Higher-carbon Sugars. Part 2.[1] The Synthesis of Some Decitols *via* the Osmylation of Unsaturated Precursors[2]

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Catalytic osmylation of (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranose (**4**) produced a mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranose (**8**) and the α-D-*ido*-D-*galacto* isomer (**9**) in the ratio *ca.* 2.5:1. Acid hydrolysis of the mixture of triacetals (**8**) and (**9**), and reduction of the resulting decoses, permitted the isolation of crystalline L-*galacto*-D-*galacto*-decitol (**10**), which was readily identified by virtue of its C_2-symmetry. By contrast, the corresponding (*Z*)-isomer (**13**) exhibited no diastereofacial selectivity on catalytic osmylation, yielding equal proportions of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*altro*-D-*galacto*-decopyranose (**14**) and the β-L-*gluco*-D-*galacto* isomer (**15**). Catalytic osmylation of (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*threo*-D-*galacto*-dec-8-enopyranose (**23**) afforded a 3:2 mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*galacto*-D-*galacto*-decopyranose (**24**) and the β-L-*ido*-D-*galacto* isomer (**25**). Samples of each of (*meso*)-*galacto*-*galacto*-decitol (**26**) (C_s-symmetry) and L-*galacto*-L-*ido*-decitol (**27**) were obtained following acid hydrolysis of this mixture and reduction of the resulting decoses.

Of those methods used to ascend the aldose series,[3] the Fischer–Kiliani cyanohydrin synthesis has been the most extensively applied to the synthesis of higher-carbon sugars.[4–6] The crowning achievement of this method was the synthesis of D-*gluco*-D-*galacto*-decose from D-glucose, through the intermediate heptose, octose, and nonose sugars.[4,7] The structure of this decose, and therefore that of the decitol (**1**) derived from it, was later inferred[4] from Maltby's generalisation[8] that the newly introduced hydroxy group at C-2 and that at C-4 of the major product have a *threo* arrangement when the precursor cyanohydrin is formed in an acid-catalysed reaction. This stereoselectivity has been rationalised on conformational grounds.[3] Nevertheless, the structures of the decitol (**1**) and a number of other higher-carbon sugars remain unproved, and serve to underline the difficulties likely to be encountered in assigning structures to higher-carbon sugars as the aldose series is ascended. Although D-*gluco*-D-*galacto*-decitol (IUPAC–IUB: L-*galacto*-L-*gulo*-decitol) (**1**) was synthesised over seventy years ago,[7] it remains the only known representative of this group of alditols containing a total of 136 stereoisomers (this number is made up of 128 chiral configurational isomers and 8 *meso* isomers).

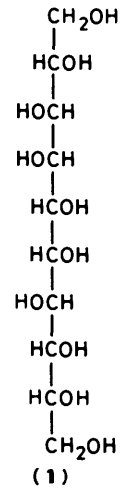
Results and Discussion

We considered that some of the octose derivatives described in the preceding paper might undergo further two-carbon extension, *via* Wittig olefination and osmylation, to give decose derivatives of identifiable stereochemistry. Initially, we set ourselves the task of preparing L-*galacto*-D-*galacto*-decitol (**10**), which could be identified by virtue of its C_2-symmetry, from 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-octodialdo-1,5-pyranose[1] (**2**).† This dialdose derivative reacted with (formylmethylene)triphenylphosphorane[9] in boiling benzene to give the (*E*)-enal (**3**) ($J_{8,9}$ 15 Hz) in excellent yield. Reduction of the (*E*)-enal (**3**) with di-isobutylaluminium hydride in methylene dichloride at 0 °C then gave (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranose (**4**). The work of Kishi and co-workers[10] has provided a good precedent for the key osmylation reaction, notably that catalytic osmylation of the (*E*)-allylic alcohol (**5**) favours the formation of the arabinitol derivative (**6**) over the xylitol derivative (**7**) by a factor of 3 (*i.e.*, the relative stereochemistry between the pre-existing hydroxy or alkoxy group and the adjacent newly introduced hydroxy group of the major product is *erythro*[10]). Catalytic osmylation[11] of the decenopyranose (**4**) produced a mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranose (**8**) and the α-D-*ido*-D-*galacto* isomer (**9**) in the ratio *ca.* 2.5:1 (determined by ^{1}H n.m.r. spectroscopy[1]). The identity of the major stereoisomer (**8**) was established by the isolation of L-*galacto*-D-*galacto*-decitol (**10**), in 47% yield, following acid hydrolysis of the mixture of triacetals (**8**) and (**9**), and reduction of the resulting decoses. In agreement with the C_2-symmetry of the decitol (**10**), only five resonances, of roughly equal intensity, were observed in its ^{13}C n.m.r. spectrum. Although the stereoselectivity for osmylation of the decenopyranose (**4**) is fairly modest, the major isomer is the one predicted by Kishi's empirical rule for osmylation[10] (*vide infra*).

