Higher-carbon Sugars. Part 8.[1] The Synthesis of Some Decitols *via* the Epoxidation of Unsaturated Precursors[2]

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Sharpless epoxidation of (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranose (**3**) with di-isopropyl L-(+)-tartrate as the chiral auxiliary furnished a mixture of 8,9-anhydro-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranose (**10**) (isolated in 63% yield) and the α-D-*ido*-D-*galacto* isomer (**11**) in the ratio ~5:1. Base-catalysed hydrolysis of the epoxy alcohol (**10**) gave, *via* preferential ring-opening of the Payne-rearrangement product (**12**), 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*altro*-D-*galacto*-decopyranose (**8**), which yielded D-*altro*-D-*galacto*-decitol (**13**) following acidic hydrolysis and reduction of the resulting decose. The epoxy alcohol (**11**) was the principal product obtained on Sharpless epoxidation of the decenopyranose (**3**) with di-isopropyl D-(−)-tartrate as the chiral auxiliary, and was similarly transformed into L-*gluco*-D-*galacto*-decitol (L-*galacto*-D-*gulo*-decitol) (**16**). The same strategy was also used in the synthesis of D-*gluco*-D-*galacto*-decitol (L-*galacto*-L-*gulo*-decitol) (**1**) and L-*altro*-D-*galacto*-decitol (**25**) from (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*threo*-D-*galacto*-dec-8-enopyranose (**18**).

In 1912, Philippe[3] reported a successful application of the cyanohydrin procedure to an amorphous nonose, previously synthesized from D-glucose by Fischer,[4] by ascending the series to two 'D-glucodeconic lactones', one of which was reduced to a crystalline decose (the so-called D-α,α,α,α-glucodecose†). Although none of the higher-carbon sugars isolated in this ascent of the series was identified, it remains to this day at the pinnacle of achievement of the cyanohydrin procedure. From a knowledge of the structure of the preceding octose (D-α,α-gluco-octose ≡ D-*erythro*-L-*galacto*-octose) and by invoking Maltby's generalization[5] (*i.e.*, in the cyanohydrin synthesis, the more abundant epimer has 2-OH and 4-OH in the *threo* relationship), Hudson[6] later deduced that the amorphous nonose probably has the D-*arabino*-D-*manno* configuration, and that the more abundant of the decoses derived from it is most likely to be D-*gluco*-D-*galacto*-decose. The crystalline decitol obtained[3] on reduction of this decose would therefore be D-*gluco*-D-*galacto*-decitol (IUPAC–IUB: L-*galacto*-L-*gulo*-decitol) (**1**), which, until very recently, was the only member of the decitols in existence.[7] That the structures of the decitol (**1**) and a number of other higher-carbon sugars have never been rigorously proved serves to underline the difficulties of identification likely to be encountered as the sugar series is ascended.[6,7] Needless to say, the synthesis of higher-carbon sugars would be far less daunting if new stereocentres could be introduced in a predictable and controlled manner.

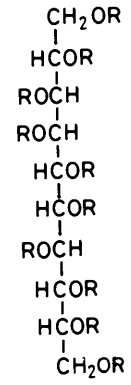
With this in mind, we set out first to examine the stereochemical outcome of the catalytic osmylation of 7-,[8] 8-,[9] 9-,[1] and 10-carbon[10] unsaturated sugars in the light of Kishi's empirical rule.‡[11] Of particular relevance to the synthesis of decitols was that, in conformity with Kishi's formulation,[11] catalytic osmylation of (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranose (**3**) provided a mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranose (**4**) (7-OH and 8-OH are *erythro*) and the α-D-*ido*-D-*galacto* isomer (**5**) in the ratio ~2.5:1.[10] The triol (**4**) was subsequently transformed into L-*galacto*-D-*galacto*-decitol (**6**). The capriciousness of the osmylation reaction was revealed when the isomeric (*Z*)-decenopyranose (**7**), which might be expected[11] to display greater diastereofacial selectivity than the (*E*)-isomer (**3**) towards osmylation, yielded equal proportions of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*altro*-D-*galacto*-decopyranose (**8**) (predicted to be the major product by Kishi's formulation[11]) and the β-L-*gluco*-D-*galacto* isomer (**9**).[10] The lack of selectivity in this reaction was not only unfortunate from a synthetic viewpoint, but also precluded a tentative assignment of structure to the individual isomers on the basis of Kishi's empirical rule. It was necessary, therefore, to seek an alternative route to the triols (**8**) and (**9**) *via* Sharpless epoxidation[12] of the (*E*)-decenopyranose (**3**).[10] Since both the (*E*)-decenopyranose (**3**) [and later (**18**)] and the epoxidising reagent[12] are chiral, the usual considerations pertaining to double asymmetric induction[13] should apply. The stereoselectivity of asymmetric epoxidation of the (*E*)-decenopyranose (**3**) can be predicted from the Sharpless model,[12] provided the diastereofacial selectivity of the chiral epoxidising reagent is large enough to outweigh that of the substrate (*i.e.*, the reaction is reagent controlled), while the stereo- and regio-chemistry of base-catalysed hydrolysis of the resulting epoxy alcohols, involving the well documented Payne rearrangement,[14] should also follow a predictable course.[15]

