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Aldol reactions on 1-deoxy-3,4:5,6-di-*O*-isopropylidene-L-fructose as a route to higher-carbon carbohydrates

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Abstract

With a view to preparing higher-carbon carbohydrates, crossed-aldol reactions of the methyl ketone 1-deoxy-3,4:5,6-di-*O*-isopropylidene-L-fructose with a representative series of aldehydes have been investigated, and the feasibility has been demonstrated of constructing a C-11 unit containing some of the key functionality found in the carbohydrate component of the herbicidins. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Aldol reaction; Higher-carbon sugars; Herbicidins

1. Introduction

The synthesis of monosaccharides possessing more than six carbon atoms, usually referred to as higher-carbon sugars, continues to be of considerable interest. In addition to widely distributed members of this class such as the octulosonic acid KDO and the aminononulosonic acids (sialic acids), there are others which are constituents of natural products possessing interesting biological properties, such as the mildiomycins [1] and tunicamycins [2], nucleoside antibiotics containing carbohydrate moieties of 10 and 11 carbon atoms, respectively. Also of particular interest are the herbicidins [3], of which herbicidin C (**1**) is a particular example, a group of nucleoside antibiotics exhibiting herbicidal activity that were isolated from *Streptomyces saganonensis* and which contain an 11-carbon sugar portion. Because of their potential as selective herbicides, compounds of this class are interesting synthetic targets and several approaches towards their synthesis have been reported [4]. Studies into the synthesis of the carbohydrate moiety have largely centred on the C-6 plus C-5 approach, and Newcombe and co-workers [4a] have successfully constructed the 11-carbon skeleton **2** with correct stereochemistry in an elegant approach based on a C-6 carbohydrate-derived enolate as the donor, and a C-5 aldehyde as the acceptor. However, construction of the enolate precursor, a bicyclic ketone, required considerable manipulation and we were led to consider an alternative C-6 plus C-5 strategy based on the retrosynthesis shown in Scheme 1, involving a straight-chain C-6 carbohydrate-derived ketone **3** containing the functionality MeCO–R and the same aldehyde **4** as used by Newcombe and co-workers, with formation of the *C*-ring occurring at a late stage in the synthesis through an alkoxide-based ring closure. The ketone **3** of our retrosynthesis is a pro-

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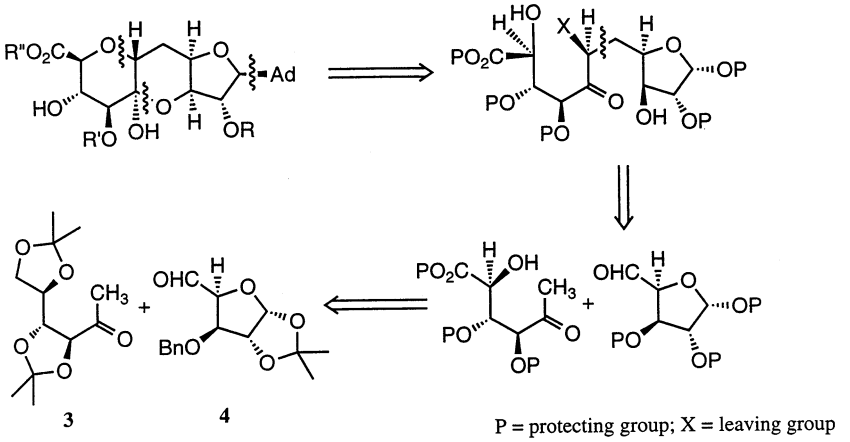


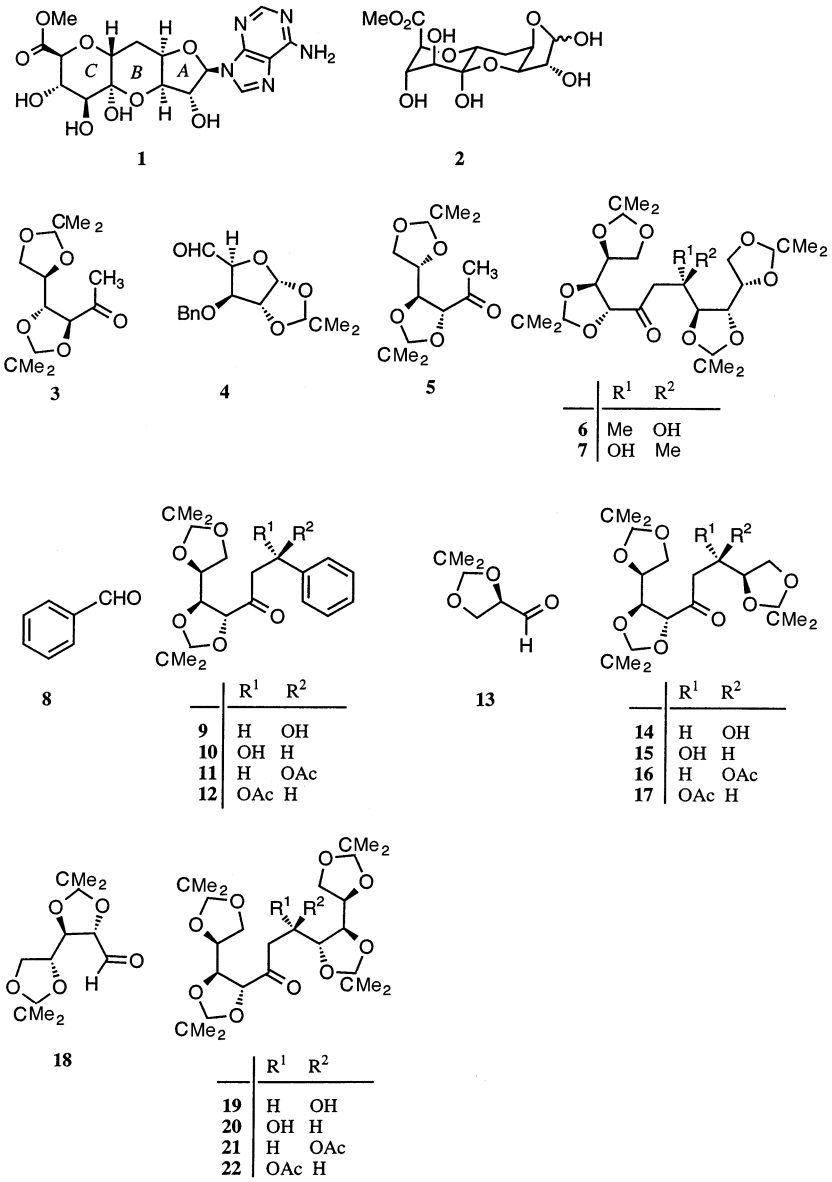
Scheme 1. A retrosynthetic analysis for the herbicidin skeleton.

tected acyclic form of 1-deoxy-D-fructose and indeed subsequent to the start of our work, Narkunan and Nagarajan [5] published their results, which employed a related approach to the synthesis of higher sugars including a Wittig–Horner reaction between a protected 1-phosphonate of 1-deoxy-D-fructose, prepared from 2,3:4,5-di-*O*-isopropylidene-D-arabinose, and aldehyde **4**. Because of the ready availability in three simple steps of the enantiomeric 1-deoxy-L-fructose in a suitable protected form **5** from commercially available L-rhamnose, we based our feasibility studies on this L-isomer and now report results of aldol reactions (Claisen–Schmidt condensations) between this ketone and a series of aldehydes including **4** (Scheme 2).

2. Results and discussion

Because in crossed-aldol reactions of the type envisaged there is the likelihood of self-addition of components, a self-aldol addition on **5** was first attempted, which was expected to give a mixture of undec-5-uloses **6** and **7**. Aqueous sodium hydroxide, potassium *t*-butoxide in tetrahydrofuran (THF) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene were unsuccessful in bringing about the desired reaction, but reaction was achieved with lithium diisopropylamide (LDA) in THF. Reaction of 1 molar equivalent of LDA with 2 molar equivalents of **5** gave one stereoisomer, based on NMR spectroscopy, of the undec-5-ulose as an oil in 30% yield with a 32% recovery of starting ketone **5**. The yield is not surprising in view of the known low concentration of dimeric product formed in aldol reactions performed with two molecules of the same ketone.

To develop suitable conditions for formation of crossed-aldol products, reaction of **5** with benzaldehyde **8** was investigated under three sets of conditions. Addition of freshly distilled benzaldehyde to the lithium enolate (from LDA) of **5** in THF solution led to complete reaction from TLC evidence, but product isolation by column chromatography gave a significant amount (21%) of **5**, presumably due to retro-aldol chemistry, a very small amount of material tentatively identified as the self-addition product (**6** or **7**), and an oil that crystallised on standing and was recrystallised to give a sharp-melting mixture of the diastereoisomeric crossed-aldol products 1-(*R*)- and 1-(*S*)-2-deoxy-4,5:6,7-di-*O*-isopropylidene-1-*C*-phenyl-L-*arabino*-hept-3-ulose (**9** and **10**, respectively, 10%) in an approximately 1:1 ratio. This allocation of overall structure was supported by the ^{1}H NMR spectrum of the product, which showed signals for protons in isopropylidene methyl groups and the phenyl groups in the ratio of 12:5 and signals for the isopropylidene methyl groups in both ^{1}H and ^{13}C NMR spectra that were attributable to the expected eight groups. In addition, the AB portions of two ABX systems could be identified centred on δ 3.08 and δ 3.09, arising in each case from the



Scheme 2.

diastereoisotopic methylene protons at C-2 coupled to the proton at the adjacent chiral centre at C-1. Analytical HPLC confirmed the presence of two isomers, though lack of a baseline separation prevented determination of an accurate isomer ratio. Use of lithium hexamethyldisilazide (LiHMDS) as the base in THF resulted in an improved yield (67%) of the combined stereoisomers **9** and **10**, again in an approximate 1:1 ratio, with only 5% recovered starting ketone **5** and no self-reaction product. In the third variation, the procedure involving the use of boron enolates [6] for aldol reactions was followed. Thus, ketone **5** in THF was added to dibutylboron triflate and triethylamine in dichloromethane followed by benzaldehyde. Chromatography afforded the combined diastereoisomers **9** and **10** in 43% yield, with an unassigned isomer ratio, estimated by ^{1}H NMR spectroscopy in the presence of a europium shift reagent, of 7:3.