Since (*Z*)-allylic alcohols invariably show a higher stereoselectivity for osmylation than the corresponding (*E*)-isomers,[10] it was of interest to examine the osmylation of (*Z*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranose (**13**). The reaction between the dialdose derivative (**2**) and (methoxycarbonylmethylene)triphenyl phosphorane[12] in methanol at *ca.* 4 °C provided a mixture containing methyl (*Z*)- and (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranuronate [(**11**) and (**12**), respectively]. The (*Z*)-enopyranuronate (**11**) was obtained in 31% yield after crystallisation from hexane. Reduction of the (*Z*)-decenopyranuronate (**11**) with lithium aluminium hydride in tetrahydrofuran (THF) furnished the (*Z*)-decenopyranose (**13**), whose ^{1}H n.m.r. spectrum distinguished it from the (*E*)-isomer (**4**). Contrary to expectation, almost equal proportions of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*altro*-D-*galacto*-decopyranose (**14**) and the β-L-*gluco*-D-*galacto* isomer (**15**) were obtained on catalytic osmylation[11] of the (*Z*)-decenopyranose (**13**). In view of the lack of stereoselectivity of the osmylation reaction, this route was not pursued further.

We also examined the osmylation of (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*threo*-D-*galacto*-dec-8-

† The nomenclature of higher-carbon sugars is discussed in a footnote in the preceding paper.



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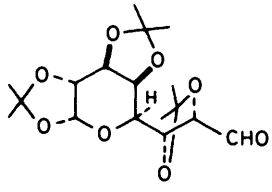

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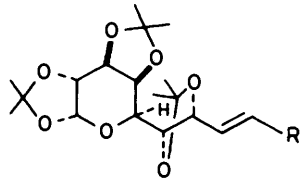
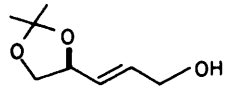


(3) R = CHO
(4) R = CH_2OH



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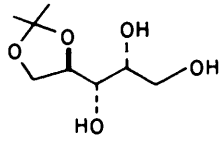

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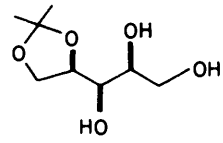

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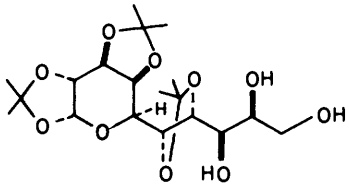

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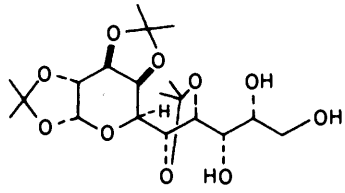

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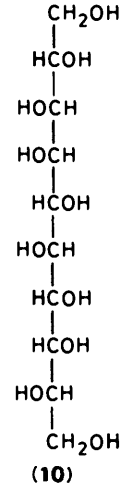

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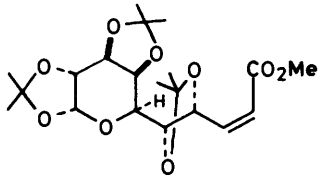

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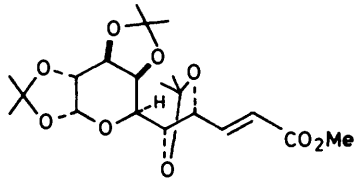

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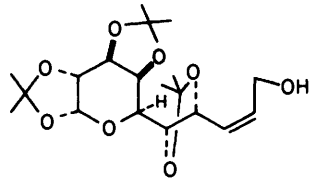

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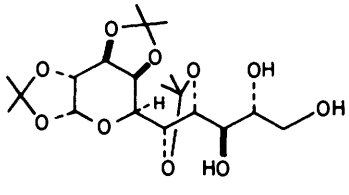

