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A SYNTHESIS OF L-*lyxo*-L-*altro*-NONITOL, A NEW NONITOL*

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ABSTRACT

Catalytic osmylation of (*E*)-6-*O*-benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-non-7-enopyranose (**15**) proceeded with good stereoselectivity to give a mixture of 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-β-L-*lyxo*-D-*galacto*-nonopyranose (**16**) and the α-D-*xylo*-D-*galacto* isomer **17** in the ratio ~8.5:1. After debenzylation of this mixture, crystalline 1,2:3,4-di-*O*-isopropylidene-β-L-*lyxo*-D-*galacto*-nonopyranose (**21**) was isolated and converted in a straightforward manner into L-*lyxo*-L-*altro*-nonitol (L-*lyxo*-D-*galacto*-nonitol) (**23**). The (*E*)-allylic alcohol **15** can be prepared by way of Wittig olefination of 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-heptodialdo-1,5-pyranose (**13**) with formylmethylenetriphenylphosphorane or (methoxycarbonylmethylene)triphenylphosphorane, followed by apppropriate reduction of the enal **14** or conjugate ester **24**.

INTRODUCTION

In previous papers in this series[2–4], we showed that catalytic osmylation of unsaturated sugars, prepared *via* Wittig olefination, provided a satisfactory route to a number of 7-, 8-, and 10-carbon sugars, whose stereochemistry could be predicted by Kishi's empirical rule for osmylation[5]. In keeping with Kishi's formulation[5], the catalytic osmylation of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-oct-7-enopyranose (**1**) gave 1,2:3,4-di-*O*-isopropylidene-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*[2]. Little, if any, of the β-L-*threo*-D-*galacto* isomer **3** was formed in this reaction. The diafacial stereoselectivity observed in this and other osmylation reactions can be rationalised by assuming that the molecule reacts in the sterically least-compressed conformation **4**, with the major product arising from preferential approach of osmium tetraoxide to the face of the olefinic linkage opposite to that of the pre-existing hydroxyl (or

*Higher-carbon Sugars, Part 7. For Part 6, see ref. 1.
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alkoxyl) group[5]. This *anti* stereoselectivity with respect to an hydroxyl group is seen clearly in the conversion of **1** into **2**.

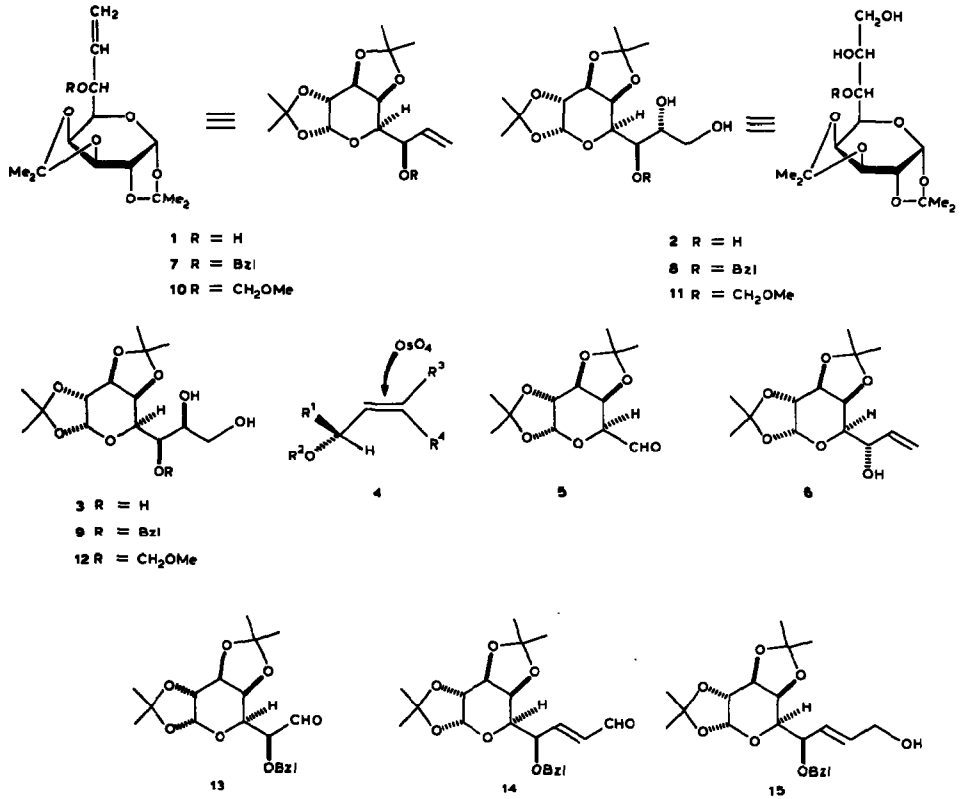
In the light of previous work[2–4], it seemed likely that suitably protected 7-carbon aldehydes (*e.g.*, **13**) might be transformed, *via* Wittig olefination, into 9-carbon, unsaturated precursors (*e.g.*, **15**) capable of undergoing stereoselective bishydroxylation. A new route would then be open to nonoses and nonitols, which hitherto have been synthesised by the cyanohydrin[6], nitroethanol[7], and diazomethane[7] methods. The fact that only three nonitols are known[8] suggests that their synthesis by traditional approaches, in which the sugar chain is extended from the reducing end, is fraught with difficulties. In many instances[2–4,9], an ascent of the series from the non-reducing end of the sugar chain offers a more flexible and stereocontrolled approach, which more than offsets the chemical manipulations required to introduce the appropriate functionality (usually an aldehyde group) at the non-reducing end and to protect the other hydroxyl groups.

