Carbohydrate Research, 202 (1990) 81–92
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

1,6-Anhydro-β-D-glucopyranose in organic synthesis: preparation of a fragment for the synthesis of rosaramycin

Garry Procter*, Denis Genin,
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Great Britain)
and Stephen Challenger
Department of Chemistry, University of Wales College at Cardiff, CF1 1XL (Great Britain)

(Received July 25th, 1989; accepted for publication, November 22nd, 1989)

ABSTRACT

1,6-Anhydro-β-D-glucopyranose has been used as the starting material for a synthesis of ethyl (*E*)-4-*C*-allyl-2,3,4,6-tetradeoxy-5,7-*O*-isopropylidene-8-*O*-methanesulphonyl-2,6-di-*C*-methyl-D-*gulo*-oct-2-enoate, which represents a synthetic unit equivalent to C-2/9 of the macrolide antibiotic rosaramycin. The synthesis involved a minimum of chromatography, and the extremely high level of regiochemical and stereochemical control was achieved by the use of epoxides at crucial C–C-bond-forming steps. A method was also developed, using tosylmethyl isocyanide, which converted a carbohydrate 6-aldehyde (**19**) directly into the corresponding homologated methyl ester.

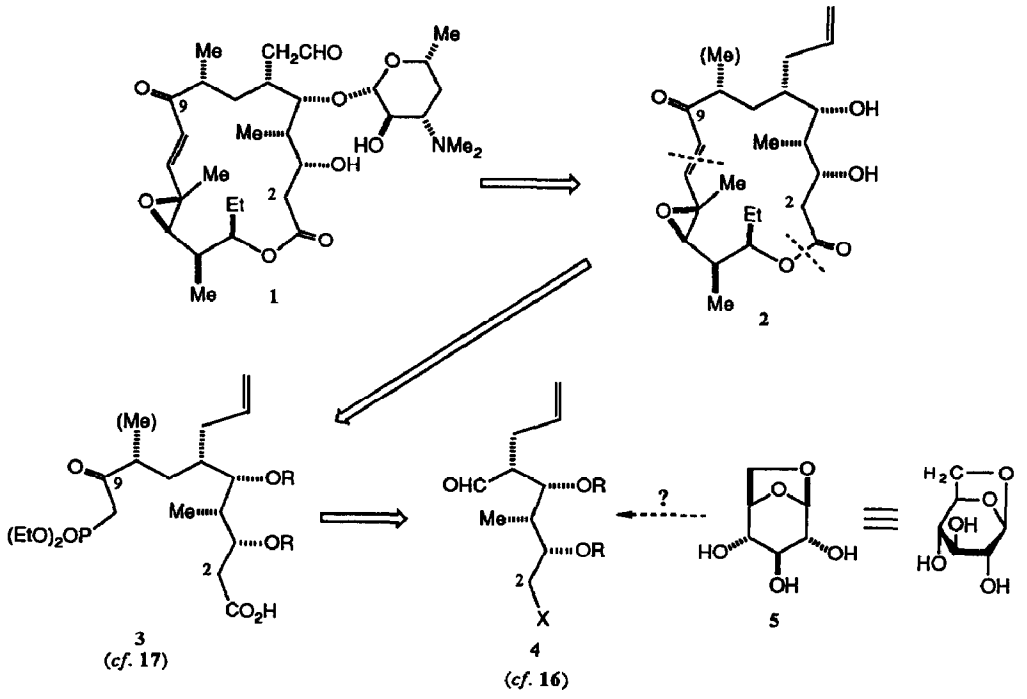
INTRODUCTION

The preparation of organic compounds in enantiomerically pure form continues to be an important area in organic synthesis. This is particularly true of natural products, and other systems, which possess biological activity. One straightforward type of asymmetric synthesis involves readily available, pure enantiomers that possess functionality which may be manipulated selectively. Carbohydrates, which have these attributes, find widespread use in the synthesis of organic compounds[1]. We have been particularly interested in the use of 1,6-anhydro-β-D-glucopyranose (**5**) for the synthesis of complex natural products[2,3], since it is readily available and has a rigid structure which can allow for high levels of regiochemical and stereochemical control[4]. In the past few years, **5** has been used in the synthesis of several natural products[5] and we have investigated its use for the preparation of sub-units of natural products. We now report the preparation of a unit which corresponds to the C-2/9 fragment of rosaramycin (**1**) (Scheme 1) and other macrolide antibiotics[6], and a method which might be of value for the homologation of glucose and related systems at C-6.

The retrosynthetic analysis, outlined in Scheme 1, follows that used by others in the synthesis of macrolides[7], and the initial problem is conversion of **5** into a synthetic equivalent of **4**. Our objective was to achieve this conversion with control of the

* Author for correspondence.

0008-6215/90/$03.50 © 1990 Elsevier Science Publishers B.V.



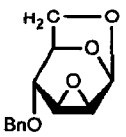
Scheme 1. Retrosynthetic analysis of rosaramycin (1).

regiochemistry and the stereochemistry of the reactions involved, and to avoid conversion of the chiral centres derived from **5** into trigonal carbons, and the possible consequent loss of stereochemical integrity. Accordingly, the chirality required was established by the use of epoxides, since the opening of epoxides in cyclic systems generally involves predictable control of regiochemistry and stereochemistry.

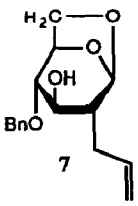
In order to introduce the group that will become the "acetaldehyde" side-chain of rosaramycin, 1,6:2,3-dianhydro-4-*O*-benzyl-β-D-mannopyranose[8] (**6**), readily obtained from **5**, was reacted with allylmagnesium chloride[9] in ether to give **7** as the sole product (^{1}H-n.m.r. data). The exclusive formation of **7** was expected, since the opening of epoxides on the rigid 1,6-anhydro-β-D-hexopyranose framework usually[4] generates *trans*-diaxial products. When tetrahydrofuran was used as the solvent in the Grignard reaction on **6**, only the chlorohydrin **8** was obtained.

It is not clear why the change of solvent in this reaction causes such a dramatic change in the product, but presumably the position of the Schlenk equilibrium, which is solvent-dependent[10], is an important factor.

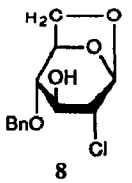
Methanolysis of **7** gave the glucoside **9**, the dimesylate (**10**) of which was *O*-debenzylated (to **11**) by treatment with sodium in liquid ammonia at −78°, conditions which do not cleave the methanesulphonate groups. Treatment of **11** with sodium methoxide gave the *allo*-3,4-epoxide **12**. The conversion of **10** into **12** could be carried out in a one-pot reaction by treatment with sodium in liquid ammonia at ~ −33°.