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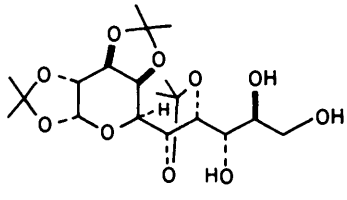
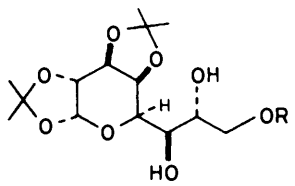
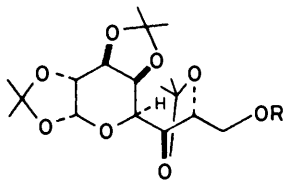


(15)

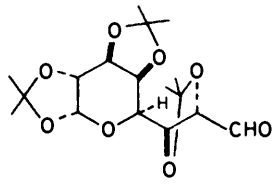
enopyranose (**23**) in the hope that it would lead to a satisfactory synthesis of (*meso*)-*galacto*-*galacto*-decitol (**26**). The decenopyranose (**23**) was prepared from 1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octopyranose (**16**), whose synthesis is described in the preceding paper. The triol (**16**) reacted selectively with chlorodiphenyl-t-butylsilane under standard conditions [13] to give the 8-*O*-(diphenyl-t-butylsilyl) derivative (**17**), which was transformed into the crystalline triacetal (**18**) on exposure to 2-methoxypropene in methylene dichloride containing a catalytic amount of toluene-*p*-sulphonic acid (PTSA). Desilylation of the



(16) R = H
(17) R = $SiPh_2CMe_3$



(18) R = $SiPh_2CMe_3$
(19) R = H



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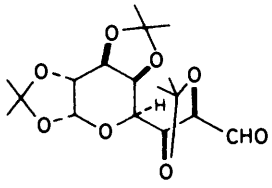

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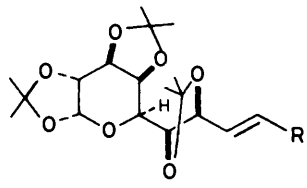
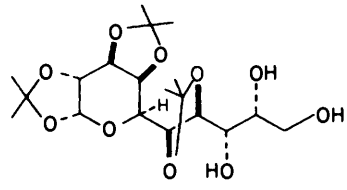


(22) R = CHO
(23) R = CH_2OH



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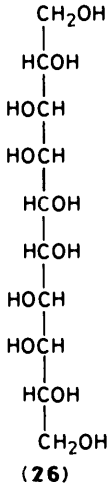

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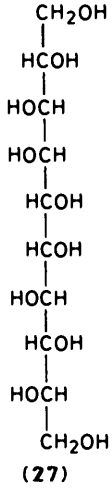

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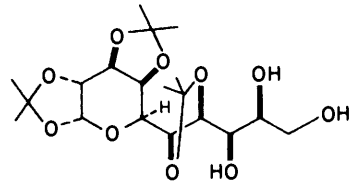

(25)

triacetal (**18**) with tetrabutylammonium fluoride in THF[14] then gave 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octopyranose (**19**). Oxidation of the latter compound with pyridinium chlorochromate (PCC)[15] gave a mixture containing the 6,7-*erythro*- and 6,7-*threo*-aldehyde (**20**) and (**21**), respectively, in the ratio *ca.* 5.5:1 (as judged from ^{1}H n.m.r. spectroscopy). Virtually complete epimerisation of the 6,7-*erythro*-aldehyde (**20**) to the more stable 6,7-*threo*-aldehyde (**21**) was brought about with potassium carbonate in methanol.[16] A Wittig reaction between the 6,7-*threo*-aldehyde (**21**) and (formylmethylene)triphenylphosphorane furnished the (*E*)-enal (**22**) ($J_{8,9}$ 15 Hz), which, on reduction with di-isobutylaluminium hydride in methylene dichloride at 0 °C, gave the (*E*)-decenopyranose (**23**). Catalytic osmylation[11] of the (*E*)-decenopyranose (**23**) produced a mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*galacto*-D-*galacto*-decopyranose (**24**) and the β-L-*ido*-D-*galacto*-isomer (**25**) in the ratio 3:2, but the predominant isomer could not be identified. Kishi's empirical rule for osmylation[10] would predict the preferential formation of the α-D-*galacto*-D-*galacto* isomer (**24**).