† The forebears of Philippe's D-α,α,α,α-glucodecose were D-α-glucoheptose, D-α,α-gluco-octose, and D-α,α,α-gluconononose, the α designation being given to the more abundant of the two epimers produced in the cyanohydrin synthesis.

‡ Kishi's empirical rule for osmylation states that the relative stereochemistry between the pre-existing hydroxy or alkoxy group and the adjacent, newly introduced hydroxy group of the major product is *erythro*.[11] The addition of osmium tetraoxide to the olefinic linkage can also be regarded as *anti* with respect to the pre-existing hydroxy (alkoxy) group.

Results and Discussion

Sharpless epoxidation[12] of the (*E*)-decenopyranose (**3**) with di-isopropyl L-(+)-tartrate [(+)-DIPT] as the chiral auxiliary at −23 °C for 5 days gave a mixture of 8,9-anhydro-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranose (**10**) (isolated in 63% yield) and the α-D-*ido*-D-*galacto* isomer (**11**) in the ratio ~5:1, respectively. In this and subsequent epoxidations, the ratios of the products were determined by integration over the resonances for the anomeric protons in the



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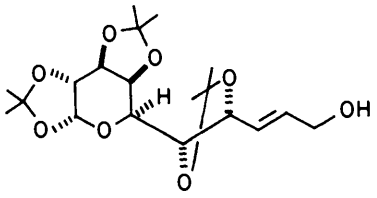
(2) R = Ac



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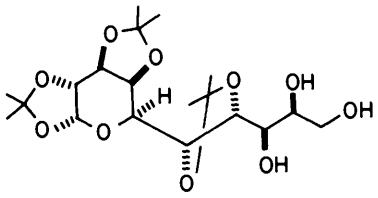

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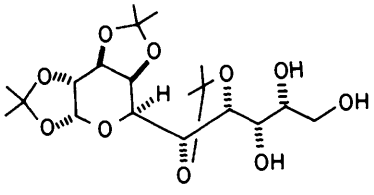

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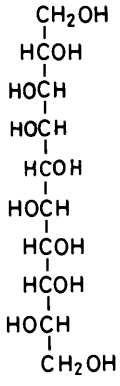

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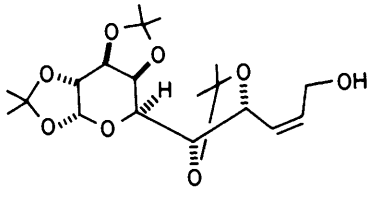

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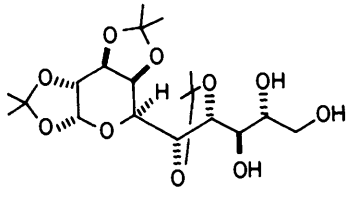

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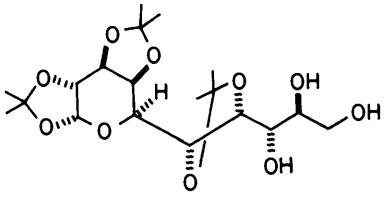

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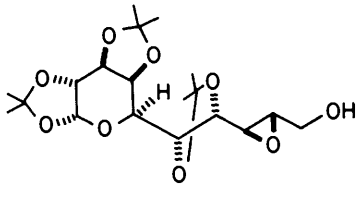

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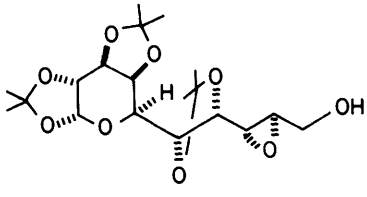

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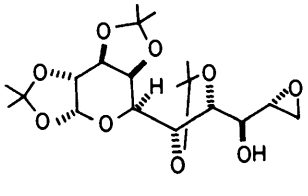

