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THE SYNTHESIS AND OSMYLATION OF 7,8-DIDEOXY-1,2:3,4-DI-*O*-ISOPROPYLIDENE-β-L-*glycero*-D-*galacto*-OCT-7-ENOPYRANOSE AND RELATED STUDIES*†

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ABSTRACT

A stereocontrolled route to 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-oct-7-enopyranose (**8**) has been developed from 6,7-anhydro-1,2:3,4-di-*O*-isopropylidene-β-L-*erythro*-D-*galacto*-octopyranose (**15**), in which the final and key step involved a facile, reductive elimination on the epoxy-iodide **18**. As predicted by Kishi's empirical rule, the major product obtained on catalytic osmylation of either **8** or its 6-*O*-benzyl derivative **21** possesses the β-L-*erythro*-D-*galacto* configuration (*i.e.*, **19** or **22**, respectively).

INTRODUCTION

Ascent of the series from the non-reducing end of the sugar chain often offers a flexible and stereocontrolled approach to higher-carbon sugars. Useful routes to a number of 7- (ref. 2), 8- (ref. 3), 9- (ref. 4), and 10-carbon sugars[5] have been developed through the catalytic osmylation of unsaturated sugars, usually prepared *via* Wittig olefination of an appropriate aldehydic precursor. With a few notable exceptions[2,3], the stereochemistry of the major products of these osmylations complies with Kishi's empirical rule[6], which predicts an *erythro* relationship between a pre-existing hydroxyl (or alkoxyl) group and the hydroxyl group introduced at an adjacent carbon atom. In keeping with Kishi's formulation[6], the catalytic osmylation of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-oct-7-enopyranose (**1**) afforded[3] 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*. Little, if any, of the corresponding β-L-*threo*-D-*galacto* isomer **3** was formed in this reaction. Catalytic osmylation of the 6-*O*-benzyl derivative **4** of **1** is similarly, though less, stereoselective, furnishing[4] a mixture of 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octopyranose (**5**) and the

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corresponding β-L-*threo*-D-*galacto* isomer **6** in the ratio ~5:1. The diafacial stereoselectivities observed in these and other osmylation reactions can be rationalised by assuming that the molecule reacts in the sterically least-compressed conformation **7**, 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 alkoxyl group[6].

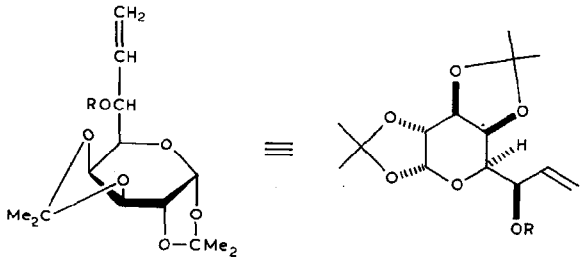
The stereochemical outcome of the catalytic osmylation of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-oct-7-enopyranose (**8**), the C-6 epimer of **1**, and its derivatives would also be of theoretical and, possibly, practical interest. Previous work[4] conducted with a 7:3 mixture of **8** and **1** indicated a modest stereoselectivity in the catalytic osmylation of **8**, but, because of severe contamination with the products derived from **1**, was unsatisfactory from a practical standpoint. We now report a stereocontrolled synthesis of **8**, together with details of its catalytic osmylation and that of the corresponding 6-*O*-benzyl derivative **21**.