RESULTS AND DISCUSSION

1,2:3,4-Di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose[10] (**5**) reacts with vinylmagnesium bromide to give[11] a 2:1 mixture of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-hept-7-enopyranose (**1**) and the corresponding β-L-*glycero*-D-*galacto* isomer **6**, from which most of **1** can be isolated by fractional crystallisation. Conventional benzylation of **1** provided the 6-*O*-benzyl derivative **7**, which, on catalytic osmylation, furnished a mixture of 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octopyranose (**8**) and the corresponding β-L-*threo*-D-*galacto* isomer **9** in the ratio ~5:1*. Following catalytic debenzylation of the mixture of **8** and **9**, the triol **2** (identified by comparison with an authentic sample[2]) was isolated in 68% yield, confirming that the major product **8** is that predicted by Kishi's empirical rule[5]. Similar osmylation of the 6-*O*-methoxymethyl derivative **10**, prepared in a conventional manner from **1**[11], yielded a mixture (80%) of two products (ratio ~4:1) in which, by analogy, 1,2:3,4-di-*O*-isopropylidene-6-*O*-methoxymethyl-α-D-*erythro*-D-*galacto*-octopyranose (**11**) was assumed to preponderate. Although the ratio of the osmylation products **8** and **9** is of theoretical interest, it did not materially affect the synthesis in hand, since the stereocentre at C-7 was destroyed in the next step, which involved periodate oxidation of the mixture to give 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-heptodialdo-1,5-pyranose (**13**) as the only product. Wittig olefination of **13** with formylmethylenetriphenylphosphorane[12,13] in boiling benzene then gave the (*E*)-enal **14**. The ^{1}H-n.m.r. spectrum of **14** contained a wide doublet ($J_{8,9}$ 7 Hz) at δ 9.60 for the aldehydic proton, while the H-8 signal at δ 6.39 was also strongly coupled ($J_{7,8}$ 15.5 Hz) to H-7, and displayed a small, long-range coupling ($J_{6,8}$ ~1.5

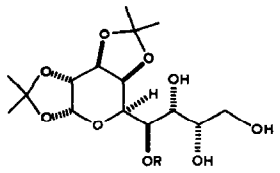
*In this and other osmylations, the ratio of the products was determined by integration over the signals for the anomeric protons in the 360-MHz ^{1}H-n.m.r. spectra.

Hz) with H-6, commensurate with the (*E*)-olefinic structure[14]. Reduction of **14** with di-isobutylaluminium hydride in dichloromethane at ~0° gave (*E*)-6-*O*-benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-non-7-enopyranose (**15**).



Catalytic osmylation[15] of **15** produced a mixture (82.5%) of **16** and **17** in the ratio ~8.5:1. The major isomer was confidently assigned the structure 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-β-L-*lyxo*-D-*galacto*-nonopyranose (**16**), on the basis of Kishi's empirical rule[5] and precedent [for example, **18**→**19** and **20** (ratio ~4:1)[5]]. Following catalytic debenzylation of the mixture of **16** and **17**, the tetraol **21** was freed from the contaminating isomer **22** by crystallisation. Acid hydrolysis of **21** and reduction of the resulting nonose gave crystalline L-*lyxo*-L-*altro*-nonitol (L-*lyxo*-D-*galacto*-nonitol) (**23**), whose ^{13}C-n.m.r. spectrum (see Experimental) was entirely compatible with the structure assigned.