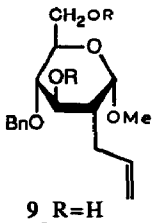
6



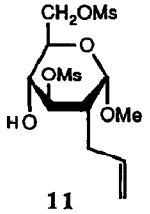
7



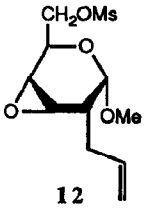
8



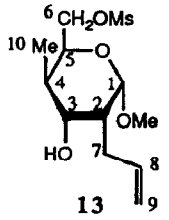
9 R=H
10 R=Ms



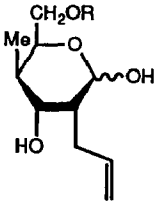
11



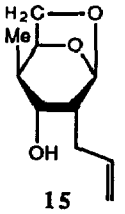
12



13



14 R=Ms
18 R=H



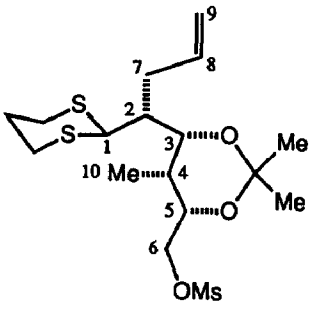
15

Although the yield of this one-pot conversion was good (~80%), that of the two-step process approached quantitative.

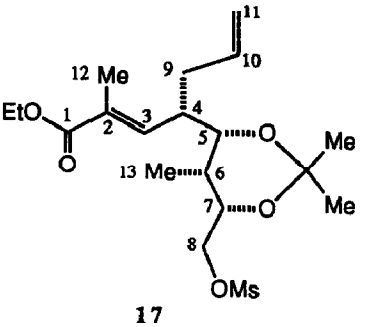
Treatment of **12** with either lithium dimethylcuprate or methylmagnesium chloride in the presence of cuprous bromide (catalytic) gave methyl 2-*C*-allyl-2,4-dideoxy-6-*O*-mesyl-4-*C*-methyl-*α*-D-gulopyranoside (**13**), the structure of which was indicated by the ^{1}H-n.m.r. data. Compound **13** is the expected product of *trans*-diaxial opening of the epoxide ring, with the tetrahydropyran ring in the most stable conformation, and has potential for the synthesis of rosaramycin and closely related macrolides, since the stereochemistry is correct and the functionality is suitable for further elaboration. The overall yield of **13** was high (>50% from **6**, ~30% from **1**), and all the reactions involved high regiochemical and stereochemical control with a minimum of chromatography (one chromatographic step in the sequence **6** → **13**).

In order to extend the chain from C-1, **13** was hydrolysed to the corresponding lactol **14**. Since lactols are known to react with stabilised phosphoranes, **14** was treated with 1-(ethoxycarbonyl)ethylidenetriphenylphosphorane. However, the product was the 1,6-anhydride **15**, which was formed also in addition to **14** when **13** was hydrolysed.

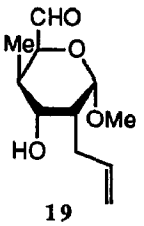
Accordingly a slightly less-direct route was investigated. Compound **13** was converted in two steps into **16**, which could be hydrolysed to the corresponding aldehyde without loss of stereochemistry, and reacted with 1-(ethoxycarbonyl)ethylidenetriphenylphosphorane to give solely alkene **17** (the proton *β* to the ester group



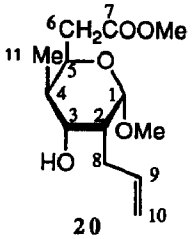
16



17



19



20

resonates at δ 6.58 typical of an *E* isomer[12]). Although the yield for the overall conversion of **13** into **17** was only moderate (28%), the sequence demonstrated that such an approach was viable and did not result in loss of stereochemical integrity.

In order to introduce the carbon that will eventually become C-1 of the macrolide (macrolide numbering), **13** requires a C_1-extension at position 6. Attempted displacement of the mesylate with cyanide ion was unsuccessful. Cyanide displacement was found also by Sunay and Fraser-Reid[13] to be difficult in their synthesis of the C-1/9 sequence of rosaramycin, and the required carbon was introduced by a Wittig reaction. However, a more direct approach was investigated here.

The diol **18** was obtained from the epoxide **12** by reaction with an excess of methylmagnesium chloride or by treatment of **13** with this Grignard reagent. The alcohol **18** was originally obtained as a by-product of the reaction, and presumably arises *via* attack of the Grignard reagent at sulphur. Hindered sulphonates will react with powerful nucleophiles to produce alcohols[14]. Oxidation of **18** to **19** and reaction with the anion of tosylmethyl isocyanide followed by work-up with methanolic HCl gave the homologated methyl ester **20** in moderate overall yield. This sequence could be useful generally for the "direct homologation" of C-6 in pyran (and related) systems, a transformation which is often troublesome.

The numbering of atoms in **7–15**, **18**, and **19** is shown in **13**, and those in **16**, **17**, and **20** as shown.

EXPERIMENTAL

I.r. spectra were recorded on Perkin–Elmer 177 and 259 spectrophotometers either for dilute solutions (chloroform or bromoform) or for Nujol mulls. ^{1}H-N.m.r.

spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) unless stated otherwise: ^1H; Perkin–Elmer R32 (90 MHz) and Bruker AM-300 (300 MHz), WM-360 (360 MHz), and WH-400 (400 MHz) (S.E.R.C. high-field n.m.r. service at Warwick University) spectrometers. ^{13}C; Bruker WM-360 (90.56 MHz) and WH-400 (100.6 MHz) spectrometers. E.i.-mass spectra were recorded on a VG 7070H mass spectrometer, and c.i.-mass spectra with a Finnegan 4500 spectrometer, using ammonia as reagent gas at a source pressure of $\sim 2.5 \times 10^{-5}$ torr. Melting points were determined on a Reichert hot-stage (Kofler) apparatus and are uncorrected. T.l.c. was performed on silica gel plates "polygram G_{254}" (Camlab), with detection by u.v. light (254 nm), iodine vapour, methanolic 7% 12-molybdophosphoric acid, or 10% ceric sulphate in M H_2SO_4). Flash chromatography was carried out with Silica Gel 60 (0.04–0.063 mm, Merck) and reagent-grade solvents which were distilled before use. Light petroleum refers to the fraction b.p. 40–60°. All reactions were run under a slight positive pressure of dry nitrogen. All solvents were dried conventionally and distilled prior to use. Alkyllithiums were standardised using diphenylacetic acid[15].