Despite the modest stereoselectivity for the osmylation reaction, it was decided to proceed to the decitols (**26**) and (**27**) since, if separable, they could be identified by ^{13}C n.m.r. spectroscopy. Acid hydrolysis of the mixture of triacetals (**24**) and (**25**) liberated the decoses, which were immediately reduced to the decitols (**26**) and (**27**) with sodium borohydride in aqueous solution. The work-up procedure used in isolation of the decitols involved the removal of sodium ions with Amberlite 1R-120(H^+) resin, which was then filtered off and washed. At this stage the filtrate appeared distinctly turbid and flecks of a white solid were observed among the beads of the resin, presumably due to the low solubility of one or both of the decitols in dilute aqueous boric acid. After the solid had been extracted from the resin with water, concentration of the aqueous solution afforded a small quantity of relatively pure (*meso*)-*galacto*-*galacto*-decitol (**26**). The C_s-symmetry of this crystalline decitol was revealed by the presence of only five resonances, of roughly equal intensity, in its ^{13}C n.m.r. spectrum. Concentration of the original filtrate and washings gave, after the removal of boric acid, a mixture (41%) containing the *meso*-decitol (**26**) and L-*galacto*-L-*ido*-decitol (L-*ido*-D-*galacto*-decitol) (**27**). The solubilities of the decitols in methanol were sufficiently different to permit the isolation of a small sample of crystalline L-*galacto*-L-*ido*-decitol (**27**) from the mixture. The structure and purity of the decitol (**27**) were confirmed by its ^{13}C n.m.r. spectrum, which contained ten resonances of roughly equal intensity.

In the preceding paper,[1] the osmylation of unsaturated precursors was shown to provide satisfactory syntheses of a number of octose sugars. The extension of this procedure to the synthesis of decose sugars has met with mixed success. Whereas iterative osmylation has provided an acceptable synthesis of

L-*galacto*-D-*galacto*-decitol (**10**), it has proved much less satisfactory in other cases because the second osmylation reaction exhibited little or no stereoselectivity. That we were able to achieve a partial separation of (*meso*)-*galacto*-*galacto*-decitol (**26**) and L-*galacto*-L-*ido*-decitol (**27**) must be regarded as somewhat fortuitous. We note, however, that the asymmetric epoxidation of allylic alcohols [*e.g.*, (**5**)] proceeds with high stereoselectivity and that a number of simple alditols have been prepared by ring-opening of the resulting epoxides.[17] In this regard, the allylic alcohols (**4**), (**13**), and (**23**) might prove to be useful intermediates *en route* to other decose derivatives.

Experimental

The general methods are described in the preceding paper, except that ^{13}C n.m.r. spectra were recorded in [$^2H_6$]dimethyl sulphoxide at 90 MHz by Edinburgh University n.m.r. service; the spectra were referenced to tetramethylsilane by taking the solvent resonance as δ_C 39.6.

(E)-8,9-*Dideoxy*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-α-D-threo-D-galacto-*dec*-8-*enodialdo*-1,5-*pyranose* (**3**).—A solution of the dialdose derivative[1] (**2**) (0.516 g, 1.44 mmol) in anhydrous benzene (12 ml) containing (formylmethylene)triphenylphosphorane[9] (0.477 g, 1.57 mmol) was heated under reflux for 70 min, cooled, and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (10:1) as eluant] gave the (*E*)-enal (**3**) (0.503 g, 91%), $[\alpha]_D$ −45° (*c* 1 in $CHCl_3$), as a clear syrup; δ_H 9.61 (1 H, d, $J_{9,10}$ 7 Hz, CHO), 6.93 (1 H, dd, $J_{7,8}$ 4, $J_{8,9}$ 15 Hz, 8-H), 6.39 (1 H, ddd, $J_{7,9}$ *ca.* 1 Hz, 9-H), 5.57 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 4.96—3.89 (6 H, m, 2-, 3-, 4-, 5-, 6-, and 7-H), and 1.53, 1.47, 1.44, 1.32, and 1.30 (18 H, 5 × s, ratio 1:1:2:1:1, 3 × CMe_2).