The crossed-aldol reaction between ketone **5** and 2,3-*O*-isopropylidene-D-glyceraldehyde (**13**) was performed using enolates prepared from **5** with LiHMDS and with dibutylboron triflate. From reaction of the lithium enolate with a slight excess of aldehyde **13**, following chromatography, starting ketone **5** (12%), the self-addition product **6** or **7** (19%) and an oily

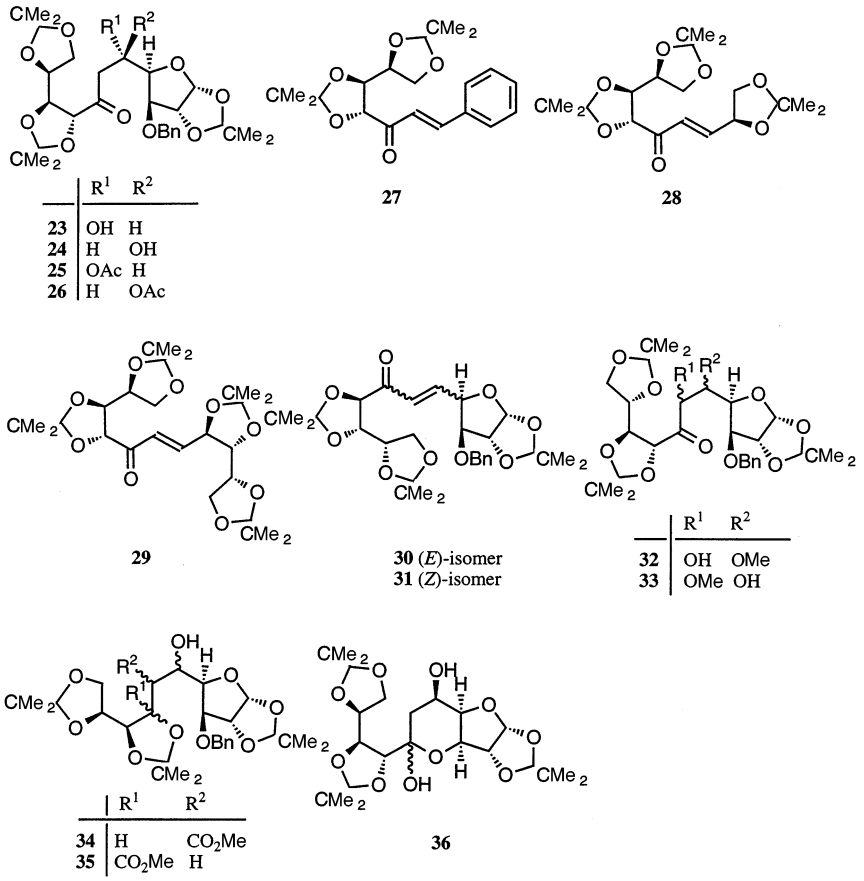
cross-reaction product as a mixture of the diasteroisomeric non-5-uloses **14** and **15** (48%) were isolated. The ^{1}H NMR spectrum of the mixture of diastereoisomers, with a consideration of relative intensities because of some signal overlap, showed 12 methyl signals and the AB parts (H-4 and H-4′) of two ABX systems (H-3, H-4 and H-4′) were discernible, centred on δ 2.90 and δ 2.91. Comparative integration of the isopropylidene methyl groups indicated the ratio of the two unassigned diastereoisomers to be approximately 1.5:1. The ^{13}C NMR spectrum of the mixture contained peaks that could readily be assigned to the 36 distinct carbon atoms expected for the mixture of isomers. Reaction of the ketone **5** and aldehyde **13** using the boron enolate procedure gave the same diastereoisomers in an approximately 1:1 ratio in 35% yield with 10% starting ketone **5** and 9% of the self-addition products **6** and **7**.

Reaction between ketone **5** and 2,3:4,5-di-*O*-isopropylidene-D-arabinose (**18**) via the lithium enolate of **5** gave, after chromatography, 12% of **5**, 13% of a mixture of **6** and **7** and the desired crossed-aldol product in 49% yield as a mixture of the diastereoisomeric undec-5-uloses **19** and **20**. Analytical HPLC indicated an unassigned isomer ratio of 1.2:1. However, separation of the two stereoisomers on an analytical HPLC column enabled an ^{1}H NMR spectrum to be obtained on each one and allowed analysis of the individual ABX systems. Performing the crossed-aldol reaction on **5** and **18** via the boron enolate procedure gave **19** and **20** in a combined yield of 80% but with a reversed isomer ratio of 1:1.6, indicating a selectivity for the isomer that had been the minor constituent in the alternative preparation.

Reaction between ketone **5** and the C-5 aldehyde 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**4**) via the lithium enolate of **5** gave the self-addition products **6** and **7** (15%) and a 25% yield of the crossed-aldol products, the undecofuranos-7-uloses **23** and **24**, in a 1:1 ratio as indicated by integration of signals for the anomeric hydrogens. Careful column chromatography of the mixture afforded a sample of one diastereoisomer. Reaction of the boron enolate of ketone **5** with aldehyde **4** gave after chromatography a mixture of the two diastereoisomers in 19% yield but also a recovery of starting ketone in 29% yield. The ratio of isomers in the condensation product was 1.5:1 from ^{1}H NMR integration measurements, and results from a subsequent reaction via the sodium enolate suggested that the predominant stereoisomer in the mixture of **23** and **24** was the 5-(*R*)-isomer **24** (Scheme 3).

Reaction of aldehyde **4** with the sodium enolate of ketone **5**, prepared in THF solution by reaction of the ketone with sodium hexamethyldisilazide (NaHMDS), gave recovered ketone **5** in 22% yield and, surprisingly, a single diastereoisomer (based on NMR spectroscopic and HPLC evidence) in 53% yield, which was tentatively identified on mechanistic argument as the L-*arabino*-α-D-*gluco*- isomer. Thus, on the reasonable assumption that a sodium ion might favour a metal ion-coordinated transition state involving the oxygen of the 3-*O*-benzyl group, the oxygen atom of the aldehydic group at C-5 in **4**, and the enolate oxygen atom, two possible intermediates *A* and *B* may be envisaged (Fig. 1), which differ in disposition of the di-*O*-isopropylidene-containing residue involving C-3 to C-6 in the parent ketone **5**. In structure *A*, this residue occupies a position lying over the furanose ring of the reactant aldehyde **4**, whereas in structure *B*, this residue is directed away from this region in space and thus may be favoured. If this is so, then the preferred stereoisomer will have the *R*-configuration at the new chiral centre and the predominant isomer will be 3-*O*-benzyl-6-deoxy-1,2:8,9:10,11-tri-*O*-isopropylidene-L-*arabino*-α-D-*gluco*-undecofuranos-7-ulose (**24**). This procedure via the sodium enolate was used in all subsequent reactions between **4** and **5**.

The route we envisaged for the transformation of **23** or **24** to the tricyclic skeleton of the herbicidins involved first, elimination of the hydroxy group at the newly formed chiral centre to give an alkene **30** or **31** with subsequent O-10 to C-6 ring closure leading to formation of ring *C* of the herbicidins. Such a closure might be achieved through alkene epoxidation followed by selective removal of the acetal group at O-10 and O-11 and then



Scheme 3.

an alkoxide-mediated attack on the epoxide involving O-10. Alternatively, in a more ambitious approach, electrophilic attack at the alkene might lead directly to formation of the six-membered ring by nucleophilic attack of O-10 at C-6 in which electrophilic character had been generated, as for example in an iodonium intermediate resulting from reaction of the alkene with *N*-iodosuccinimide. In this approach, prior cleavage of the 10,11-acetal is not required; examples are known [7] where just such functionality is involved in ring closure. Reliable methods exist for the removal of the group introduced at C-5 during ring closure, for example, hydroxy or iodo, and control of the stereochemistry at C-6 may be possible in view of the carbonyl group in the α-position (C-7). Deprotection at O-3 should then lead to spontaneous formation of ring *B* and completion of the tricylic skeleton found in herbicidins. In view of the central position of alkene **30** or **31** in the proposed synthetic sequence, elimination reactions were investigated on the mixed-aldol products **9** and **10**, **14** and **15**, **19** and **20**, **23** and **24**, and the single stereoisomer thought to be **24**, in order to develop the most favourable reaction conditions.

Treatment of the isomer mixture **9** and **10** with acetic anhydride–pyridine led to production of the (*E*)-hept-1-en-3-ulose **27** (50%) in addition to the expected acetates **11** and **12**

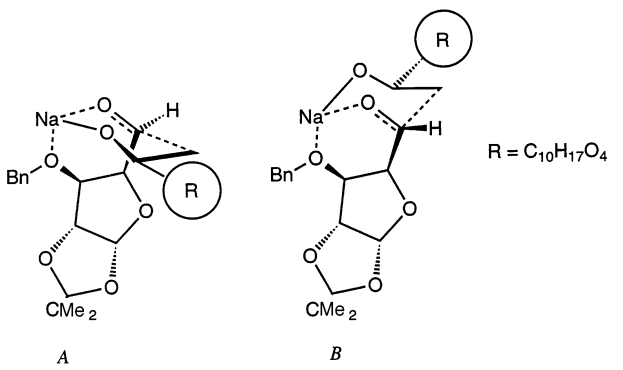


Fig. 1. Possible intermediates in the aldol reaction between sodium enolate of ketone **5** and aldehyde **4**.

(identified spectroscopically), the proportion of **27** increasing with time. The structure of the alkene was supported by elemental analysis and its NMR parameters, with the *E*-configuration indicated by the 16.2 Hz coupling constant between the alkene protons.

Acetylation of the mixed stereoisomers **14** and **15** under the same conditions gave the mixed 3-acetates **16** and **17** (6%) and an elimination product, the (*E*)-non-3-en-5-ulose (**28**) in 39% yield, the *E*-configuration being confirmed by the large coupling constant for the alkenic protons of 15.5 Hz.

Acetylation of the mixed stereoisomers **19** and **20** followed a similar path affording a mixture of the expected 7-acetates **21** and **22** (19%), as identified by their spectroscopic properties, and an elimination product, the (*E*)-undec-6-en-5-ulose **29** (13%) ($J_{6,7}$ 15.5 Hz), as well as a considerable amount of recovered starting materials. An elimination reaction on the mixture of **19** and **20** using *p*-tolylsulphonyl chloride in pyridine gave the enone **29** in an improved yield of 27% and recovered starting materials in 29% yield.

Dehydration of the mixed aldol adducts **23** and **24** was investigated under a variety of conditions in view of the likely importance of the elimination product for further transformations. Reaction of the mixed alcohols with acetic anhydride–pyridine at room temperature gave after 6 days and chromatographic separation the starting alcohols (16%), the diastereoisomeric acetates **25** and **26** (10%) as identified by NMR spectroscopy, and the (*E*)-undec-5-enofuranos-7-ulose (**30**) ($J_{5,6}$ 15.8 Hz) in 46% yield. TLC analysis of the progress of the reaction indicated that the alkene **30** was formed via the acetates, verification being obtained when a sample of the mixed acetates was converted to the alkene **30** when subject to the original acetylation conditions. The yield of **30** was raised to 61% by conducting the acetylation at 45 °C for 8 h, and to 72% when 4-dimethylaminopyridine (DMAP) was present in the acetylation medium with reaction at room temperature for 70 h, but in the latter case the chromatographically recovered alkene was found to contain approximately 5% of the *Z*-isomer **31** ($J_{5,6}$ 11.9 Hz).

Our synthetic strategy involving elaboration of **30** or **31** to form the *C*-ring of the herbicidins via alkene epoxidation was thwarted by an alternative sequence of reactions undergone by the epoxide. Thus, treatment of the enone **30** with alkaline hydrogen peroxide reagents in methanol gave a mixture of five products, as indicated by methoxy resonances in the ^{1}H NMR spectrum, and these products were only partially separable by chromatography. NMR spectroscopic data suggested that the products arose from the required epoxide (or epoxides), four being stereoisomers (see **32** and **33**) resulting from methoxide cleavage of epoxides (MeO resonances at δ 3.22, 3.24, 3.27, and 3.28) and one being a methyl ester (see **34** and **35**) (MeO resonance at δ 3.71) resulting from a Favorskii rearrangement of the epoxide. Examples of the latter type of rearrangement in such systems have been documented previously [8]. Use of a milder base (K_2CO_3), afforded the methoxy derivatives and no rearranged product. Reaction in THF with H_2O_2–$NaHCO_3$, a reportedly mild procedure for the epoxidation of enones [9], gave a product that was tentatively identified by ^{1}H NMR and IR spectroscopy was tentatively as a carboxylic acid (rather than a methyl ester), resulting presumably from a Favorskii rearrangement of an epoxide.