2-C-Allyl-1,6-anhydro-4-O-benzyl-β-D-glucopyranose (**7**). — 3-Chloropropene (0.7 mL, 8.54 mmol) was added dropwise to a stirred suspension of magnesium (245 mg, 8.54 mmol) in dry ether (17 mL) at room temperature under nitrogen. After 30 min, a solution of 1,6:2,3-dianhydro-4-*O*-benzyl-β-D-mannopyranose[8] (**6**; 1 g, 4.27 mmol) in dry ether (24 mL) was added dropwise. The mixture was stirred and heated under reflux for 4 h, then cooled, poured into saturated aqueous ammonium chloride (25 mL), and extracted with dichloromethane (3 × 25 mL). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate (25 mL) and saturated aqueous sodium choride (25 mL), dried ($MgSO_4$), filtered, and concentrated. Column chromatography (ethyl acetate–light petroleum, 1:2) of the residue gave **7** (1.06 g, 90%), isolated as a colourless oil, $[\alpha]_D$ −18° (*c* 1, chloroform); R_F 0.44 (ethyl acetate–light petroleum, 1:1); ν_{max} 3530 (b, OH) and 1640 cm^{-1} (C=C). N.m.r. data: ^1H (400 MHz), δ 1.74 (br.t, 1 H, $J_{2,7A}$ 7.1 Hz, $J_{2,7B}$ 7.1 Hz, H-2), 2.21–2.33 (m, 2 H, H-7A, 7B), 2.60 (br.d, 1 H, $J_{3,OH}$ 7.2 Hz, OH), 3.34 (br.s, 1 H, H-4), 3.63 (dd, 1 H, $J_{6exo,6endo}$ 7.4 g $J_{5,6exo}$ 5.3 Hz, H-6*exo*), 3.66–3.68 (br.s, 1 H, H-3), 4.01 (d, 1 H, $J_{6exo,6endo}$ 7.4 Hz, H-6*endo*), 4.52 (br.d, 1 H, $J_{5,6exo}$ 5.3 Hz, H-5), 4.53 (d, 1 H, $J_{A,B}$ 12.1 Hz, PhCH_AH$_B$O), 4.61 (d, 1 H, $J_{A,B}$ 12.1 Hz, PhCH$_A$$H_B$O), 5.03 (dm, 1 H, $J_{8,9cis}$ 10.2 Hz, H-9*cis*), 5.04 (dm, 1 H, $J_{8,9trans}$ 17.1 Hz, H-9*trans*), 5.39 (br.s, 1 H, H-1), 5.75 (ddt, 1 H, $J_{8,9trans}$ 17.1, $J_{8,9cis}$ 10.2, $J_{8,7A}$ 7.0, $J_{8,7B}$ 7.0 Hz, H-8), 7.21–7.30 (m, 5 H, Ar-H); ^{13}C (100.6 MHz), δ 33.44 (t, 1 C, C-7), 45.65 (d, 1 C, C-2), 65.36 (t, 1 C, C-6), 69.03 (d, 1 C, C-3), 71.34 (t, 1 C, PhCH_2O), 74.77 (d, 1 C, C-5), 79.08 (d, 1 C, C-4), 103.26 (d, 1 C, C-1), 117.02 (t, 1 C, C-9), 127.44 (d, 2 C, *ortho*-ArC), 127.64 (d, 1 C, *para*-ArC), 128.32 (d, 1 C, C-8), 135.72 (s, 1 C, $C_{substituted}$ ArC). F.d.-mass spectrum: *m/z* 276 (M^+, 100%) and 277 ($M^+ + 1$, 32).

This reaction was repeated on a scale of up to 7.5 g of epoxide without loss in yield. The crude alcohol was routinely used without further purification.

Anal. Calc. for $C_{16}H_{20}O_4$: C, 69.5; H, 7.3;. Found: 69.6; H, 7.3.

1,6-Anhydro-4-O-benzyl-2-chloro-2-deoxy-β-D-glucopyranose (**8**). – 3-Chloropropene (0.17 mL, 2.14 mmol) was added dropwise to a stirred suspension of magnesium

(52 mg, 2.14 mmol) in anhydrous tetrahydrofuran (4.3 mL) at room temperature. After 30 min, a solution of **6** (250 mg, 1.07 mmol) in anhydrous tetrahydrofuran (6 mL) was added dropwise at room temperature. The mixture was heated under reflux for 5 h, then allowed to cool, poured into saturated aqueous ammonium chloride (10 mL), and extracted with dichloromethane (3 × 10 mL). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate (10 mL) and saturated aqueous sodium chloride (10 mL), dried ($MgSO_4$), filtered, and concentrated. Flash chromatography (ethyl acetate–light petroleum, 1:2) of the residue yielded **8** (220 mg, 76%), isolated as a colourless oil; R_F 0.52 (ethyl acetate–light petroleum, 1:1); ν_{max} 3535 cm^{-1} (b, OH). N.m.r. data: ^1H (360 MHz), δ 2.44 (d, 1 H, $J_{3,OH}$ 6 Hz, OH), 3.39 (br.s, 1 H, H-2), 3.71 (dd, 1 H, $J_{6exo,6endo}$ 7.5, $J_{5,6exo}$ 5.4 Hz, H-6*exo*), 3.72 (br.s, 1 H, H-4), 3.96 (d, 1 H, $J_{6exo,6endo}$ 7.5 Hz, H-6*endo*), 4.62–4.64 (br.s, 1 H, H-3), 4.63 (d, 1 H, $J_{5,6exo}$ 5.4 Hz, H-5), 4.67 (d, 1 H, $J_{A,B}$ 12.1 Hz, PhCH_AH_BO), 4.75 (d, 1 H, $J_{A,B}$ 12.1 Hz, PhCH_AH_BO), 5.55 (br.s, 1 H, H-1), 7.31–7.40 (m, 5 H, ArH); ^{13}C (100.6 MHz), δ 58.15 (d, 1 C, C-2), 66.36 (t, 1 C, C-6), 71.79 (t, 1 C, PhCH_2O), 72.33 (d, 1 C, C-3), 75.29 (d, 1 C, C-5), 78.73 (d, 1 C, C-4), 102.22 (d, 1 C, C-1), 127.86 (d, 2 C, *ortho*-ArC), 128.00 (d, 1 C, *para*-ArC), 128.55 (d, 2 C, *meta*-ArC), 137.48 (s, 1 C, $C_{substituted}$ ArC); F.d.-mass spectrum: *m/z* 270 ($M^{+\,35}Cl$, 100), 271 ($M^+ + 1$, 15) and 272 ($M^{+\,37}Cl$, 42).

Anal. Calc. for $C_{13}H_{15}ClO_4$: C, 57.7; H, 5.6. Found: C, 57.8; H, 5.6.