(E)-8,9-*Dideoxy*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-α-D-threo-D-galacto-*dec*-8-*enopyranose* (**4**).—To a cooled (0 °C) and stirred solution of the enal (**3**) (0.8 g, 2.08 mmol) in anhydrous methylene dichloride (5 ml) under nitrogen was gradually added di-isobutylaluminium hydride in methylene dichloride (3.1 ml of a M solution, 3.1 mmol), and the reaction mixture was stirred at 0 °C for 1 h. The excess of the reagent was then destroyed by the careful addition of saturated aqueous ammonium chloride, and the solution was diluted with methylene dichloride (50 ml) and filtered through glass wool. The filtrate was washed with a little water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (2:1) as eluant] gave the (*E*)-decenopyranose (**4**) (0.505 g, 63%), $[\alpha]_D$ −45° (*c* 1.2 in $CHCl_3$), as a viscous syrup; δ_H (*inter alia*) 5.87 (2 H, m, CH=CH), 5.56 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), and 1.53, 1.44, 1.33, and 1.28 (18 H, 4 × s, ratio 1:3:1:1, 3 × CMe_2).

L-galacto-D-galacto-*Decitol* (**10**).—A solution of the (*E*)-decenopyranose (**4**) (1.2 g, 3.1 mmol) in acetone–water (8:1, 16 ml) containing *N*-methylmorpholine *N*-oxide monohydrate (0.84 g, 6.2 mmol) and osmium tetraoxide (0.066 g, 0.26 mmol) was stirred for 2 h at room temperature. Methylene dichloride (100 ml) was then added, and the solution was washed with 5M-hydrochloric acid (3 ml) and was then shaken vigorously with 45% aqueous sodium metabisulphite (6 ml) for a few minutes. After being dried ($MgSO_4$), the solution was concentrated under reduced pressure. Percolation of a solution of the residue in methylene dichloride–acetone (1:2) through silica gel removed the remaining inorganic impurities and, on concentration, gave a mixture (0.964 g, 74%) containing 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranose (**8**) (δ_H 5.62, $J_{1,2}$ 5 Hz, 1-H) and the α-D-*ido*-D-*galacto* isomer (**9**) (δ_H 5.60, $J_{1,2}$ 5 Hz, 1-H) in the ratio *ca.* 2.5:1.

A solution of the triacetals (**8**) and (**9**) (1.2 g, 2.85 mmol) in trifluoroacetic acid (TFA)–water (9:1, 15 ml) was kept at room temperature for 15 min, whereafter it was concentrated under reduced pressure with occasional addition of water. To a cooled (0 °C) solution of the residue in water (48 ml) was gradually added sodium borohydride (0.588 g, 15.5 mmol), and the reaction mixture was stirred for 2 h at 0 °C and then overnight at room temperature. Sodium ions were removed from the reaction mixture with Amberlite IR-120(H^+) resin (20 g), the resin was filtered off and washed thoroughly with water, and the filtrate and washings were combined and concentrated under reduced pressure. Methanol was then added to, and distilled from, the residue several times to remove boric acid. The resulting solid was suspended in a little warm methanol and filtered to give the *decitol* (**10**) (0.402 g, 47%), m.p. 224.5—226 °C (after recrystallisation from aqueous ethanol); $[\alpha]_D$ −0.5 ± 0.2° (*c* 0.8 in H_2O) (Found: C, 39.7; H, 7.2. $C_{10}H_{22}O_{10}$ requires C, 39.7; H, 7.3%); δ_C 70.40, 70.08, 70.06, 69.69, and 63.27.

Methyl (Z)-8,9-*Dideoxy*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-α-D-threo-D-galacto-*dec*-8-*enopyranuronate* (**11**).—(Methoxycarbonylmethylene)triphenylphosphorane[12] (1.84 g, 5.5 mmol) was added gradually to a cooled (4 °C) and stirred solution of the dialdose derivative[1] (**2**) (1.8 g, 5 mmol) in anhydrous methanol (33 ml), and the reaction mixture was stirred at *ca.* 4 °C for 2 h, and was then concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (20:1) as eluant] afforded a mixture (1.75 g, 84%) of the (*Z*)- and (*E*)-decenopyranuronate (**11**) and (**12**). Crystallisation from hexane gave the (*Z*)-*decenopyranuronate* (**11**) (0.641 g, 31%), m.p. 134.5—136 °C (after recrystallisation from hexane); $[\alpha]_D$ −79° (*c* 1.4 in $CHCl_3$) (Found: C, 58.15; H, 7.5. $C_{20}H_{30}O_9$ requires C, 58.0; H, 7.3%); δ_H 6.01 (2 H, m, CH=CH), 5.56 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 4.62—3.78 (6 H, m, 2-, 3-, 4-, 5-, 6-, and 7-H), 3.73 (3 H, s, CO_2Me), and 1.54, 1.46, 1.39, 1.32, and 1.19 (18 H, 5 × s, ratio 1:2:1:1:1, 3 × CMe_2).