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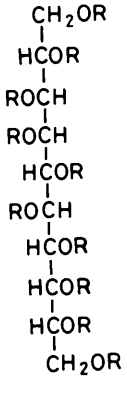
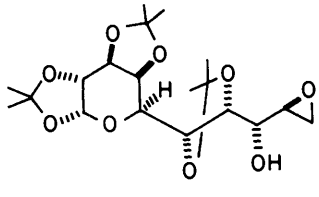


(13) R = H
(14) R = Ac



(15)

360 MHz ^{1}H n.m.r. spectra. The structure assigned to the epoxy alcohol (**10**) on the basis of the Sharpless model[12] was reinforced when similar epoxidation of the (*E*)-decenopyranose (**3**) with di-isopropyl D-(−)-tartrate [(−)-DIPT] as the chiral auxiliary furnished a mixture containing the isomeric epoxy alcohol (**11**) as the preponderant product [ratio (**11**):(**10**) ~ 4:1]. The degree of stereochemical control exerted in the reactions of the chiral epoxidising reagents and the decenopyranose (**3**) was not nearly so marked as with other chiral substrates, for which values in excess of 20:1 have been

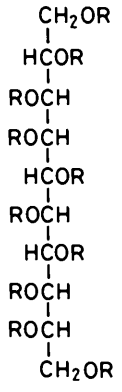
recorded,[15] but it is of the same order of magnitude as that of a closely related system (see later).

Hydrolysis of the epoxy alcohol (**10**) with sodium hydroxide in aqueous 1,4-dioxane at 70 °C yielded the triol (**8**), which, by analogy,[15] was considered to be formed by preferential opening of the epoxide (**12**) [the product of a Payne rearrangement[14] of (**10**) *in situ*] at the terminal position with hydroxide ion. Acidic hydrolysis of the triol (**8**) and reduction of the resulting decose then gave D-*altro*-D-*galacto*-decitol (**13**), which was characterised as the deca-acetate (**14**). Although neither of the compounds (**13**) and (**14**) is crystalline, their ^{13}C n.m.r. spectra were entirely compatible with the structures assigned, and the presence of ten acetoxy groups in the deca-acetate (**14**) was demonstrated convincingly by 360 MHz ^1H n.m.r. spectroscopy (see Experimental section).

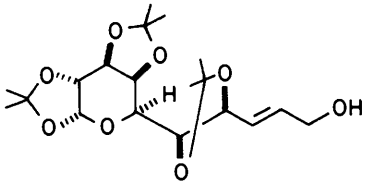
Basic hydrolysis of the mixture of epoxy alcohols enriched in the α-D-*ido*-D-*galacto* isomer (**11**) gave, *via* preferential ring-opening of the Payne-rearrangement[14] product (**15**) at the terminal position with hydroxide ion,[15] 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*gluco*-D-*galacto*-decopyranose (**9**). This product was contaminated (≤ 20%) with the isomeric triol (**8**), most of which would have been formed from the epoxy alcohol (**10**) present in the original mixture. Acidic hydrolysis of the triol (**9**) and reduction of the resulting decose gave L-*gluco*-D-*galacto*-decitol (IUPAC–IUB: L-*galacto*-D-*gulo*-decitol) (**16**), which was characterised as the deca-acetate (**17**). Compounds (**16**) and (**17**) are crystalline, and their spectroscopic properties (see Experimental section) were in accord with the structures assigned; in particular, ten acetoxy resonances were visible in the 360 MHz ^1H n.m.r. spectrum of the deca-acetate (**17**).

The foregoing results indicated that it should be possible to synthesize D-*gluco*-D-*galacto*-decitol (**1**) from (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*threo*-D-*galacto*-dec-8-enopyranose (**18**), which has also become available by chain-extension of the non-reducing end of a D-galactose derivative.[10] Such a synthesis would finally settle the structure of D-*gluco*-D-*galacto*-decitol (**1**), which would then have been elaborated in a complementary fashion from both D-glucose[3] and D-galactose, without disruption of the original stereocentres.

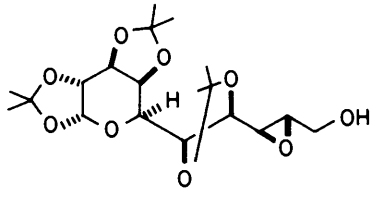
Sharpless epoxidation[12] of the (*E*)-decenopyranose[10] (**18**)



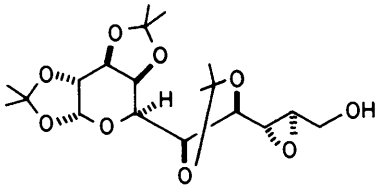
(**16**) R = H
(**17**) R = Ac



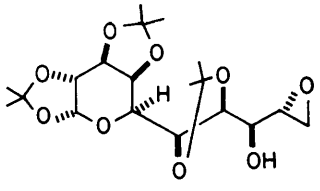
(**18**)