*Methyl-2-*C*-allyl-4-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**9**). — A saturated solution of hydrogen chloride in methanol (20 mL) was added to a stirred solution of **7** (0.68 g, 2.47 mmol) in methanol (3 mL) at 0°. The mixture was stirred at room temperature overnight, then concentrated to dryness. The solid residue was triturated with di-isopropyl ether to give **9** (0.731 g, 96%) as a colourless solid which was used without further purification. A sample for analysis, crystallised from ethyl acetate–light petroleum as colourless needles, had m.p. 128–131°, $[\alpha]_D$ +92.7° (*c* 1, chloroform); ν_{max} 3650–3100 (b, OH) and 1640 cm^{-1} (C=C). N.m.r. data: ^1H (360 MHz), δ 1.72–1.79 (m, 1 H, H-2), 2.06–2.17 (m, 2 H, H-7A, 7B), 3.30 (s, 3 H, OCH_3), 3.39 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 3.64 (dt, 1 H, $J_{3,4}$ 9.6, $J_{2,3}$ 3, $J_{3,OH}$ 3 Hz, H-3), 3.72–3.87 (m, 3 H, H-5, 6A, 6B), 4.58 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.72 (d, 1 H, $J_{A,B}$ 11.5 Hz, PhCH_AH_BO), 4.77 (d, 1 H, $J_{A,B}$ 11.5 Hz, PhCH_AH_BO), 5.03 (br.d, 1 H, $J_{8,9cis}$ 9.7 Hz, H-9*cis*), 5.09 (br.d, 1 H, $J_{8,9trans}$ 17.1 Hz, H-9*trans*), 5.73–5.85 (m, 1 H, H-8), 7.28–7.42 (m, 5 H, ArH); ^{13}C (90.56 MHz), δ 31.89 (t, 1 C, C-7), 45.97 (d, 1 C, C-2), 54.93 (q, 1 C, OCH_3), 62.03 (t, 1 C, C-6), 70.84 (d, 1 C, C-3), 72.92 (d, 1 C, C-5), 74.73 (t, 1 C, PhCH_2O), 79.61 (d, 1 C, C-4), 99.89 (d, 1 C, C-1), 116.58 (t, 1 C, C-9), 127.92 (d, 2 C, *ortho*-ArC), 127.97 (d, 1 C, *para*-ArC), 128.62 (d, 2 C, *meta*-ArC), 136.31 (d, 1 C, C-8), 138.31 (s, 1 C, $C_{substituted}$ ArC); F.d.-mass spectrum: *m/z* 308 (M^+, 100%) and 309 ($M^+ + 1$, 38).

Anal. Calc. for $C_{17}H_{24}O_5$: C, 66.2; H, 7.8. Found: C, 65.9; H, 7.8.

*Methyl-2-*C*-allyl-4-*O*-benzyl-2-deoxy-3,6-di-*O*-methanesulphonyl-α-*D*-glucopyranoside* (**10**). — Mesyl chloride (0.53 mL, 6.9 mmol) was added dropwise to a stirred solution of **9** (607 mg, 1.97 mmol) and triethylamine (1.2 mL) in anhydrous tetrahydrofuran (40 mL) at 0°. After 2 h at 0°, water (10 mL) was added dropwise followed by dichloromethane (20 mL). The organic phase was separated and the aqueous phase was

extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (10 mL) and saturated aqueous sodium chloride (10 mL), dried ($MgSO_4$), filtered, and concentrated. Flash chromatography of the residue (ethyl acetate–light petroleum, 1:2) yielded **10** (832 mg, 92%), isolated as a colourless oil, $[\alpha]_D$ +86° (*c* 1.3, chloroform), R_f 0.65 (ethyl acetate–light petroleum, 1:1); ν_{max} 1645 (C=C) and 1360 cm^{-1} (–SO_2–O–, mesylate). N.m.r. data: ^1H (360 MHz), δ 1.98 (tt, 1 H, $J_{2,3}$ 11, $J_{2,7A}$ 11, $J_{1,2}$ 3.4, $J_{2,7B}$ 3.4 Hz, H-2), 2.18–2.27 (m, 1 H, H-7A), 2.43–2.49 (m, 1 H, H-7B), 2.94 (s, 3 H, SO_2CH_3), 3.04 (s, 3 H, SO_2CH_3), 3.32 (s, 3 H, OCH_3), 3.61 (t, 1 H, $J_{3,4}$ 9.5, $J_{4,5}$ 9.5 Hz), 3.91 (dt, 1 H, $J_{4,5}$ 9.5 Hz, $J_{5,6A}$ 2.8 Hz, $J_{5,6B}$ 2.8 Hz, H-5), 4.67 (d, 1 H, $J_{A,B}$ 10.9 Hz, PhC$H_A$$H_B$O), 4.68 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.84 (d, 1 H, $J_{A,B}$ 10.9 Hz, PhC$H_A$$H_B$O), 4.84 (dd, 1 H, $J_{2,3}$ 11, $J_{3,4}$ 9.5 Hz, H-3), 5.09 (br.d, 1 H, $J_{8,9cis}$ 10.4 Hz, H-9*cis*), 5.13 (br.d, 1 H, $J_{8,9trans}$ 18 Hz, H-9*trans*), 5.65–5.77 (m, 1 H, H-8), 7.26–7.36 (m, 5 H, ArH); ^{13}C (90.56 MHz), δ 31.90 (t, 1 C, C-7), 37.65 (q, 1 C, SO_2CH_3), 38.63 (q, 1 C, SO_2CH_3), 45.26 (d, 1 C, C-2), 55.29 (q, 1 C, OCH_3), 68.38 (t, 1 C, C-6), 69.42 (d, 1 C, C-5), 74.70 (t, 1 C, PhCH_2O), 77.21 (d, 1 C, C-4), 83.06 (d, 1 C, C-3), 99.51 (d, 1 C, C-1), 117.79 (t, 1 C, C-9), 127.63 (d, 2 C, *ortho*-ArC), 128.15 (d, 1 C, *para*-ArC), 128.61 (d, 2 C *meta*-ArC), 134.54 (d, 1 C, C-8), 136.89 (s, 1 C, $C_{substituted}$ ArC). F.d.-mass spectrum: *m/z* (M^+, 100%) and 465 (M^++1, 37).

Anal. Calc. for $C_{19}H_{28}O_9S_2$: C, 49.1; H, 6.1. Found: C, 49.5; H, 6.1.