(Z)-8,9-*Dideoxy*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-α-D-threo-D-galacto-*dec*-8-*enopyranose* (**13**).—To a stirred solution of the enopyranuronate (**11**) (0.414 g, 1 mmol) in anhydrous THF (6 ml) was gradually added lithium aluminium hydride (0.05 g, *ca.* 1.3 mmol), and the reaction mixture was stirred for 2 h at room temperature. The excess of the reagent was then destroyed with wet ethyl acetate, inorganic material was filtered off and washed thoroughly with ethyl acetate, and the filtrate and washings were combined, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (2:1) as eluant] gave the (*Z*)-allylic alcohol (**13**) (0.312 g, 81%), $[\alpha]_D$ −41° (*c* 1.45 in $CHCl_3$), as a thick syrup; δ_H 5.78 (2 H, m, CH=CH), 5.54 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 4.87 and 4.64—3.79 (8 H, t and m, 2-, 3-, 4-, 5-, 6-, 7-, and 10-H), and 1.51, 1.42 (with shoulder), 1.31, and 1.29 (18 H, 4 × s, ratio 1:3:1:1, 3 × CMe_2). The ^1H n.m.r. spectra readily distinguished between the (*E*)-and (*Z*)-isomer (**4**) and (**13**).

Catalytic Osmylation of (Z)-8,9-*Dideoxy*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-α-D-threo-D-galacto-*dec*-8-*enopyranose* (**13**).—A solution of the decenopyranose (**13**) (0.318 g, 0.82 mmol) in acetone–water (8:1; 4 ml) containing *N*-methylmorpholine *N*-oxide monohydrate (0.223 g, 1.65 mmol) and osmium tetraoxide (0.025 g, 0.098 mmol) was stirred at room temperature for 4.5 h and then processed as described previously. Chromatography of the resulting residue on silica gel [methylene dichloride–acetone (1:2) as eluant] gave an unidentified compound (0.041 g) and then a mixture (0.266 g, 77%) containing almost equal proportions of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*altro*-D-*galacto*-decopyranose (**14**) and the β-L-*gluco*-D-*galacto* isomer

(**15**). The anomeric protons appeared as overlapping doublets centred at δ_H 5.57 and 5.56, each with $J_{1,2}$ 4.7 Hz, in the 360 MHz n.m.r. spectrum of the mixture.

8-O-(*Diphenyl-t-butylsilyl*)-1,2:3,4-*di*-O-*isopropylidene*-α-D-erythro-D-galacto-*octopyranose* (**17**).—A solution of the triol[1] (**16**) (0.16 g, 0.5 mmol) in anhydrous *NN*-dimethylformamide (4 ml) containing imidazole (0.076 g, 1.1 mmol) and chlorodiphenyl-t-butylsilane (0.145 ml, 0.56 mmol) was stirred overnight at room temperature, and was then poured into methylene dichloride (50 ml). The resulting solution was washed successively with dil. hydrochloric acid and water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (10:1) as eluant] gave the silyl derivative (**17**) (0.274 g, 98%), $[\alpha]_D$ −41° (*c* 1.2 in $CHCl_3$), as a syrup; δ_H (*inter alia*) *ca.* 7.50 (10 H, m, 2 × Ph), 5.47 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 1.43, 1.32, 1.27, and 1.24 (12 H, 4 × s, 2 × CMe_2), and 1.04 (9 H, s, CMe_3).

8-O-(*Diphenyl-t-butylsilyl*)-1,2:3,4:6,7-*tri*-O-*isopropylidene*-α-D-erythro-D-galacto-*octopyranose* (**18**).—A solution of the silyl derivative (**17**) (0.27 g, 0.48 mmol) in anhydrous methylene dichloride (5 ml) containing 2-methoxypropene (0.2 ml, 2.1 mmol) and PTSA (0.01 g) was stirred at room temperature for 30 min, and was then diluted with methylene dichloride (25 ml). The solution was washed successively with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (25:1) as eluant] gave the *triacetal* (**18**) (0.212 g, 73%), m.p. 133—135 °C [from light petroleum (b.p. 40—60 °C)]; $[\alpha]_D$ −57° (*c* 0.9 in $CHCl_3$) (Found: C, 66.0; H, 7.9. $C_{33}H_{46}O_8Si$ requires C, 66.2; H, 7.7%); δ_H (*inter alia*) *ca.* 7.53 (10 H, m, 2 × Ph), 5.31 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 1.40, 1.33, and 1.16 (18 H, 3 × s, ratio 4:1:1, 3 × CMe_2), and 1.04 (9 H, s, CMe_3).