RESULTS AND DISCUSSION

Previously, **8** has been synthesised[7] by partial reduction of the minor product* obtained on ethynylation of 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**10**), which also undergoes ethenylation[8] to give a 2:1 mixture of **1** and **8**. Whereas most of **1** can be isolated from this mixture by fractional crystallisation, efforts to obtain pure **8** by further fractional crystallisation or chromatography were unavailing. We therefore sought to prepare **8** by a more expedient route involving inversion of the configuration at C-6 of either **1** or the related methanesulphonate **9**. However, a complex mixture of products was obtained when attempts were made to invert the configuration of **1** under Mitsunobu conditions[9] (triphenylphosphine, diethyl azodicarboxylate, and benzoic acid in tetrahydrofuran at room temperature), forcing us to abandon this approach. By contrast, the methanesulphonate **9** underwent a much cleaner displacement with sodium benzoate in *N,N*-dimethylformamide at 90° to give a major product that was identified as (*E*)-8-*O*-benzoyl-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enopyranose (**11**), since it afforded the known[3] (*E*)-allylic alcohol **12** on debenzoylation. The isomeric methanesulphonate[7] **13** also gave the transposed benzoate **11** on reaction with sodium benzoate under similar conditions. In each instance, the benzoate **11** presumably arises from an SN2′ displacement on the original methanesulphonate, although an SN2 displacement and subsequent allylic rearrangement of the initially formed benzoate cannot be ruled out.

A final assault on this problem was made using a procedure[10] designed to

* *Note added in proof.* Improved syntheses of this product, namely 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-oct-7-ynopyranose, have been reported recently {S. Jarosz, J. Glodek, and A. Zamojski, *Carbohydr. Res.*, 163 (1987) 289–296; S. Czernecki and J.-M. Valéry, *Abstracts 4th European Carbohydrate Symposium*, Darmstadt, 1987, A-60}.



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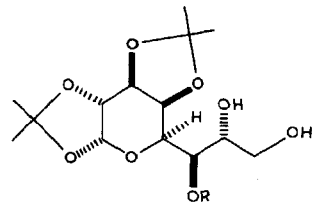
4 R = Bzl
9 R = Ms



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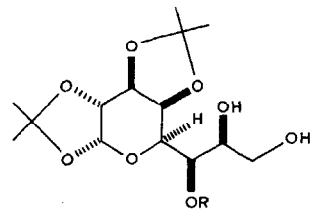
5 R = Bzl



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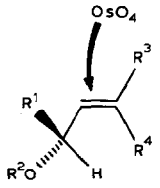
6 R = Bzl



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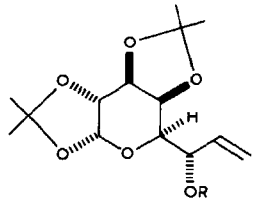
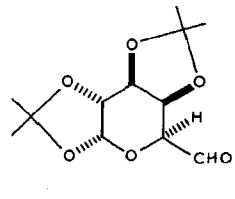


8 R = H
13 R = Ms
21 R = Bzl



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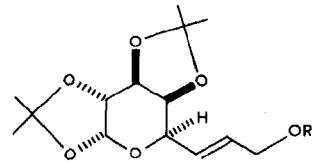