*Methyl 2-C-allyl-2-deoxy-3,6-di-O-methanesulphonyl-α-*D*-glucopyranoside* (**11**). — Sodium (0.54 g, 23.4 mmol) was added in one portion to a stirred solution of **10** (4.34 g, 9.35 mmol) in anhydrous tetrahydrofuran (3 mL) and liquid ammonia (~60 mL) at −78°. The reaction was quenched after the disappearance of the blue colour (~5 min) by the addition of solid ammonium chloride (0.5 g) at −78°. Ethyl acetate (25 mL) was added, and, after warming to room temperature, the mixture was dried ($MgSO_4$), filtered, and concentrated to give **11** (3.4 g, 97% crude) as a pale-yellow oil. The crude product was used without purification. A sample for analysis was purified by flash chromatography (ethyl acetate–light petroleum, 1:1), to give a colourless oil; ν_{max} 3600–3200 (b, OH) 1640 (C=C), and 1350 cm^{-1} (–SO_2–O–, mesylate). N.m.r. data: ^1H (360 MHz), δ 1.97 (tt, 1 H, $J_{2,3}$ 10.8, $J_{2,7A}$ 10.8, $J_{1,2}$ 3.6, $J_{2,7B}$ 3.6 Hz, H-2), 2.16–2.25 (m, 1 H, H-7A), 2.38–2.44 (m, 1 H, H-7B), 3.09 (s, 3 H, SO_2CH_3), 3.15 (s, 3 H, SO_2CH_3), 3.29–3.31 (br.s, 1 H, OH), 3.34 (s, 3 H, OCH_3), 3.70 (br.t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 8.8 Hz, H-4), 3.83 (dm, 1 H, $J_{4,5}$ 8.8 Hz, H-5), 4.44 (dd, 1 H, $J_{5,6A}$ 1.8 Hz, $J_{6A,6B}$ 11.4 Hz, H-6A), 4.60 (dd, 1 H, $J_{5,6B}$ 3.8, $J_{6A,6B}$, 11.4 Hz, H-6B), 4.69 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.74 (dd, 1 H, $J_{1,2}$ 10.8, $J_{3,4}$ 8.8 Hz, H-3), 5.08 (br.d, 1 H, $J_{8,9cis}$ 10 Hz, H-9*cis*), 5.12 (br.d, 1 H, $J_{8,9trans}$ 18 Hz, H-9*trans*), 5.66–5.74 (m, 1 H, H-8); ^{13}C (90.56 MH), δ 31.83 (t, 1 C, C-7), 37.48 (q, 1 C, SO_2CH_3), 38.53 (q, 1 C, SO_2CH_3), 44.28 (d, 1 C, C-2), 55.29 (t, 1 C, OCH_3), 68.66 (t, 1 C, C-6), 68.99 (d, 1 C, C-4),* 69.90 (d, 1 C, C-5),* 83.81 (d, 1 C, C-3), 99.56 (d, 1 C, C-1), 117.68 (t, 1 C, C-9), 134.53 (d, 1 C, C-8). F.d.-mass spectrum: *m/z* 374 (M^+, 100%) and 375 [(M^++1), 77].

Anal. Calc. for $C_{12}H_{22}O_9S_2$: C, 38.5; H, 5.9. Found C, 38.6; H, 5.8.

* These assignments may be reversed.

Methyl-2-C-allyl-3,4-anhydro-2-deoxy-6-O-methanesulphonyl-α-D-allopyranoside (**12**). — Sodium (442 mg, 19.2 mmol) in methanol (12 mL) was added dropwise to a stirred solution of **11** (1.5 g, 4.8 mmol) in anhydrous dichloromethane (28 mL) at 0°. The mixture was stirred at room temperature for 24 h and then diluted with water (50 mL), and the dichloromethane phase was separated. The aqueous phase was extracted with dichloromethane (3 × 25 mL), and the combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (25 mL) and saturated aqueous sodium chloride (25 mL), dried ($MgSO_4$), filtered, and concentrated to afford **12** (1.07 g, 83% crude) which was used without purification. A sample for analysis was purified by flash chromatography (ethyl acetate–light petroleum, 1:2) and isolated as a colourless oil, $[\alpha]_D$ +25° (*c* 2.2, chloroform); ν_{max} 1640 (C=C) and 1355 cm^{-1} (–SO_2–O–, mesylate). N.m.r. data: ^1H (360 MHz), δ 2.16–2.22 (m, 1 H, H-2), 2.32–2.38 (m, 2 H, H-7A, 7B), 3.06 (s, 3 H, SO_2CH_3), 3.25 (dd, 1 H, $J_{3,4}$ 5, $J_{2,3}$ 2 Hz, H-3), 3.29 (d, 1 H, $J_{3,4}$ 5Hz, H-4), 3.32 (s, 3 H, OCH_3), 4.22 (t, 1 H, $J_{5,6A}$ 4, $J_{5,6B}$ 4 Hz, H-5), 4.48 (d, 2 H, $J_{5,6A}$ 4, $J_{5,6B}$ 4 Hz, H-6A, 6B), 4.58 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 5.11 (dm, 1 H, $J_{8,9cis}$ 10 Hz, H-9*cis*), 5.18 (dm, 1 H, $J_{8,9trans}$ 17 Hz, H-9*trans*), 5.82 (ddt, 1 H, $J_{8,9trans}$ 17, $J_{8,9cis}$ 10, $J_{8,7A}$ 7, $J_{8,7B}$ 7 Hz, H-8); ^{13}C (90.56 MHz) δ 32.28 (t, 1 C, C-7), 37.67 (q, 1 C, SO_2CH_3), 38.13 (d, 1 C, C-2), 51.57 (d, 1 C, C-3),* 51.85 (d, 1 C, C-4),* 56.75 (t, 1 C, OCH_3), 65.69 (d, 1 C, C-5), 69.92 (t, 1 C, C-6), 98.81 (d, 1 C, C-1), 117.55 (t, 1 C, C-9), 134.87 (d, 1 C, C-8). F.d.-mass spectrum: *m/z* 246 [M^+-32, ($-CH_3CH$), 100%], 278 (M^+, 71) and 279 (M^++1, 19).

Anal. Calc. for $C_{11}H_{18}O_6S$: C, 47.5; H, 6.5. Found: C, 47.5; H, 6.6.

Methyl-2-C-allyl-2,4-dideoxy-6-O-methanesulphonyl-4-C-methyl-α-D-allopyranoside (**13**). — (*a*) Methylmagnesium chloride (0.14 mL of a 2.9M solution in tetrahydrofuran, 0.4 mmol) was added dropwise to a stirred solution of **12** (59 mg, 0.2 mmol) and cuprous bromide (1.4 mg, 0.01 mmol) in anhydrous tetrahydrofuran (1.1 mL) at 0° under nitrogen. The mixture was stirred for 9 h at 0°, quenched by the dropwise addition of saturated aqueous ammonium chloride (10 mL), and extracted with chloroform (10 mL). The aqueous phase was extracted with chloroform (3 × 10 mL), and the combined chloroform extracts were washed with saturated aqueous sodium chloride (10 mL), dried ($MgSO_4$), filtered, and concentrated to give **13** (54 mg, 92% crude) as a colourless oil: ν_{max} 3600–3200 (b, OH), 1640 (C=C), and 1315 cm^{-1} (–SO_2–O–, mesylates). N.m.r. data: ^1H (360 MHz), δ 0.93 (d, 3 H, $J_{4,10}$ 7.2 Hz, H-10), 1.85–1.92 (m, 1 H, H-2), 1.92–1.99 (m, 1 H, H-4), 2.21–2.29 (m, 2 H, H-7A, 7B), 3.06 (s, 3 H, SO_2CH_3), 3.39 (s, 3 H, OCH_3), 3.43 [d, 1 H, $J_{3,OH}$ 2 Hz, OH (D_2O exchange)], 3.57 (br.d, 1 H, $J_{3,OH}$ 2 Hz, H-3), 4.20 (dd, 1 H, $J_{5,6A}$ 2.7 Hz, $J_{6A,6B}$ 10 Hz, H-6A), 4.29 (dd, 1 H, $J_{5,6B}$ 8.4 Hz, $J_{6A,6B}$ 10 Hz, H-6B), 4.35 (dt, 1 H, $J_{5,6B}$ 8.4, $J_{5,6A}$ 2.7, $J_{4,5}$ 2.7 Hz, H-5), 4.65 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 5.07 (br.d, 1 H, $J_{8,9cis}$ 10 Hz, H-9*cis*), 5.13 (br.d, 1 H, $J_{8,9trans}$ 17 Hz, H-9*trans*), 5.75 (ddt, 1 H, $J_{8,9trans}$ 17, $J_{8,9cis}$ 10, $J_{8,7A}$ 7, $J_{8,7}$ 7 Hz, H-8); ^{13}C (90.56 MHz), δ 10.72 (q, 1 C, C-10), 31.62 (t, 1 C, C-7), 36.92 (d, 1 C, C-2),* 37.25 (d, 1 C, C-4),* 37.53 (q, 1 C, SO_2CH_3), 55.61 (q, 1 C, OCH_3), 63.80 (d, 1 C, C-3), 70.58 (t, 1 C, C-6), 72.65 (d, 1 C, C-5), 101.36 (d, 1 C, C-1), 117.20 (t, 1 C, C-9), 135.17 (d, 1 C, C-8).