1,2:3,4:6,7-*Tri*-O-*isopropylidene*-α-D-erythro-D-galacto-*octopyranose* (**19**).—To a solution of the silyl derivative (**18**) (1.07 g, 1.8 mmol) in anhydrous THF (5 ml) was added a M solution of tetrabutylammonium fluoride in THF (5 ml, 5 mmol), and the reaction mixture was kept overnight and then concentrated under reduced pressure. The residue was extracted with methylene dichloride, and the extract was washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (10:1) as eluant] gave the *alcohol* (**19**) (0.533 g, 83%), m.p. 82—83.5 °C [from light petroleum (b.p. 40—60 °C)]; $[\alpha]_D$ −91.5° (*c* 1.4 in $CHCl_3$) (Found: C, 56.8; H, 7.5. $C_{17}H_{28}O_8$ requires C, 56.65; H, 7.8%); δ_H (*inter alia*) 5.53 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), and 1.58, 1.44, 1.39, and 1.34 (18 H, 4 × s, ratio 1:2:2:1, 3 × CMe_2).

1,2:3,4:6,7-*Tri*-O-*isopropylidene*-β-L-threo-D-galacto-*octodialdo*-1,5-*pyranose* (**21**).—A solution of the alcohol (**19**) (2.99 g, 8.3 mmol) in anhydrous methylene dichloride (43 ml) was added to a stirred solution of PCC[15] (5.4 g, 25 mmol) in anhydrous methylene dichloride (21 ml) containing 3Å molecular sieves[18] (4.27 g) at room temperature. The reaction mixture was stirred at room temperature for 4 h, and was then poured into anhydrous diethyl ether (375 ml). The supernatant solution was decanted from the spent oxidant and concentrated under reduced pressure. The residue was extracted with diethyl ether, and the ethereal solution was filtered and concentrated; this procedure was repeated (with charcoaling). Percolation of a solution of the residue in methylene dichloride–acetone (20:1) through silica gel removed the remaining inorganic impurities to give a mixture (2.01 g, 68%) containing the aldehydes (**20**) and (**21**) in the ratio *ca.* 5.5:1; δ_H (major isomer) 9.77 (1 H, s, CHO), 5.49 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), and 1.57, 1.52, 1.47, 1.42, 1.38, and 1.33 (18 H, 6 × s, 3 × CMe_2).

A solution of the foregoing aldehydes (0.485 g, 1.35 mmol) in anhydrous methanol (9 ml) containing anhydrous potassium carbonate (0.64 g, 4.6 mmol) was stirred at room temperature for 2.5 h and then filtered. The filtrate was neutralised with saturated aqueous ammonium chloride, and was then concentrated under reduced pressure. The residue was extracted with chloroform, and the extract was washed with a little water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (15:1) as eluant] gave the 6,7-*threo*-aldehyde (**21**) (0.362 g, 75%), $[\alpha]_D$ −62° (*c* 1.3 in $CHCl_3$), as a clear syrup; δ_H 9.75 (1 H, s, CHO), 5.56 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 4.76—4.29 and 3.81 (6 H, m and dd, 2-, 3-, 4-, 5-, 6-, and 7-H), and 1.56, 1.53, 1.51, 1.47, 1.42, and 1.40 (18 H, 6 × s, 3 × CMe_2).