11 R = Bz
12 R = H

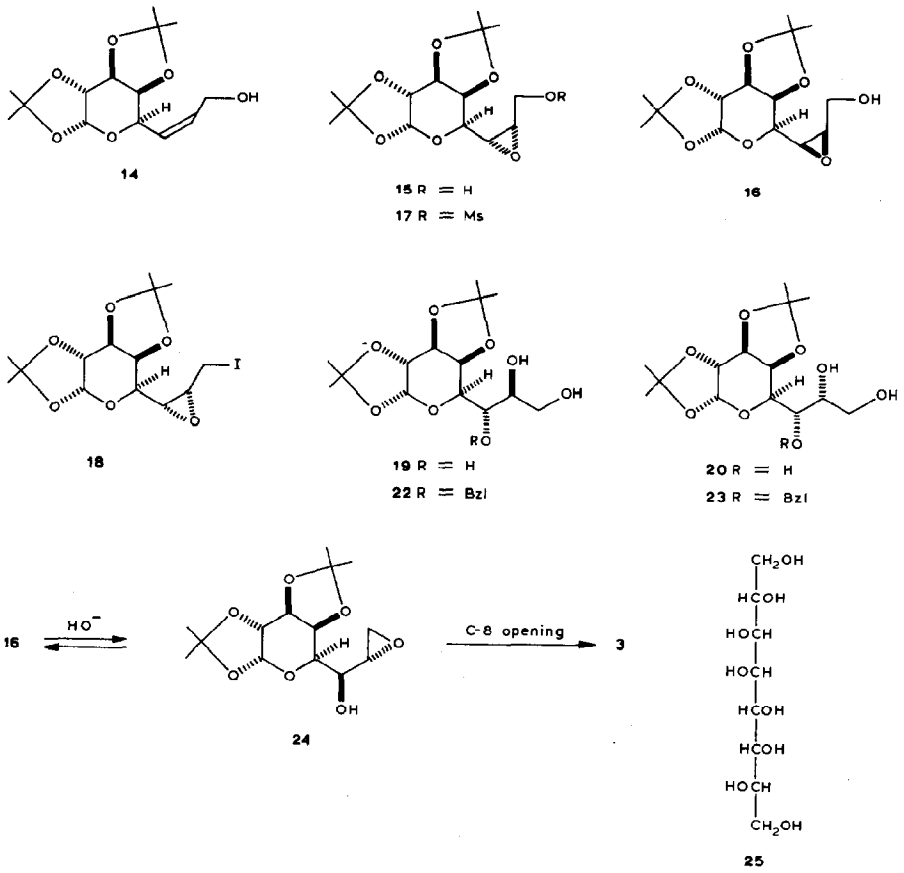
effect a 1,3-transposition of the allylic system of the readily accessible (*Z*)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enopyranose[3] (**14**). Epoxidation of **14** with *m*-chloroperoxybenzoic acid furnishes[11] a ~3:1 mixture of the epoxy-alcohols **15** and **16**, which can be separated without difficulty by a combination of fractional crystallisation and chromatography (see Experimental). Significantly, the oxygen atom is already installed in the required configuration at C-6 of the major β-L-*erythro*-D-*galacto* isomer **15**, which was transformed in a straightforward manner into the epoxy-iodide **18**, *via* the methanesulphonate **17**. A reductive elimination on **18** in ethanol using a zinc–copper couple then provided **8** in 78% yield. Although the physical data found for **8** {m.p. 76–77°, $[\alpha]_D$ −66° (*c* 1, chloroform)} differ somewhat from those {m.p. 64–66°, $[\alpha]_D$ −61° (*c* 1, chloroform)} reported in the literature[7], the p.m.r. spectrum of **8** was identical to that reported[7], and methanesulphonylation of **8** gave **13** (ref. 7).

Catalytic osmylation[12] of **8** produced a mixture of 1,2:3,4-di-*O*-isopropylidene-β-L-*erythro*-D-*galacto*-octopyranose (**19**) and the α-D-*threo*-D-*galacto* isomer **20** in the ratio ~3:1 (determined by 360-MHz p.m.r. spectroscopy). The identities of the products were revealed when the addition of authentic **20** (ref. 11) to a ~3:1 mixture of **19** and **20** was observed (p.m.r. spectroscopy) to produce an increase in the proportion of the minor isomer. Similar osmylation[12] of the 6-*O*-benzyl derivative **21** provided **22** and **23** in the ratio ~4:1; debenzylation of this mixture gave **19** and **20** in the ratio ~4:1. Both osmylations proceed in accordance with Kishi's empirical rule[6], although their diafacial stereoselectivities are modest. Fortunately, the ratio of the osmylation products **22** and **23** does not compromise further ascent of the series along the lines used in our recent synthesis of L-*lyxo*-L-*altro*-nonitol[4].