An attempt to bring about ring closure on **30** by an iodonium-ion-mediated cyclisation was not successful; only starting material was recovered on prolonged treatment of the alkene with *N*-iodosuccinimide in dichloromethane or with molecular iodine in THF.

In view of the difficulties encountered in forming ring *C* at an early stage, prior formation of ring *B* was investigated. Elaboration of a fused furano–pyrano ring system from **23** or **24** to mimic the *A*/*B* fused ring system found in the herbicidins requires removal of the benzyl protecting group, which should lead to spontaneous hemiacetal formation and thus the pyrano ring *B*. Hydrogenolysis of the benzyl group in **24** was readily achieved using palladium black as catalyst in acidic methanol to give **36** as a crystalline solid in high yield. No carbonyl absorption was apparent in the IR spectrum of this product, in contrast to the

absorption at 1720 cm^{-1} found in the starting material. A signal in the ^{13}C NMR spectrum at 96.2 ppm was assigned to the carbon at the newly created hemiacetal centre (C-7), the reaction evidently affording a single isomer at this centre. Thus, the number of peaks in the ^{1}H and ^{13}C NMR spectra was consistent with only one isomer. The axial orientation of the hydroxy group at C-7 and therefore also the equatorial orientation of the C-8 to C-11 side chain might reasonably be expected to be more favoured rather than the reverse arrangement.

Although the eventual aim of this project has still to be achieved, current results indicate that our approach leads to facile formation of an undecose in a usefully functionalised form and that closure to give ring *B* is not problematical. The crucial step of ring *C* formation is being pursued by reaction of enone **30** with alternative more powerful electrophiles and by a strategy involving cyclisation of the 10,11-diol formed by the partial deprotection of **30**.

3. Experimental

General methods.—^{1}H NMR spectra were recorded on a Jeol EX90 FT spectrometer, a Jeol EX270 FT spectrometer or a Varian Gemini 2000 FT spectrometer in $CDCl_3$ with Me_4Si as internal standard. Where appropriate, signal assignments were deduced by DEPT, COSY and HETCOR NMR experiments. In ^{1}H NMR spectra of products containing two diastereoisomers, protons at related centres in the isomers that give rise to resolved and assignable signals are distinguished by subscripts 'a' and 'b', otherwise no distinction is made. Optical rotations were measured at 20 °C with a Perkin–Elmer 141 polarimeter. High-resolution mass spectra were recorded by the EPSRC Mass Spectrometry Service at the University College of Swansea. Low-resolution EI mass spectra and elemental analyses were performed by A.W.R. Saunders at the University of East Anglia. HPLC was performed on Pye Unicam apparatus using a PU 4015 pump connected to a PU 4025 UV detector operating at 300 nm unless otherwise stated. HPLC grade solvents were used on a Spherisorb S5W normal phase column. Thin-layer chromatography (TLC) was performed on pre-coated plates of silica gel with fluorescent indicator (Machery–Nagel SIL G UV_{254}. Detection was either by viewing under UV light (254 nm), or by spraying with a 10% H_2SO_4, 1.5% molybdic acid, 1% ceric sulfate spray followed by heating to 150 °C. Column chromatography was performed on Matrex Silica 60 (70–200 μm mesh, Fisons) or Kieselgel 60 (70–230 μm mesh, E. Merck). Solvents for reactions and column chromatography were SLR grade or better and were dried appropriately when required anhydrous. Thus, THF was dried by storage over and distillation from sodium wire; CH_2Cl_2, pyridine and Et_3N were obtained anhydrous by distilling from CaH_2 and storage over 4 Å molecular sieves; MeOH was dried by distillation from magnesium methoxide (formed by reaction with activated magnesium) and stored over powdered 3 Å molecular sieves. Light petroleum refers to the fraction with a boiling range of 40–60 °C, unless stated otherwise. When mixed solvents were used, the ratios given are v/v except if otherwise stated. Solvent A is 6:1 light petroleum–EtOAc, and solvent B is 4:1 light petroleum–EtOAc. Organic solutions were dried over anhydrous Na_2SO_4. L-Rhamnitol was prepared from L-rhamnose by adapting the procedure described by Wolfrom and Thompson for the preparation of galactitol from D-galactose [10] and was then converted into 1,2:3,4-di-*O*-isopropylidene-L-rhamnitol as described by Bukhari and co-workers [11]. 2,3-*O*-Isopropylidene-D-glyceraldehyde (**13**) was prepared from 1,2:5,6-di-*O*-isopropylidene-D-mannitol [12,13] by periodate cleavage according to the procedure of Jackson [14]. 2,3:4,5-Di-*O*-isopropylidene-D-arabinose (**18**) was synthesised by the method of Inch and co-workers [15] from 1,2:3,4-di-*O*-isopropylidene-D-mannitol [16]. 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**4**) was prepared either by oxidative cleavage of the 5,6-diol in 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose [17], as described by Anderson and Fraser-Reid [18], or by the method of Lemieux and Howard [19], directly from 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose [20].

1-Deoxy-3,4:5,6-di-O-*isopropylidene*-L-*fructose* (**5**).—To a stirred soln of oxalyl chloride (2 mL, 20.8 mmol) in anhyd CH_2Cl_2 (40 mL) at −50 °C under N_2, was added an anhyd soln of Me_2SO (3.5 mL, 48.9 mmol) in CH_2Cl_2 (10 mL) and the solution was then cooled to −78 °C. A soln of 1,2:3,4-di-*O*-isopropylidene-L-rhamnitol (4.88 g, 20.0 mmol) in anhyd CH_2Cl_2 (20 mL) was then added dropwise over 10 min. After 15 min, Et_3N (14.0 mL, 0.10 mol) was added and after a further 5 min, the stirred reaction mixture was allowed to warm to room temperature (rt) when water (100 mL) was added. The organic and aqueous layers were separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic layers were washed consecutively with satd aq NaCl (200 mL), 0.1 M HCl (200 mL), aq Na_2CO_3 (5% w/v; 200 mL) and water (50 mL). The dried organic solution was concentrated to give a pale yellow oil (5.0 g). Column chromatography (solvent A) gave ketone **5** as a mobile liquid (4.17 g, 85%); $[\alpha]_D$ −0.10° (*c* 1.2, $CHCl_3$), lit. ~0° (*c* 4.2, $CHCl_3$) [15] and lit. 0.0° (*c* 1.5, $CHCl_3$) [21]; IR (film): *v* 1730 (C=O), 1370 and 1385 ($C(CH_3)_2$) , no absorption near 3300 cm^{-1} (OH); ^1H NMR (90 MHz): δ 1.34, 1.36, 1.40, 1.45 (4 × s, 4 × 3 H, 2 × $C(CH_3)_2$), 2.29 (s, 3 H, H_3C-1), 3.92–4.38 (complex, 5 H, H-3, 4, 5, 6, 6′); ^{13}C NMR (67.9 MHz): δ 24.9 (C-1), 26.0, 26.3, 26.5, 26.9 (2 × $C(CH_3)_2$), 66.4 (C-6), 76.3, 77.9 (C-4, 5), 83.1 (C-3), 109.7, 111.1 (2 × $C(CH_3)_2$), 207.2 (C=O). Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.0; H, 8.25. Found: C, 59.2; H, 8.4.

General procedures for aldol reactions on **5**.—(a) Method 1: using LiHMDS. A solution of **5** (1 molar equivalent) in anhyd THF was added to LiHMDS (1.0 M solution in THF; 1.3 molar equiv) at −78 °C under N_2, and the reaction mixture was stirred at −78 °C for 20 min. Freshly distilled aldehyde (1.1–1.3 molar equiv) was added either neat, in one portion, or as a concd soln in anhyd THF. After 20 min at −78 °C, the mixture was allowed to warm to rt, satd aq $NaHCO_3$ was added, and the solution was extracted repeatedly with Et_2O. The combined extracts were dried, concentrated, and the resulting oil was purified by column chromatography (light petroleum–EtOAc mixture).

(b) Method 2: using dibutylboron triflate/Et_3N. The procedure for the crossed-aldol reaction via the boron enolate was essentially that described by Paterson and co-workers [6] but using dibutylboron triflate in place of dicyclohexylboron chloride. A soln of **5** (1 molar equiv) in anhyd THF was added, dropwise, to a stirred soln of dibutylboron triflate (1.0 M soln in CH_2Cl_2; 1.5 molar equiv) and freshly distilled Et_3N (8–10 molar equiv) in anhyd THF (3 mL/mmol of boron reagent) at −78 °C under N_2. The soln was allowed to warm to 0 °C, stirred at this temperature for 45 min and then re-cooled to −78 °C. Freshly distilled aldehyde (1.2–3 molar equiv) was added either neat or as a concd soln in anhydrous THF. After a further 30 min at −78 °C, the mixture was stored at −30 °C for 14 h then brought to rt and partitioned between equal volumes (10 mL/mmol of **5**) of pH 7 buffer solution and Et_2O. The aq layer was extracted further with Et_2O and the combined organic layers were concd to give a crude product which was dissolved in equal volumes (6 mL/mmol of **5**) of MeOH and pH 7 buffer soln. To this soln was cautiously added 30% aq H_2O_2 (3 mL/mmol of **5**). The resulting mixture was stirred until TLC (light petroleum–EtOAc mixture) indicated the absence of the boron-coordinated products, which remained on or near the baseline on TLC in such solvent systems employed; typically between 1 and 3 h were required. Extraction of the solution with CH_2Cl_2 (3 × 8 mL for 1 mmol of **5**) and concentration of the dried organic soln gave crude material that was purified by column chromatography (light petroleum–EtOAc mixture).

Where alternative procedures to (a) or (b) have been used, the methods are described in full.

