of Sharpless[12] and Teranishi[13]. Epoxidation of the double bond of these allylic alcohols under Sharpless conditions[14] was not effective. Opening of the oxirane ring in the higher sugar epoxyalcohols did not follow the general rules established for simpler compounds and is probably connected with steric factors.

EXPERIMENTAL

General. — Optical rotations were measured with a Perkin–Elmer 141 polarimeter on solutions in ethyl acetate at 20°. ^{1}H-N.m.r. spectra (the data for **2, 3, 12, 13, 15,** and **16** are shown in Tables II and III) were recorded with Bruker AM-500 and WX 300 spectrometers for solutions in $CDCl_3$ (internal Me_4Si). The ^{13}C-n.m.r. spectrum was recorded with a JEOL FX 90 Q on a solution in $CDCl_3$. Column chromatography was performed on silica gel (Merck, 230–400 mesh; and Macherey–Nagel, 70–270 mesh). Organic solutions were dried over anhydrous magnesium sulfate.

Epoxidation of higher sugar allylic alcohols with 3-chloroperoxybenzoic acid. — To a solution of the allylic alcohol (**1** or **11**) in dichloromethane (5 mL) at room temperature was added 3-chloroperoxybenzoic acid (1.5 equiv.). The reaction was monitored by t.l.c. [light petroleum–ether–methanol (5:5:1), 2 developments]. After 24 h, the mixture was diluted with ether (30 mL), washed with aqueous 5% sodium hydrogencarbonate and water, dried, and concentrated.

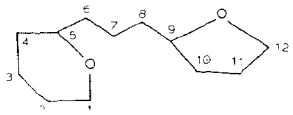
*5,6-Anhydro-3-O-benzyl-6-C-(1,2:3,4-di-O-isopropylidene-*D-glycero-α-D-galacto-*hexopyranos-6-yl)-1,2-O-isopropylidene-*L-glycero-α-D-gluco- (**2**) *and* -D-glycero-β-L-ido-*hexo-1,4-furanose* (**3**). — Epoxidation of **1** (950 mg, 1.78 mmol)

TABLE II

^{1}H-N.M.R. DATA FOR **2, 3, 15,** AND **16**[a]

Compound	*Chemical shifts (δ)*											
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*	*H-9*	*H-10*	*H-11*	*H-12*
2	5.54	4.29	4.61	4.47	3.81	4.01	3.31	3.50	3.86	4.04	4.60	5.90
3	5.47	4.30	4.63	4.48	3.75	3.90	3.23	3.46	3.90	3.96	4.60	5.97
15	5.68	4.39	4.63	4.63	4.61		3.91	3.41	3.94	4.06	4.62	5.95
16	5.68	4.38	4.62	4.55	4.50		4.03	3.52	4.17	4.07	4.62	5.95
	Coupling constants (Hz)											
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$	$J_{8,9}$	$J_{9,10}$	$J_{10,11}$	$J_{11,12}$	
2	5.0	2.4	8.0	1.8	7.4	3.4	2.2	7.3	3.2	0	3.7	
3	5.0	2.4	8.0	1.8	9.0	2.4	2.4	5.2	3.4	0	3.8	
15	5.0	n.d.	8.0	2.3			1.8	6.3	3.3	0	3.6	
16	5.0	2.5	7.7	2.0			1.9	3.9	3.9	0	3.8	

[a]The numbering is as follows:



followed by column chromatography (light petroleum–ether, 3:1) afforded **2** (143 mg, 14.6%), isolated as an oil, $[\alpha]_D$ −48° (*c* 2).

Anal. Calc. for $C_{28}H_{38}O_{11}$: C, 61.1; H, 7.0. Found: C, 61.1; H, 7.1.

Eluted second was **3** (601 mg, 61.2%), m.p. 131–132° (from hexane–ether, 1:1), $[\alpha]_D$ −45° (*c* 1). Mass spectrum: *m/z* 550 (M^+) and 535.2179 [(M^+ − 15); calc. 535.2190].

Anal. Found: C, 61.0; H, 7.1.

*6,7-Anhydro-3-*O*-benzyl-7-*C*-(6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-*L*-glycero-α-*D*-galacto-hexopyranos-6-yl)-1,2-*O*-isopropylidene-*L*-threo-* (**12**) *and* -*D*-threo-α-*D*-gluco-hepto-1,4-furanose* (**13**). — Epoxidation of **11** (826 mg, 1.26 mmol) followed by column chromatography (toluene–acetone, 95:5) afforded **12** (126 mg, 15.1%), isolated as an oil, $[\alpha]_D$ −31° (*c* 3).

