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THE SYNTHESIS OF SOME SEVEN-CARBON SUGARS *via* THE OSMYLATION OF OLEFINIC SUGARS*,†

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ABSTRACT

The stereochemical outcome of the catalytic osmylation of 6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hept-6-enopyranose (**10**), 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose, (*E*)- and (*Z*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-enofuranose (**20** and **27**, respectively), methyl (*Z*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-enofuranuronate (**26**), (*E*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hept-5-enofuranose, benzyl (*E*)- and (*Z*)-5,6-dideoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hept-5-enofuranoside (**46** and **50**, respectively), and methyl [benzyl (*Z*)-5,6-dideoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hept-5-enofuranosid]uronate (**49**) has been examined. Such oxidations led to satisfactory syntheses of L-*glycero*-D-*gluco*-heptose and the corresponding heptitol (from **20**), L-*glycero*-D-*gulo*-heptitol (from **26**), D-*glycero*-D-*gluco*-heptitol (from **27**), D-*glycero*-D-*galacto*-heptitol (from **10** and **46**), (*meso*)-*glycero*-*gulo*-heptitol (from **49**), and D-*glycero*-D-*manno*-heptitol (from **50**).

INTRODUCTION

In Part 1 of this series[2], we showed that the catalytic osmylation of octenopyranose derivatives, prepared *via* Wittig olefination, provided satisfactory routes to a number of 8-carbon sugars, whose stereochemistry could be predicted by Kishi's empirical rule for osmylation[3]. In accord with Kishi's formulation[3], the catalytic osmylation of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-oct-7-enopyranose‡ (**1**) gave, as the major product, 1,2:3,4-di-*O*-isopropyl-

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†Higher-carbon Sugars, Part 3. For Part 2, see ref. 1.
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‡This and other higher-carbon sugars are named according to the IUPAC–IUB Tentative Rules for Carbohydrate Nomenclature[4], which specify the highest-numbered stereocentre as the reference atom regardless of chain length. According to the British–American Rules of Carbohydrate Nomenclature[5], **1** would be given the alternative name 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-oct-7-enopyranose. Both names are unambiguous.

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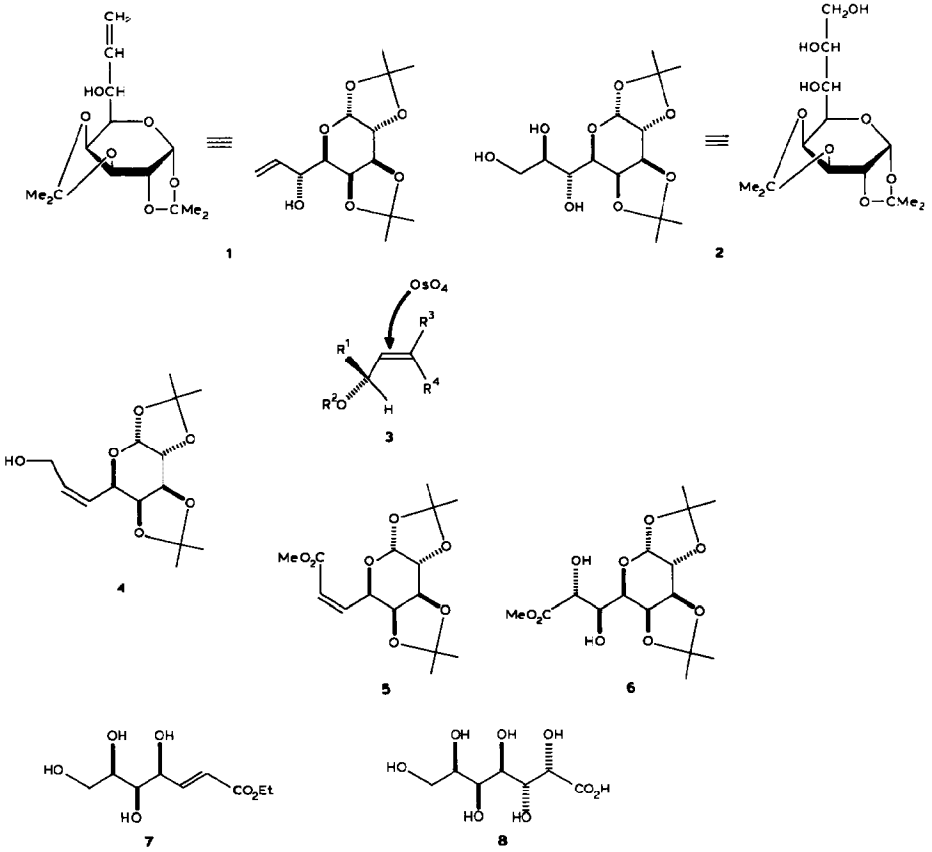
idene-α-D-*erythro*-D-*galacto*-octopyranose (**2**) in which the relative stereochemistry between the pre-existing HO-6 and the newly introduced HO-7 is *erythro*[3]. The observed stereoselectivity of the osmylation reaction can be rationalised by assuming that the molecule reacts in the sterically least-compressed conformation **3**, with the major product arising from the preferential approach of osmium tetraoxide to the face of the olefinic linkage opposite to that of the pre-existing hydroxyl (or alkoxyl) group[3]. This *anti* stereoselectivity with respect to a hydroxyl group is seen clearly in the conversion of **1** into **2**. The osmylation reaction is also *anti* stereoselective with respect to a pyranose ring-oxygen atom, which may be regarded as influencing the stereochemical outcome of the reaction in the same way as does an alkoxyl group. Thus, the major product obtained[2,6] on catalytic osmylation of (*Z*)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enopyranose (**4**) is also **2**. Also of interest is the failure of methyl (*Z*)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enopyranuronate (**5**) to conform to Kishi's formulation[3], the major product of catalytic osmylation being methyl 1,2:3,4-di-*O*-isopropylidene-β-L-*erythro*-D-*galacto*-octopyranuronate[2,6] (**6**).

With the foregoing examples as a guide, it appeared that Wittig olefination and subsequent *cis*-hydroxylation of the olefinic linkage might provide an attractive route to 7-carbon sugars of predictable stereochemistry. The synthesis of higher-carbon sugars by this approach is not new[7], although its efficiency depends critically on the stereoselectivities of both the Wittig and hydroxylation reactions. The catalytic osmylation of the α,β-unsaturated aldonic ester **7** in the presence of chloric acid, reported by Kochetkov and co-workers[8], is of particular interest since subsequent lactonisation and reduction afforded a mixture of D-*glycero*-L-*galacto*-heptose and D-*glycero*-L-*ido*-heptose in the ratio 5:1. The preferential formation of D-*glycero*-L-*galacto*-heptonic acid (**8**) under the acid conditions used for osmylation is in agreement with Kishi's empirical rule[3]. Other general procedures for the synthesis of 7-carbon sugars have been extensively reviewed[9].