Anal. Calc. for $C_{12}H_{22}O_5S$: C, 48.9; H, 7.5. Found: C, 48.9; H, 7.3.

(*b*) Methyl-lithium (1.6 mL of a 1.55M solution in ether, 2.5 mmol) was added

dropwise to a stirred suspension of cuprous iodide (246 mg, 1.29 mmol) in anhydrous ether (1.5 mL) at 0° under nitrogen. After 30 min, a solution of **12** (180 mg, 0.64 mmol) in anhydrous ether (0.4 mL) was added dropwise and the mixture was stirred at 0° for 4.5 h. The reaction was quenched by the dropwise addition of saturated aqueous ammonium chloride (5 mL), followed by chloroform (10 mL). The aqueous phase was extracted with chloroform (3 × 10 mL). The combined chloroform extracts were washed with saturated aqueous sodium chloride (10 mL), dried ($MgSO_4$), filtered, and concentrated to give **13** (154 mg, 81% crude) as a colourless oil.

Hydrolysis of **13**. — 2M Hydrochloric acid (1.5 mL) was added to a stirred solution of **13** (300 mg, 1.0 mmol) in acetone (2.7 mL) at room temperature. The mixture was stirred at 40° for 16 h, then diluted with ethyl acetate (5 mL), and neutralised with solid sodium hydrogen carbonate at 0°. The aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined ethyl acetate extracts were dried ($MgSO_4$), filtered, and concentrated to give a ~12:1 mixture (n.m.r. data) of crude *αβ*-**14** (222 mg, 79%) which was used without purification. N.m.r. data: ^1H (360 MHz), δ (major diastereoisomer) 0.94 (d, 3 H, $J_{4,10}$ 7 Hz, H-10), 1.83–1.89 (m, 1 H, H-2), 1.93–2.01 (m, 1 H, H-4), 2.26–2.33 (m, 2 H, H-7A, 7B), 2.70–2.90 (br.m, 2 H, 2 OH), 3.09 (s, 3 H, SO_2CH_3), 3.78 (br.m, 1 H, H-3), 4.20 (dd, 1 H, $J_{6A,6B}$ 10.8, $J_{5,6A}$ 3.8 Hz, H-6A), 4.24–4.28 (m, 1 H, H-5), 4.31 (dd, 1 H, $J_{6A,6B}$ 10.8, $J_{5,6B}$ 8 Hz, H-6B), 5.09 (br.d, 1 H, $J_{8,9cis}$ 8.8 Hz, H-9*cis*), 5.16 (br.d, 1 H, $J_{8,9trans}$ 17 Hz, H-9*trans*), 5.74–5.82 (m, 1 H, H-8).

The crude product was contaminated with a variable amount (<10%) of a second component. A small sample of this product was isolated by flash chromatography (ethyl acetate–light petroleum, 1:1) and is suggested to be 2-*C*-allyl-1,6-anhydro-2,4-dideoxy-4-*C*-methyl-*α*-D-glucopyranose (**15**); ν_{max} ($CDCl_3$) 3600–3200 (b, OH) and 1640 cm^{-1} (C=C). N.m.r. data: ^1H (360 MHz), δ 0.99 (d, 3 H, $J_{4,10}$ 6.8 Hz, H-10), 1.46–1.49 (br.m, 1 H, OH, D_2O exchange), 1.95–2.01 (m, 1 H, H-2), 2.10–2.18 (m, 2 H, H-4, 7A), 2.37–2.42 (m, 1 H, H-7B), 3.57 (dd, 1 H, $J_{6exo,6endo}$ 7.3, $J_{5,6exo}$ 5 Hz, H-6*exo*), 3.77–3.80 (br.m, 1 H, H-3), 3.86 (d, 1 H, $J_{6exo,6endo}$ 7.3 Hz, H-6*endo*), 4.25 (dd, 1 H, $J_{5,6exo}$ 5, $J_{4,5}$ 4 Hz, H-5), 5.06 (d, 1 H, $J_{8,9cis}$ 10 Hz, H-9*cis*), 5.14 (d, 1 H, $J_{8,9trans}$ 17 Hz, H-9*trans*), 5.78–5.88 (m, 1 H, H-8).

*2-C-Allyl-2,4-dideoxy-3,5-O-isopropylidene-6-O-methanesulphonyl-4-C-methyl-*D-*gulose propane-1,3-diyl dithioacetal* (**16**). — Boron trifluoride etherate (0.1 mL, 0.9 mmol) was added dropwise to a stirred solution of **13** (130 mg, 0.45 mmol) and propane-1,3-dithiol (0.09 mL, 0.9 mmol) in anhydrous dichloromethane (3 mL) at 0°. The mixture was stirred at 0° for 4 h, diluted with saturated aqueous sodium hydrogen carbonate (5 mL), stirred at 0° for a further 30 min, and then diluted with dichloromethane (25 mL). The aqueous phase was extracted with dichloromethane (3 × 25 mL), and the combined dichloromethane extracts were washed with saturated aqueous sodium chloride (25 mL), dried ($MgSO_4$), and concentrated. A solution of the crude dithioacetal in 2,2-dimethoxypropane (0.5 mL) was stirred with *p*-toluenesulphonic acid (10 mg, 0.05 mmol) for 20 h at room temperature, then diluted with chloroform (10 mL), washed with saturated aqueous sodium hydrogen carbonate (5 mL), and saturated aqueous sodium chloride (5 mL), dried ($MgSO_4$), filtered, and concentrated. Flash

