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Preparation of higher-carbon sugars by stereoselective osmylation of related allylic alcohols*

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ABSTRACT

The catalytic osmylation of the following higher-carbon sugar allylic alcohols and enones was examined. 3-*O*-Benzyl-5-deoxy-5-*C*-[(*E*)-7-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-heptopyranos-6-ulos-7-ylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose (**5**) afforded 93% of 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*- (**10**) and -D-*glycero*-β-L-*ido*-hexofuranose (**11**) in the ratio 2:3. 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 (**6**) gave 75% of 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*- (**12**) and -D-*glycero*-β-L-*ido*-hexofuranose (**13**) in the ratio 4:1. The L-*glycero* isomer (**7**) of **6** afforded 75% of 3-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*glycero*-α-D-*gluco*- (**14**) and -D-*glycero*-β-L-*ido*-hexofuranose (**15**) in the ratio 53:47. 3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-6-*C*-[methyl (*E*)-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranosid-6-ylidene]-α-D-*xylo*-hexofuranos-5-ulose (**8**) gave 65% of 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*C*-[methyl 2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-*gluco*-hexopyranosid-6-yl]-α-D-*gluco*- (**19**) and -[L-*glycero*-α-D-*gluco*-]-β-L-*ido*-hexofuranos-5-ulose (**20**) in the ratio 55:45. 3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-6-*C*-[methyl (*E*)-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranosid-6-ylidene]-α-D-glucofuranose (**9**) afforded 71% of 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*C*-[methyl 2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-*gluco*-hexopyranosid-6-yl]-D-*glycero*-α-D-*gluco*- (**21**) and -[L-*glycero*-α-D-*gluco*-]-L-*glycero*-α-D-*gluco*-hexofuranose (**22**) in the ratio 9:1. The configurations of all new compounds were assigned by X-ray, chemical, and spectral correlations. These reactions followed Kishi's rule, except that of **5** which afforded mainly the *anti*-Kishi product **11**.

INTRODUCTION

Higher-carbon sugars containing more than ten carbon atoms have gained considerable attention in recent years[1], since they are components of some antibiotics and can be used in biochemical studies as non-metabolised analogues of disaccharides. We have developed a general method for the preparation of *trans*-allylic alcohols (with the *R* or *S* configuration at the carbon atom carrying the hydroxyl group) substituted at both ends with *different* monosaccharide units[2]. These versatile synthons can be converted into higher-carbon sugars by stereoselective oxidation of the double bond.

* These compounds are C_{12} 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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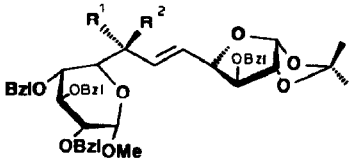
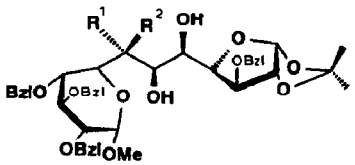
Model studies of the epoxidation[3] and osmylation[4] of this type of compound showed that the former process was difficult to control. However, the stereochemistry of the latter process could be predicted, with few exceptions, by Kishi's empirical rule[5]. Because this method appears to provide a simple and *predictable* route to C_{12} higher-carbon sugars, further examples have been studied to determine how general is this approach.

RESULTS AND DISCUSSION

The stereochemistry of the osmylation of allylic alcohols (or ethers) is controlled by the oxygen function (OR group) on the carbon α to the double bond[5]. The attack of osmium tetraoxide is postulated to occur from the side opposite to the hydroxyl (alkoxyl) group. Stereochemical effects observed in this process are additive and the presence of two hydroxyl (alkoxyl) groups (α to the double bond) acting in the same direction usually increases the proportion of one of the stereoisomers. Preliminary results on the osmylation of 3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-5-*C*-[methyl (*E*)-2,3,4-tri-*O*-benzyl-7-deoxy-α-D-*gluco*-heptopyranosid-6-ulos-7-ylidene]-α-D-xylofuranose (**1**) and 3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-5-*C*-[methyl (*E*)-2,3,4-tri-*O*-benzyl-7-deoxy-D-*glycero*-α-D-*gluco*-heptopyranosid-7-ylidene]-α-D-xylofuranose (**2**) were in accordance with Kishi's rule. In each reaction, the product resulting from *anti* (with respect to the hydroxyl group and/or ring oxygen atom) attack of osmium tetraoxide on the double bond (**3** and **4**, respectively) preponderated, and the stereoselectivity of osmylation of **2** was much higher than that of **1** (84:16 *vs.* 68:32)[4].