RESULTS AND DISCUSSION

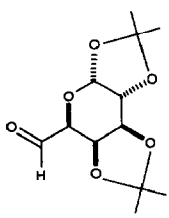
Besides the approach from unsaturated, acyclic derivatives, such as **7**, two other approaches to 7-carbon sugars can be envisaged. One of them involves the *cis*-hydroxylation of such unsaturated pyranose derivatives as 6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hept-6-enopyranose[10] (**10**), which was readily prepared by one-carbon extension of the hexodialdose derivative **9**[11] using methylenetriphenylphosphorane (a modified procedure for the preparation of **10** is given in the Experimental section). Catalytic osmylation[12] of **10** produced a mixture (94%) of 1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-heptopyranose (**11**) and the β-L-*glycero*-D-*galacto* isomer **12** in the ratio ~2.5:1. Once again, the osmylation reaction is *anti* stereoselective with respect to the oxygen atom of the pyranose ring. In this and all subsequent oxidations, the ratio of the products was determined by integration over the signals for the anomeric protons in the 90- or



360-MHz p.m.r. spectra. The identity of the major isomer **11** was established by the isolation of the known[13] D-*glycero*-D-*galacto*-heptitol (perseitol, **13**), in 54% yield, following acid hydrolysis of the mixture of **11** and **12**, and reduction of the resulting heptoses. The ^{13}C-n.m.r. spectrum (D_2O) of **13** was indistinguishable from that reported[14] for an authentic sample, and **13** was further characterised as the hepta-acetate **14**[13]*. Perseitol (**13**) occurs naturally in the avocado[15]; the best source of perseitol is the seed of the avocado[16], but the crystalline heptitol has also been obtained from the leaves[17] and wound exudates[18] of the avocado tree.

The synthesis of other 7-carbon sugars by the foregoing procedure would entail starting from a hexodialdose derivative different from **9**. Although undoubtedly feasible, this approach was not pursued since contemporary studies had uncovered a much more versatile and stereoselective route that involved two-carbon extension of the chain of pentodialdofuranose derivatives (*e.g.*, **18**). The

*Since the specific optical rotations of heptitols in aqueous solution are invariably very low[9], ^{13}C-n.m.r. spectroscopy[14] and/or derivatisation afforded the most reliable means of confirming the structure indicated by the melting point of the heptitol.



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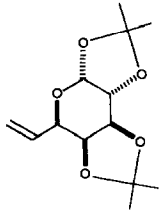

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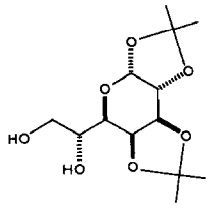

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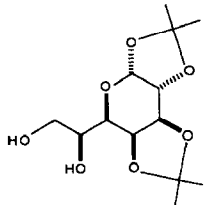

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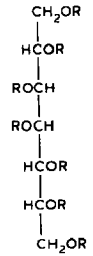
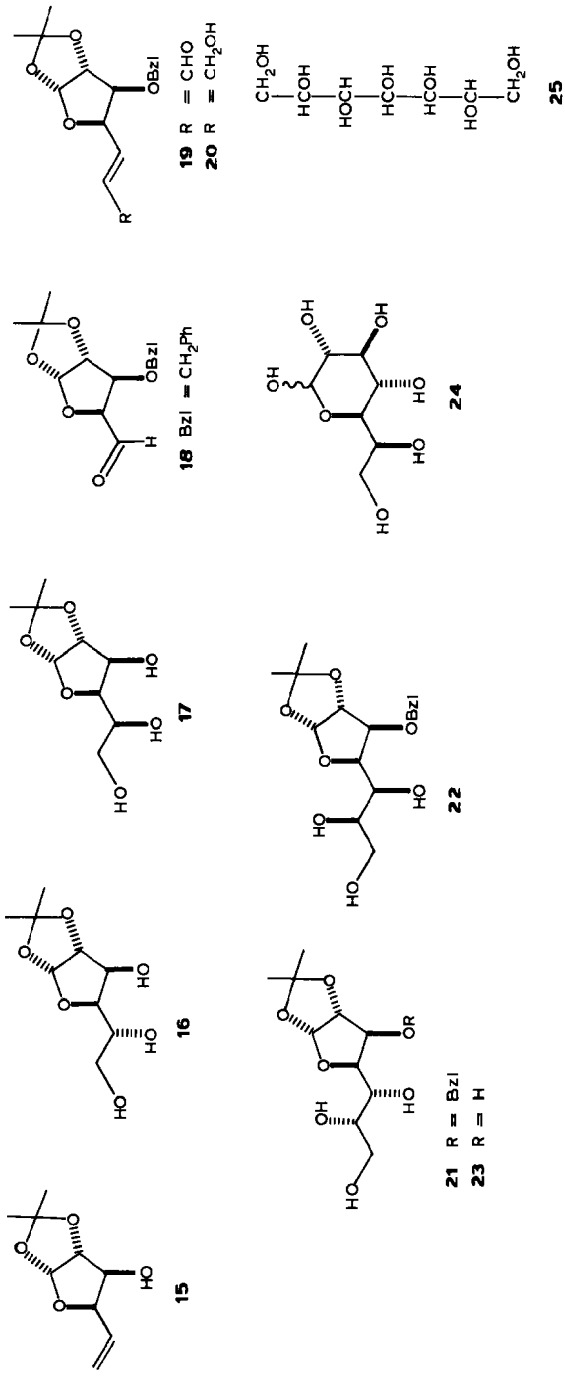


13 R = H
14 R = Ac

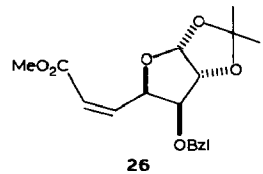
incentive to explore this route came from the catalytic osmylation[12] of 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose[19] (**15**), which provided a mixture (71%) of 1,2-*O*-isopropylidene-α-D-glucofuranose (**16**) and the β-L-idofuranose **17** in the ratio ~3:1. In conformity with Kishi's formulation[3], the osmylation of **15** is *anti* stereoselective with respect to the furanose ring-oxygen atom (*i.e.*, O-4 and O-5 of **16** are *erythro*). Encouraged by this result, we went on to examine the osmylation of (*E*)- and (*Z*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-enofuranose (**20** and **27**, respectively), methyl (*Z*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-enofuranuronate (**26**), (*E*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hept-5-enofuranose (**39**), benzyl (*E*)- and (*Z*)-5,6-dideoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hept-5-enofuranoside (**46** and **50**, respectively), and methyl [benzyl (*Z*)-5,6-dideoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hept-5-enofuranosid]uronate (**49**). The introduction of the benzyl group at C-3 of compounds **20, 26, 27**, and **39** was a deliberate ploy to increase the solubility of the osmylation products in organic solvents; otherwise, they were much too soluble in water and unacceptable losses were incurred during their isolation.