The reaction of aldehydes, such as **5**, with (methoxycarbonylmethylene)triphenylphosphorane[16] in methanol often yields the (*Z*)-conjugate ester as the principal or exclusive product, thereby providing a convenient route to (*Z*)-allylic alcohols[2–4,17]. Such was not the case with the 7-carbon aldehyde **13**, which reacted



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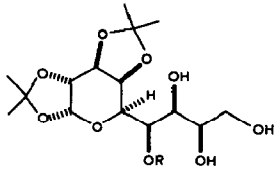
21 R = H



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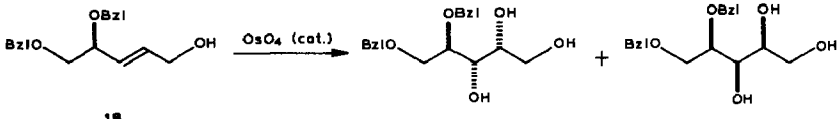
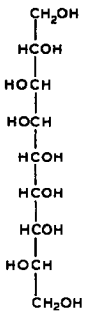
22 R = H



18 19 20



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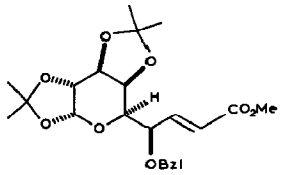

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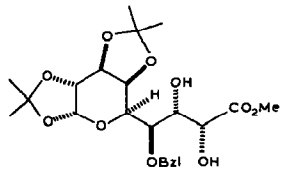

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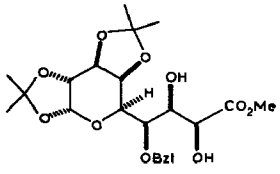

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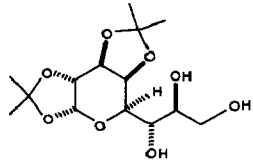

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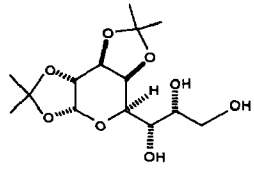

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cleanly with this Wittig reagent either in methanol at 0° or in boiling benzene to give almost entirely methyl (*E*)-6-*O*-benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-non-7-enopyranuronate (**24**). The (*E*) configuration of **24**, which was apparent from the strong coupling ($J_{7,8}$ 15.8 Hz) between H-7 and H-8, was confirmed when reduction of **24** furnished the (*E*)-allylic alcohol **15**. Catalytic osmylation[15] of **24** produced a mixture (96%) of methyl 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-β-L-*lyxo*-D-*galacto*-nonopyranuronate (**25**) and the corresponding α-D-*xylo*-D-*galacto* isomer **26** (ratio ~17:1), from which **25** crystallised. The configuration of the major isomer **25** was readily correlated with that of the crystalline tetraol **21** by reduction of the ester group and debenzylation. Latterly, we have adopted the route **13**→**24**→**25**→**16**→**21** in preference to the original route to **21** proceeding through the (*E*)-enal **14**. Interestingly, the catalytic

osmylation of the conjugate ester **24** is highly stereoselective and the major product **25** is that predicted by Kishi's empirical rule[5]. This is not always so with conjugate esters, and several exceptions have been noted[2,5].

Finally, we note that catalytic osmylation[15] of a mixture enriched in the *β*-L-*glycero*-D-*galacto* isomer **6*** gave two new products (ratio ~3:1), which were identified as 1,2:3,4-di-*O*-isopropylidene-*β*-L-*erythro*-D-*galacto*-octopyranose (**27**) and the *α*-D-*threo*-D-*galacto* isomer **28**, respectively, by comparison of the 360-MHz ^{1}H-n.m.r. spectrum with those of authentic samples[1]. Once again, the major isomer **27** is that predicted by Kishi's empirical rule for osmylation[5].