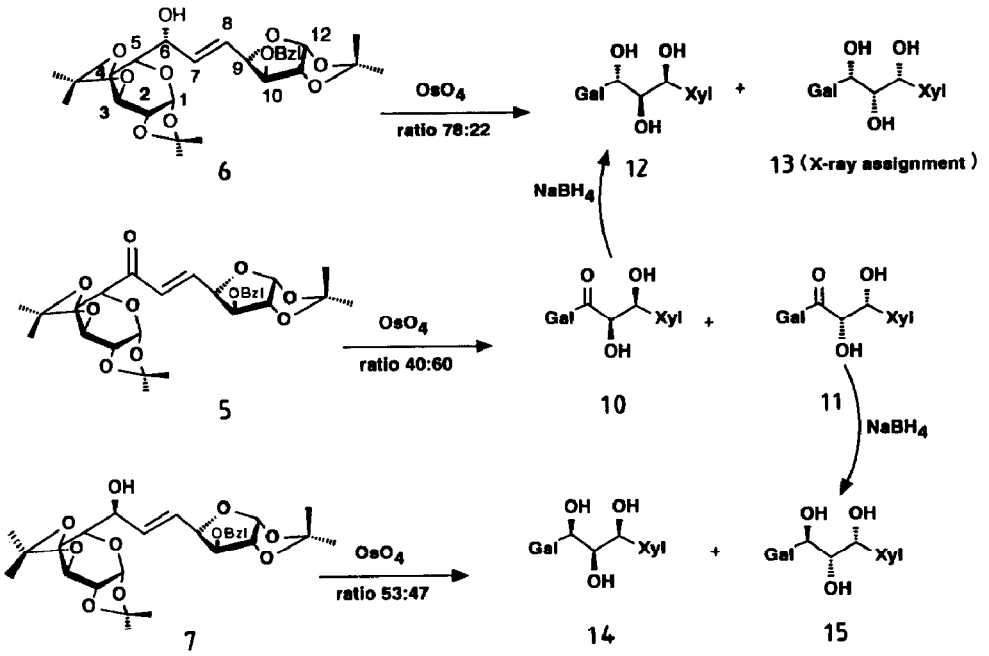


1 $R^1, R^2 = O$ **3** $R^1, R^2 = O$

2 $R^1 = OH$, $R^2 = H$ **4** $R^1 = OH$, $R^2 = H$

For the *directed* synthesis of higher-carbon sugars, it is important to determine if Kishi's rule[5] is generally applicable in the oxidation of such complicated molecules, and further examples of higher-sugar precursors, namely **5**[2c], **6**[2c], **7**[2c], **8**, and **9**, have now been studied.