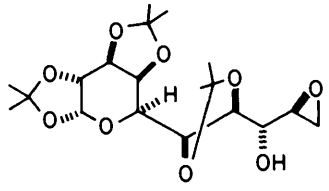
(**19**)



(**20**)



(**21**)



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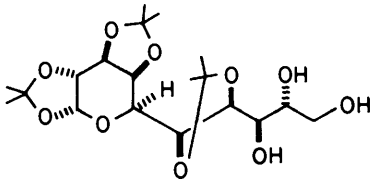
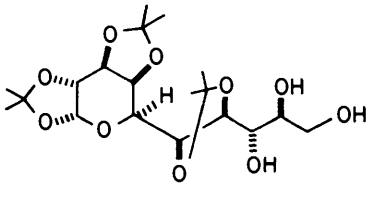
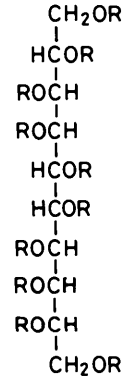


(**23**)



(**24**)



(**25**) R = H
(**26**) R = Ac

with (+)-DIPT as the chiral auxiliary at −23 °C for 4 days provided mixture of 8,9-anhydro-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*ido*-D-*galacto*-decopyranose (**19**) and the α-D-*galacto*-D-*galacto* isomer (**20**) in the ratio ~4:1, respectively. The subsequent chemistry confirmed these assignments, which were based initially on the Sharpless model.[12] Basic hydrolysis of the mixture of the epoxy alcohols (**19**) and (**20**) gave an inseparable mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*gluco*-D-*galacto*-decopyranose (**23**) and the β-L-*altro*-D-*galacto* isomer (**24**) in the ratio ~5:1, formed mostly *via* the Payne-rearrangement[14] products (**21**) and (**22**), respectively. The slight increase in the proportion of the major isomer from that present originally is likely to reflect the extent of ring-opening of the minor epoxy alcohol (**20**) at C-8, with inversion of the configuration at this centre (see below). Acidic hydrolysis of the triols (**23**) and (**24**), and reduction of the resulting decoses, permitted the isolation of D-*gluco*-D-*galacto*-decitol (**1**) in 70% yield. The physical constants of this decitol and its crystalline deca-acetate (**2**), whose structures are now confirmed, were in good agreement with literature values.[3]

With (−)-DIPT as the chiral auxiliary, Sharpless epoxidation[12] of the (*E*)-decenopyranose[10] (**18**) at −23 °C gave, after 4 days, a mixture of 8,9-anhydro-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*galacto*-D-*galacto*-decopyranose (**20**) and the β-L-*ido*-D-*galacto* isomer (**19**) (≤10%), from which the former crystallised in 61% yield. Basic hydrolysis of the epoxy alcohol (**20**) furnished a mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*altro*-D-*galacto*-decopyranose (**24**) [formed *via* the Payne-rearrangement[14] product (**22**)] and the α-D-*gluco*-D-*galacto* isomer (**23**) [formed directly from the epoxy alcohol (**20**)] in the ratio ~6:1, respectively. Acidic hydrolysis of this mixture of triols and reduction of the resulting decoses gave crystalline L-*altro*-D-*galacto*-decitol (**25**), whose ^{13}C n.m.r. spectrum was compatible with the structure assigned and distinguishable from that of D-*gluco*-D-*galacto*-decitol (**1**). Acetylation of L-*altro*-D-*galacto*-decitol (**25**) furnished the amorphous deca-acetate (**26**), whose ^{1}H and ^{13}C n.m.r. spectra firmly established the presence of ten acetoxy groups in the molecule.

The comparatively modest selectivities obtained on asymmetric epoxidation of the (*E*)-decenopyranoses (**3**) and (**18**) are compensated to some extent by the versatility of this approach. Each of the (*E*)-decenopyranoses has been transformed stereoselectively and without difficulty into two decitols of predictable stereochemistry, and further diversification may be possible using procedures employed jointly by Sharpless[12] and Masamune[13] in the synthesis of lower monosaccharides.

Experimental

T.l.c. was performed on Kieselgel G, and spots were detected with 1% aqueous sulphuric acid. ^{1}H N.m.r. spectra were recorded for solutions in deuteriochloroform (internal tetramethylsilane) at 360 MHz by Edinburgh University n.m.r. service. ^{13}C N.m.r. spectra were recorded for solutions in [$^{2}H_6$]-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. A Perkin-Elmer Model 141 automatic polarimeter and 1 dm tubes were used for the measurement of specific optical rotations. M.p.s were measured on a Reichert hot-plate apparatus and are uncorrected.