Self-addition of ketone **5** *to give 6-deoxy-1,2:3,4:8,9:10,11-tetra*-O-*isopropylidene*-7-C-*methyl*-L-arabino-L-manno-*undec*-5-*ulose* (**6**) *and 6-deoxy-1,2:3,4:8,9:10,11-tetra*-O-*isopropylidene*-7-C-*methyl*-L-arabino-D-gulo-*undec*-5-*ulose* (**7**).—To a stirred soln of diisopropylamine (0.17 mL, 0.12 g, 1.2 mmol) in anhyd THF (5 mL) at 0 °C under nitrogen was added dropwise *n*-butyllithium (2.5 M soln in hexane; 0.5 mL, 1.25 mmol). After 10

min at 0 °C, the soln was cooled to −78 °C and a soln of **5** (0.50 g, 2.05 mmol) in anhyd THF (5 mL) was added dropwise in two approximately equal portions, at such a rate that the temperature remained below −65 °C. After a further 30 min stirring at −78 °C, satd aq $NaHCO_3$ (10 mL) was added and the mixture was allowed to warm to rt. Extraction of the aq soln with Et_2O (3 × 15 mL) and concentration of the combined, dried organic solutions gave a pale yellow oil, which was shown by TLC (solvent B) to contain starting material (R_f 0.46) and another component (R_f 0.3). Column chromatography (solvent B) yielded **5** (0.16 g, 32%) and the less mobile component which, on spectroscopic evidence, was a single diastereoisomer, the aldol product **6** or **7** as an oil (0.15 g, 30%); IR (film): *v* 3480 (OH), 1720 (C=O), 1380 and 1370 cm^{-1} ($C(CH_3)_2$); ^1H NMR (270 MHz): δ 1.32, 1.33, 1.35 (× 2), 1.37, 1.39, 1.43 (× 2), 1.45 (9 × s, 9 × 3 H, 4 × $C(CH_3)_2$ and H_3C-7), 1.92 (br s, 1 H, OH), 2.97 (s, 2 H, H-6, 6′), 3.60–4.42 (complex, 10 H, H-1, 1′, 2, 3, 4, 8, 9, 10, 11, 11′); ^{13}C NMR (67.9 MHz): δ 23.2 (H_3C-7), 25.2, 25.3, 26.3, 26.4, 26.6, 27.1, 27.2 (× 2) (4 × $C(CH_3)_2$), 47.0 (C-6), 66.7, 67.5 (C-1, 11), 71.4 (C-7), 76.6, 76.8, 77.6, 77.9 (C-2, 3, 9, 10), 83.7, 84.2 (C-4, 8), 109.3, 109.9, 110.0, 111.4 (4 × $C(CH_3)_2$), 208.9 (C=O); EIMS: *m*/*z* 473 (0.7, M − 15). Anal. Calcd for $C_{24}H_{40}O_{10}$: C, 59.0; H, 8.25. Found: C, 58.7; H, 8.2.

Reaction of ketone **5** *with benzaldehyde. Preparation of 1-(*R*)- and 1-(*S*)-2-deoxy-4,5:6,7-di-*O*-isopropylidene-1-*C*-phenyl-*L*-arabino-hept-3-ulose* (**9**) *and* (**10**), *respectively*.—(a) Using LDA: to a stirred soln of diisopropylamine (0.6 mL, 0.43 g, 4.3 mmol) in anhyd THF (10 mL) at −78 °C under N_2, was added *n*-butyllithium (2.5 M soln in hexane; 1.8 mL, 4.5 mmol). The mixture was stirred for 15 min and then a soln of **5** (1.00 g, 4.09 mmol) in anhyd THF (5 mL) was added dropwise, over 10 min. After 15 min, freshly distilled benzaldehyde (0.42 mL, 4.09 mmol) was added neat in one portion. The mixture was stirred at −78 °C for 30 min and then allowed to warm to rt when TLC (solvent A) confirmed the disappearance of **5** (R_f 0.34) and formation of two components (R_f 0.20 and 0.11). The reaction was quenched with water (25 mL), extracted with CH_2Cl_2 (3 × 25 mL) and the combined organic extracts were dried and concentrated to give an oil (1.37 g), which on column chromatography (solvent A) gave three components. The first, ketone **5** (0.21 g, 21%) presumably arose by a retro-aldol reaction on the silica column. The second material (R_f 0.20; 4 mg) was tentatively identified as a mixture of **6** and **7**. The least mobile component (R_f 0.11; 0.28 g), isolated as an oil, crystallised on storage under high vacuum and was recrystallised from light petroleum–EtOAc to give a product shown to be an approximately equimolar mixture of the two diastereoisomeric crossed-aldol products, **9** and **10** (0.14 g, 10%), mp 62–63 °C; IR (Nujol): *v* 3480 (OH), 1720 (C=O), 1380 and 1370 cm^{-1} ($C(CH_3)_2$); ^1H NMR (270 MHz): δ 1.33, 1.34 (× 2), 1.37, 1.40, 1.42, 1.44 (× 2) (8 × s, 8 × 3 H, 4 × $C(CH_3)_2$), 3.00 (dd, 1 H, $J_{1a,2a}$ 3.3, $J_{2a,2'a}$ 17.8 Hz, H-2a), 3.03 (dd, 1 H, $J_{1b,2b}$ 4.0, $J_{2b,2'b}$ 18.5 Hz, H-2b), 3.12 (dd, 1 H, $J_{1b,2'b}$ 8.6 Hz, H-2′b), 3.13 (br s, 2 × 1 H, 2 × OH), 3.17 (dd, 1 H, $J_{1a,2'a}$ 9.2, H-2′a), 3.96 (complex, 2 × 1 H, H-7), 4.08–4.22 (complex, 2 × 3 H, H-5, 6, 7′), 4.37 and 4.39 (2 × d, 2 × 1 H, $J_{4a,5a}$ 2.6, $J_{4b,5b}$ 3.0 Hz, H-4a and H-4b), 5.20 (complex, 2 × 1 H, H-1), 7.26–7.37 (complex, 2 × 5 H, 2 × C_6H_5); ^{13}C NMR (67.9 MHz): δ 25.1 (× 2), 26.1, 26.2, 26.5 (× 2) and 27.0 (× 2) (4 × $C(CH_3)_2$), 48.1 (2 × C-2), 66.7, 66.8 (2 × C-7), 69.6, 69.8, (2 × C-6), 76.4, 76.5 (2 × C-1), 78.1, 78.2, 83, 83.2 (2 × C-4, 5), 110.0 (× 2), 111.5 and 111.6 (4 × $C(CH_3)_2$), 125.6, 125.7, 127.7, 127.8, 128.6, 142.8 (C-aromatic), 209.2 and 209.5 (2 × C=O). Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.1; H, 7.5. Found: C, 65.1; H, 7.4.

Analytical HPLC (detection at 254 nm) indicated the presence of two isomers, but a baseline separation was not obtained in a variety of solvent systems. However, ^1H and ^{13}C NMR spectroscopy showed that the ratio of the isomers was approximately 1:1.

(b) Using LiHMDS: reaction of ketone **5** (0.75 g, 3.07 mmol) with benzaldehyde (0.35 mL, 3.43 mmol) under Method 1 conditions gave, after column chromatography (solvent B), starting ketone **5** (0.04 g, 5%) followed by the mixed crossed-aldol products **9** and **10**

(0.72 g, 67%). Recrystallisation of the mixture of two diastereoisomers from light petroleum–EtOAc gave material with mp 60–64 °C. The product was identical by IR, ^{1}H and ^{13}C NMR spectroscopy to the sample of the crossed-aldol product, prepared as in (a). ^{1}H NMR spectroscopy indicated the isomer ratio as approximately 1:1.

(c) Using dibutylboron triflate–Et_3N: reaction of ketone **5** (0.15 g, 0.61 mmol) with benzaldehyde (0.20 mL, 1.79 mmol) under Method 2 conditions gave, after column chromatography (solvent B), the crossed-aldol product as a pale yellow oil (0.12 g), which solidified on storage. Recrystallisation from light petroleum–EtOAc, gave a mixture of **9** and **10** (92 mg, 43%), mp 57–61 °C. The isomeric ratio (unassigned) in this preparation as determined by ^{1}H NMR spectroscopy in the presence of Eu(fod)$_3$ was 7:3. No self-condensation aldol products **6** or **7**, or ketone **5** were obtained, although unreacted benzaldehyde was isolated (0.11 g, 58% recovery).

Reaction of ketone **5** *with 2,3-*O*-isopropylidene-*D*-glyceraldehyde* (**13**). *Preparation of 4-deoxy-1,2:6,7:8,9-tri-*O*-isopropylidene-*L*-glycero-*L*-galacto-non-5-ulose* (**14**) *and 4-deoxy-1,2:6,7:8,9-tri-*O*-isopropylidene-*L*-glycero-*L*-gulo-non-5-ulose* (**15**).—(a) Using LiHMDS: reaction of ketone **5** (2.0 g, 8.19 mmol) and aldehyde **13** (1.17 g, 9.0 mmol) under Method 1 conditions gave, after column chromatography (solvent B), starting ketone **5** (0.24 g, 12%), a product shown by comparison with a known sample (TLC, and IR and NMR spectroscopy) to be **6** and/or **7** (0.38 g, 19%) and finally, as an oil, a mixture of the title compounds **14** and **15** (1.48 g, 48%); IR (film): ν 3470 (OH), 1720 (C=O), 1380 and 1370 cm^{-1} (C(CH$_3$)$_2$); ^{1}H NMR (270 MHz): δ 1.33 ($\times$ 2), 1.35 ($\times$ 4), 1.38, 1.39, 1.41, 1.42, 1.43 and 1.46 (12 $\times$ s, 12 $\times$ 3 H, 6 $\times$ C(CH$_3$)$_2$), 2.74 (dd, 1 H, $J_{3a,4a}$ 2.3, $J_{4a,4'a}$ 16.2 Hz, H-4a), 2.82 (dd, 1 H, $J_{3b,4b}$ 8.3, $J_{4b,4'b}$ 18.2 Hz, H-4b), 2.99 (dd, 1 H, $J_{3b,4'b}$ 9.2 Hz, H-4′b), 3.00 (br d, 21 H, $J_{3,OH}$ 3.6 Hz, 2 $\times$ OH), 3.05 (dd, 1 H, $J_{3a,4'a}$ 2.6 Hz, H-4′a), 3.82–4.23 (complex, 2 $\times$ 8 H, H-1, 1′, 2, 3, 7, 8, 9, 9′), 4.34–4.42 (complex, 2 $\times$ 1 H, H-6); ^{13}C NMR (67.9 MHz): δ 25.1 ($\times$ 4), 26.2, 26.3, 26.4, 26.5 ($\times$ 2), 26.6 and 27.0 ($\times$ 2) (6 $\times$ C(*C*H$_3$)$_2$), 42.5, 42.9 (2 $\times$ C-4), 65.5, 66.7 ($\times$ 3), 67.6, 68.7 (2 $\times$ C-1, 3, 9), 76.4, 76.5, 77.6, 77.7, 78.0, 78.3 (2 $\times$ C-2, 7, 8), 83.1, 83.3 (2 $\times$ C-6), 109.5, 109.6, 110.0 ($\times$ 2), 111.5 and 111.6 (6 $\times$ *C*(CH$_3$)$_2$), 208.5, 209.8 (2 $\times$ C=O); EIMS: m/z 374 (0.8, M$^+$), 359 (7.6, M − 15). Anal. Calcd for $C_{18}H_{30}O_8$: C, 57.7; H, 8.1. Found: C, 57.5; H, 8.1.

By comparison of the integration values of certain peaks in the ^{1}H NMR spectrum in the presence of Eu(fod)$_3$, the ratio of isomers (unassigned) was estimated as approximately 1.5:1.

(b) Using dibutylboron triflate–Et_3N: reaction of ketone **5** (0.61 g, 2.50 mmol) with aldehyde **13** (0.36 g, 2.77 mmol) under Method 2 conditions gave, after column chromatography (solvent B), **5** (62 mg, 10% recovery), a small amount of the self-aldol product **6** and/or **7** (54 mg, 9%) and, as an oil, a mixture of the crossed-aldol reaction products **14** and **15** (0.33 g, 35%). Spectroscopic data (IR, and ^{1}H and ^{13}C NMR) on this material agreed with that for the mixture of **14** and **15** prepared in (a), but differing peak intensities reflected a different ratio of diastereoisomers. Analytical HPLC in hexane-2-propanol (24:1) gave two peaks at R_t 11.62 min and R_t 13.19 min in a ratio of 13:12.