(E)-8,9-*Dideoxy*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-β-L-threo-D-galacto-*dec*-8-*enodialdo*-1,5-*pyranose* (**22**).—A solution of the dialdose derivative (**21**) (0.72 g, 2 mmol) in anhydrous benzene (15 ml) containing (formylmethylene)triphenylphosphorane[9] (0.682g, 2.24 mmol) was heated under reflux for 2.5 h, whereafter it was processed as described in the preparation of compound (**3**). Chromatography of the residue on silica gel [methylene dichloride–acetone (20:1) as eluant] gave the (*E*)-enal (**22**) (0.595 g, 77%), $[\alpha]_D$ −101° (*c* 1.4 in $CHCl_3$), as a syrup; δ_H (*inter alia*) 9.60 (1 H, d, $J_{9,10}$ 7 Hz, CHO), 6.93 (1 H, dd, $J_{7,8}$ 4, $J_{8,9}$ 15 Hz, 8-H), 6.40 (1 H, ddd, $J_{7,9}$ *ca.* 1 Hz, 9-H), 5.51 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), and 1.53, 1.46, and 1.36 (18 H, 3 × s, ratio 1:3:2, 3 × CMe_2).

(E)-8,9-*Dideoxy*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-β-L-threo-D-galacto-*dec*-8-*enopyranose* (**23**).—This *compound*, $[\alpha]_D$ −75.5° (*c* 1.2 in $CHCl_3$), was prepared from the (*E*)-enal (**22**), in 65% yield, essentially as described for the isomeric compound (**4**); δ_H (*inter alia*) 5.91 (2 H, m, CH=CH), 5.48 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), and 1.53, 1.44, 1.40, 1.34, and 1.32 (18 H, 5 × s, ratio 1:2:1:1:1, 3 × CMe_2).

(meso)-galacto-galacto-*Decitol* (**26**) and L-galacto-L-ido-*Decitol* (**27**).—A solution of the (*E*)-decenopyranose (**23**) (0.48 g, 1.24 mmol) in acetone–water (8:1; 6.25 ml) containing *N*-methylmorpholine *N*-oxide monohydrate (0.336 g, 2.48 mmol) and osmium tetraoxide (0.035 g, 0.14 mmol) was stirred at room temperature for 2 h. Processing and chromatography, as described previously, afforded a mixture (0.396 g, 76%) containing 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*galacto*-D-*galacto*-decopyranose (**24**) (δ_H 5.54, $J_{1,2}$ 5 Hz, 1-H) and the β-L-*ido*-D-*galacto* isomer (**25**) (δ_H 5.52, $J_{1,2}$ 5 Hz, 1-H) in the ratio *ca.* 3:2.

A solution of the triacetals (**24**) and (**25**) (0.39 g, 0.93 mmol) in TFA–water (9:1; 5 ml) was kept at room temperature for 20 min, and was then concentrated under reduced pressure with occasional addition of water. To a cooled (0 °C) solution of the residue in water (15 ml) was gradually added sodium borohydride (0.2 g, 5.3 mmol), and the reaction mixture was stirred for 2 h at 0 °C and for 3 h at room temperature. Water (20 ml) was then added and the solution was stirred with Amberlite IR-120(H^+) resin (7 g) for 30 min to remove sodium ions. The resin was filtered off (Buchner funnel), washed with hot water (*ca.* 100 ml), and retained for further washing (see below). The filtrate (which was distinctly turbid) and washings were combined and concentrated under reduced pressure. The residue was freed from boric acid as before by use of methanol to give a solid (0.114 g, 41%) composed of the decitols (**26**) and (**27**); the presence of both alditols was readily apparent from the ^{13}C n.m.r. spectrum. The solid was extracted with a small volume of hot methanol and the undissolved material was filtered off. After a time, the methanolic solution deposited

crystals of L-*galacto*-L-*ido*-decitol (**27**) (11 mg, 4%), m.p. 181—184 °C (Found: C, 39.6; H, 7.1. $C_{10}H_{22}O_{10}$ requires C, 39.7; H, 7.3%); δ_C 72.21, 71.61, 70.73, 70.43, 69.66, 69.55, 68.67, 68.55, 63.34, and 62.95.

Inspection of the acid resin revealed flecks of a white solid adhering to the beads. A suspension of the resin in water (100 ml) was stirred for 30 min at room temperature, the resin was filtered off, and the filtrate was concentrated under reduced pressure. Methanol was distilled several times from the residue, and the resulting solid was suspended in warm methanol and filtered to give essentially pure (>95%) (meso)-galacto-galacto-*decitol* (**26**) (24 mg, 8.5%), m.p. > 280 °C (decomp.) (Found: C, 39.55; H, 7.3%); δ_C 70.46, 69.77, 68.81, 68.71, and 63.34. ^{13}C N.m.r. spectroscopy revealed a trace of the decitol (**27**) as the principal impurity.

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