The structure of the epoxy-alcohol **15** has been established[11] by means of base-catalysed hydrolysis, thus paving the way for the present work, which also furnished the isomeric epoxy-alcohol **16**. Evidence corroborating the structure of **16** was also obtained by base-catalysed hydrolysis. Thus, on treatment with sodium hydroxide in aqueous 1,4-dioxane, **16** gave 1,2:3,4-di-*O*-isopropylidene-β-L-*threo*-D-*galacto*-octopyranose (**3**), *via* preferential ring-opening of the Payne-rearrangement[13] product **24** at C-8. The stereochemistry assigned to **3** was founded on the conversion of **3** into L-*threo*-D-*galacto*-octitol[8] (**25**) following acid hydrolysis and reduction of the resulting octose.

EXPERIMENTAL

General methods. — T.l.c. was performed on Kieselgel G, and detection was effected with 1% sulphuric acid. P.m.r. spectra were recorded for solutions in deuteriochloroform (internal Me_4Si) either with a Bruker Spectrospin (90 MHz) spectrometer or by the Edinburgh University N.M.R. Service (360 MHz). Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter, using 1-dm tubes. Melting points are uncorrected. Light petroleum refers to the fraction boiling in the range 40–60°, unless otherwise indicated.



7,8-Dideoxy-1,2:3,4-di-O-*isopropylidene-6*-O-*methanesulphonyl*-β-L-glycero-D-galacto-*oct-7-enopyranose* (**13**). — To a solution of vinylmagnesium bromide [prepared from magnesium (9.72 g) and vinyl bromide (30 mL)] in anhydrous tetrahydrofuran (240 mL) was added a solution of **10** (ref. 14) (17.1 g, 66.2 mmol) in anhydrous tetrahydrofuran (60 mL), and the mixture was then boiled under reflux for 1.5 h. After cooling, ether (300 mL) was added to the solution and the excess of the reagent was decomposed by the gradual addition of water. Inorganic material was filtered off and washed with ether, and the filtrate and washings were combined, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 10:1 dichloromethane–acetone) gave a mixture of **1** and **8** from which **1** crystallised upon the addition of light petroleum and seeding. Recrystallisation from ether–light petroleum gave pure **1** (refs. 4,7,8) (6.9 g, 36%), m.p. and mixture m.p. 106–107°. Concentration of the mother liquor and recrystallisation of the resulting solid from ether–light petroleum afforded a 3:7 mixture of **1** and **8** (2.7 g, 14%).

To a stirred and cooled (0°) solution of the foregoing mixture of **1** and **8** (1.56 g, 5.45 mmol) in anhydrous pyridine (12 mL) was added methanesulphonyl chloride (0.9 mL, ~11.6 mmol), and the reaction mixture was stirred for 2 h at 0° and then kept overnight in a refrigerator (~4°). After the addition of water (1 mL), the mixture was stirred at room temperature for 1 h and then poured into ice-water. The precipitate was filtered off, washed with water, and recrystallised from ethanol–light petroleum to give **13** (0.94 g, 47%), m.p. 121–122°, $[\alpha]_D$ −64° (*c* 1, chloroform); lit.[7] m.p. 121.5–122.5°, $[\alpha]_D$ −61° (*c* 1.3, chloroform).

*7,8-Dideoxy-1,2:3,4-di-*O*-isopropylidene-6-*O*-methanesulphonyl-α-*D*-glycero-*D*-galacto-oct-7-enopyranose* (**9**). — To a stirred and cooled (0°) solution of **1** (1 g, 3.49 mmol) in anhydrous pyridine (10 mL) was added methanesulphonyl chloride (0.55 mL, ~7 mmol), and the mixture was stirred at ~0° for 1 h and then kept overnight in a refrigerator (~4°). Conventional aqueous work-up and chromatography of the residue on silica gel (40:1 dichloromethane–acetone) gave **9** (1.12 g, 88%), $[\alpha]_D$ −91° (*c* 0.8, chloroform), as a syrup that decomposed with time. P.m.r. data: δ 5.99 (m, 3 H, CH = CH_2), 5.58 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 3.01 (s, 3 H, OMs), and 1.51, 1.42, and 1.33 (3 s, 12 H, ratio 1:1:2, 2 CMe_2). This compound was used immediately in the next experiment.