3M-t-Butyl hydroperoxide refers to a solution in toluene. 1,4-Dioxane and 0.5M-sodium hydroxide used for hydrolysis of the epoxy alcohols were deoxygenated prior to use by the passage of a rapid stream of nitrogen for at least 30 min.

The experimental and chromatographic procedures used in the synthesis of D-*altro*-D-*galacto*-decitol (**13**) are typical of those used in the synthesis of the other decitols.

8,9-*Anhydro*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-β-L-galacto-D-galacto-*decopyranose* (**10**).—A 100 ml round-bottom flask equipped with a Teflon-coated bar magnet was oven-dried and then fitted with a serum cap and flushed with nitrogen. The flask was charged with anhydrous methylene dichloride (40 ml, distilled from calcium hydride) and cooled to −23 °C (solid CO_2–carbon tetrachloride). Titanium(IV) isopropoxide (1.77 ml, 6.77 mmol) and a solution of (+)-DIPT (1.75 g, 7.47 mmol) in anhydrous methylene dichloride (2 ml) were then added in turn by syringe, and the mixture was stirred for 5—10 min prior to the addition of solutions of the (*E*)-decenopyranose (**3**)[10] (1.9 g, 4.92 mmol) in anhydrous methylene dichloride (5 ml) and 3M-t-butyl hydroperoxide (5 ml, 15 mmol). The flask was then stoppered and kept for 5 days in a freezer at −23 °C. It was then placed in a cooling bath at −23 °C, and 10% aqueous tartaric acid (16 ml) was added to the stirred solution. The mixture, containing the solidified aqueous layer, was stirred at −23 °C for 30 min and then at room temperature for 1 h. After dilution with methylene dichloride, the organic layer was separated, washed with a little water, dried (Na_2SO_4), and concentrated under reduced pressure. A solution of the residue in diethyl ether (48 ml) was cooled (0 °C) and stirred with M-sodium hydroxide (19.2 ml) for 30 min. More diethyl ether was then added, and the ethereal layer was separated, washed with a little aqueous sodium chloride, dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (2:1) as eluant] furnished a mixture of the epoxy alcohols (**10**) and (**11**) in the ratio ~5:1, respectively. Crystallisation from diethyl ether–hexane gave the *epoxy alcohol* (**10**) (1.25 g, 63%), m.p. 128—128.5 °C; $[\alpha]_D$ −58° (*c* 0.9 in $CHCl_3$) (Found: C, 56.4; H, 7.5. $C_{19}H_{30}O_9$ requires C, 56.7; H, 7.5%); δ_H 5.52 (1 H, d, $J_{1,2}$ 4.9 Hz, 1-H), 3.19 (2 H, m, CH–CHO), and 1.47, 1.41, 1.38, 1.37, and 1.28 (18 H, 5 s, proportions 1:1:1:1:2, 3 × CMe_2).

1,2:3,4:6,7-*Tri*-O-*isopropylidene*-α-D-altro-D-galacto-*decopyranose* (**8**).—A solution of the epoxy alcohol (**10**) (0.3 g, 0.745 mmol) in 0.5M-sodium hydroxide (4 ml) and 1,4-dioxane (0.5 ml; if necessary, more co-solvent may be added to effect solution) was heated at 70 °C for 22 h. It was then diluted with water, neutralised with Amberlite IR-120(H^+) resin (1 g), and concentrated under reduced pressure. The residue was extracted with chloroform, and the extract was dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (1:1) as eluant] gave the *triol* (**8**) (0.198 g, 63%), $[\alpha]_D$ −50° (*c* 1.3 in $CHCl_3$) (Found: C, 54.6; H, 7.9. $C_{19}H_{32}O_{10}$ requires C, 54.3; H, 7.7%); δ_H 5.56 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), and 1.49, 1.45, 1.40, 1.31, and 1.30 (18 H, 5 s, proportions 1:1:2:1:1, 3 × CMe_2).