Anal. Calc. for $C_{36}H_{46}O_{12}$: C, 64.5; H, 6.9. Found: C, 64.3; H, 7.0.

Eluted second was **13** (467 mg, 55.6%), isolated as an oil, $[\alpha]_D$ −27° (*c* 1.5).

Anal. Found: C, 64.2; H, 7.1.

*5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-β-*L*-idofuranose*[7] (**4**). — ^{1}H-N.m.r. data: δ 5.93 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.57 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 3.85 (d, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 3.73 (dd, 1 H, $J_{4,5}$ 5.6 Hz, H-4), 3.15 (m, 1 H, H-5), 2.67 (dd, 1 H, $J_{5,6}$ 3.0, $J_{6,6}$ 6.0 Hz, H-6), and 4.45 (dd, 1 H, $J_{5,6}$ 2.4 Hz, H-6).

*5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-glucofuranose*[8] (**5**). — ^{1}H-n.m.r. data: δ 5.83 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.52 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 3.93 (d, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 3.57 (dd, 1 H, $J_{4,5}$ 7.6 Hz, H-4), 3.17 (m, 1 H, H-5), 2.88 (dd, 1 H, $J_{5,6}$ 3.6, $J_{6,6}$ 5.6 Hz, H-6), and 2.75 (dd, 1 H, $J_{5,6}$ 2.0 Hz, H-6).

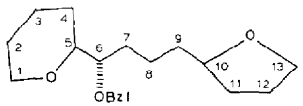
Oxidation of the epoxyalcohols **2**, **3**, *and* **13**. — The Swern procedure[15] was used. To a solution of oxalyl chloride (0.1 mL) in dichloromethane (5 mL) at −78°

TABLE III

^{1}H-N.M.R. DATA FOR **12** AND **13**[a]

Compound	*Chemical shifts (δ)*												
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*	*H-9*	*H-10*	*H-11*	*H-12*	*H-13*
12	5.61	4.28	4.58	4.44	3.93	3.55	3.35	3.39	4.16	4.06	4.10	4.61	5.95
13	5.56	4.29	4.58	4.42	3.90	4.16	3.40	3.38	4.02	3.92	4.16	4.60	5.95
	Coupling constants (Hz)												
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$	$J_{8,9}$	$J_{9,10}$	$J_{10,11}$	$J_{11,12}$	$J_{12,13}$	
12	5.0	2.1	8.0	1.4	8.0	6.8	2.3	3.6	7.9	3.0	0	3.8	
13	5.0	2.2	8.0	1.0	8.1	2.4	2.7	2.5	7.0	2.8	0	3.8	

[a]The numbering is as follows:



was added methyl sulfoxide (0.4 mL) followed immediately by a solution of the epoxyalcohol (~0.2 mmol) in dichloromethane (5 mL). The mixture was stirred for 30 min at −78°, triethylamine (1.5 mL) was added, and the mixture was allowed to attain room temperature and was then diluted with ether (30 mL). The organic phase was washed with M HCl and water, dried, and concentrated. The residue was subjected to column chromatography (light petroleum–ethyl acetate, 4:1 for **15** and **16**; and toluene–acetone, 95:5 for **18**).

*5,6-Anhydro-3-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-α-*D*-galacto-hexopyranos-6-ulos-6-yl)-1,2-*O*-isopropylidene-*L*-glycero-α-*D*-gluco-hexo-1,4-furanose* (**15**). — Prepared (75%) from **2, 15** was isolated as an oil, $[\alpha]_D$ −71° (*c* 3). See Table II for the ^{1}H-n.m.r. data.

Anal. Calc. for $C_{28}H_{36}O_{11}$: C, 61.3; H, 6.6. Found: C, 60.9; H, 6.9.

*5,6-Anhydro-3-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-α-*D*-galacto-hexopyranos-6-ulos-6-yl)-1,2-*O*-isopropylidene-*D*-glycero-β-*L*-ido-hexo-1,4-furanose* (**16**). — Prepared (78%) from **3, 16** was isolated as an oil, $[\alpha]_D$ −54° (*c* 3). See Table II for the ^{1}H-n.m.r. data.