(E)-*6,7-Dideoxy-1,2:3,4-di-*O*-isopropylidene-α-*D*-galacto-oct-6-enopyranose* (**12**). — A solution of **9** (0.7 g, 1.92 mmol) in anhydrous *N,N*-dimethylformamide (30 mL) containing sodium benzoate (0.83 g, 5.76 mmol) was stirred for 65 h at 90°. After cooling, chloroform (50 mL) was added, and the resulting solution was washed with water (3 × 10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (40:1 dichloromethane–acetone) gave (*E*)-8-*O*-benzoyl-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-*D*-*galacto*-oct-6-enopyranose (**11**; 0.374 g, 50%), $[\alpha]_D$ −85.5° (*c* 0.9, chloroform), as a syrup. P.m.r. data: δ ~7.76 (m, 5 H, Ph), 5.98 (m, 2 H, CH = CH), 5.58 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), and 1.53, 1.46, and 1.33 (3 s, 12 H, ratio 1:1:2, 2 CMe_2). A similar reaction on 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-6-*O*-methanesulphonyl-β-L-*glycero*-*D*-*galacto*-oct-7-enopyranose (**13**) for 72 h provided **11** in 73% yield.

To a solution of **11** (0.39 g, ~1 mmol) in anhydrous methanol (15 mL) was added a small piece of sodium, and the mixture was kept for 1 h at room temperature before being neutralised with Amberlite IR-120(H^+) resin. The resin was filtered off and washed thoroughly with methanol, and the filtrate and washings were combined and concentrated under reduced pressure. Chromatography of the residue on silica gel (4:1 dichloromethane–acetone) furnished **12** (0.272 g, 95%), $[\alpha]_D$ −108° (*c* 0.9, chloroform), which was indistinguishable (i.r. and p.m.r. spectra) from an authentic sample; lit.[3] $[\alpha]_D$ −108° (*c* 1, chloroform).

*6,7-Anhydro-1,2:3,4-di-*O*-isopropylidene-β-L-erythro-D-galacto-octopyranose* (**15**) *and the* α-D-erythro-D-galacto *isomer* **16**. — The following modified procedure was used to prepare the title compounds.

m-Chloroperoxybenzoic acid (85%; 4.51 g, 22.2 mmol) was added gradually to a stirred and cooled (0°) solution of **14** (ref. 3) (4.6 g, 16.1 mmol) in anhydrous

dichloromethane (220 mL), and the mixture was then kept overnight in a refrigerator (~4°). After dilution with dichloromethane (150 mL), the solution was washed with M sodium hydroxide (2 × 20 mL) and saturated, aqueous sodium chloride, dried ($MgSO_4$), and concentrated under reduced pressure. Crystallisation of the residue from ether–hexane gave **15** (2.1 g, 43%), m.p. and mixture m.p. 123–124°; lit.[11] m.p. 124–125.5°. Chromatography of the mother liquor on silica gel (2:1 ethyl acetate–hexane) gave **16** (0.82 g, 17%), m.p. 84–86° (from ether–hexane), $[\alpha]_D$ −88° (*c* 1, chloroform); lit.[15] m.p. 85–87°, $[\alpha]_D$ −92° (*c* 0.15, chloroform). Continued elution provided an additional quantity of **15** (0.84 g, total yield 60%).