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose[20] (**18**) (readily prepared by periodate oxidation of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose) reacted with formylmethylenetriphenylphosphorane[21] in boiling benzene to give the known[22] (*E*)-enal **19**, which furnished **20** on reduction with di-isobutylaluminium hydride in dichloromethane at ~0°. Catalytic osmylation[12] of **20** afforded a mixture of 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*glycero*-D-*gluco*-heptofuranose (**21**) and the α-D-*glycero*-L-*ido* isomer **22** in the ratio ~5:1. After catalytic debenzylation of the mixture of **21** and **22**, 1,2-*O*-isopropylidene-β-L-*glycero*-D-*gluco*-heptofuranose (**23**) was isolated in crystalline form and in ~55% yield. The identities of **21** and **23** were revealed when acid hydrolysis of **23** gave L-*glycero*-D-*gluco*-heptose (**24**), whose physical constants showed the expected correspondence with those of the D enantiomer[23]. The heptitol **25**[13] derived from **24** provided further proof of identification.

The reaction between **18** and (methoxycarbonylmethylene)triphenylphosphorane[24] in methanol at ~0° furnished the (*Z*)-heptenofuranuronate **26** in 89% yield. The *Z* configuration of the olefinic linkage followed from the reduction of **26**,


19 R = CHO
20 R = CH2OH
18 Bzl = CH2Ph
17
16
15
21 R = Bzl
23 R = H
22
24
25

with lithium aluminium hydride, to give the (*Z*)-heptenofuranose **27**, whose p.m.r. spectrum readily distinguished it from the (*E*)-isomer **20** of established stereochemistry. Besides **27**, the reduction of **26** gave an unidentified product that was not removed by chromatography. The 7-acetate **28** was obtained in a chromatographically homogeneous form after acetylation of the products, and provided **27** on deacetylation.



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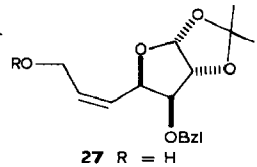
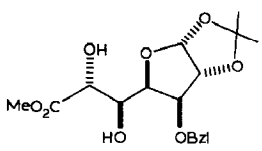


27 R = H
28 R = Ac



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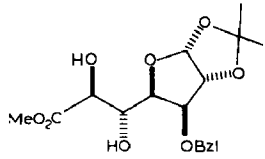

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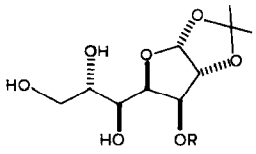
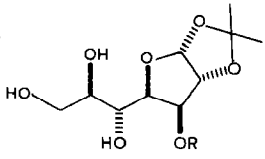
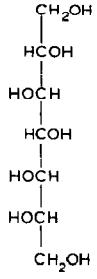


31 R = Bzl
33 R = H



32 R = Bzl
34 R = H



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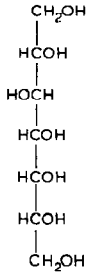

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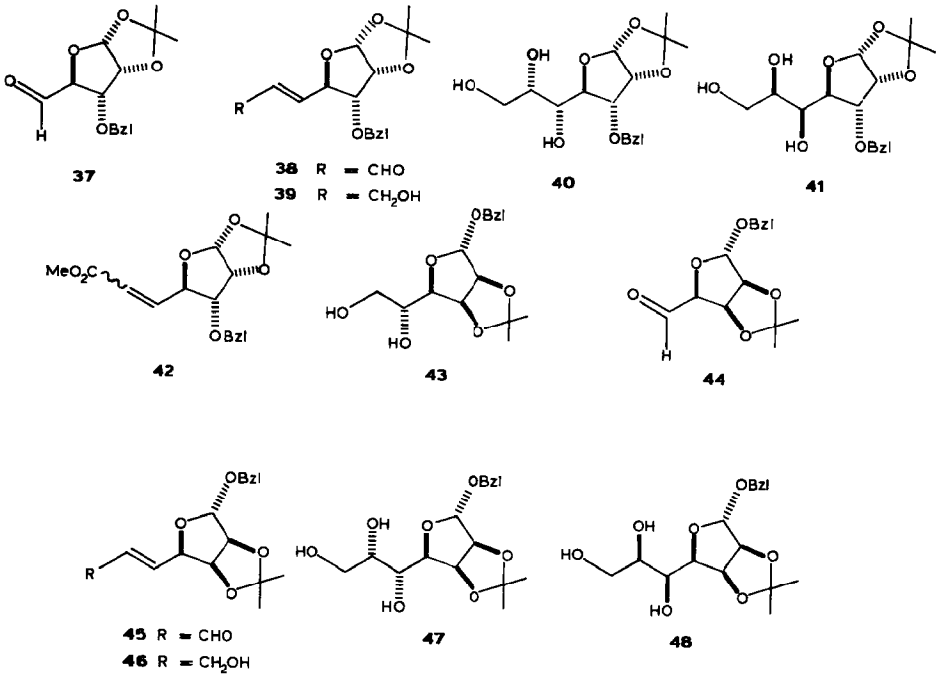
Catalytic osmylation[12] of **26** produced a mixture (94%) of methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*glycero*-L-*ido*-heptofuranuronate (**29**) and the α-D-*glycero*-D-*gluco* isomer **30** in the ratio ~1.5:1. Reduction of the mixture of **29** and **30**, with lithium aluminium hydride in tetrahydrofuran, gave a mixture of 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*glycero*-L-*ido*-heptofuranose (**31**) and the α-D-*glycero*-D-*gluco* isomer **32**, which then yielded crystalline **32** and a syrup substantially enriched in **31**. The structure of **32** was established following its preparation by a more expeditious route described later. Debenzylation of the mixture enriched in **31** gave principally **33**, which yielded L-*glycero*-D-*gulo*-heptitol (L-*glycero*-L-*ido*-heptitol) (**35**), in 38% yield, following acid hydrolysis and reduction of the resulting heptoses. The crystalline heptitol **35** was identified by comparison (m.p. and ^{13}C-n.m.r. spectrum) with the D enantiomer[25].

When subjected to catalytic osmylation[12], the (*Z*)-heptenofuranose **27** afforded a mixture of **31** and **32** in the ratio ~1:7, from which 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*glycero*-D-*gluco*-heptofuranose (**32**) crystallised. Catalytic debenzylation of **32** gave **34**, which, for the purpose of identification, was transformed into the known[26] D-*glycero*-D-*gluco*-heptitol (**36**).