D-altro-D-galacto-*Decitol* (**13**).—A solution of the decopyranose (**8**) (0.436 g, 1.04 mmol) in trifluoroacetic acid–water (9:1; 6 ml) was kept for 15 min at room temperature and then concentrated under reduced pressure with occasional additions of water. To a cooled (0 °C) and stirred solution of the residue in water (16 ml) was gradually added sodium borohydride (0.2 g, ~5.3 mmol), and the reaction mixture was stirred at 0 °C for 2 h and then overnight at room temperature. Sodium ions were removed with Amberlite IR-120(H^+) resin (7 g), the resin was filtered off and washed thoroughly with water, and the filtrate and washings were combined and concentrated under reduced pressure. Several distillations of methanol from the residue removed boric acid and left the decitol (**13**) (0.288 g, 92%), $[\alpha]_D$ ~ +0.6° (*c* 2.3 in H_2O), as a syrup probably contaminated with ≤2% boric acid.[16] The ^{13}C n.m.r. spectrum of the decitol (**13**) exhibited ten resonances, of roughly equal intensity, at δ_C 73.24, 71.84, 71.37, 70.79, 70.07, 69.92, 69.68, 69.38, 63.22, and 62.84.

D-altro-D-galacto-*Decitol Deca-acetate* (**14**).—A solution of the decitol (**13**) (0.315 g, 1.04 mmol) in pyridine (15 ml) and acetic anhydride (12 ml) was heated at 100 °C for 3 h. After being cooled, the solution was poured into water and the aqueous solution was extracted with chloroform. The extract was washed successively with dil. hydrochloric acid, saturated aqueous sodium hydrogen carbonate, 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 *deca-acetate* (**14**) (0.55 g, 73%), $[\alpha]_D$ +27° (*c* 1.3 in $CHCl_3$), as a syrup (Found: C, 49.7; H, 6.0. $C_{30}H_{42}O_{20}$ requires C, 49.9; H, 5.9%); δ_H 2.222, 2.111, 2.090, 2.047, 2.020, 2.012, 1.982, 1.979, 1.969, and 1.963 (30 H, 10 s, 10 × OAc); δ_C 170.32, 170.30, 170.24, 170.18, 170.10, 169.81, 169.57, 169.55, 169.50, and 169.17 (C=O groups), 70.00, 68.28, 67.70, 67.56, 67.48 (× 2), 67.00, 66.74, 62.14, and 61.45 (chain-carbon atoms), and 20.53, 20.48 (× 3), 20.44, 20.38, 20.35, 20.31, 20.22, and 20.19 (Me groups).

L-galacto-D-gulo-*Decitol* (**16**).—Using the standard procedure, Sharpless epoxidation of the (*E*)-decenopyranose[10] (**3**) (2.295 g, 5.94 mmol) with titanium(IV) isopropoxide (2.26 ml, 8.65 mmol), (−)-DIPT (2.23 g, 9.52 mmol), and 3M-t-butyl hydroperoxide (6.4 ml, 19.2 mmol) in anhydrous methylene dichloride (total volume 56 ml) at −23 °C for 6 days produced an inseparable mixture (1.69 g, 71%) of 8,9-anhydro-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*ido*-D-*galacto*-decopyranose (**11**) and the β-L-*galacto*-D-*galacto* isomer (**10**) in the ratio ~4:1, respectively; δ_H [for (**11**)] 5.51 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), ~3.09 (2 H, m, CH–CHO), and 1.47, 1.41, 1.40, 1.38, and 1.28 (18 H, 5 s, proportions 1:1:1:1:2, 3 × CMe_2).

Base-catalysed hydrolysis of the foregoing mixture of epoxy alcohols (1.69 g, 3.98 mmol) in 0.5M-sodium hydroxide (34 ml) and 1,4-dioxane (7 ml) at 70 °C for 24 h gave, after the usual work-up and chromatography, a mixture (0.85 g, 51%) of 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*gluco*-D-*galacto*-decopyranose (**9**) and the α-D-*altro*-D-*galacto* isomer (**8**) in the ratio ~4:1, respectively; δ_H [for (**9**)] 5.54 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), and 1.49, 1.43, 1.41, 1.30, and 1.29 (18 H, 5 s, proportions 1:2:1:1:1, 3 × CMe_2).

Hydrolysis of the foregoing mixture of triols (0.63 g, 1.5 mmol) with trifluoroacetic acid–water (9:1; 8.6 ml), and reduction of the resulting decoses in water (23 ml) with sodium borohydride (0.288 g, ~7.6 mmol) gave the crystalline *decitol* (**16**) (0.17 g, 37%), following trituration of the final residue with methanol and warming. After recrystallisation from aqueous ethanol, L-galacto-D-gulo-*decitol* (**16**) had m.p. 155—156.5 °C; $[\alpha]_D$ −2° (*c* 1 in H_2O) (Found: C, 39.6; H, 7.2. $C_{10}H_{22}O_{10}$ requires C, 39.7; H, 7.3%); δ_C 75.24, 72.77, 71.49, 71.39, 70.03, 69.45, 68.74, 68.68, 63.53, and 63.35.