*6,7-Anhydro-1,2:3,4-di-*O*-isopropylidene-8-*O*-methanesulphonyl-β-*L*-erythro-*D*-galacto-octopyranose* (**17**). — To a stirred and cooled (0°) solution of **15** (3.6 g, 11.9 mmol) and *N*-ethyldi-isopropylamine (1.8 mL, 10.3 mmol) in anhydrous dichloromethane (90 mL) was added methanesulphonyl chloride (1.9 mL, −24.5 mmol), and the mixture was stirred at 0° for 2.5 h and then kept overnight in a refrigerator (~4°). After dilution with dichloromethane (50 mL), the solution was washed with water (2 × 20 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (10:1 dichloromethane–acetone) furnished **17** (3.72 g, 82%), m.p. 155–156° (from ethyl acetate–hexane), $[\alpha]_D$ −66.5° (*c* 0.9, chloroform) (Found: C, 47.3; H, 6.2; S, 8.3. $C_{15}H_{24}O_9S$ calc.: C, 47.4; H, 6.4; S, 8.4%). P.m.r. data: δ 5.58 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 3.12 (s, 3 H, OMs), and 1.49, 1.36, and 1.33 (3 s, 12 H, ratio 2:1:1, 2 CMe_2).

*7,8-Dideoxy-1,2:3,4-di-*O*-isopropylidene-β-*L*-glycero-*D*-galacto-oct-7-enopyranose* (**8**). — A solution of **17** (1.68 g, 4.42 mmol) in anhydrous acetone (80 mL) containing sodium iodide (5.35 g, 35.7 mmol) was stirred for 72 h at room temperature and then concentrated under reduced pressure. The residue was extracted with chloroform, and the extract was washed with water, aqueous 2% sodium thiosulphate (2 × 20 mL), and water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (15:1 dichloromethane–acetone) gave 6,7-anhydro-8-deoxy-8-iodo-1,2:3,4-di-*O*-isopropylidene-β-*L*-*erythro*-*D*-*galacto*-octopyranose (**18**; 1.35 g, 74%), $[\alpha]_D$ +15° (*c* 0.5, chloroform), as a straw-coloured syrup that was used immediately in the next step. P.m.r. data: δ 5.59 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), and 1.51, 1.38, and 1.34 (3 s, 12 H, ratio 2:1:1, 2 CMe_2).

A solution of **18** (1.34 g, 3.25 mmol) in anhydrous ethanol (100 mL) containing a zinc–copper couple[16] (5.7 g) was boiled under reflux for 1.5 h, cooled, and filtered, and the filtrate was concentrated under reduced pressure. Chromatography of the residue on silica gel (10:1 dichloromethane–acetone) gave **8** (0.725 g, 78%), m.p. 76–77° [from light petroleum (b.p. 80–100°)], $[\alpha]_D$ −66° (*c* 1, chloroform); lit.[7] m.p. 64–66°, $[\alpha]_D$ −61° (*c* 1, chloroform) (Found: C, 58.9; H, 7.8. $C_{14}H_{22}O_6$ calc.: C, 58.7; H, 7.75%). The p.m.r. spectrum of **8** was indistinguishable from that recorded[7] previously, and the methanesulphonate **13** derived from **8** had m.p. and mixture m.p. 122–123°.

*6-*O*-Benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-β-*L*-glycero-*D*-galacto-oct-7-enopyranose* (**21**). — Sodium hydride (0.3 g, ~12.5 mmol) was added to a

stirred solution of **8** (0.3 g, 1.05 mmol) in anhydrous tetrahydrofuran (6 mL) followed, after 15 min, by benzyl bromide (0.6 mL, ~5 mmol). The mixture was stirred overnight at room temperature, methanol was then added to remove the excess of the reagents, and the solution was concentrated under reduced pressure. The residue was extracted with chloroform, and the extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (50:1 dichloromethane–acetone) furnished **21** (0.32 g, 81%), b.p. 125–130° (bath)/0.05 mmHg, $[\alpha]_D$ −66° (*c* 0.9, chloroform) (Found: C, 67.2; H, 7.6. $C_{21}H_{28}O_6$ calc.: C, 67.0; H, 7.5%). P.m.r. data: δ ~7.29 (m, 5 H, Ph), 5.93 and 5.42 (2 m, 3 H, $CH=CH_2$), 5.58 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.62 (s, 2 H, $PhCH_2$), and 1.51, 1.41, 1.29, and 1.27 (4 s, 12 H, 2 CMe_2).