In the light of the foregoing results, it seemed likely that other 7-carbon sugars would be accessible from 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*ribo*-pentodialdo-1,4-furanose[27] (**37**) (obtained by periodate oxidation of 3-*O*-benzyl-1,2-*O*-

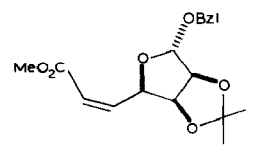
isopropylidene-α-D-allofuranose). The literature procedure[22] was used to transform **37** into the (*E*)-enal **38**, which, as before, was reduced to the (*E*)-heptenofuranose **39**. Catalytic osmylation[12] of **39** provided a mixture (~70%) containing almost equal proportions of 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*glycero*-D-*allo*-heptofuranose (**40**) and the α-D-*glycero*-L-*talo* isomer **41**. In view of the lack of stereoselectivity of the osmylation reaction, this route to 7-carbon sugars was not pursued. In comparing the osmylation of **20** and **39**, it is noticeable that the configuration at C-3 has a pronounced effect on the stereoselectivity of the reaction. This effect is presumably steric in origin. If the osmylation reaction prefers to be *anti* stereoselective with respect to the furanose ring-oxygen atom, then the bulky benzyloxy group of **39** may lie more in the path of the incoming reagent than that of **20**. Equally unpromising was the finding that the reaction between **37** and (methoxycarbonylmethylene)triphenylphosphorane[24] in methanol produced an inseparable mixture containing roughly equal proportions of methyl (*Z*)- and (*E*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hept-5-enofuranuronate (**42**).



The catalytic osmylation[12] of the (*E*)-heptenofuranoside **46**, which was prepared in a straightforward manner from benzyl 2,3-*O*-isopropylidene-α-D-mannofuranoside[27] (**43**), was also examined. Thus, oxidation of **43** with ~1.5 equiv. of sodium periodate in aqueous 1,4-dioxane furnished the pentodialdofuranose derivative **44**, which reacted with formylmethylenetriphenylphosphorane[21] in boiling benzene to give the (*E*)-enal **45**. The *E* configuration assigned to **45** was

based on analogy[28] and spectroscopic evidence. The p.m.r. spectrum of **45** showed a wide doublet ($J_{6,7}$ 7 Hz) at δ 9.64 for the aldehydic proton; the H-6 signal at δ 6.38 was strongly coupled ($J_{5,6}$ 15 Hz) to H-5, and displayed a small, long-range coupling ($J_{4,6}$ ~1 Hz) with H-4, indicative of the (*E*)-olefinic structure[22]. The structure assigned to **45** was validated by the subsequent chemistry. Following reduction of **45** to **46**, catalytic osmylation[12] gave a mixture (92%) of benzyl 2,3-*O*-isopropylidene-β-L-*glycero*-D-*manno*-heptofuranoside (**47**) and the α-D-*glycero*-L-*gulo* isomer **48** in the ratio 7:1. Catalytic debenzylation* of the mixture of **47** and **48**, acid hydrolysis, and reduction gave D-*glycero*-D-*galacto*-heptitol** (perseitol)[13] (**13**) in 55% overall yield.

The reaction between **44** and (methoxycarbonylmethylene)triphenylphosphorane[24] furnished the (*Z*)-olefin **49**, which, on reduction with 3 equiv. of di-isobutylaluminium hydride in dichloromethane at ~0°, gave the (*Z*)-heptenofuranoside **50**. P.m.r. spectroscopy readily distinguished between **50** and the (*E*)-isomer **46**. Catalytic osmylation of **49** produced a mixture (98%) of methyl (benzyl 2,3-*O*-isopropylidene-α-D-*glycero*-D-*manno*-heptofuranosid)uronate (**51**) and the β-L-*glycero*-L-*gulo* isomer **52** in the ratio ~1.5:1. Reduction of the mixture of **51** and **52**, with lithium aluminium hydride in tetrahydrofuran, provided a mixture of **53** and **54**, in the ratio ~1.5:1, from which benzyl 2,3-*O*-isopropylidene-β-L-*glycero*-L-*gulo*-heptofuranoside (**54**) crystallised; the removal of the minor component by crystallisation was readily monitored by p.m.r. spectroscopy. Debenzylation of **54**, acid hydrolysis, and reduction afforded the known[29] (*meso*)-*glycero*-*gulo*-heptitol (**55**), which ^{13}C-n.m.r. spectroscopy also identified by virtue of its C_s-symmetry[14].



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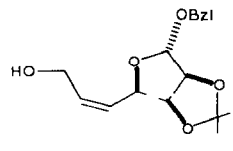

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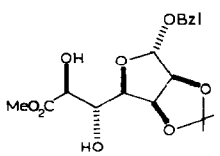

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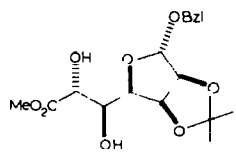

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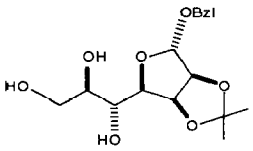

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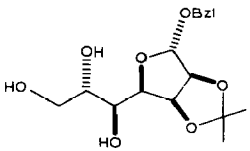
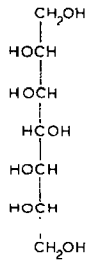


54



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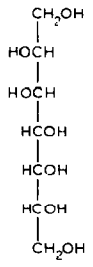

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*Removal of the glycosidic substituent by hydrogenolysis, prior to acid-catalysed deacetalation, was preferred to its removal with acid during deacetalation, since it avoided contamination of the products with the highly involatile benzyl alcohol.

An alternative, though less correct[4], name for **13 is L-*glycero*-D-*manno*-heptitol, which, in this instance, provides a much clearer indication of the relationship between **13** and **47**.

TABLE I

THE PRODUCTS OF CATALYTIC OSMYLATION OF SOME OLEFINIC SUGARS AND THE HEPTITOLS DERIVED THEREFROM

Olefinic sugar	*Products[a] (ratio)*	*Heptitol isolated[b]*
10	**11/12** (2.5:1)	D-*glycero*-D-*galacto*-heptitol (**13**)
15	**16/17** (3:1)	
20	**21/22** (5:1)	L-*glycero*-D-*galacto*-heptitol (**25**)
26	**30/29** (1:1.5)	L-*glycero*-D-*gulo*-heptitol (**35**)
27	**32/31** (7:1)	D-*glycero*-D-*gluco*-heptitol (**36**)
39	**40/41** (1:1)	
46	**47/48** (7:1)	D-*glycero*-D-*galacto*-heptitol (**13**)
49	**51/52** (1.5:1)	(*meso*)-*glycero*-*gulo*-heptitol (**55**)
50	**53/54** (6:1)	D-*glycero*-D-*manno*-heptitol (**56**)

[a]The product predicted by Kishi's empirical rule for osmylation[3] is given first. [b]This column refers to the crystalline heptitol ultimately obtained from the osmylation products.

Finally, catalytic osmylation[12] of **50** yielded a mixture (75%) of **53** and **54**, in the ratio ~6:1, which on debenzylation, acid hydrolysis, and reduction afforded D-*glycero*-D-*manno*-heptitol[26] (volemitol, **56**) in 29% overall yield. Volemitol, originally isolated from the mushroom *Lactarius volemus*[30], has also been found in certain lichens[31], algae[32], *Sedum* plants[33], the roots of various *Primulae*[34], and avocado seeds[35].

The products obtained on catalytic osmylation of the olefinic sugars examined, together with the heptitols that can be isolated in crystalline form after appropriate manipulations on them, are summarised in Table I.