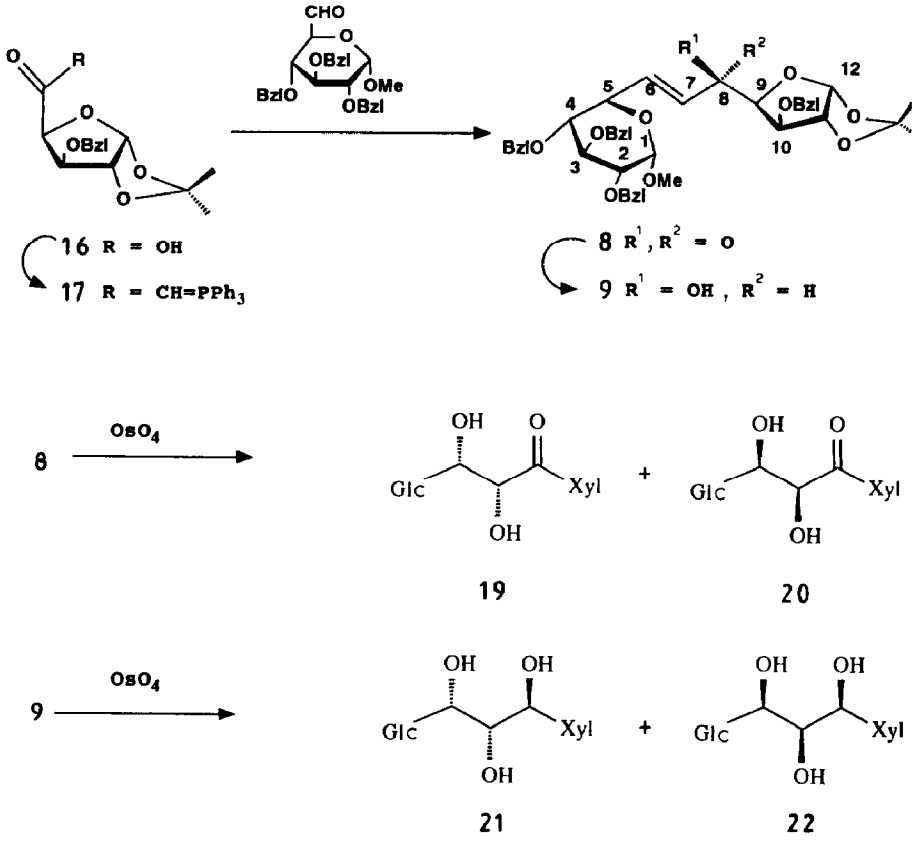
Catalytic osmylation of 3-*O*-benzyl-5-deoxy-5-*C*-[(*E*)-7-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-heptopyranos-6-ulos-7-ylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose (**5**) afforded 93% of 3-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexopyranos-6-ulos-6-yl)-1,2-*O*-isopropylidene-L-*glycero*-α-D-*gluco*- (**10**) and -D-*glycero*-β-L-*ido*-hexofuranose (**11**) in the ratio 2:3. Likewise, 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 (**6**) gave 75% of 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*- (**12**) and -D-*glycero*-β-L-*ido*-hexofuranose (**13**) in the ratio 4:1, and the L-*glycero* isomer (**7**) of **6** afforded 75% of 3-*O*-benzyl-6-*C*-(1,2:3,4-di-*O*-isopropylidene-L-*glycero*-α-D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*glycero*-α-D-*gluco*- (**14**) and -D-*glycero*-β-L-*ido*-hexofuranose (**15**) in the ratio 53:47.

The configurations of **10–15** were established by crystallography and chemical correlations. X-Ray analysis[6] of the minor product (**13**) of the oxidation of **6** revealed the D-*xylo* configuration of the internal triol system (C-6,7,8). Consequently, the configuration of this moiety in **12** was assigned as L-*arabino*. Reduction of the minor product (**10**) of the osmylation of **5** with sodium borohydride afforded **12**, which established the L- and D-*threo* configurations of the C-7, 8-diol in **10** and **11**, respectively. Reduction of **11** with sodium borohydride afforded **15**, indicating the D-*lyxo* and L-*xylo* configurations of the C-6,7,8-triol in **15** and **14**, respectively.

Oxidation of **6** (both OR groups on the same side of the double bond) followed Kishi's rule, but oxidation of **5** was an exception since the diol **11** was the main product. No exceptions were found in the osmylations of **8** and **9**, which were synthesised by a reported method[2b]. Thus, conversion of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranuronic acid (**16**) into the stable ylid **17** (see Experimental) followed by reaction with methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranoside[7] (**18**) afforded 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-6-*C*-[methyl (*E*)-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranosid-6-ylidene]-α-D-*xylo*-hexofuranos-5-ulose (**8**). Reduction of **8** with zinc borohydride[8] afforded (as the only product) the expected[2b] alcohol **9**. The *R*



configuration at C-8 (for numbering see formula **9**) was proved by (*a*) degradation to 3,5-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (benzylation of the free hydroxyl group followed by cleavage of the double bond with $OsO_4/NaIO_4$ and reduction of the resulting aldehyde with sodium borohydride, see Experimental), and (*b*) isolation of the known[4] triol **22** (see below) from the osmylation reaction of **9**.

Catalytic osmylation of **8** afforded 65% of 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*C*-[methyl 2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-*gluco*-hexopyranosid-6-yl]-α-D-*gluco*- (**19**) and -[L-*glycero*-α-D-*gluco*-]-β-L-*ido*-hexo-1,4-furanos-5-ulose (**20**) in the ratio 55:45. Osmylation of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-6-*C*-[methyl (*E*)-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranosid-6-ylidene]-α-D-glucofuranose (**9**) afforded 71% of 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*C*-[methyl 2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-*gluco*-hexopyranosid-6-yl]-D-*glycero*-α-D-*gluco*- (**21**) and -[L-*glycero*-α-D-*gluco*-]-L-*glycero*-α-D-*gluco*-hexofuranose (**22**) in the ratio 9:1.