Added in proof. — Confirmation of the stereochemistry of 1,2:3,4-di-*O*-isopropylidene-*β*-L-*lyxo*-D-*galacto*-nonopyranose (**21**) at C-6 to C-8 has been achieved by correlation with that of 1,2,3,4,5-penta-*O*-methyl-L-arabinitol (-lyxitol) [for the D enantiomer, see N. Allentoff and G. F. Wright, *J. Org. Chem.*, 22 (1957) 1–6]. Thus, methylation of the tetraol **21** gave the corresponding tetra-*O*-methyl derivative [m.p. 64–65° (without recrystallisation), $[\alpha]_D$ −53° (*c* 0.9, chloroform)], which was transformed into 1,2,3,4,5-penta-*O*-methyl-L-arabinitol (identified by ^{1}H- and ^{13}C-n.m.r. spectroscopy) following (i) acid hydrolysis (CF_3CO_2H–H_2O), (ii) reduction ($NaBH_4$), (iii) periodate oxidation, (iv) reduction ($NaBH_4$), and (v) methylation (MeI–NaH–$HCONMe_2$). Identification of the final permethylated product by ^{13}C-n.m.r. spectroscopy is particularly easy because it lacks the C_s symmetry possessed by the permethylated derivatives of ribitol and xylitol.

EXPERIMENTAL

General methods. — T.l.c. was performed on Kieselgel G, and detection was effected with 1% sulphuric acid. ^{1}H-N.m.r. spectra were recorded for solutions in deuteriochloroform (internal Me_4Si), unless otherwise indicated, either with a Bruker (90 MHz) spectrometer or by the Edinburgh University WH-360 N.m.r. service. ^{13}C-N.m.r. (90 MHz) spectra were recorded for solutions in $(CD_3)_2SO$ by the Edinburgh University N.m.r. service; the spectra were referenced to Me_4Si by means of the solvent resonance at *δ* 39.6. Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter, using 1-dm tubes. Melting points are uncorrected.

6-O-Benzyl-7,8-dideoxy-1,2:3,4-di-O-isopropylidene-α-D-glycero-D-galacto-oct-7-enopyranose (**7**). — To a stirred solution of **1**[11] (3 g, 10.5 mmol) in anhydrous tetrahydrofuran (60 mL) was gradually added sodium hydride (60% dispersion in mineral oil; 3 g, ~75 mmol) followed, after 30 min, by benzyl bromide (4 mL, 33.6 mmol). The mixture was stirred overnight at room temperature, methanol was then added cautiously to destroy the excess of reagents, and the solvents were removed 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 (elution first with dichloro-

*Following fractional crystallisation of **1** (see text), the material remaining consisted of a mixture of **1** and **6** in the ratio ~3:7.

methane to remove traces of benzyl bromide, and then with 50:1 dichloromethane–acetone) gave **7** (3.5 g, 89%), b.p. ~135° (bath)/0.05 mmHg, $[\alpha]_D$ −66° (*c* 1, chloroform) (Found: C, 67.2; H, 7.4. $C_{21}H_{28}O_6$ calc.: C, 67.0; H, 7.5%). ^{1}H-N.m.r. data: *inter alia*, δ ~7.33 (m, 5 H, Ph), 5.93 (m, 1 H, C*H*=CH_2), 5.44 (m overlying d, 3 H, $J_{1,2}$ 5 Hz, CH=CH_2 and H-1), 4.56 (ABq, 2 H, J_{AB} 12 Hz, PhCH_2), and 1.49, 1.44, 1.36, and 1.29 (4 s, 12 H, 2 CMe_2).

*7,8-Dideoxy-1,2:3,4-di-*O*-isopropylidene-6-*O*-methoxymethyl-α-*D*-glycero-*D*-galacto-oct-7-enopyranose* (**10**). — A solution of **1**[11] (0.3 g, 1.05 mmol) in anhydrous dichloromethane (6 mL) containing ethyldi-isopropylamine (0.4 mL, 2.3 mmol) and methoxymethyl chloride (0.2 mL, 2.6 mmol) was stirred at room temperature for 60 h and then concentrated under reduced pressure. The residue was extracted with dichloromethane, and the extract was washed with dilute hydrochloric acid and water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 50:1 dichloromethane–acetone) gave **10** (0.342 g), b.p. ~90° (bath)/0.05 mmHg, $[\alpha]_D$ −107° (*c* 0.7, chloroform), in virtually quantitative yield (Found: C, 58.5; H, 7.6. $C_{16}H_{26}O_7$ calc.: C, 58.2; H, 7.9%). ^{1}H-N.m.r. data: *inter alia*, δ 5.52 (m overlying d, 4 H, $J_{1,2}$ 5 Hz, $CH=CH_2$ and H-1), 3.40 (s, 3 H, OMe), and 1.51, 1.46, 1.33, and 1.31 (4 s, 12 H, 2 CMe_2).