Reaction between ketone **5** *and 2,3:4,5-di-*O*-isopropylidene-*D*-arabinose* (**18**). *Preparation of 6-deoxy-1,2:3,4:8,9:10,11-tetra-*O*-isopropylidene-*D*-arabino-*L*-manno-undec-5-ulose* (**19**) *and 6-deoxy-1,2:3,4:8,9:10,11-tetra-*O*-isopropylidene-*D*-arabino-*D*-gulo-undec-5-ulose* (**20**).—(a) Using LiHMDS: reaction of ketone **5** (0.40 g, 1.64 mmol) with aldehyde **18** (0.41 g, 1.78 mmol) under Method 1 conditions gave, after column chromatography (solvent B), ketone **5** (48 mg, 12% recovery), the self-aldol product **6** and/or **7** (52 mg, 13%) and, as a colourless oil, a mixture of the title compounds **19** and **20** (0.38 g, 49%); IR (film): ν 3470 (OH), 1720 (C=O), 1385 and 1375 cm^{-1} (C(CH$_3$)$_2$); ^{1}H NMR (270 MHz): δ 1.34–1.48 (complex, 48 H, 8 $\times$ C(CH$_3$)$_2$), 2.88 (dd, 1 H, $J_{6a,6'a}$ 17.5, $J_{6a,7a}$ 8.9 Hz, H-6a), 2.92 (br s, 2 $\times$ 1 H, 2 $\times$ OH), 2.97 (2 $\times$ d, 2 H, $J_{6b,7b}$ 6.3, $J_{6'b,7b}$ 4.6 Hz, H-6b and H-6′b), 3.06 (dd, 1 H, $J_{6'a,7a}$ 3.6 Hz, H-6′a), 3.60–4.41 (complex, 2 $\times$ 11 H, H-1, 1′, 2, 3, 4, 7, 8, 9, 10, 11, 11′); ^{13}C NMR (67.9 MHz): δ 25.1–27.1 (8 $\times$

$C(CH_3)_2$), 42.9, 43.6 (2 × C-6), 66.4, 66.6, 67.7, 67.8 (2 × C-1, 11), 68.9 (2 × C-7), 76.4–83.4 (2 × C-2, 3, 4, 8, 9, 10), 109.5, 109.6, 109.7, 109.8, 109.9, 110.2, 111.4, 111.5 (8 × $C(CH_3)_2$), 208.5, 208.6 (2 × C=O); EIMS: m/z 474 (0.3, M^+), 459 (2.7, M − 15). Anal. Calcd for $C_{23}H_{38}O_{10}$: C, 58.2; H, 8.1. Found: C, 57.9; H, 8.1.

Analytical HPLC (49:1 hexane–2-propanol) showed two isomers (R_t 12.5 min and R_t 13.6 min) in a ratio of 1.2:1, respectively. Preparative HPLC was used to isolate pure samples of both stereoisomers in order to obtain an ^{1}H NMR spectrum of each one.

Data for isomer with R_t 12.5 min; ^{1}H NMR (270 MHz): δ 1.35, 1.36, 1.38, 1.39, 1.41, 1.43 (× 2) and 1.46 (8 × s, 8 × 3 H, 4 × $C(CH_3)_2$), 2.82 (br d, 1 H, $J_{7,OH}$ 6.3 Hz, OH), 2.88 (dd, 1 H, $J_{6,6'}$ 17.5, $J_{6,7}$ 8.9 Hz, H-6), 3.06 (dd, 1 H, $J_{6',7}$ 3.6 Hz, H-6′), 3.89–4.58 (complex, 10 H, H-1, 1′, 2, 3, 7, 8, 9, 10, 11, 11′), 4.41 (d, 1 H, $J_{3,4}$ 3.3 Hz, H-4).

Data for isomer with R_t 13.6 min; ^{1}H NMR (270 MHz): δ 1.36 (× 4), 1.37, 1.44 (× 2), 1.46 (8 × s, 8 × 3 H, 4 × $C(CH_3)_2$), 2.97 (2 × d, 2 H, $J_{6,7}$ 6.3, $J_{6',7}$ 4.6 Hz, H-6, 6′), 3.55 (br d, 1 H, $J_{7,OH}$ 1.6 Hz, OH), 3.73–4.30 (complex, 10 H, H-1, 1′, 2, 3, 7, 8, 9, 10, 11, 11′), 4.41 (d, 1 H, $J_{3,4}$ 5.6 Hz, H-4).

(b) Using dibutylboron triflate–Et_3N: reaction of ketone **5** (1.00 g, 4.09 mmol) with aldehyde **18** (1.04 g, 4.52 mmol) under Method 2 conditions gave, after column chromatography (solvent B), only the crossed-aldol reaction products **19** and **20** (1.57 g, 80%). The spectroscopic data for a mixed-isomer sample agreed with those for the previous sample, differing only because of its different diastereoisomeric ratio.

Analytical HPLC (49:1 hexane-2-propanol) showed two isomers (R_t 12.7 min and R_t 13.7 min) in a ratio of 1:1.6, respectively.

Reaction of ketone **5** *with 3-*O*-benzyl-1,2-*O*-isopropylidene-α-*D*-xylo-pentodialdo-1,4-furanose* (**4**). *Preparation of 3-*O*-benzyl-6-deoxy-1,2:8,9:10,11-tri-*O*-isopropylidene-*L*-arabino-β-*L*-ido-undecofuranos-7-ulose* (**23**) *and 3-*O*-benzyl-6-deoxy-1,2:8,9:10,11-tri-*O*-isopropylidene-*L*-arabino-α-*D*-gluco-undecofuranos-7-ulose* (**24**).—(a) Using LiHMDS: reaction of ketone **5** (0.42 g, 1.72 mmol) with aldehyde **4** (0.50 g, 1.80 mmol) under Method 1 conditions gave, after column chromatography (solvent B), first the self-aldol reaction product **6** and/or **7** (60 mg, 15%) and secondly, as an oil, a mixture of the title compounds **23** and **24** (0.20 g, 25%). By re-chromatography of the mixture of crossed-aldol isomers **23** and **24**, (solvent A), the faster running isomer[1] could be obtained pure (61 mg, 7%); IR (film): ν 3470 (OH), 1720 (C=O), 1610 (weak, C_6H_5), 1380 and 1370 cm^{-1} ($C(CH_3)_2$); ^{1}H NMR (270 MHz): δ 1.31, 1.33, 1.34, 1.42, 1.44 and 1.48 (6 × s, 6 × 3 H, 3 × $C(CH_3)_2$), 2.89 (br s, 1 H, OH), 2.93 (dd, 1 H, $J_{5,6}$ 8.9, $J_{6,6'}$ 18.1 Hz, H-6), 3.12 (dd, 1 H, $J_{5,6'}$ 2.6 Hz, H-6′), 3.94–4.73 (complex, 9 H, H-2, 3, 4, 5, 8, 9, 10, 11, 11′), 4.59 (d, 1 H, J_{AB} 11.6 Hz, $C_6H_5CH_AH_B$), 4.71 (d, 1 H, $C_6H_5CH_AH_B$), 5.89 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 7.16–7.36 (complex, 5 H, C_6H_5); ^{13}C NMR (67.9 MHz): δ 25.2, 26.2, 26.3, 26.5, 26.8 and 27.0 (3 × $C(CH_3)_2$), 43.5 (C-6), 64.9 (C-11), 72.4 ($C_6H_5CH_2$), 66.7, 76.5, 78.0, 81.3, 81.9, 82.5, 83.3 (C-2, 3, 4, 5, 8, 9, 10), 105.1 (C-1), 109.9, 111.5, 111.8 (3 × $C(CH_3)_2$), 127.9, 128.1, 128.6, 137.4 (C-aromatic), 210.2 (C=O); EIMS: m/z 273 (0.8, M − 249), 249 (1.3, M − 273). Anal. Calcd for $C_{27}H_{38}O_{10}$: C, 62.1; H, 7.3. Found: C, 61.7; H, 7.15.

Integration of the signals for H-1 in the NMR spectrum of the original isomeric mixture of **23** and **24**, gave an approximate diastereoisomeric ratio of 1:1.

(b) Using dibutylboron triflate–Et_3N: reaction of ketone **5** (1.00 g, 4.09 mmol) with aldehyde **4** (1.23 g, 4.42 mmol) under Method 2 conditions gave, on column chromatography (solvent B) as the first eluted material, ketone **5** (0.29 g, 29%). Further elution gave, as a mixture of isomers, the crossed-aldol products **23** and **24** (0.41 g, 19%). The spectroscopic data for this mixture of isomers were identical, except for differences resulting from a different diastereoisomeric ratio, to those described above in (a) for the aldol product obtained from the reaction using LiHMDS.

[1] By comparison with the single-isomer sample obtained via the sodium enolate of **5**, which is tentatively assigned as **24**, this material obtained from chromatography is also **24**.

Integration of the signals for H-1 in the NMR spectrum of the original isomeric mixture of **23** and **24** gave an approximate diastereoisomeric ratio of 1.5:1. The major isomer was identical to the single isomer sample prepared as described in (c) below, which is tentatively assigned as **24**.

(c) Using NaHMDS: to a stirred soln of NaHMDS (1.0 M in THF; 25 mL, 25 mmol) under argon at −78 °C was added dropwise a soln of ketone **5** (5.00 g, 20.5 mmol) in anhyd THF (50 mL) such that the temperature of the reaction mixture remained below −65 °C. The soln was stirred at −78 °C for 30 min and then a concd soln of aldehyde **4** (6.56 g, 23.6 mmol) in anhyd THF (10 mL) was added in three rapidly consecutive portions. After 20 min at −78 °C, the reaction mixture was allowed to warm to −20 °C and after a further 10 min, it was quenched by the addition of satd aq $NaHCO_3$ (100 mL). Separation of the two phases, extraction of the aq phase with Et_2O (3 × 100 mL) and concentration of the combined, dried organic solutions gave a syrup (10.86 g). This material mainly contained the desired aldol products **23** and **24** plus some of the starting materials **4** and **5**, as indicated by TLC (solvent B); for further transformations it could be used in this crude form or purified by column chromatography in solvent B. Such purification on a portion of the crude syrup (1.0 g) yielded as the first-eluted material ketone **5** (0.10 g; 22%), then a single isomer (as indicated by NMR spectroscopy and analytical HPLC) of the crossed-aldol product, tentatively assigned (see Section 2) as **24** (0.52 g, 53%); $[\alpha]_D$ −18.7° (*c* 6.3, $CHCl_3$). Other spectroscopic data were identical to those for the related component in the previously separated sample of mixed isomers.