The configurations of compounds **19–22** were established by chemical and spectral correlations. Since the L-*xylo* configuration has been assigned[4] to the internal triol system in **22**, the configuration at C-6,7,8 in **21** is L-*lyxo*. Furthermore, reduction of **19** afforded **21**, thus proving the L-*threo* configuration of the C-6,7 unit in **19**.

Thus, from this and the previous[2a] study, it is concluded that osmylation of higher sugar allylic alcohols affords higher-carbon sugars in good yield. The configurations of the main isomers can be assigned safely on the basis of Kishi's rule if both oxygen functions, *i.e.*, the hydroxyl group and the ring oxygen atom (flanking the double bond), are on the same side of the molecule. The stereochemistry of the osmylation reaction of higher sugar enones is not as clear; the configuration of the main isomers usually results from the attack of osmium tetraoxide *anti* to the ring oxygen atom, but an exception is **8** where predominant *syn* attack occurs.

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 **10–14** are shown in Table I) were recorded with a Bruker AM-500 spectrometer for solutions in $CDCl_3$

TABLE I

^{1}N-N.m.r. data for **11–15**

Compound	*Chemical shifts (δ, p.p.m.)*											
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*	*H-9*	*H-10*	*H-11*	*H-12*
10	5.65 d	4.34 dd	4.73 dd	4.64 dd	4.53 d	–	n.d.	3.92 dd	4.28 dd	4.24 d	4.60 d	5.99 d
11	5.63 d	4.28 dd	4.65		4.59 d	–	4.67	3.53	4.37 dd	4.10 d	n.d.	5.96 d
12	5.52 d	4.34 dd	4.63 dd	4.53 dd	3.98 bs	4.0 m			4.27 dd	4.20 d	4.61 d	5.94 d
13	5.50 d	4.32 dd	4.63 dd	4.49 dd	3.97 dd	4.02 d	3.94	4.19 dd	4.44 dd	4.12 d	4.67 d	5.97 d
14	5.56 d	4.34 dd	4.60 dd	4.37 dd	4.01 dd	4.06 dd	n.d.	n.d.	4.27 t	4.12 d	4.59 d	5.93 d
15	5.62 d	4.32 dd	4.60 dd	4.41 dd	4.17 t	4.06 dd	3.81 dd	n.d.	4.37 dd	4.10 d	4.62 d	6.00 d

	Coupling constants (J, *Hz*)										
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$	$J_{8,9}$	$J_{9,10}$	$J_{10,11}$	$J_{11,12}$
10	4.9	2.5	7.9	2.0	–	–	3.4	6.4	3.2	0	3.8
11	5.0	2.4	n.d.	2.1	–	–	0	7.5	3.2	0	3.8
12	5.0	2.5	8.0	1	n.d.	n.d.	n.d.	7.6	3.2	0	3.8
13	4.9	2.5	8.0	1.8	9.2	0	2.1	6.0	3.6	0	3.8
14	5.0	2.4	8.0	1.8	7.2	2.2	n.d.	2.5	2.5	0	3.7
15	5.0	2.4	8.0	1.5	1.5	8.5	3.5	3.6	3.6	0	3.9

(internal Me_4Si). Reactions were monitored by t.l.c. (hexane–ethyl acetate: *A* 2:1, *B* 3:2, *C* 1:1, *D* 2:3, and *E* 1:4). Column chromatography was performed on silica gel (Merck, 230–400 mesh). Organic solutions were dried over anhydrous $MgSO_4$.

Osmylation reactions. — To a solution of 1.0 mmol of the allylic alcohol (**6**, **7**, or **9**) or enone (**5** or **8**) in tetrahydrofuran (8 mL), *tert*-butyl alcohol (0.8 mL), and water (0.1 mL) was added *N*-methylmorpholine *N*-oxide (160 mg) followed by osmium tetraoxide (0.5 mL of a ~ 2% solution in *tert*-butyl alcohol). The mixture was stirred for 24–48 h at room temperature, then diluted with methanol (20 mL), stirred with aqueous 40% sodium hydrogen sulfite (3 mL) for 30 min, filtered, concentrated, and subjected to column chromatography (solvent *C*), or diluted with ether (40 mL), washed twice with aqueous 5% mannitol, followed by concentration and column chromatography (solvent *B*).