L-galacto-D-gulo-*Decitol Deca-acetate* (**17**).—Acetylation of the decitol (**16**) (0.06 g, ~0.2 mmol) in pyridine (3 ml) and acetic anhydride (2.4 ml) at 100 °C for 3 h gave, after the usual work-up and chromatography, the *deca-acetate* (**17**) (0.102 g, 71%), m.p. 139—141 °C (from diethyl ether–hexane); $[\alpha]_D$ −23° (*c* 1 in $CHCl_3$) (Found: C, 50.0; H, 5.6. $C_{30}H_{42}O_{20}$ requires C, 49.9; H, 5.9%); δ_H 2.103, 2.097, 2.079, 2.064, 2.049, 2.037, 2.030, 2.009, 1.983, and 1.970 (30 H, 10 s, 10 × OAc); δ_C 170.64, 170.27, 170.21 (× 2), 169.78 (× 2), 169.71, 169.57, 169.51, and 169.32 (C=O groups), 69.71, 69.23, 68.54, 68.19, 67.69, 67.36 (× 2), 67.09, 62.15, and 61.35 (chain-carbon atoms), and 20.61, 20.49, 20.43 (× 4), 20.38, 20.34, 20.23, and 20.21 (Me groups).

L-galacto-L-gulo-*Decitol* (**1**).—Using the standard procedure, Sharpless epoxidation of the (*E*)-decenopyranose[10] (**18**) (1.71 g, 4.42 mmol) with titanium(IV) isopropoxide (1.68 ml, 6.43 mmol), (+)-DIPT (1.66 g, 7.09 mmol), and 3M-t-butyl hydroperoxide (4.8 ml, 14.4 mmol) in anhydrous methylene dichloride (total volume 36 ml) at −23 °C for 4 days gave, after work-up and chromatography, a mixture (1.42 g, 80%) of 8,9-anhydro-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*ido*-D-*galacto*-decopyranose (**19**) and the α-D-*galacto*-D-*galacto* isomer (**20**) in the ratio ~4:1, respectively; δ_H [for (**19**)] 5.43 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 3.19 and 3.12 (2 H, m, CH–CHO), and 1.47, 1.42, 1.35, 1.33, and 1.29 (18 H, 5 s, proportions 1:2:1:1:1, 3 × CMe_2).

Base-catalysed hydrolysis of the foregoing mixture of epoxy alcohols (1.3 g, 3.23 mmol) in 0.5M-sodium hydroxide (29 ml) and 1,4-dioxane (6 ml) at 70 °C for 26 h gave, after the usual work-up and chromatography, a mixture (0.57 g, 42%) of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*gluco*-D-*galacto*-decopyranose (**23**) and the β-L-*altro*-D-*galacto* isomer (**24**) in the ratio ~5:1, respectively; δ_H [for (**23**)] 5.47 (1 H, d, $J_{1,2}$ 4.9 Hz, 1-H), and 1.51, 1.44, 1.42, 1.38, 1.33, and 1.31 (18 H, 6 s, 3 × CMe_2).

Hydrolysis of this mixture of the triols (**23**) and (**24**) (0.45 g, 1.07 mmol) with trifluoroacetic acid–water (9:1; 6 ml), and reduction of the resulting decoses in water (16 ml) with sodium borohydride (0.2 g, ~5.3 mol), gave the crystalline decitol (**1**) (0.226 g, 70%), following trituration of the final residue with methanol and warming. Recrystallisation from aqueous ethanol gave L-*galacto*-L-*gulo*-decitol (**1**) having m.p. 217—219 °C; $[\alpha]_D$ +1° (saturated solution in H_2O) {lit.,[3] m.p. 222 °C; $[\alpha]_D$ +1.2° (H_2O)}; δ_C 74.22, 72.97, 71.71, 70.47, 69.82, 68.94, 68.71, 68.02, 63.35, and 63.30.

L-galacto-L-gulo-*Decitol Deca-acetate* (**2**).—Acetylation of the decitol (**1**) (0.078 g, 0.26 mmol) in pyridine (4 ml) and acetic anhydride (3 ml) at 100 °C for 3 h gave, after the usual work-up and chromatography, the deca-acetate (**2**) (0.173 g, 93%), m.p. 149—150 °C (from diethyl ether–hexane); $[\alpha]_D$ +15.5° (*c* 1 in $CHCl_3$) {lit.,[3] m.p. 149—150 °C; $[\alpha]_D$ +16° (*c* 5 in $CHCl_3$)}; δ_H 2.114, 2.109, 2.057 (× 2), 2.047, 2.046, 2.042, 2.000, 1.991, and 1.982 (30 H, 9 s, 10 × OAc); δ_C 170.23 (× 2), 170.03, 169.90, 169.86, 169.77, 169.56, 169.54, and 169.36 (× 2) (C=O groups), 68.31, 67.95, 67.92, 67.89, 67.47 (× 2), 67.34, 66.10, 61.88, and 61.50 (chain-carbon atoms), and 20.55, 20.43, 20.40, and 20.21 (Me groups).