Catalytic osmylations of **8** *and* **21**. — (*a*) A solution of **8** (0.202 g, 0.71 mmol) in acetone–water (8:1, 9 mL) containing *N*-methylmorpholine *N*-oxide monohydrate (0.2 g, 1.48 mmol) and osmium tetraoxide (0.015 g, 0.06 mmol) was stirred for 3 h at room temperature and then kept overnight. Work-up of the reaction mixture in the usual way[3] and purification of the final residue by percolation through silica gel (1:2 dichloromethane–acetone) gave a mixture (0.17 g, 75%) containing 1,2:3,4-di-*O*-isopropylidene-β-L-*erythro*-D-*galacto*-octopyranose (**19**) [δ 5.58 (d, $J_{1,2}$ 5 Hz, H-1)] and the α-D-*threo*-D-*galacto* isomer **20** [δ 5.54 (d, $J_{1,2}$ 5 Hz, H-1)] in the ratio ~3:1. Identification of the minor isomer **20** was achieved by the addition of authentic **20** (ref. 11) to the solution used to record the p.m.r. spectrum of the mixture and then re-measuring the spectrum.

(*b*) A solution of **21** (0.245 g, 0.65 mmol) in acetone–water (8:1, 9 mL) containing *N*-methylmorpholine *N*-oxide monohydrate (0.18 g, 1.33 mmol) and osmium tetraoxide (0.012 g, 0.05 mmol) was stirred at room temperature for 3 h and then worked-up in the usual way[3]. Percolation of the final residue through silica gel (2:1 dichloromethane–acetone) gave a mixture (0.257 g, 96%) containing 6-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-β-L-*erythro*-D-*galacto*-octopyranose (**22**) [δ 5.56 (d, $J_{1,2}$ 5 Hz, H-1)] and the α-D-*threo*-D-*galacto* isomer **23** [δ 5.59 (d, $J_{1,2}$ 5 Hz, H-1)] in the ratio ~4:1. The identities of **22** and **23** were established when conventional debenzylation (5% Pd/C in methanol) furnished a mixture of **19** and **20** in the ratio ~4:1.

L-threo-D-galacto-*Octitol* (**25**). — A stirred solution of **16** (0.5 g, 1.65 mmol) in 0.5M sodium hydroxide (7.5 mL) and 1,4-dioxane (1.5 mL) (both solvents were deoxygenated by the passage of a rapid stream of nitrogen before use) was heated for 24 h at ~70°, cooled, diluted with water, and neutralised with Amberlite IR-120(H^+) resin. The resin was filtered off and washed with water, and the filtrate and washings were combined and concentrated under reduced pressure. The residue was extracted with chloroform, and the extract was washed with a little water, dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography of the residue on silica gel (1:2 dichloromethane–acetone) gave 1,2:3,4-di-*O*-isopropylidene-β-L-*threo*-D-*galacto*-octopyranose (**3**) (0.223 g, 42%), $[\alpha]_D$ ~ −53° (*c* 0.5, chloroform). P.m.r. data: δ 5.52 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), and 1.55, 1.44, 1.36, and

1.32 (4 s, 12 H, 2 CMe_2).

Acid hydrolysis of **3** and reduction of the resulting octose, as previously described[3], gave L-*threo*-D-*galacto*-octitol (**25**, 52%), m.p. 220–223°; lit. m.p. 233–236° (ref. 3), m.p. (D enantiomer) 230° (ref. 17). Although the melting point of **25** was lower than that obtained[3] previously, the ^{13}C-n.m.r. spectrum [$(CD_3)_2SO$] of **25** (C_2 symmetry) was indistinguishable from that of an authentic sample[3].

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