Anal. Calc. for $C_{28}H_{36}O_{11}$: C, 61.3; H, 6.6. Found: C, 61.0; H, 7.0.

*6,7-Anhydro-3-*O*-benzyl-7-*C*-(6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-*L*-glycero-α-*D*-galacto-hexopyranos-6-yl)-1,2-*O*-isopropylidene-*D*-threo-α-*D*-xylo-hepto-1,4-furanos-5-ulose* (**18**). — Prepared (79%) from **13, 18** was isolated as an oil, $[\alpha]_D$ −30° (*c* 1.3). ^{1}H-N.m.r. data: *inter alia* δ 6.05 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-13), 5.51 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 4.90 (d, 1 H, $J_{10,11}$ 3.0 Hz, H-10), 4.05 (d, 1 H, $J_{7,8}$ 2.5 Hz, H-8), 3.90 (m, 2 H, H-5,6), 3.40 (bs, 1 H, H-7).

Anal. Calc. for $C_{36}H_{44}O_{12} \cdot H_2O$: C, 63.0; H, 6.8. Found: C, 62.7; H, 7.1.

Determination of the configuration of **3**. — To a solution of **3** (210 mg, 0.38 mmol) in dry xylene (10 mL) and benzyl alcohol (1 mL) was added titanium tetraisopropoxide (0.3 mL), and the mixture was boiled under reflux for 30 h. T.l.c. (light petroleum–ether–methanol, 5:5:1; 2 developments) then showed that **3** had disappeared with formation of a slightly less polar product. Water (3 mL) was added to the cooled mixture which was stirred for 30 min, then filtered through Celite. The organic phase was separated, dried, and concentrated. Xylene was evaporated from the residue *in vacuo* at 40° and benzyl alcohol at 85°/0.1 Torr. Column chromatography (light petroleum–ether, 1:1) of the residue gave **8** (135 mg, 55%), which did not react with sodium periodate and was contaminated with side-products. Acetylation afforded the diacetate **8-Ac**. ^{1}H-N.m.r. data: *inter alia* δ 5.63 (dd, 1 H, $J_{7,8}$ 6.6, $J_{8,9}$ 8.7 Hz, H-8), 5.54 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.51 (dd, 1 H, $J_{5,6}$ 10, $J_{6,7}$ 5.3 Hz, H-6), 4.52 (dd, 1 H, $J_{3,4}$ 8.0, $J_{4,5}$ 2.5 Hz, H-4), 4.31 (dd, 1 H, $J_{2,3}$ 2.4 Hz, H-2), 4.19 (dd, 1 H, $J_{9,10}$ 2.0 Hz, H-9), 2.08 and 1.99 (2 s, 6 H, 2 OAc). This compound was also contaminated with side-products (detectable by 500-MHz ^{1}H-n.m.r. spectroscopy, but not by t.l.c. in various solvents).

A solution of **8** (112 mg, 0.17 mmol) in *N,N*-dimethylformamide (5 mL) was treated with sodium hydride (1 mmol) and 1-bromobutane (1 mL) overnight. The product was hydrogenolysed in ethyl acetate over 10% Pd/C, overnight (in order to

remove benzyl groups), then hydrolysed in boiling AcOH–tetrahydrofuran–water (1:1:1, 10 mL) for 6 h. The mixture was diluted with ether (20 mL) and neutralised with aqueous 5% sodium hydrogencarbonate. Sodium periodate (300 mg) was added and the heterogeneous mixture was stirred for 3 h. The organic phase was separated, washed with water, dried, and concentrated. A solution of the residue in tetrahydrofuran–water (1:1, 5 mL) was treated with sodium borohydride (30 mg) for 2 h at room temperature. The usual work-up gave **9**, which was tritylated (pyridine, TrCl, and 4-dimethylaminopyridine for 24 h), butylated (as described above), detritylated (in methanol, in the presence of a catalytic amount of toluene-*p*-sulfonic acid), and acetylated (Ac_2O/pyridine/4-dimethylaminopyridine). Flash chromatography (hexane–ether, 5:1) of the crude product gave 1,5-di-*O*-acetyl-2,3,4-tri-*O*-butylribitol (**10**; 15 mg, 23%), which was identical (h.p.l.c., i.r. spectrum) with the authentic compound[11]. The achiral structure of **10** was also proved by the ^{13}C-n.m.r. spectrum which contained only single signals for $COCH_3$ (170.83 p.p.m.) and CH_2OAc (63.99 p.p.m.).

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