Catalytic osmylation of **10** (0.15 g, 0.45 mmol), as described for **7** in the next experiment, gave, after chromatography (ethyl acetate), a mixture (0.132 g, 80%) of 1,2:3,4-di-*O*-isopropylidene-6-*O*-methoxymethyl-α-*D*-*erythro*-*D*-*galacto*-octopyranose **11** [δ 5.47 (d, $J_{1,2}$ 5 Hz, H-1)] and the corresponding β-*L*-*threo*-*D*-*galacto* isomer **12** [δ 5.49 (d, $J_{1,2}$ 5 Hz, H-1)] in the ratio ~4:1.

*1,2:3,4-Di-*O*-isopropylidene-α-*D*-erythro-*D*-galacto-octopyranose* (**2**). — A solution of **7** (3.2 g, 8.5 mmol) in acetone–water (8:1, 54 mL) containing *N*-methylmorpholine *N*-oxide monohydrate (2.4 g, 17.8 mmol) and osmium tetraoxide (0.07 g, 0.275 mmol) was stirred at room temperature for 3 h and then diluted with chloroform (300 mL). The resulting solution was washed with 5M hydrochloric acid (15 mL) and saturated, aqueous sodium metabisulphite (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) furnished a mixture (3.22 g, 92%) of 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-*D*-*erythro*-*D*-*galacto*-octopyranose (**8**) [δ 5.49 (d, $J_{1,2}$ 5 Hz, H-1)] and the corresponding β-*L*-*threo*-*D*-*galacto* isomer **9** [δ 5.50 (d, $J_{1,2}$ 5 Hz, H-1)] in the ratio ~5:1.

A solution of the foregoing mixture of **8** and **9** (0.37 g, 0.9 mmol) in anhydrous methanol (20 mL) containing 5% Pd/C (0.6 g) was shaken overnight at room temperature under a slight overpressure of hydrogen, and the catalyst and the solvent were then removed. Chromatography of the residue on silica gel (elution with 2:1 ethyl acetate–methanol) afforded a mixture (0.26 g, 90%) of **2** and **3** (ratio ~5:1). Crystallisation from ethyl acetate–hexane gave **2** (0.195 g, 68%), m.p. 116–117°, $[\alpha]_D$ −61° (*c* 1, chloroform); lit.[2] m.p. 117–118°, $[\alpha]_D$ −61° (*c* 0.75, chloroform). The ^{1}H-n.m.r. and i.r. spectra of **2** were indistinguishable from those of an authentic sample[2].

6-O-Benzyl-1,2:3,4-di-O-isopropylidene-α-D-glycero-D-galacto-heptodialdo-1,5-pyranose (**13**). — Sodium periodate (2.4 g, 11.2 mmol) was added to a stirred solution of a 5:1 mixture of **8** and **9** (3.2 g, 7.8 mmol; prepared from **7**) in 50% aqueous 1,4-dioxane (90 mL), and the resulting suspension was stirred at room temperature for 2 h. Inorganic material was then filtered off, the filtrate was concentrated under reduced pressure, and the residue was extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 50:1 dichloromethane–acetone) gave **13** (2.93 g), b.p. ~155° (bath)/0.05 mmHg, $[\alpha]_D$ −59° (*c* 0.3, chloroform), in essentially quantitative yield. The 360-MHz ^{1}H-n.m.r. spectrum of **13** was identical to that recently reported by Danishefsky and coworkers[18], who used an essentially similar route in the preparation of **13**.