With the exception of those derived from **26** and **39**, the major products are as predicted by Kishi's empirical rule for osmylation[3]; notably, the reaction is *anti* stereoselective with respect to the furanose (or pyranose) ring-oxygen atom. In most cases, the stereoselectivity is reasonably good. A possible cause for the lack of stereoselectivity displayed in the osmylation of the D-*ribo*-heptenose **39** was suggested earlier. Of the two heptenouronates examined, the osmylation of the D-*lyxo* compound **49** shows a slight bias in favour of the predicted product **51**, whereas an equally slight bias against the formation of the predicted product **30** is evinced by the D-*xylo* compound **26**. However, Kishi *et al.*[3] have pointed out that the empirical rule for osmylation should be applied with caution to conjugated carbonyl compounds, since there are exceptions. As the data in Table I show, the osmylation of olefinic sugars provides satisfactory syntheses of a number of heptitols and nicely complements existing procedures[9]. Moreover, some of the 7-carbon sugars (*e.g.*, **32**) and partially deprotected derivatives thereof (*e.g.*, **23**) are isolated in a form that should prove amenable to chemical manipulation.

EXPERIMENTAL

General methods. — T.l.c. was performed on Kieselgel G, and detection was effected with 1% sulphuric acid. I.r. spectra were recorded for Nujol mulls or liquid films with a Perkin–Elmer Model 298 spectrometer, and p.m.r. spectra were recorded for solutions in deuteriochloroform (internal Me_4Si) with a Bruker Spectrospin (90 MHz) spectrometer, unless otherwise indicated. ^{13}C-N.m.r. spectra were recorded for solutions in deuterium oxide (external Me_4Si) at 90 MHz by the Edinburgh University N.m.r. Service. Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter, using 1-dm tubes. Melting points are uncorrected. Light petroleum refers to the fraction boiling in the range 40–60°.

General procedure for catalytic osmylation[12]. — A solution of the olefinic sugar (1 equiv.), *N*-methylmorpholine *N*-oxide monohydrate (2 equiv.), and osmium tetraoxide (~0.05–0.1 equiv.) in acetone–water (8:1, 5 mL/mmol of substrate) was stirred at room temperature until t.l.c. indicated that the reaction was complete (usually within 3–6 h). The mixture was then diluted with chloroform (50 mL/mmol of substrate), washed with 5M hydrochloric acid (2 mL/mmol of substrate), and shaken vigorously for several minutes with aqueous 45% sodium metabisulphite (3 mL/mmol of substrate). After drying ($MgSO_4$) and concentration under reduced pressure, a solution of the residue in ethyl acetate (unless otherwise indicated) was passed down a column of silica gel to remove inorganic impurities, without effecting a separation of the osmylation products. After concentration, the ratio of the products was determined by integration over the resonances for the anomeric protons in the 90- or 360-MHz p.m.r. spectrum.

General procedures for debenzylation, acid hydrolysis, and reduction. — A solution of the benzylated product(s) (3 mmol) in anhydrous methanol (40 mL) containing 5% Pd/C (1.3 g) was shaken overnight at room temperature under a slight overpressure of hydrogen. After removal of the catalyst and the solvent, chromatography of the residue on silica gel in an appropriate solvent gave the debenzylated material.

A solution of this product (2.5 mmol) in trifluoroacetic acid–water (9:1, 12 mL) was kept at room temperature for 20 min, and then concentrated under reduced pressure with occasional additions of water. To a cooled (0°) and stirred solution of the resulting heptose(s) in water (30 mL) was gradually added sodium borohydride (0.4 g, 10.6 mmol), and the reaction mixture was stirred at 0° for 3 h and then overnight at room temperature. Amberlite IR-120 (H^+) resin (7.5 g) was added to remove sodium ions, and the resin was filtered off and washed thoroughly with water. The filtrate and washings were combined and concentrated under reduced pressure, and methanol was added to, and distilled from, the residue until no boric acid remained. Finally, the heptitol was crystallised (or recrystallised) from the solvent specified.

*6,7-Dideoxy-1,2:3,4-di-*O*-isopropylidene-α-*D*-galacto-hept-6-enopyranose* (**10**). — Methyltriphenylphosphonium bromide (3.08 g, 8.6 mmol) was added to a

solution of sodium amide (0.331 g, 8.5 mmol) in liquid ammonia (15 mL) under nitrogen, and, after stirring for 15 min, the ammonia was allowed to evaporate. A solution of the residue in ether (15 mL) was boiled under reflux for 30 min, and a solution of **9**[11] (2.13 g, 8.25 mmol) in ether (15 mL) was added to the boiling solution during 30 min. The mixture was then boiled for a further 15 min, cooled, and filtered, and the filtrate was washed with dilute sulphuric acid and water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 20:1 dichloromethane–acetone) gave **10** (1.33 g, 63%), b.p. ~93° (bath)/0.1 mmHg, $[\alpha]_D$ −93° (*c* 1.8, chloroform), ν_{max} 1645 cm^{-1} (C=C); lit.[10] b.p. 85–87°/0.4 mmHg, $[\alpha]_{578}$ −200.2° (chloroform). P.m.r. data: δ ~5.91 (m, 3 H, $CH{=}CH_2$), 5.58 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), and 1.52, 1.44, and 1.33 (3 s, ratios 1:1:2, 12 H, 2 CMe_2).

*Catalytic osmylation of 5,6-dideoxy-1,2-*O*-isopropylidene-α-*D-xylo-*hex-5-enofuranose* (**15**). — Catalytic osmylation of **15**[19] (0.304 g, 1.6 mmol) and chromatography of the residue on silica gel (7:3 ethyl acetate–methanol) produced a mixture (0.254 g, 71%) of 1,2-*O*-isopropylidene-α-D-glucofuranose (**16**) and the β-L-idofuranose derivative **17** in the ratio ~3:1. The identity of the major component was readily established by comparison of the p.m.r. spectrum of the mixture with that of an authentic sample of **16**[36].

(E)-*3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-*D-xylo-*hept-5-enofuranose* (**20**). — To a cooled (−10°) and stirred solution of **19**[22] (1.15 g, 3.8 mmol) in anhydrous dichloromethane (10 mL) under nitrogen was gradually added a M solution of di-isobutylaluminium hydride in dichloromethane (5.7 mL, 5.7 mmol), while the internal temperature was maintained at ~ −5°. The mixture was stirred at 0° for 2 h, the excess of the reagent was then destroyed with saturated, aqueous ammonium chloride, and dichloromethane (200 mL) was added. Insoluble material was filtered off through glass wool, and the filtrate was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave **20** (0.8 g, 69%), $[\alpha]_D$ −62° (*c* 1.1, chloroform), as a thick syrup. P.m.r. data: δ 7.29 (m, 5 H, Ph), 5.91 (m overlying d, 3 H, $J_{1,2}$ 4 Hz, CH=CH and H-1), and 1.47 and 1.29 (2 s, 6 H, CMe_2).