chromatography (silica gel pre-treated with triethylamine; ethyl acetate–light petroleum, 1:3) gave **16** (103 mg, 56% from **7**), isolated as a colourless oil. N.m.r. data: ^{1}H (360 MHz), δ 0.84 (d, 3 H, $J_{4,10}$ 6.8 Hz, H-10), 1.41 (s, 3 H, O_2CCH_3), 1.45 (s, 3 H, O_2CCH_3), 1.77–1.90 (m, 1 H, H-2), 1.98–2.16 (m, 4 H, $SCH_2CH_2CH_2S$, H-7A, 7B), 2.40–2.45 (m, 1 H, H-4), 2.80–2.88 (m, 4 H, $SCH_2CH_2CH_2S$), 3.04 (s, 3 H, SO_2CH_3), 3.97 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 1.7 Hz, H-3), 4.13 (dd, 1 H, $J_{6A,6B}$ 8.5 Hz, $J_{5,6A}$ 1.9 Hz, H-6A), 4.20–4.26 (m, 2 H, H-5, 6B), 4.55 (d, 1 H, $J_{1,2}$ 2.3 Hz, H-1), 5.02 (br.d, 1 H, $J_{8,9cis}$ 10 Hz, H-9*cis*), 5.08 (br.d, 1 H, $J_{8,9trans}$ 18 Hz, H-9*trans*), 5.86–5.99 (m, 1 H, H-8). F.d.-mass spectrum: *m/z* 410 (M^+, 100) and 411 (M^++1, 31).

Ethyl (E)-*4-C-allyl-2,3,4,6-tetradeoxy-5,7-O-isopropylidene-8-O-methanesulphonyl-2,6-di-C-methyl-*D*-gulo-oct-2-enoate* (**17**). — Methyl iodide (0.5 mL) was added to a stirred solution of **16** (57 mg, 0.14 mmol) and calcium carbonate (50 mg) in acetonitrile (1 mL) and water (0.5 mL) at room temperature. The mixture was stirred at room temperature for 16 h, diluted with chloroform (10 mL), dried ($MgSO_4$), filtered, and concentrated. To a solution of the crude aldehyde (43 mg) in chloroform (10 mL) was added 1-(ethoxycarbonyl)ethylidenetriphenylphosphorane (100 mg, 0.28 mmol) in one portion. The mixture was stirred for 20 h at room temperature, then diluted with chloroform (10 mL), filtered through silica gel, and concentrated. Flash chromatography (ethyl acetate–light petroleum, 1:2.5) of the residue gave **17** (30 mg, 53% from **16**), isolated as a colourless oil. N.m.r. data: ^{1}H (360 MHz), δ 0.91 (d, 3 H, $J_{6,13}$ 6.8 Hz, H-13), 1.30 (t, 3 H, J_{CH_2,CH_3} 7 Hz, CH_2CH_3), 1.33 (s, 3 H, O_2CCH_3), 1.37 (s, 3 H, O_2CCH_3), 1.65–1.71 (m, 1 H, H-6), 1.82 (d, 3 H, $J_{3,12}$ 1.4 Hz, H-12), 1.91–2.02 (m, 1 H, H-9A), 2.18–2.23 (m, 1 H, H-9B), 2.62 (ddd, 1 H, $J_{4,5}$ 9, $J_{4,9A}$ 4, $J_{4,9B}$ 4.0 Hz, H-4), 3.05 (s, 3 H, SO_2CH_3), 3.77 (dd, 1 H, $J_{4,5}$ 9, $J_{5,6}$ 2 Hz, H-5), 4.13–4.27 (m, 5 H, H-7, 8A, 8B and OCH_2CH_3), 5.01 (br.d, 1 H, $J_{10,11cis}$ 10 Hz, H-11*cis*), 5.04 (br.d, 1 H, $J_{10,11trans}$ 18 Hz, H-11*trans*), 5.67 (ddt, 1 H, $J_{10,11trans}$ 18, $J_{10,11cis}$ 10, $J_{10,9A}$ 7, $J_{10,9B}$ 7 Hz, H-10), 6.58 (dd, 1 H, $J_{3,4}$ 9.8, $J_{3,12}$ 1.4 Hz, H-3). F.d.-mass spectrum: *m/z* 404 (M^+, 100) and 405 (M^++1, 28).

*Methyl 2-C-allyl-2,4-dideoxy-4-C-methyl-α-*D*-gulopyranoside* (**18**). — Methylmagnesium chloride (21 mL of a 2.9M solution in tetrahydrofuran, 61 mmol) was added dropwise to a stirred solution of **12** (5.26 g, 18.9 mmol) and cuprous bromide (0.13 g, 0.9 mmol) in anhydrous tetrahydrofuran (95 mL) at 0° under nitrogen. The mixture was stirred at 0° for 1 h, then at room temperature for 22 h. More Grignard reagent solution (7 mL, 20.3 mmol) was added dropwise at room temperature and the mixture stirred thereat for a further 4 h, followed by heating under reflux for 1 h. The mixture was quenched at 0° by the dropwise addition of saturated aqueous ammonium chloride (3 mL) followed by the addition of M hydrochloric acid (100 mL). The mixture was extracted with ethyl acetate (3 × 100 mL), and the combined extracts were washed with water (3 × 100 mL) and saturated aqueous sodium chloride (100 mL), dried ($MgSO_4$), and filtered. Flash chromatography (ethyl acetate–light petroleum, 1:1), of the residue (3.2 g) gave **18** (2.31 g, 57%), isolated as a clear oil, $[\alpha]_D$ +66° (*c* 3.4, chloroform); ν_{max} 3680–3200 (b, OH) and 1640 (C=C) cm^{-1}. N.m.r. data: ^{1}H (360 MHz), δ 0.87 (d, 3 H, $J_{4,10}$ 7.2 Hz, H-10), 1.84–1.92 (m, 2 H, H-2,4), 2.08 (br.m, 1 H, OH, D_2O exchange), 2.22–2.27 (m, 2 H, H-7A, 7B), 3.38 (s, 3 H, OCH_3), 3.47 (d, 1 H, $J_{3,OH}$ 10 Hz, OH, D_2O

exchange), 3.51–3.57 (m, 2 H, H-3, 6A), 3.72 (br.t, 1 H, $J_{6A,6B} = J_{5,6B} = 8.6$ Hz, H-6B), 4.15 (dt, 1 H, $J_{5,6B}$ 8.6 Hz, $J_{5,6A} = J_{4,5} = 3.0$ Hz, H-5), 4.63 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 5.05 (br.d, 1 H, $J_{8,9cis}$ 10 Hz, H-9*cis*), 5.11 (br.d, 1 H, $J_{8,9trans}$ 17 Hz, H-9*trans*), 5.67 (ddt, 1 H, $J_{8,9trans}$ 17, $J_{8,9cis}$ 10, $J_{8,7A}$ 7 Hz, $J_{8,7B}$ 7 Hz, H-8).

Anal. Calc. for $C_{12}H_{22}O_5S$: 61.1; H, 9.3. Found: C, 60.6; H, 9.1.