1,2:3,4-Di-O-isopropylidene-β-L-lyxo-D-galacto-nonopyranose (**21**). — A solution of **13** (1.9 g, 5 mmol) in anhydrous benzene (40 mL) containing formylmethylenetriphenylphosphorane[12] (1.8 g, 5.9 mmol) was boiled under reflux for 3 h and then concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave **14** (1.83 g, 90%), $[\alpha]_D$ −48° (*c* 1.6, chloroform), isolated as a pale-yellow syrup that was sufficiently pure for use in subsequent experiments. ^{1}H-N.m.r. data: *inter alia*, δ 9.60 (d, 1 H, $J_{8,9}$ 7 Hz, CHO), ~7.33 (m, 5 H, Ph), 6.97 (dd, 1 H, $J_{6,7}$ 5, $J_{7,8}$ 15.5 Hz, H-7), 6.39 (ddd, 1 H, $J_{6,8}$ ~1.5 Hz, H-8), 5.48 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.58 (s, 2 H, PhCH_2), and 1.44, 1.36, and 1.28 (3 s, ratio 2:1:1, 12 H, 2 CMe_2).

To a cooled (−10°) and stirred solution of **14** (1.2 g, 3 mmol) in anhydrous dichloromethane (10 mL) under nitrogen was gradually added a M solution of diisobutylaluminium hydride in dichloromethane (7 mL, 7 mmol) while the internal temperature was maintained at ~ −5°. The mixture was stirred at 0° for 2 h, the excess of reagent was then decomposed with saturated, aqueous ammonium chloride, and dichloromethane (50 mL) was added. Insoluble material was filtered off through glass wool and washed thoroughly with dichloromethane, and the filtrate and washings were combined, washed with a little water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave **15** (0.85 g, 70.5%), $[\alpha]_D$ −72.5° (*c* 1, chloroform), isolated as a thick syrup. ^{1}H-N.m.r. data (360 MHz), *inter alia*, δ 7.36–7.23 (m, 5 H, Ph), 5.95 (dt, 1 H, $J_{7,8}$ 15, $J_{8,9} = J_{8,9'}$ = 5 Hz, H-8), 5.68 (qt, 1 H, $J_{6,7}$ 7.5, $J_{7,9} = J_{7,9'}$ = 1.5 Hz, H-7), 5.48 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), and 1.49, 1.43, 1.35, and 1.29 (4 s, 12 H, 2 CMe_2).

A solution of **15** (0.85 g, 2.1 mmol) in acetone–water (8:1, 18 mL) containing *N*-methylmorpholine *N*-oxide monohydrate (0.56 g, 4.1 mmol) and osmium tetraoxide (0.026 g, 0.1 mmol) was stirred at room temperature for 3 h, and then processed by the procedure described in an earlier experiment. Chromatography of the residue on silica gel (ethyl acetate) gave a mixture (0.76 g, 82.5%) of 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-*β*-L-*lyxo*-D-*galacto*-nonopyranose (**16**) [δ 5.48 (d, $J_{1,2}$ 5 Hz, H-1)] and the *α*-D-*xylo*-D-*galacto* isomer **17** [δ 5.49 (d, $J_{1,2}$ 5 Hz, H-1)] in the ratio ~8.5:1.

Debenzylation of the foregoing mixture of **16** and **17** (0.76 g, 1.7 mmol) in

anhydrous methanol (40 mL) containing 5% Pd/C (1 g), using the procedure described in an earlier experiment, and chromatography of the residue on silica gel (elution with 2:1 chloroform–methanol) afforded a mixture (0.6 g, 99%) of the debenzylated compounds **21** and **22** in the ratio ~8.5:1. Crystallisation from ethyl acetate–hexane gave **21** (0.48 g, 79%), m.p. 119–120° (after further recrystallisation), $[\alpha]_D$ −52° (*c* 1, methanol) (Found: C, 51.7; H, 7.7. $C_{15}H_{26}O_9$ calc.: C, 51.4; H, 7.5%). ^{1}H-N.m.r. data (CD_3OD): *inter alia*, δ 5.51 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), and 1.56, 1.42, 1.36, and 1.33 (4 s, 12 H, 2 CMe_2).

L-lyxo-L-altro-*Nonitol* (L-lyxo-D-galacto-*nonitol*) (**23**). — A solution of **21** (0.5 g, 1.4 mmol) in trifluoroacetic acid–water (9:1, 10 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 nonose in water (25 mL) was gradually added sodium borohydride (0.27 g, ~7 mmol), and the reaction mixture was stirred at 0° for 3 h and then overnight at room temperature. Amberlite IR-120 (H^+) resin (7 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. The crude nonitol **23** (~0.38 g, ~98%) crystallised upon the addition of ethanol to the residue. Recrystallisation from aqueous methanol gave pure **23**, m.p. 169–171°, $[\alpha]_D$ +2.5° (*c* 0.7, water) (Found: C, 40.0; H, 7.1. $C_9H_{20}O_9$ calc.: C, 39.7; H, 7.4%). ^{13}C-N.m.r. data: δ 71.95, 71.35, 70.74, 70.38, 70.11, 69.15, 69.07, 63.36, and 62.95.