*1,2-*O*-Isopropylidene-β-*L-glycero-D-gluco-*heptofuranose* (**23**). — Catalytic osmylation of **20** (1.07 g, 3.5 mmol) produced a mixture (0.938 g, 79%) containing 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*glycero*-D-*gluco*-heptofuranose (**21**) [δ 5.90 (d, $J_{1,2}$ 4 Hz, H-1)] and the α-D-*glycero*-L-*ido* isomer **22** [δ 5.97 (d, $J_{1,2}$ 4 Hz, H-1)] in the ratio ~5:1.

Debenzylation of the mixture of **21** and **22** (1.2 g, 3.5 mmol) and crystallisation of the residue from methanol–ethyl acetate gave **23** (0.49 g, 55.5%), m.p. 163–165°, $[\alpha]_D$ −9° (*c* 0.5, methanol) (Found: C, 47.8; H, 7.2. $C_{10}H_{18}O_7$ calc.: C, 48.0; H, 7.25%). P.m.r. data (D_2O, external Me_4Si): δ 6.00 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), and 1.33 and 1.50 (2 s, 6 H, CMe_2).

L-glycero-D-gluco-*Heptose* (**24**). — Acid hydrolysis of **23** (0.329 g, 1.3 mmol) gave **24** (0.201 g, 73%), m.p. 193–194° (from aqueous ethanol), $[\alpha]_D$ +24 (10 min)

→ +52° (final; *c* 1.9, water); lit. (D enantiomer)[23] m.p. 196–197°, $[\alpha]_D$ −19 → −54° (water).

L-glycero-D-galacto-*Heptitol* (**25**). — Reduction of **24** (0.07 g, 0.33 mmol) and crystallisation of the residue from aqueous ethanol at ~0° gave **25** (0.055 g, 78%), m.p. 141–142° (from aqueous ethanol); lit.[13] m.p. 141°. The ^{13}C-n.m.r. spectrum of **25** was indistinguishable from that reported[14] for the D enantiomer.

Methyl (Z)-*3*-O-*benzyl-5,6-dideoxy-1,2*-O-*isopropylidene-α*-D-xylo-*hept-5-enofuranuronate* (**26**). — To a cooled (0°) and stirred solution of **18**[20] (0.86 g, 3.1 mmol) in anhydrous methanol (15 mL) was added (methoxycarbonylmethylene)triphenylphosphorane[24] (1.17 g, 3.5 mmol), and the mixture was then stirred at 0° for 4 h. Removal of the solvent under reduced pressure and chromatography of the residue on silica gel (ethyl acetate) gave **26** (0.915 g, 89%), b.p. ~170° (bath)/0.03 mmHg, $[\alpha]_D$ −165.5° (*c* 1.5, chloroform) (Found: C, 64.7; H, 6.6. $C_{18}H_{22}O_6$ calc.: C, 64.7; H, 6.6%). P.m.r. data: δ ~7.29 (m, 5 H, Ph), 6.41 (dd, 1 H, $J_{4,5}$ 6.5, $J_{5,6}$ 12 Hz, H-5), 6.00 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.91 (dd, 1 H, $J_{4,6}$ ~1 Hz, H-6), 3.63 (s, 3 H, CO_2Me), 1.51 and 1.31 (2 s, 6 H, CMe_2).

L-glycero-D-gulo-*Heptitol* (**35**). — Catalytic osmylation of **26** (4.77 g, 14.3 mmol) produced a mixture (4.93 g, 94%) containing methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*glycero*-L-*ido*-heptofuranuronate (**29**) [δ 5.98 (d, $J_{1,2}$ 4 Hz, H-1)] and the α-D-*glycero*-D-*gluco* isomer **30** [δ 5.89 (d, $J_{1,2}$ 4 Hz, H-1)] in the ratio ~1.5:1.

A solution of the foregoing mixture of **29** and **30** (4.5 g, 12.2 mmol) in anhydrous tetrahydrofuran (60 mL) containing lithium aluminium hydride (2 g, ~53 mmol) was stirred at room temperature for 3 h, and the excess of the reagent was then carefully destroyed with wet ethyl acetate. Inorganic material was filtered off and washed thoroughly with ethyl acetate, and the filtrate and washings were combined, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) furnished a mixture of 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*glycero*-L-*ido*-heptofuranose (**31**) and the α-D-*glycero*-D-*gluco* isomer **32** in the ratio ~1.5:1. Crystallisation from ethyl acetate–hexane gave **32** (1 g, 24%), which was identical (m.p. and p.m.r. spectrum) with a sample prepared by another route (see later). The mother liquor (1.5 g, 36%), substantially enriched in **31**, was used in the next stage.

Debenzylation of the compounds in the mother liquor (1 g, 2.95 mmol) and chromatography of the products on silica gel (2:1 ethyl acetate–methanol) afforded a mixture (0.55 g, 75%) containing 1,2-*O*-isopropylidene-β-L-*glycero*-L-*ido*-heptofuranose (**33**) and a trace of **34**.

Acid hydrolysis of this mixture (0.48 g, 1.9 mmol), reduction, and crystallisation of the product from methanol at ~0° gave **35** (0.154 g, 38% overall), m.p. 129–131° (from aqueous methanol); lit. (D enantiomer)[25] m.p. 128–129°. The ^{13}C-n.m.r. spectrum of **35** was indistinguishable from that reported[14] for the D enantiomer.

(Z)-*3*-O-*Benzyl-5,6-dideoxy-1,2*-O-*isopropylidene-α*-D-xylo-*hept-5-enofura-*

nose (**27**). — A solution of **26** (5 g, 14.95 mmol) in anhydrous tetrahydrofuran (60 mL) containing lithium aluminium hydride (0.8 g, ~21 mmol; added during 20 min) was stirred at room temperature for 5 h, and the excess of the reagent was then destroyed with wet ethyl acetate. Inorganic material was filtered off and washed thoroughly with ethyl acetate, and the filtrate and washings were combined, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave a syrup (3.32 g) containing **27** and an unidentified component (as judged from p.m.r. spectroscopy).

A solution of the syrup (3.32 g) in pyridine (15 mL) containing acetic anhydride (7.5 mL) was kept at room temperature for 4 h and then worked-up conventionally. Chromatography of the product on silica gel (25:1 dichloromethane–acetone) gave (*Z*)-7-*O*-acetyl-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hept-5-enofuranose (**28**; 2.83 g, 54% from **26**), $[\alpha]_D$ −79° (*c* 1.3, chloroform), as a homogeneous syrup. P.m.r. data: ~7.33 (m, 5 H, Ph), 5.87 (m overlying d, 3 H, $J_{1,2}$ 4 Hz, CH=CH and H-1), 2.00 (s, 3 H, OAc), and 1.50 and 1.31 (2 s, 6 H, CMe_2).