8,9-*Anhydro*-1,2:3,4:6,7-*tri*-O-*isopropylidene*-α-D-galacto-D-galacto-*decopyranose* (**20**).—Using the standard procedure, Sharpless epoxidation of the (*E*)-decenopyranose[10] (**18**) (1.14 g, 2.95 mmol) with titanium(IV) isopropoxide (1.13 ml, 4.32 mmol), (−)-DIPT (1.12 g, 4.78 mmol), and 3M-t-butyl hydroperoxide (3.2 ml, 9.6 mmol) in anhydrous methylene dichloride (total volume 56 ml) at −23 °C for 4 days gave, after work-up and chromatography, the *epoxy alcohol* (**20**), (0.73 g, 61.5%), m.p. 121.5—122.5 °C (from diethyl ether–hexane); $[\alpha]_D$ −65° (*c* 1 in $CHCl_3$) (Found: C, 57.0; H, 7.5. $C_{19}H_{30}O_9$ requires C, 56.7; H, 7.5%); δ_H 5.46 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 3.26 and 3.22 (2 H, 2 m, CH–CHO), and 1.50, 1.43, 1.42, 1.38, 1.34, and 1.31 (18 H, 6 s, 3 × CMe_2). The ^1H n.m.r. spectrum revealed the presence of a trace of the β-L-*ido*-D-*galacto* isomer (**19**), which persisted after several recrystallisations.

L-altro-D-galacto-*Decitol* (**25**).—Base-catalysed hydrolysis of the epoxy alcohol (**20**) (1.31 g, 3.26 mmol) in 0.5M-sodium hydroxide (29 ml) and 1,4-dioxane (6 ml) at 70 °C for 24 h gave, after the usual work-up and chromatography, a mixture (0.697 g, 51%) of 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*altro*-D-*galacto*-decopyranose (**24**) and the α-D-*gluco*-D-*galacto* isomer (**23**) in the ratio ~6:1, respectively; δ_H [for (**24**)] 5.49 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), and 1.52, 1.44, 1.43, 1.37, 1.35, and 1.32 (18 H, 6 s, 3 × CMe_2).

Hydrolysis of the foregoing mixture of triols (0.655 g, 1.56 mmol) in trifluoroacetic acid–water (9:1, 9 ml), and reduction of

the resulting decoses in water (23 ml) with sodium borohydride (0.288 g, ~7.6 mmol), gave the crystalline *decitol* (**25**) (0.258 g, 55%), following trituration of the final residue with methanol and warming. After recrystallisation from boiling water (or aqeuous ethanol), L-altro-D-galacto-*decitol* (**25**) had m.p. 246—247.5 °C (Found: C, 39.4; H, 7.1. $C_{10}H_{22}O_{10}$ requires C, 39.7; H, 7.3%); δ_C 73.39, 72.16, 70.42, 70.38, 69.57, 68.95, 68.54, 68.27, 63.36, and 62.99. The very low solubility of the decitol (**25**) in cold water precluded the measurement of a meaningful specific optical rotation.

L-altro-D-galacto-*Decitol Deca-acetate* (**26**).—Acetylation of the decitol (**25**) (0.091 g, 0.3 mmol) in pyridine (4.5 ml) and acetic anhydride (3.6 ml) at 100 °C for 5.5 h gave, after the usual work-up and chromatography [methylene dichloride–acetone (5:1) as eluant], the *deca-acetate* (**26**) (0.19 g, 87%), $[\alpha]_D$ ~ −27° (*c* 1.4 in $CHCl_3$), as an amorphous solid (Found: C, 49.7; H, 6.1. $C_{30}H_{42}O_{20}$ requires C, 49.9; H, 5.9%); δ_H 2.047 (× 2), 2.044, 2.043, 2.027, 2.021, 2.020, 1.991, 1.989, and 1.977 (30 H, 9 s, 10 × OAc); δ_C 170.33, 170.18, 169.87, 169.83, 169.70, 169.61, 169.57, 169.55, 169.49, and 169.12 (C=O groups), 69.34, 68.79, 67.93, 67.84, 67.66, 66.90, 66.86, 66.38, 61.97, and 61.56 (chain-carbon atoms), and 20.64, 20.53, 20.51, 20.45, 20.42, and 20.39 (Me groups).

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