(E)-*1,2-Dideoxy-4,5:6,7-di*-O-*isopropylidene-1*-C-*phenyl*-L-arabino-*hept-1-en-3-ulose* (**27**).—A solution of aldol adducts **9** and **10** (130 mg, 0.37 mmol) and Ac_2O (0.15 mL, 0.11 g, 1.08 mmol) in pyridine (2 mL) was stored at rt (18 °C) for 45 h and water (0.3 mL) and satd aq $NaHCO_3$ (2.5 mL) were then added sequentially. After being stirred for 30 min, the soln was extracted with CH_2Cl_2 (2 × 10 mL) and the combined organic solutions were washed with 0.1 M HCl (5 mL), water (5 mL), satd aq $NaHCO_3$ (5 mL) and water (5 mL). The dried organic soln was co-evaporated with toluene (2 × 15 mL) to remove residual pyridine and then concentrated to give a crude syrup (87 mg) containing three components. Column chromatography (solvent A) yielded, initially, as an oil, alkene **27** (62 mg, 50%); $[\alpha]_D$ −17.0° (*c* 5.3, $CHCl_3$); IR (film): *ν* 1700 (C=O), 1630 (C=C), 1595 (C_6H_5), 1380 and 1370 cm^{-1} ($C(CH_3)_2$); ^1H NMR (270 MHz): *δ* 1.37, 1.38, 1.43 and 1.51 (4 × s, 4 × 3 H, 2 × $C(CH_3)_2$), 4.01 (dd, 1 H, $J_{6,7}$ 5.0, $J_{7,7'}$ 8.6 Hz, H-7), 4.14 (dd, 1 H, $J_{6,7'}$ 6.3 Hz, H-7′), 4.25 (ddd, 1 H, $J_{5,6}$ 7.0 Hz, H-6), 4.35 (dd, 1 H, $J_{4,5}$ 5.3 Hz, H-5), 4.62 (d, 1 H, H-4), 7.20 (d, 1 H, $J_{1,2}$ 16.2 Hz, H-2), 7.39–7.42 and 7.58–7.62 (complex, 5 H, C_6H_5), 7.76 (d, 1 H, H-1); ^{13}C NMR (67.9 MHz): *δ* 25.2, 26.3, 26.6 and 27.2 (2 × $C(CH_3)_2$), 66.7 (C-7), 76.6 (C-6), 78.5 (C-5), 82.6 (C-4), 109.9 and 111.4 (2 × $C(CH_3)_2$), 121.6 (C-2), 128.6, 128.9, 130.8, 134.5 (C-aromatic), 144.4 (C-1), 197.6 (C=O); EIMS: *m/z* 332 (1.9, M^+), 317 (7.3, M − 15). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.7; H, 7.3. Found: C, 68.4; H, 7.3.

Further elution gave a mixture of the 1-(*R*)- and 1-(*S*)-acetates, **11** and **12**, respectively, combined with alkene **27**, from which, by re-chromatography, could be obtained as an oily material identified by NMR spectroscopy as one of the acetates **11** or **12** (6.5 mg, 5%); ^1H NMR (270 MHz): *δ* 1.41, 1.55 and 1.56 and 1.57 (4 × s, 4 × 3 H, 2 × $C(CH_3)_2$), 1.99–2.17 (complex, 2 H, and H-2, 2′), 2.03 (s, 3 H, CH_3CO), 3.67–4.14 (complex, 6 H, H-1, 4, 5, 6, 7, 7′), 7.26–7.47 (complex, 5 H, C_6H_5); ^{13}C NMR (75.4 MHz): *δ* 21.0 ($COCH_3$), 25.1, 25.9, 26.5 and 26.7 (2 × $C(CH_3)_2$), 60.0 (C-2), 67.8 (C-7), 73.1, 76.5 (C-5, 6), 77.1 (C-4), 80.8 (C-1), 110.3 and 111.0 (2 × $C(CH_3)_2$), 128.1, 129.8, 129.0, 135.7 (C-aromatic), 169.5 (CH_3C=O), 209.4 (C=O).

Finally, a mixture of starting materials **9** and **10** (2.7 mg, 2%) was recovered.

3-O-*Acetyl-4-deoxy-1,2:6,7:8,9-tri*-O-*isopropylidene*-L-glycero-L-galacto-*non-5-ulose* (**16**), *3*-O-*acetyl-4-deoxy-1,2:6,7:8,9-tri*-O-*isopropylidene*-L-glycero-L-gulo-*non-5-ulose* (**17**), *and* (E)-*3,4-dideoxy-1,2:6,7:8,9-tri*-O-*isopropylidene*-L-gluco-*non-3-en-5-ulose* (**28**).—To a soln of a mixture of **14** and **15** (0.30 g,

0.80 mmol) in pyridine (3 mL) was added Ac_2O (0.15 mL, 0.11 g, 1.09 mmol) and the reaction mixture was stored at rt (18 °C) for 2 h. Product isolation, as described for the preparation of **27**, gave a syrup (0.20 g) containing [TLC (solvent B)] three components, R_f 0.34 (major), R_f 0.23 (minor), and R_f 0.11 (**14** and **15**). On column chromatography (solvent B), first eluted as an oil was alkene **28** (0.11 g, 39%); $[\alpha]_D + 13.6°$ (*c* 0.93, $CHCl_3$); IR (film): *v* 1700 (C=O), 1630 (C=C), 1380 and 1370 cm^{-1} ($C(CH_3)_2$); ^1H NMR (270 MHz): δ 1.35 (× 2), 1.42 (× 2) 1.46 and 1.47 (6 × s, 6 × 3 H, 3 × $C(CH_3)_2$), 3.68 (dd, 1 H, $J_{1,1'}$ 7.6, $J_{1,2}$ 7.6 Hz, H-1), 3.96 (dd, 1 H, $J_{8,9}$ 4.6, $J_{9,9'}$ 8.6 Hz, H-9), 4.09–4.30 (complex, 4 H, H-1′, 7, 8, 9′), 4.53 (d, 1 H, $J_{6,7}$ 5.3 Hz, H-6), 4.71 (m, 1 H, H-2), 6.81 (dd, 1 H, $J_{2,3}$ 5.6, $J_{3,4}$ 15.5 Hz, H-3), 6.97 (dd, 1 H, $^4J_{2,4}$ 5.0 Hz, H-4); ^{13}C NMR (67.9 MHz): δ 25.1, 25.6, 26.2, 26.4, 26.5 and 27.1 (3 × $C(CH_3)_2$), 66.6 (C-9), 68.6 (C-1), 75.1, 76.4 (C-7, 8), 78.2 (C-2), 82.2 (C-6), 109.8, 110.2 and 111.4 (3 × $C(CH_3)_2$), 125.5 (C-4), 144.6 (C-3), 197.1 (C=O); EIMS: *m/z* 356 (1.9, M^+), 341 (18.1, M − 15), 255 (1.2, M − 101), 155 (4.7, M − 201); HRMS: calcd for $C_{18}H_{28}O_7$: 356.1835; found: *m/z* 356.1835. Anal. Calcd for $C_{18}H_{28}O_7$: C, 60.7; H, 7.9. Found: C, 60.25; H, 7.8.

Further elution gave, as an oil, the mixture of stereoisomers, **16** and **17**, (21 mg, 6%); IR (film): *v* 1760–1700 (br, C=O), 1380 and 1370 cm^{-1} ($C(CH_3)_2$); ^1H NMR (270 MHz): δ 1.24–1.44 (complex, 18 H, 3 × $C(CH_3)_2$), 1.98, 2.00 (2 × s, 3 H in total, $COCH_3$), 3.67–4.74 (complex, 10 H, H-1, 1′, 2, 4, 4′, 6, 7, 8, 9, 9′), 5.31–5.47 (complex, 1 H, H-3); ^{13}C NMR (67.9 MHz): δ major isomer: 20.8 ($COCH_3$), 25.1 (× 2), 26.1, 26.2, 26.3 and 26.4 (3 × $C(CH_3)_2$), 48.8 (C-4), 65.8, 66.4 (C-1, 9), 69.3, 71.7, 74.5, 77.9 (C-2, 3, 7, 8), 82.6 (C-6), 109.7, 109.8 and 110.0 (3 × $C(CH_3)_2$), 169.7 ($COCH_3$), 207.5 (C=O); minor isomer: 20.9 ($COCH_3$), 25.1, 25.2, 25.3, 26.0, 27.0 and 27.1 (3 × $C(CH_3)_2$), 48.2 (C-4), 65.6, 67.0 (C-1, 9), 69.0, 74.1, 75.9, 78.0 (C-2, 3, 7, 8), 84.2 (C-6), 109.8, 109.9, 112.4 (3 × $C(CH_3)_2$), 170.0 (CH_3C=O), 205.1 (C=O); EIMS: *m/z* 417 (1.8, $M^+ + 1$), 401 (2.7, $M^+ - 15$). Anal. Calcd for $C_{20}H_{32}O_9$: C, 57.7; H, 7.7. Found: C, 58.0; H, 8.0. From the ^{13}C NMR spectrum the two isomers were in a ratio of 2:1.

Eluted last as an inseparable mixture were starting materials **14** and **15** (30 mg, 10%).

(E)-*6,7-Dideoxy-1,2:3,4:8,9:10,11-tetra*-O-*isopropylidene*-D-erythro-L-manno-*undec-6-en-5-ulose* (**29**).—(a) A solution of **19** and **20**, (0.15 g, 0.32 mmol) and Ac_2O (0.10 mL, 0.72 mmol) in pyridine (2 mL) was stored at rt for 48 h, and the reaction mixture then worked-up as in the preparation of **27** to yield a crude oil (0.12 g), which was subjected to column chromatography (solvent B). First eluted, as a colourless oil (R_f 0.60), was the alkene **29** (19 mg, 13%); $[\alpha]_D - 15.1°$ (*c* 1.65, $CHCl_3$); IR (film): *v* 1695 (C=O), 1630 (C=C), 1380 and 1370 cm^{-1} ($C(CH_3)_2$); ^1H NMR (270 MHz): δ 1.33, 1.34, 1.35, 1.39, 1.41, 1.43 (× 2), 1.47 (8 × s, 8 × 3 H, 4 × $C(CH_3)_2$), 3.65–4.30 (complex, 8 H, H-1, 1′, 2, 3, 9, 10, 11, 11′), 4.53 (d, 1 H, $J_{3,4}$ 5.0 Hz, H-4), 4.58 (ddd, 1 H, $^4J_{6,8}$ 1.7, $J_{7,8}$ 4.3, $J_{8,9}$ 7.9 Hz, H-8), 6.89 (dd, 1 H, $J_{6,7}$ 15.5 Hz, H-6), 7.09 (dd, 1 H, H-7); ^{13}C NMR (67.9 MHz): δ 25.2 (× 2), 26.3, 26.5, 26.7, 26.8, 27.0 and 27.2 (4 × $C(CH_3)_2$), 66.7, 67.5 (C-1, 11), 76.5, 77.0, 78.3, 79.4 (C-2, 3, 9, 10), 81.2, 82.4 (C-4, 8), 109.9, 110.0, 110.3 and 111.5 (4 × $C(CH_3)_2$), 124.7 (C-6), 145.2 (C-7), 197.5 (C=O); EIMS: *m/z* 456 (3.5, M^+), 441 (23.4, M − 15). Anal. Calcd for $C_{23}H_{36}O_9$: C, 60.5; H, 7.95. Found: C, 60.5; H, 8.1.