A small piece of sodium was added to a solution of **28** (2.28 g, 6.55 mmol) in anhydrous methanol (35 mL), and the solution was kept at room temperature for 1 h and then neutralised with Amberlite IR-120 (H^+) resin. The resin was filtered off and washed with methanol, and the filtrate and washings were combined and concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave **27** (1.96 g, 98%), $[\alpha]_D$ −78° (*c* 1.8, chloroform), as a syrup. P.m.r. data: ~7.31 (m, 5 H, Ph), 5.84 (m overlying d, 3 H, $J_{1,2}$ 4 Hz, CH=CH and H-1), and 1.47 and 1.27 (2 s, 6 H, CMe_2); the p.m.r. spectrum of **27** was readily distinguishable from that of the (*E*)-isomer **20** of established stereochemistry.

*3-O-Benzyl-1,2-O-isopropylidene-α-*D-glycero-D-gluco-*heptofuranose* (**32**). — Catalytic osmylation of **27** (1.96 g, 6.4 mmol) gave a mixture containing **32** and the β-L-*glycero*-L-*ido* isomer **31** in the ratio ~7:1. Crystallisation from ethyl acetate–hexane gave **32** (1.57 g, 72%), m.p. 124.5–125.5°, $[\alpha]_D$ −22° (*c* 1, ethyl acetate) (Found: C, 60.0; H, 7.0. $C_{17}H_{24}O_7$ calc.: C, 60.0; H, 7.1%). P.m.r. data (CD_3OD): δ ~7.38 (m, 5 H, Ph), 5.89 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.67 (s, 2 H, $PhCH_2$), and 1.44 and 1.29 (2 s, 6 H, CMe_2).

D-glycero-D-gluco-*Heptitol* (**36**). — Debenzylation of **32** (1 g, 2.9 mmol) and chromatography of the residue on silica gel (2:1 chloroform–methanol) gave 1,2-*O*-isopropylidene-α-D-*glycero*-D-*gluco*-heptofuranose (**34**; 0.63 g, 86%), $[\alpha]_D$ −14° (*c* 1.3, methanol), as a thick syrup.

Acid hydrolysis of **34** (0.63 g, 2.5 mmol), reduction of the resulting heptose, and crystallisation of the product from aqueous ethanol gave **36** (0.238 g, 45%), m.p. 128.5–129.5° (from aqueous ethanol); lit.[26] m.p. 128–129°. The ^{13}C-n.m.r. spectrum of **36** was indistinguishable from that reported[14] for an authentic sample.

(E)-*3-O-Benzyl-5,6-dideoxy-1,2-O-isopropylidene-α-*D-ribo-*hept-5-enofuranose* (**39**). — This compound, $[\alpha]_D$ +47° (*c* 1.1, chloroform), was prepared in 69% yield by reduction of (*E*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-

hept-5-enodialdo-1,4-furanose[22] (**38**) with di-isobutylaluminium hydride, as described for the preparation of **20**. P.m.r. data: δ ~7.31 (m, 5 H, Ph), ~5.71 (m overlying d, $J_{1,2}$ 4 Hz, CH=CH and H-1), 4.60 (ABq, 2 H, J_{AB} 12 Hz, PhCH_2), and 1.58 and 1.31 (2 s, 6 H, CMe_2).

Catalytic osmylation of **39** and chromatography of the product on silica gel (2:1 acetone–dichloromethane) gave an inseparable mixture (69.5%) containing equimolar proportions of 3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*glycero*-D-*allo*-heptofuranose (**40**) and the α-D-*glycero*-L-*talo* isomer **41** (δ 5.75 and 5.72, 2 d, each with $J_{1,2}$ ~3.7 Hz, H-1).

*Benzyl 2,3-*O*-isopropylidene-α-*D*-lyxo-pentodialdo-1,4-furanoside* (**44**). — A solution of benzyl 2,3-*O*-isopropylidene-α-D-mannofuranoside[27] (**43**; 4 g, 12.9 mmol) in aqueous 1,4-dioxane (1:1, 120 mL) containing sodium periodate (4 g, 18.7 mmol) was stirred for 1 h at room temperature, filtered, and concentrated under reduced pressure. The residue was extracted with chloroform, and the extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave **44** (3.46 g, 96.5%), m.p. 80–81° (from light petroleum) (Found: C, 64.5; H, 6.4. $C_{15}H_{18}O_5$ calc.: C, 64.7; H, 6.5%). P.m.r. data: δ 9.68 (d, 1 H, $J_{4,5}$ ~1 Hz, CHO), ~7.31 (m, 5 H, Ph), 5.28 (s, 1 H, H-1), 4.60 (ABq, 2 H, J_{AB} 11 Hz, CH_2Ph), and 1.41 and 1.27 (2 s, 6 H, CMe_2). The optical rotation of **44** in chloroform (stabilised with 1% of ethanol) changed with time, presumably due to the formation of a hemiacetal or a related species.

Benzyl (E)-*5,6-dideoxy-2,3-*O*-isopropylidene-α-*D*-lyxo-hept-5-enodialdo-1,4-furanoside* (**45**). — A solution of **44** (0.5 g, 1.8 mmol) in anhydrous benzene (12 mL) containing formylmethylenetriphenylphosphorane[21] (0.6 g, 2 mmol) was boiled under reflux for 2.5 h and then concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave **45** (0.52 g, 95%), m.p. 98–99° (from hexane), $[\alpha]_D$ +20.5° (*c* 1, chloroform) (Found: C, 67.0; H, 6.8. $C_{17}H_{20}O_5$ calc.: C, 67.1; H, 6.6%). P.m.r. data: δ 9.64 (d, 1 H, $J_{6,7}$ 7 Hz, CHO), 7.33 (m, 5 H, Ph), 6.84 (dd, 1 H, $J_{4,5}$ 5, $J_{5,6}$ 15 Hz, H-5), 6.38 (ddd, 1 H, $J_{4,6}$ ~1 Hz, H-6), 5.18 (s, 1 H, H-1), 4.60 (ABq, 2 H, J_{AB} 12 Hz, PhCH_2), and 1.40 and 1.29 (2 s, 6 H, CMe_2).

Benzyl (E)-*5,6-dideoxy-2,3-*O*-isopropylidene-α-*D*-lyxo-hept-5-enofuranoside* (**46**). — This compound, m.p. 45–47° (without recrystallisation), $[\alpha]_D$ +31.5° (*c* 1, chloroform), was obtained in 74% yield on reduction of **45** with di-isobutylaluminium hydride, as described for the preparation of **20** (Found: C, 65.6; H, 7.2. $C_{17}H_{22}O_5$ calc.: C, 66.6; H, 7.2%). P.m.r. data: δ ~7.31 (m, 5 H, Ph), 5.93 (m, 2 H, CH=CH), 5.07 (s, 1 H, H-1), 4.57 (ABq, 2 H, J_{AB} 12 Hz, PhCH_2), and 1.43 and 1.27 (2 s, 6 H, CMe_2).