*Methyl 2-*C*-allyl-2,4-dideoxy-4-*C*-methyl-α-*D*-gulo-hexodialdo-1,5-pyranoside* (**19**). — Sulphur trioxide–pyridine complex (3.29 g, 20.7 mmol) was added to a solution of **18** (1.37 g, 6.3 mmol) in dry Me_2SO (17 mL) and triethylamine (13.5 mL, 96.7 mmol) with stirring at room temperature. The mixture was stirred vigorously at this temperature for 15 min, then water (30 mL) was added, the mixture was extracted with dichloromethane (3 × 30 mL), and the combined extracts were washed with water (3 × 30 mL) and saturated aqueous sodium chloride (30 mL), dried ($MgSO_4$), filtered, and concentrated. Flash chromatography (ethyl acetate–light petroleum, 1:1) of the residue (1.66 g) gave **19** (1.01 g, 4.7 mmol, 75%), isolated as a somewhat unstable oil which was used immediately; $[\alpha]_D$ +75° (*c* 2, chloroform); ν_{max} 3600–3200 (b, OH), 1730 (C=O), 1630 cm^{-1} (C=C). N.m.r. data: ^1H (300 MHz), δ 0.92 (d, 3 H, $J_{3,10}$ 8.0 Hz, H-10), 1.85–1.94 (m, 1 H, H-2), 2.19–2.15 (m, 2 H, H-7A, 7B), 2.30–2.40 (m, 1 H, H-4), 3.37 (s, 3 H, OCH_3), 3.58–3.63 (br.m, 2 H, H-3 and OH, D_2O exchange), 4.58 (d, 1 H, $J_{4,5}$ 3.0 Hz, H-5), 4.77 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1), 5.08 (br.d, 1 H, $J_{8,9cis}$ 10 Hz, H-9*cis*), 5.11 (br.d, 1 H, $J_{8,9trans}$ 17 Hz, H-9*trans*), 5.64–5.82 (m, 1 H, H-8), 9.63 (s, 1 H, H-6).

*Methyl (methyl-2-*C*-allyl-2,4,6-trideoxy-4-*C*-methyl-α-*D*-gulo-heptopyranosid)-uronate* (**20**). — Tosylmethyl isocyanide (1.05 g, 5.4 mmol) was added to a suspension of potassium *tert*-butoxide (1.20 g, 10.7 mmol) in dry tetrahydrofuran (22 mL) at 10°. The mixture was stirred at 10° for 10 min and then cooled to −10°, and a solution of **19** (1.05 g, 4.9 mmol) in dry tetrahydrofuran (10 mL) was added dropwise. The mixture was stirred for 8 min at −10°, quenched with methanolic HCl [from methanol (125 mL) and acetyl chloride (1.75 mL)] at −10°, stirred for 2 h at room temperature, and concentrated, and the residue was extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with water (2 × 50 mL) and saturated aqueous sodium chloride (50 mL), dried ($MgSO_4$), filtered, and concentrated. Flash chromatography (ethyl acetate–light petroleum 1:9) of the residue (1.57 g) gave **20** (0.44 g, 35%), isolated as a colourless oil, $[\alpha]_D$ +86° (*c* 2, chloroform); ν_{max} 3550–3400 (b, OH), 1735 (C=O), 1640 cm^{-1} (C=C). N.m.r. data: ^1H (300 MHz), δ 0.88 (d, 3 H, $J_{4,11}$ 7.0 Hz, H-11), 1.8–1.88 (m, 2 H, H-2,4), 2.21 (br.t, 2 H, $J_{2,8}$ 7.0 Hz, H-8A, 8B), 2.29 (dd, 1 H, $J_{5,6A}$ 3.5, $J_{6A,6B}$ 15.0 Hz, H-6A), 2.55 (dd, 1 H, $J_{5,6B}$ 10.0, $J_{6A,6B}$ 15.0 Hz, H-6B), 3.34 (s, 3 H, OCH_3), 3.67 (s, 3 H, CO_2CH_3), 4.54 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 4.64 (dt, 1 H, $J_{4,5}$ 3.5, $J_{5,6A}$ 3.5, $J_{5,6B}$ 10.0 Hz, H-5), 5.01 (br.d, 1 H, $J_{9,10cis}$ 10 Hz, H-10*cis*), 5.07 (br.d, 1 H, $J_{9,10}$ 17 Hz, H-10*trans*), 5.71–5.79 (1 H, m, H-9). C.i.-mass spectrum: *m/z* 209 [(M + H)$^+$, 100], 210 [(M+1+H)$^+$, 26].

ACKNOWLEDGMENTS

We thank the S.E.R.C. for a CASE studentship (to S.C.) (with Glaxo Group Research Greenford) and a Postdoctoral Research Assistantship (to D.G.), and Dr. A. H. Davidson and Professor S. M. Roberts for valuable discussions.

REFERENCES

1 S. Hanessian, *Total Synthesis of Natural Products: The "Chiron" Approach*, Pergamon, Oxford, 1983.
2 S. Challenger and G. Procter, *Tetrahedron Lett.*, 27 (1986) 391–394.
3 P. J. Hodges and G. Procter, *Tetrahedron Lett.*, 26 (1985) 4111–4114.
4 M. Cerny and J. Stanek, *Adv. Carbohydr. Chem. Biochem.*, 34 (1977) 23–175.
5 M. P. Edwards, S. V. Ley, S. G. Lister, and B. D. Palmer, *J. Chem. Soc., Chem. Commun.*, (1983) 630–633; A. F. Sviridov, M. S. Ermolento, D. V. Yashunsky, V. S. Borodkin, and N. K. Kochetkov, *Tetrahedron Lett.*, 28 (1987) 3835–3838 and 3839–3842.
6 I. Paterson and M. M. Mansuri, *Tetrahedron*, 41 (1985) 3569–3624.
7 K. C. Nicolaou, S. P. Seitz, and M. R. Pavia, *J. Am. Chem. Soc.*, 103 (1981) 1224–1226; R. H. Schlessinger, M. A. Poss, and S. Richardson, *ibid.*, 108 (1986) 3112–3114; W. C. Still and V. J. Novack, *ibid.*, 106 (1984) 1148–1149.
8 M. Cerny and T. Trinka, *Collect. Czech. Chem. Commun.*, 36 (1971) 2216–2225.
9 A. G. Kelly and J. S. Roberts, *J. Chem. Soc., Chem. Commun.*, (1980) 228–229.
10 B. J. Wakefield, *Adv. Inorg. Chem. Radiochem.*, 11 (1968) 341–425.
11 B. Fraser-Reid, R. D. Dawe, and D. B. Tulshian, *Can. J. Chem.*, 57 (1979) 1746–1749.
12 M. D. Nair and R. Adams, *J. Am. Chem. Soc.*, 83 (1961) 922–926; L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, (1960) 2886–2890.
13 U. Sunay and B. Fraser-Reid, *Tetrahedron Lett.*, 27 (1986) 5335–5338.
14 S. Umezawa, T. Tsuchiya, and H. Hineno, *Bull. Chem. Soc. Jpn.*, 43 (1970) 1212–1218.
15 W. Kofron and L. M. Baclawski, *J. Org. Chem.*, 41 (1976) 1879–1880.