Further elution gave an unseparated mixture of two slower-running components (R_f 0.25 and 0.28) as an oil, shown by spectroscopy to be an approximately equimolar mixture of the two isomers **21** and **22** (32 mg, 19%); IR (film): *v* 1710 (br, C=O), 1380 and 1375 ($C(CH_3)_2$), no absorption near 3400 cm^{-1} (OH); ^1H NMR (270 MHz): δ 1.32–1.47 (complex, 16 × 3 H, 8 × $C(CH_3)_2$), 2.04, 2.06 (2 × s, 2 × 3 H, 2 × $COCH_3$), 2.88 (dd, 1 H, $J_{6a,6'a}$ 17.1, $J_{6a,7a}$ 3.4 Hz, H-6a), 2.97 (d, 2 H, $J_{6b,7b}$ 6.2, $J_{6'b,7b}$ 6.2 Hz, H-6b, 6′b), 3.07 (dd, 1 H, $J_{6a,6'a}$ 8.8, $J_{6'a,7a}$ 8.8 Hz, H-6′a), 3.66–4.87 (complex, 2 × 11 H, H-1, 1′, 2, 3, 4, 7, 8, 9, 10, 11, 11′); ^{13}C NMR (22.4 MHz)): δ 25.2 and 25.4 (2 × $COCH_3$), 26.4–27.5 (8 × $C(CH_3)_2$), 52.0, 54.7 (2 × C-6), 65.8–84.8 (2 × C-1, 2, 3, 4, 7, 8, 9, 10, 11), 109.4–112.0 (8 × $C(CH_3)_2$), 175.3 and 175.4 (2 × CH_3C=O), 204.9 and 209.7 (2 × C=O).

Further elution with 2:1 light petroleum–EtOAc gave a mixture of starting materials **19** and **20** (33 mg, 22%).

(b) Treatment of **19** and **20** (0.207 g, 0.44 mmol) in pyridine (2 mL) with *p*-tolylsulfonyl chloride (0.102 g, 0.54 mmol) at rt for 5 days and conventional work-up gave a crude oil (0.13 g) which, when subjected to column chromatography (solvent B), gave as an oil alkene **29** (54 mg, 27%).

Further elution (2:1 light petroleum–EtOAc) gave a mixture of **19** and **20** (61 mg, 29% recovery). No products of *O*-*p*-tolylsulfonylation could be identified.

(E)-*3*-O-*Benzyl*-*5,6*-*dideoxy*-*1,2:8,9:10,11*-*tri*-O-*isopropylidene*-L-erythro-α-D-gluco-*undec*-*5*-*enofuranos*-*7*-*ulose* (**30**).—Acetylation/elimination reactions on the mixed isomer sample of the aldol adducts **23** and **24** to give the α,β-unsaturated ketone and an isomeric mixture of the corresponding acetates **25** and **26** were carried out under four different reaction conditions to optimise the yield and to increase the rate of the reaction. That performed in the presence of a catalytic quantity of DMAP was adopted for the bulk preparation of product and was also used to acetylate and eliminate the single-isomer sample of the aldol adduct (i.e., the isomer presumed to be **24**) to give **26** and (*E*)-enone **30**.

Acetylation of a solution of **23** and **24** (137 mg, 0.26 mmol) with Ac_2O (0.12 mL, 0.87 mmol) in pyridine (2 mL) for 6 days, and product isolation, as described in the preparation of **27**, gave a crude syrup (119 mg), which on column chromatography (solvent A) yielded initially, as an oil, the enone **30** (62 mg, 46%); $[\alpha]_D - 44.9°$ (*c* 4.5, $CHCl_3$); IR (film): *v* 1700 (C=O), 1640 (C=C), 1620 (C_6H_5), 1385 and 1370 cm^{-1} ($C(CH_3)_2$); ^1H NMR (300 MHz) δ 1.32, 1.33, 1.35, 1.42, 1.45 and 1.49 (6 × s, 6 × 3 H, 3 × $C(CH_3)_2$), 3.97 (dd, 1 H, $J_{10,11}$ 4.8, $J_{11,11'}$ 8.5 Hz, H-11), 4.00 (d, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 4.12 (dd, 1 H, $J_{10,11'}$ 6.2 Hz, H-11′), 4.19 (ddd, 1 H, $J_{9,10}$ 6.9 Hz, H-10), 4.29 (dd, 1 H, $J_{8,9}$ 5.4 Hz, H-9), 4.47 (d, 1 H, J_{AB} 12.0 Hz, $C_6H_5H_AH_B$), 4.54 (d, 1 H, H-8), 4.60 (d, 1 H, $C_6H_5H_AH_B$), 4.65 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-2), 4.84 (ddd, 1 H, $J_{4,5}$ 4.8, $^4J_{4,6}$ 1.6 Hz, H-4), 6.01 (d, 1 H, H-1), 6.88 (dd, 1 H, $J_{5,6}$ 15.8 Hz, H-5), 7.06 (dd, 1 H, H-6), 7.24–7.36 (complex, 5 H, C_6H_5); ^{13}C NMR (75.4 MHz): δ 25.2, 26.2, 26.3, 26.6, 26.9 and 27.2 (3 × $C(CH_3)_2$), 66.9 ($C_6H_5CH_2$), 72.3 (C-11), 76.8, 78.4, 80.0, 82.5, 83.0, 83.2 (C-2, 3, 4, 8, 9, 10), 105.2 (C-1), 110.1, 111.8 and 112.1 (3 × $C(CH_3)_2$), 126.9 (C-6), 128.0, 128.8, 128.3, 137.3 (C-aromatic), 141.9 (C-5), 197.3 (C=O); HRMS: calcd for $C_{27}H_{36}O_9$: *m*/*z*, 504.2359; found: 504.2360.

Further elution gave, according to NMR spectroscopy, a mixture of the isomeric acetates **25** and **26** containing a small amount of the elimination product **30**. Re-chromatography of the mixture gave a sample mostly comprising one of the acetates (presumably isomer **26**, as shown by comparison with the single isomeric *O*-acetate isolated in a similar reaction conducted in the presence of DMAP on the compound tentatively identified as **24**, see later) containing approximately 10 mol% of the second isomer **25** (15 mg, 10%); IR (film): *v* 1745 (CH_3C=O), 1720 (C=O), 1375 and 1365 cm^{-1} ($C(CH_3)_2$); ^1H NMR (300 MHz) major isomer: δ 1.24, 1.31, 1.34, 1.42 (× 2) and 1.47 (6 × s, 6 × 3 H, 3 × $C(CH_3)_2$), 1.93 (s, 3 H, CH_3C=O), 3.12 (dd, 1 H, $J_{5,6}$ 7.0, $J_{6,6'}$ 18.0 Hz, H-6), 3.21 (dd, 1 H, $J_{5,6'}$ 4.2, $J_{6,6'}$ Hz, H-6′), 3.92–4.37 (complex, 7 H, H-2, 3, 4, 9, 10, 11, H-11′), 4.47 (d, 1 H, J_{AB} 11.5 Hz, $C_6H_5CH_AH_B$), 4.58 (d, 1 H, $J_{8,9}$ 3.6 Hz, H-8), 4.60 (d, 1 H, $C_6H_5CH_AH_B$), 5.60 (ddd, 1 H, $J_{4,5}$ 5.6 Hz, H-5), 5.91 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 7.27–7.37 (complex, 5 H, C_6H_5); minor isomer: 1.25 (× 2), 1.34, 1.39 and 1.45 (× 2) (6 × s, 6 × 3 H, 3 × $C(CH_3)_2$), 1.95 (s, 3 H, CH_3C=O), 2.74 (dd, 1 H, $J_{5,6}$ 8.2, $J_{6,6'}$ 16.2 Hz, H-6), 2.98 (dd, 1 H, $J_{5,6'}$ 3.3 Hz, H-6′), 3.90–4.34 (complex, 7 H, H-2, 3, 4, 9, 10, 11, 11′), 4.48 (d, 1 H, J_{AB} 11.8 Hz, $C_6H_5CH_AH_B$), 4.54 (d, 1 H, $J_{8,9}$ 5.3 Hz, H-8), 4.62 (d, 1 H, $C_6H_5CH_AH_B$), 5.53 (ddd, 1 H, $J_{4,5}$ 6.3 Hz, H-5), 6.01 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 7.27–7.37 (complex, 5 H, C_6H_5); ^{13}C NMR (75.4 MHz) (for **26**): δ 21.0 (CH_3CO), 25.2, 26.1, 26.3, 26.5, 26.9, 27.1 (3 × $C(CH_3)_2$), 40.3 (C-6), 66.7, 67.6, 77.3, 78.0, 80.7, 81.7, 82.1 and 83.1 (C-2, 3, 4, 5, 8, 9, 10, 11), 72.3 ($C_6H_5CH_2$), 105.2 (C-1), 110.1, 111.6, 112.1 (3 × $C(CH_3)_2$), 128.3, 128.7, 128.8, 137.2 (C-aromatic), 170.3 (CH_3C=O), 206.5 (C=O); EIMS: *m*/*z* 473 (2.2, M − 91).

Finally, the starting alcohols **23** and **24** were recovered (22 mg, 16%).

The isomeric mixture of acetates **25** and **26** was subjected to the same acetylation conditions used in their preparation. Monitoring of the reaction by TLC (solvent A) revealed slow conversion of acetates **26** and **26** to an elimination product. After 3 days, the concentration of the starting acetate was negligible, and the major product was confirmed as (*E*)-enone **30**, by TLC and NMR spectroscopic comparison with an authentic sample.

Repetition of the reaction on the mixture of **23** and **24** at 45 °C for 8 h gave (*E*)-enone **30** (0.17 g, 61%) and the mixed acetates **25** and **26** (55 mg, 18%). Acetylation at 60 °C gave a negligible amount of **25** and **26**, and (*E*)-enone **30** in 40% yield. Reaction of the single stereoisomer, presumed to be **24**, with Ac_2O–pyridine containing DMAP for 70 h at 18 °C gave a 20:1 mixture of the (*E*)- and (*Z*)-enones **30** and **31** in 72% yield. Thus, the 300 MHz ^1H NMR spectrum of the product showed alkenic couplings of 11.9 and 15.8 Hz. Additional peaks that could be assigned to the (*Z*)-enone **31** are: δ_H 5.56 (ddd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 6.7, $^4J_{4,6}$ 1.6 Hz, H-4), 5.98 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 6.48 (dd, 1 H, $J_{5,6}$ 11.9 Hz, H-5), 6.77 (dd, 1 H, H-6). Negligible quantities of both the acetate **26** and starting material **24** were obtained from the column separation. However, if this reaction was quenched after shorter reaction times then, in addition to the enones **30** and **31**, a single acetate **26** was obtained; $[\alpha]_D - 26.3°$ (*c* 4.75, $CHCl_3$). The ^1H and ^{13}C NMR spectra of this material were identical to those of the major isomer obtained by column chromatography of the product of acetylation of the mixture of **23** and **24** with Ac_2O–pyridine.