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- (**10**) *and* -D-glycero-β-L-ido-*hexofuranose* (**11**). — Osmylation of **5** (440 mg, 0.827 mmol) afforded the following amorphous products.

Compound **10** (173 mg, 37%), $[\alpha]_D$ − 94° (*c* 1.2).

Anal. Calc. for $C_{28}H_{38}O_{12}\cdot 0.5H_2O$: C, 58.4; H, 6.8. Found: C, 58.4; H, 7.2.

Compound **11** (265 mg, 56.6%), $[\alpha]_D$ − 31° (*c* 2.6).

Anal. Calc. for $C_{28}H_{38}O_{12}\cdot H_2O$: C, 57.5; H, 6.9. Found: C, 57.9; H, 6.7.

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- (**12**) *and* -D-glycero-β-L-ido-*hexofuranose* (**13**). — Osmylation of **6** (1.04 g, 1.95 mmol) afforded the following products.

Compound **12** (665 mg, 60%), amorphous, $[\alpha]_D$ − 42° (*c* 1.7).

Anal. Calc. for $C_{28}H_{40}O_{12}$: C, 59.1; H, 7.1. Found: C, 59.0; H, 7.3.

Compound **13** (166 mg, 15.1%), m.p. 160–162° (from ethyl acetate–hexane), $[\alpha]_D$ − 48° (*c* 1.0).

Anal. Found: C, 58.9; H, 7.3.

3-O-*Benzyl*-6-C-(*1,2:3,4-di*-O-*isopropylidene*-L-glycero-α-D-galacto-*hexopyranos-6-yl*)-*1,2*-O-*isopropylidene*-L-glycero-α-D-gluco- (**14**) *and* -D-glycero-β-L-ido-*hexofuranose* (**15**). — Osmylation of **7** (540 mg, 1.01 mmol) afforded the following amorphous products.

Compound **14** (230 mg, 40%), $[\alpha]_D$ − 40° (*c* 1.4).

Anal. Calc. for $C_{28}H_{40}O_{12}$: C, 59.1; H, 7.1. Found: C, 59.3; H, 7.3.

Compound **15** (200 mg, 35%), $[\alpha]_D$ − 54° (*c* 1.9).

Anal. Calc. for $C_{28}H_{40}O_{12}\cdot 0.5H_2O$: C, 58.2; H, 7.2. Found: C, 58.6; H, 7.4.

3-O-*Benzyl*-1,2-O-*isopropylidene-6*-C-*[methyl 2,3,4-tri*-O-*benzyl*-D-glycero-α-D-gluco-*hexopyranosid-6-yl*]-α-D-gluco- (**19**) *and* -[L-glycero-α-D-gluco-]-β-L-ido-*hexo-1,4-furanos-5-ulose* (**20**). — Osmylation of **8** (510 mg, 0.69 mmol) afforded the following products.

Compound **19** (192 mg, 36%), oil, $[\alpha]_D$ + 6° (*c* 1). ^{1}H-N.m.r. data: δ 6.05 (d, 1 H, $J_{11,12}$ 3.6 Hz, H-12), 4.90 (d, 1 H, $J_{9,10}$ 3.6 Hz, H-9), 4.54 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.39 (d, 1 H, H-10), 4.04 (t, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.2 Hz, H-3), 3.82 (dd, 1 H, $J_{4,5}$ 9.7, $J_{5,6}$ 7.7 Hz, H-5),

3.61 (dd, 1 H, H-4), 3.51 (dd, 1 H, H-2), 3.40 (s, 3 H, OMe), 1.47 and 1.41 (2 s, 6 H, CMe_2).

Anal. Calc. for $C_{44}H_{50}O_{12}$: C, 68.6, H, 6.5. Found: C, 68.3; H, 6.6.