D-glycero-D-galacto-*Heptitol* (*perseitol*, **13**). — (*a*) Catalytic osmylation of **46** (0.78 g, 2.55 mmol) yielded a mixture (0.8 g, 92%) of benzyl 2,3-*O*-isopropylidene-β-L-*glycero*-D-*manno*-heptofuranoside (**47**) (δ 5.08, s, H-1) and the α-D-*glycero*-L-*gulo* isomer **48** (δ 5.14, s, H-1) in the ratio ~7:1.

Debenzylation of the foregoing mixture, acid hydrolysis, and reduction gave perseitol (**13**, 55% overall), m.p. 186–187° (from aqueous methanol); lit.[13] m.p. 187°.

(*b*) Catalytic osmylation of **10** (1.025 g, 4 mmol) and chromatography of the product on silica gel (2:1 dichloromethane–acetone) gave a mixture (1.09 g, 94%) of 1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-heptopyranose (**11**) [δ 5.47 (d, $J_{1,2}$ 5 Hz, H-1)] and the β-L-*glycero*-D-*galacto* isomer (**12**) [δ 5.55 (d, $J_{1,2}$ 5 Hz, H-1)] in the ratio ~2.5:1.

Acid hydrolysis of the foregoing mixture and reduction of the resulting heptoses afforded perseitol (**13**, 54% overall), m.p. 186–187° (from aqueous methanol); this sample was indistinguishable by the usual criteria from that prepared in (*a*).

D-glycero-D-galacto-*Heptitol hepta-acetate* (**14**). — A solution of **13** (0.1 g, 0.47 mmol) in anhydrous pyridine (3 mL) and acetic anhydride (2.5 mL) was heated at 100° for 3 h and then poured into ice–water. The precipitate was collected and recrystallised from aqueous ethanol to give **14** (0.16 g, 67%), m.p. 118–119°, $[\alpha]_D$ −13° (*c* 1, chloroform); lit.[13] m.p. 119°, $[\alpha]_D$ −13.3° (chloroform).

Methyl [*benzyl* (Z)-*5,6-dideoxy-2,3*-O-*isopropylidene*-α-D-lyxo-*hept-5-enofuranosid*]*uronate* (**49**). — A solution of **44** (2.5 g, 9 mmol) and (methoxycarbonylmethylene)triphenylphosphorane[24] (3.3 g, 9.9 mmol) in methanol (40 mL) was stirred at 0° for 2 h and then concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave **49** (2.95 g, 98%), b.p. ~155° (bath)/0.03 mmHg, $[\alpha]_D$ −27° (*c* 1, chloroform) (Found: C, 65.0; H, 6.6. $C_{18}H_{22}O_6$ calc.: C, 64.7; H, 6.6%). P.m.r. data: δ ~7.32 (m, 5 H, Ph), 6.37 (dd, 1 H, $J_{4,5}$ 6, $J_{5,6}$ 11 Hz, H-5), 5.97 (dd, 1 H, $J_{4,6}$ ~1 Hz, H-6), 5.12 (s, 1 H, H-1), 4.58 (ABq, 2 H, J_{AB} 12 Hz, PhCH_2), 3.70 (s, 3 H, CO_2Me), and 1.43 and 1.27 (2 s, 6 H, CMe_2).

Benzyl 2,3-O-*isopropylidene*-β-L-glycero-L-gulo-*heptofuranoside* (**54**). — Catalytic osmylation of **49** (4 g, 12 mmol) produced a mixture (4.31 g, 98%) containing methyl (benzyl 2,3-*O*-isopropylidene-α-D-*glycero*-D-*manno*-heptofuranosid)uronate (**51**) (δ 5.01, s, H-1) and the β-L-*glycero*-L-*gulo* isomer (**52**) (δ 5.14, s, H-1) in the ratio ~1.5:1.

A solution of the foregoing mixture (4.31 g, 11.7 mmol) in anhydrous tetrahydrofuran (70 mL) containing lithium aluminium hydride (2.8 g, ~73.8 mmol; added during 20 min) was stirred at room temperature for 3 h and then processed as described in an earlier experiment. Chromatography on silica gel (ethyl acetate) afforded a mixture containing **54** (δ 5.16, s, H-1) and benzyl 2,3-*O*-isopropylidene-α-D-*glycero*-D-*manno*-heptofuranoside (**53**) (δ 5.11, s, H-1). Crystallisation from ethyl acetate–hexane gave **54** (1.1 g, 28%), m.p. 100–101° (after several recrystallisations from ethyl acetate–light petroleum), $[\alpha]_D$ +81° (*c* 0.7, chloroform) (Found: C, 60.0; H, 7.1. $C_{17}H_{24}O_7$ calc.: C, 60.0; H, 7.1%). P.m.r. data: δ ~7.33 (m, 5 H, Ph), 5.16 (s, 1 H, H-1), 4.62 (ABq, 2 H, J_{AB} 12 Hz, PhCH_2), and 1.45 and 1.28 (2 s, 6 H, CMe_2); p.m.r. spectroscopy also revealed the presence of a trace of **53**.

(meso)-glycero-gulo-*Heptitol* (**55**). — Debenzylation of **54**, acid hydrolysis,

and reduction yielded **55** (33% overall), m.p. 126–127°; lit.[29] m.p. 126.5–128°. The ^{13}C-n.m.r. spectrum of **55** was indistinguishable from that reported[14] for an authentic sample.

*Benzyl (Z)-5,6-dideoxy-2,3-O-isopropylidene-α-*D-lyxo*-hept-5-enofuranoside* (**50**). — To a stirred and cooled (−10°) solution of **49** (0.71 g, 2.1 mmol) in anhydrous dichloromethane (10 mL) under nitrogen was gradually added a M solution of di-isobutylaluminium hydride in dichloromethane (6.3 mL, 6.3 mmol), and the mixture was then stirred at ~0° for 3 h. After processing (as described for the preparation of **20**) and chromatography of the product on silica gel (ethyl acetate), **50** (0.5 g, 77%), $[\alpha]_D$ +38° (*c* 1.7, chloroform), was obtained as a syrup. P.m.r. data: δ ~7.29 (m, 5 H, Ph), 5.80 (m, 2 H, CH=CH), 5.06 (s, 1 H, H-1), and 1.41 and 1.25 (2 s, 6 H, CMe_2).

D-glycero-D-manno-*Heptitol* (*volemitol*, **56**). — Catalytic osmylation of **50** (0.84 g, 2.7 mmol) gave a mixture (0.7 g, 75%) of **53** (δ 5.11, s, H-1) and **54** (δ 5.16, s, H-1) in the ratio ~6:1.

Debenzylation of the foregoing mixture, acid hydrolysis, reduction, and crystallisation of the product from aqueous ethanol gave volemitol (**56**, 29% overall), m.p. 150–152° (from aqueous ethanol), $[\alpha]_D$ +3° (*c* 1, water); lit.[26] m.p. 152–153°, $[\alpha]_D$ +2.15° (water).

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