Attempted epoxidation of (E)-*3*-O-*benzyl-5,6- dideoxy - 1,2:8,9:10,11 - tri* - O - *isopropylidene*-L-erythro-α-D-gluco-*undec-5-enofuranos-7-ulose* (**30**).—(a) Using hydrogen peroxide and NaOH in MeOH: to a stirred solution of **30** (101 mg, 0.20 mmol) and aq 30% H_2O_2 (0.1 mL) in MeOH (5 mL), at 0 °C was added aq 2.5 M NaOH (0.1 mL, 0.25 mmol). The mixture was then allowed to warm to rt and TLC (solvent B) indicated that after 2 h, all the starting material had been consumed and five new, closely-running materials were formed, all with lower R_f values than **30**. The reaction mixture was then poured into cold water (5 mL), the aqueous solution was extracted with Et_2O (3 × 5 mL) and the combined organic solutions were washed with water (10 mL), dried and then concentrated to give a syrup (81 mg). Column chromatography (solvent A) allowed only mixtures of the components to be isolated.

A fast-running fraction appeared to contain three distinct but inseparable isomeric components in a ratio of approximately 1:1:1. Evidence as to the structure of these components was based solely on the ^1H NMR spectrum of the mixture. Two of these isomers appeared to result from opening of an epoxide by methoxide to yield two of the eight possible stereoisomers depicted by **32** and **33**. The third component in the faster-running mixture, on the basis of its ^1H NMR spectrum, was a 6- or 7-*C*-methoxycarbonyl derivative of a stereoisomer of 3-*O*-benzyl-6-deoxy-1,2:7,8:9,-10-tri-*O*-isopropylidene-L-decafuranose, **34** and **35**, originating from Favorskii rearrangement of the intermediate epoxide [8] (11 mg, 11%); ^1H NMR (300 MHz): δ 1.31–1.52 (complex, 18 H, 3 × $C(CH_3)_2$), 1.60 (br s, 1 H, OH), 2.20–3.33 (complex), 3.27, 3.28 and 3.71 (3s, 3 H, 2 × CH_3O (**32**, **33**) and CO_2CH_3 (**34**, **35**), respectively), 3.85–4.75 (complex), 5.86, 5.88 and 5.91 (3 × d, 1 H, $J_{1,2}$ 3.9, 3.7 and 3.7, respectively, H-1), 7.27–7.37 (complex, 5 H, C_6H_5).

A slower-running fraction was shown by ^1H NMR spectroscopy to contain two further components in a ratio of 2:1, tentatively identified from the ^1H NMR spectrum to be two other stereoisomers of **32**, **33** (19 mg, 17%); major isomer: ^1H NMR (270 MHz): δ 1.32, 1.33, 1.35, 1.47 (× 2) and 1.49 (6 × s, 6 × 3 H, 3 × $C(CH_3)_2$), 1.65 (br s, 1 H, OH), 2.69–3.19 (complex, 2 H), 3.24 (s, 3 H, CH_3O), 3.99–4.18 (complex, 6 H), 4.34 (ddd, 1 H, $J_{9,10}$ 5.6, $J_{10,11}$ 5.6, $J_{10,11'}$ 5.6 Hz, H-10), 4.49 (d, 1 H, J_{AB} 11.6 Hz, $C_6H_5CH_AH_B$), 4.65, (d, 1 H, $J_{8,9}$ 4.0 Hz, H-8), 4.73 (d, 1 H, $C_6H_5CH_AH_B$), 6.01 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 7.26–7.38 (complex, 5 H, C_6H_5); minor isomer: ^1H NMR (270 MHz): δ 1.25, 1.33, 1.39, 1.47, 1.50 and 1.51 (6s, 6 × 3 H, 3 × $C(CH_3)_2$), 1.65 (br s, 1 H,

OH), 2.69–3.19 (complex, 2 H), 3.22 (s, 3 H, CH_3O), 3.84–4.18 complex 6 H), 4.30 (ddd, 1 H, $J_{9,10}$ 5.6, $J_{10,11}$ 5.6, $J_{10,11'}$ 5.6 Hz, H-10), 4.52 (d, 1 H, J_{AB} 11.9 Hz, $C_6H_5CH_AH_B$), 4.65 (d, 1 H, $J_{8,9}$ 4.0 Hz, H-8), 4.74 (d, 1 H, $C_6H_5CH_AH_B$), 6.02 (d, 1 H, $J_{1,2}$ 2.5 Hz, 1-H), 7.26–7.38 (complex, 5 H, C_6H_5); EIMS: m/z 537 (0.3, M − 15,), 534 (0.3, M − 18).

(b) Using hydrogen peroxide and potassium carbonate in MeOH: treatment of **30** (41 mg, 81 μmol) with aq 30% H_2O_2 (0.05 mL) in MeOH (2 mL) and water (1 mL) at 0 °C containing K_2CO_3 led to loss of starting material, (TLC). Product isolation gave crude material which by ^{1}H NMR spectroscopy was consistent with it containing four possible isomers of **32**, **33**: ^{1}H NMR (300 MHz): δ 1.26–1.55 (complex, 18 H, 3 × $C(CH_3)_2$), 1.60 (br s, 1 H, OH), 2.77–5.29 (complex 12 H,), 3.22, 3.24, 3.28 and 3.29 (4 × s, 3 H total, CH_3O), 5.86, 5.90, 6.01, and 6.22 (4 × d, 1 H total, $J_{1,2}$ 4.1, 3.9, 3.9, and 3.7, respectively, H-1), 7.20–7.45 (complex, 5 H, C_6H_5). No products due to Favorskii rearrangement were observed in the crude mixture.

(c) Using hydrogen peroxide and $NaHCO_3$ in THF [9]: treatment of **30** (195 mg, 0.39 mmol) with aq 30% H_2O_2 (0.1 mL) in a THF (5 mL)/satd aq $NaHCO_3$ (0.1 mL) mixture at 0 °C gave [TLC (solvent B)] a product running as a single component in an approximately equal proportion to remaining starting material. Column chromatography (14:1 toluene–acetone) gave initially **30** (86 mg, 44%) and a new component (11 mg, 5%), tentatively identified, on the basis of its IR and ^{1}H NMR spectra, as a mixture of 6- and/or 7-*C*-carboxy derivatives of a stereoisomer of 3-*O*-benzyl-6-deoxy-1,2:7,8:9,10-tri-*O*-isopropylidene-L-deca-1,4-furanose arising from the Favorskii rearrangement of the intermediate epoxide [8]; IR (film): ν 3400 (br, CO_2H), 1750–1600 cm^{-1} (C=O and C_6H_5); ^{1}H NMR (300 MHz): δ 1.22–1.54 (complex, 18 H, 3 × $C(CH_3)_2$), 1.59 (br s, 1 H, OH), 1.70–2.02 (complex, 2 H, H-6, 6′), 3.78–4.79 (complex, 10 H), 5.52–5.58 (complex, 1 H, H-1), 7.10–7.38 (complex, 5 H, C_6H_5), 8.55 (CO_2H).

Attempted iodonium-induced cyclisation reaction on (E)-*3*-O-*benzyl-5,6-dideoxy-1,2:8,9:10,11-tri*-O-*isopropylidene*-L-erythro-α-D-gluco-*undec-5-enofuranos-7-ulose* (**30**).—(a) Using *N*-iodosuccinimide (NIS): a soln of **30** (78 mg, 0.15 mmol) in anhyd CH_2Cl_2 (5 mL) containing NIS (129 mg, 0.57 mmol) was stirred under N_2 at rt. TLC (solvent B) indicated that after 2 weeks, only starting material was present; the mixture was filtered through Kieselguhr and then concentrated to give **30** (59 mg, 76%).

(b) Using iodine: a soln of **30** (54 mg, 0.11 mmol) in anhyd THF (2 mL) containing resublimed iodine (0.14 g, 0.55 mmol) and $NaHCO_3$ (0.10 g, 1.19 mmol) was stirred at rt. TLC (solvent B) indicated that only starting material was apparent after 6 days. The mixture was filtered through Kieselguhr and partitioned between water (5 mL) and CH_2Cl_2 (5 mL). The dried organic solution was concentrated to yield **30** (21.6 mg, 40%).

6-Deoxy-1,2:8,9:10,11-tri-O-*isopropylidene*-L-arabino-α-D-gluco-*undecofuranos-7-ulo-7,3-pyranose* (**36**).—(a) Using H_2 and palladium black, catalysed by a trace amount of acid: to a soln of **24** (307 mg, 0.59 mmol) in anhyd MeOH (5 mL) containing palladium black (50 mg) was added a 0.014 M soln of HCl in anhyd MeOH (1.5 mL). The reaction mixture was stirred under H_2 at rt and atmospheric pressure for 4 h after which time TLC (1:1 light petroleum–EtOAc) indicated that all starting material (R_f 0.72) had reacted to give a single product (R_f 0.47). The suspension was filtered through a pad of Kieselguhr and the filtrate, which was slightly acidic to moist indicator paper, was stirred with Amberlite IRA-400 ion-exchange resin (HO^- form; 5 mL) for 1 h. After removal of the resin by filtration, the solution was concentrated to a colourless oil. Dissolution of this oil in Et_2O and subsequent removal of the solvent under vacuum resulted in crystallisation to give a single anomer of the title product **36** (201 mg, 79%) mp 145.5–148°C; $[\alpha]_D$ + 11.9° (c 1.0, $CHCl_3$); IR (Nujol): ν 3400 (br, OH), 1380 and 1375 cm^{-1} ($C(CH_3)_2$); ^{1}H NMR (270 MHz): δ 1.33, 1.35, 1.36, 1.38, 1.48 and 1.52 (6 × s, 6 × 3 H, 3 × $C(CH_3)_2$), 1.84 (dd, 1 H, $J_{5,6}$ 4.6 and $J_{6,6'}$ 12.6 Hz, H-6), 2.02 (ddd, 1 H, $J_{5,6'}$ 11.9, $^4J_{6',8}$ 2.0 Hz, H-6′), 2.13 (d, 1 H, $J_{5,OH}$ 10.6 Hz, 5-OH), 3.76 (d, 1 H, $J_{8,9} \sim 0$, $J_{9,10}$ 7.6 Hz, H-9), 4.02–4.30 (complex, 5 H,

H-5, 10 11, 11′, 7-OH), 4.31 (d, 1 H, $J_{2,3} \sim 0$, $J_{3,4}$ 2.0 Hz, H-3), 4.40 (dd, 1 H, $J_{3,4}$ and $J_{4,5}$ 3.0 Hz, H-4), 4.56 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-2), 4.81 (d, 1 H, H-8), 5.87 (d, 1 H, H-1); ^{13}C NMR (67.9 MHz): δ 25.0, 26.3 ($\times$ 2), 26.4, 26.8 and 27.0 ($3 \times C(CH_3)_2$), 35.2 (C-6), 63.8 (C-11), 67.9, 74.9, 75.7, 76.5, 77.4, 84.4, 84.8 (C-2, 3, 4, 5, 8, 9, 10), 96.2 (C-7), 105.1 (C-1), 109.6, 110.4 and 112.2 ($3 \times C(CH_3)_2$); EIMS: 417 (2.6, M − 15), 399 (0.7, M − 33), 289 (1.2, M − 143), 143 (17.2, M − 289); HRMS: calcd for $C_{19}H_{29}O_{10}$ (M − 15): 417.1761; found: m/z 417.1760. Anal. Calcd for $C_{20}H_{32}O_{10}$: C, 55.55; H, 7.5. Found: C, 56.0; H, 7.85.

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