Compound **20** (154 mg, 29%),oil, $[\alpha]_D$ +20° (*c* 1). ^{1}H-n.m.r. data: δ 5.61 (d, 1 H, $J_{11,12}$ 3.6 Hz, H-12), 4.91 (d, 1 H, $J_{9,10}$ 3.7 Hz, H-9), 4.81 (d, 1 H, H-11), 4.65 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.24 (d, 1 H, H-10), 3.99 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 9.3 Hz, H-3), 3.76 (dd, 1 H, $J_{4,5}$ 9.9, $J_{5,6}$ 1.1 Hz, H-5), 3.60 (dd, 1 H, H-4), 3.48 (dd, 1 H, H-2), 3.40 (s, 3 H, OMe), 1.42 and 1.24 (2 s, 6 H, CMe_2).

Anal. Calc. for $C_{44}H_{50}O_{12}\cdot H_2O$: C, 67.0; H, 6.6. Found: C, 66.5; H, 6.6.

*3-O-Benzyl-1,2-O-isopropylidene-6-C-[methyl 2,3,4-tri-O-benzyl-*D-glycero-α-D-gluco-*hexopyranosid-6-yl]*-D-glycero-α-D-gluco- (**21**) *and* -[L-glycero-α-D-gluco-]-L-glycero-α-D-gluco-*hexofuranose* (**22**). — Osmylation of **9** (605 mg, 0.82 mmol) afforded the following products.

Compound **21** (405 mg, 64%), oil, $[\alpha]_D$ +11° (*c* 2.5). ^{1}H-N.m.r. data: δ 5.95 (d, 1 H, $J_{11,12}$ 3.8 Hz, H-12), 4.60 (d, 1 H, H-11), 4.55 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.29 (1 H, $J_{8,9}$ 7.4 Hz, H-9), 4.18 (d, 1 H, $J_{9,10}$ 3.2 Hz, H-10), 4.04 (t, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.2 Hz, H-3), 3.88 (dd, 1 H, $J_{4,5}$ 9.8, $J_{5,6}$ 6.2 Hz, H-5), 3.53 (dd, 1 H, H-4) 3.51 (dd, 1 H, H-2), 3.40 (s, 3 H, OMe), 1.42 and 1.30 (2 s, 6 H, CMe_2).

Anal. Calc. for $C_{44}H_{52}O_{12}\cdot H_2O$: C, 66.8; H, 6.9. Found: C, 66.6; H, 7.1.

Compound **22** (46 mg, 7.3%), oil, identical with the product described previously[4].

3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-6-C-[methyl (E)*-2,3,4-tri-O-benzyl-6-deoxy-α-D-glucopyranosid-6-ylidene]-α-*D-xylo-*hexofuranos-5-ulose* (**8**). — A solution of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose[9] (6.0 g, 21.6 mmol) in acetone (200 mL) was titrated with the Jones reagent[10] until reaction was complete (t.l.c., solvent *C*). Water (300 mL) was added, the product was extracted with ether (2 × 200 mL), the combined extracts were washed with aqueous 2% NaOH, and the extract was acidified to pH ~1 with aqueous 10% sulfuric acid and extracted with chloroform. The combined extracts were washed with water (2 × 200 mL), dried, and concentrated to yield 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranuronic acid (**16**; 5.35 g, 84%), m.p. 141–142° (from hexane–ethyl acetate), $[\alpha]_D$ −27° (*c* 3).

Anal. Calc. for $C_{15}H_{18}O_6$: C, 61.2; H, 6.2. Found: 61.3; H, 6.3.

To a suspension of 1,1-carbonyldi-imidazole (2.1 g, 12.96 mmol, 1.15 equiv.) in dry benzene (50 mL) was added a solution of **16** (3.3 g, 11.2 mmol; dried by evaporation of toluene thrice therefrom) in dry benzene (50 mL). The mixture was stirred for 30 min at room temperature, then added dropwise to a stirred solution of methylenetriphenylphosporane [2.5 equiv., generated from methyltriphenylphosphonium iodide (11.3 g) and 1.6M butyl-lithium in hexane (17.5 mL), in dry benzene (250 mL)] during ~30 min. After 1 h, water (50 mL) was added, the aqueous phase was extracted with ethyl acetate (2 × 50 mL), and the combined organic solutions were dried and concentrated. Column chromatography (solvent *C* and *E*) of the residue gave the ylid **17** (3.71 g) as an oil, to a solution of which in dry benzene (50 mL) was added methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranoside[7] (3.24 g, 7.01 mmol). The mixture was boiled under