Methyl (E)-*6-O-benzyl-7,8-dideoxy-1,2:3,4-di*-O-*isopropylidene*-α-D-glycero-D-galacto-*non-7-enopyranuronate* (**24**). — A solution of **13** (2.93 g, 7.7 mmol) and (methoxycarbonylmethylene)triphenylphosphorane[16] (2.84 g, 8.5 mmol) in anhydrous methanol (65 mL) was kept at ~4° for 20 h and then concentrated under reduced pressure. Chromatography of the residue on silica gel (ethyl acetate) gave **24** (2.52 g, 75%), m.p. 127–128° (from ethyl acetate–hexane), $[\alpha]_D$ −62.5° (*c* 1, chloroform) (Found: C, 63.4; H, 6.8. $C_{23}H_{30}O_8$ calc.: C, 63.6; H, 7.0%). ^{1}H-N.m.r. data (360 MHz): *inter alia*, δ 7.36–7.25 (m, 5 H, Ph), 7.00 (dd, 1 H, $J_{6,7}$ 5.8, $J_{7,8}$ 15.8 Hz, H-7), 6.13 (dd, 1 H, $J_{6,8}$ 1.3 Hz, H-8), 5.47 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 3.73 (s, 3 H, CO_2Me), and 1.46, 1.44, 1.35, and 1.29 (4 s, 12 H, 2 CMe_2).

The conjugate ester **24**, m.p. and mixture m.p. 127–128°, was isolated in 89% yield when a similar Wittig reaction was conducted in boiling, anhydrous benzene (51 mL) for 3 h and then processed as described above.

Reduction of **24** in tetrahydrofuran with lithium aluminium hydride, in the usual way[2], gave **15** (78%), having a ^{1}H-n.m.r. spectrum indistinguishable from that of the material prepared from the (*E*)-enal **14**.

Methyl *6-O-benzyl-1,2:3,4-di*-O-*isopropylidene*-β-L-lyxo-D-galacto-*nono-pyranuronate* (**25**). — A solution of **24** (0.5 g, 1.15 mmol) in acetone–water (8:1, 18 mL) containing *N*-methylmorpholine *N*-oxide monohydrate (0.3 g, 2.2 mmol) and osmium tetraoxide (0.021 g, 0.08 mmol) was stirred at room temperature for 20 h, and then processed in the usual way. Chromatography of the residue on silica gel (ethyl acetate) gave a mixture (0.52 g, 96%) of **25** [δ 5.50 (d, $J_{1,2}$ 5 Hz, H-1)] and

the α-D-*xylo*-D-*galacto* isomer **26** [δ 5.47 (d, $J_{1,2}$ 5 Hz, H-1)] in the ratio ~17:1. Crystallisation from ethyl acetate–hexane gave **25** (0.41 g, 76%), m.p. 107–108°, $[\alpha]_D$ −44° (*c* 1, chloroform) (Found: C, 59.3; H, 7.0. $C_{23}H_{32}O_{10}$ calc.: C, 59.0; H, 6.9%). ^{1}H-N.m.r. data (360 MHz): *inter alia*, δ 7.36–7.25 (m, 5 H, Ph), 5.50 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.77 (ABq, 2 H, J_{AB} 11 Hz, PhCH_2), 3.78 (s, 3 H, CO_2Me), and 1.52, 1.48, 1.37, and 1.31 (4 s, 12 H, 2 CMe_2).

Reduction of **25** in tetrahydrofuran with lithium aluminium hydride, in the usual way[2], and chromatography of the residue on silica gel (ethyl acetate) gave **16** (71%), having a ^{1}H-n.m.r. spectrum indistinguishable from that of the major isomer obtained on catalytic osmylation of the allylic alcohol **15**. Catalytic debenzylation of **16**, as described earlier, gave **21**, m.p. (from ethyl acetate–hexane) and mixture m.p. 119–120°, in virtually quantitative yield.

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