reflux for 5 h, the solvent was evaporated, and chromatography (solvent *A*) of the residue afforded enone **8**, isolated as an oil (3.71 g, 45% from **16**), $[\alpha]_D$ + 30° (*c* 2). ^{1}H-N.m.r. data: δ 7.10 (dd, 1 H, $J_{5,6}$ 4.4, $J_{6,7}$ 15.8 Hz, H-6), 6.82 (dd, 1 H, $J_{5,7}$ 1.8 Hz, H-7), 6.03 (d, 1 H, $J_{11,12}$ 3.6 Hz, H-12), 4.76 (d, 1 H, $J_{9,10}$ 3.6 Hz, H-9), 4.60 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.57 (d, 1 H, $J_{10,11}$ 0 Hz, H-10), 4.28 (m, 1 H, H-5), 4.00 (t, 1 H, $J_{3,4}$ 9.0, $J_{4,5}$ 9.1 Hz, H-4), 3.0 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.31 (s, 3 H, OMe), 3.17 (dd, 1 H, H-3), 1.46 and 1.42 (2 s, 6 H, CMe_2).

Anal. Calc. for $C_{44}H_{48}O_{10}\cdot H_2O$: C, 70.0; H, 6.7. Found: C, 70.2; H, 6.7.

3-O-Benzyl-6-deoxy-1,2-O-isopropylidene-6-C-[methyl (E)-*2,3,4-tri-O-benzyl-6-deoxy-α-D-glucopyranosid-6-ylidene]-α-D-glucofuranose* (**9**). — To a solution of **8** (1.5 g., 2.038 mmol) in dry ether (50 mL) at 0° was added an ethereal ~M solution of zinc borohydride[8] (3 mL). After 15 min, water was added, and **9** was isolated as usual[2b]. Column chromatography (solvent *B*) afforded **9** (1.35 g, 90%), isolated as an oil, $[\alpha]_D$ + 29° (*c* 2.6). ^{1}H-N.m.r. data: δ 5.98 (d, 1 H, $J_{11,12}$ 3.8, H-12), 5.92 (dd, 1 H, $J_{7,8}$ 5.5, $J_{6,7}$ 15.5 Hz, H-7), 5.83 (dd, 1 H, $J_{5,6}$ 6.4 Hz, H-6), 4.60 (d, 1 H, H-11), 4.57 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.46 (t, 1 H, $J_{8,9}$ 6 Hz, H-8), 4.10 (dd, 1 H, $J_{9,10}$ 3.4, $J_{8,9}$ 12.0 Hz, H-9), 4.08 (dd, 1 H, $J_{4,5}$ 9.3 Hz, H-5), 4.06 (d, 1 H, H-10), 3.98 (t, 1 H, $J_{3,4}$ 9.2, H-4), 3.53 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.37 (s, 3 H, OMe), 3.24 (t, 1 H, H-3), 1.44 and 1.31 (2 s, 6 H, CMe_2).

Anal. Calc. for $C_{44}H_{50}O_{10}$: C, 71.5; H, 6.8. Found: C, 71.3; H, 6.9.

Determination of the configuration of **9**. — To a solution of **9** (150 mg, 0.203 mmol) in dry *N,N*-dimethylformamide (5 mL) was added sodium hydride (50 mg of 50% suspension in mineral oil) followed by benzyl chloride (0.5 mL), and the mixture was stirred at room temperature for 1 h. The product was isolated in the usual manner and purified by column chromatography (hexane–ethyl acetate, 9:1). To its solution in 1,4-dioxane–water (4:1, 5 mL) was added sodium periodate (100 mg) followed by osmium tetraoxide (1 drop of ~2% solution in *tert*-butyl alcohol). The mixture was stirred overnight at room temperature, the solvent was evaporated *in vacuo*, and the crude product was extracted with ether and reduced with sodium borohydride (20 mg). Isolation of the product in the usual way, followed by column chromatography (solvent *A*), afforded known 3,5-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[11] (64 mg) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[7] (65 mg).

Reduction of **10**, **11**, *and* **19**. — A solution of **10** (80 mg, 0.104 mmol) in tetrahydrofuran–methanol (1:1, 5 ,L) was treated with sodium borohydride (20 mg) for 30 min at room temperature. Isolation of the product in the usual manner, followed by column chromatography (solvent *C*), afforded **12** (65 mg) identical (n.m.r. spectra) with the product prepared previously[4]. Likewise, **11** afforded 85% of **13**, and **19** gave 80% of **21**.

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