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A Stereoselective Route to the Sugar-Cinnamate Unit of Hygromycin A

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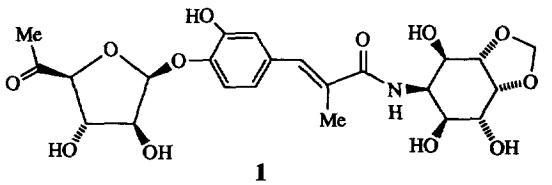
Abstract: Various aryl 6-deoxy-5-keto-β-D-*arabino*-hexofuranosides, including one (**42**) corresponding to the sugar-cinnamate unit of Hygromycin A (**1**) have been synthesized by a method in which 6-deoxy-β-D-glucofuranosides are first prepared, followed by configurational inversion at positions 2 and 3 *via* 2,3-anhydro-6-deoxy-β-D-mannofuranosyl intermediates.

The antibiotic hygromycin A, produced by various strains of *Streptomyces*, was first isolated in 1953,[1] and its structure was established as **1** by a combination of degradative[2] and spectroscopic studies.[3] Hygromycin A has a relatively broad spectrum of moderate activity against Gram-positive and Gram-negative bacteria,[1] but the compound has attracted renewed interest in recent years due to its prevention of haemagglutination by an enterotoxic strain of *E.coli*,[4] and in particular its activity both *in vitro*[5] and *in vivo*[6] against *Serpulinia (Treponema) hyodysenteriae*, the causative agent of swine dysentery, a disease of considerable economic significance. This antitreponemal activity has led to considerable semisynthetic effort in Pfizer laboratories to determine structure-activity relationships in hygromycin analogues,[7] leading to the conclusion, *inter alia*, that the 6-deoxy-5-keto-β-D-*arabino*-hexofuranosyl unit can be replaced by an allyl ether without loss of activity against *S. hyodysenteriae*.[8]



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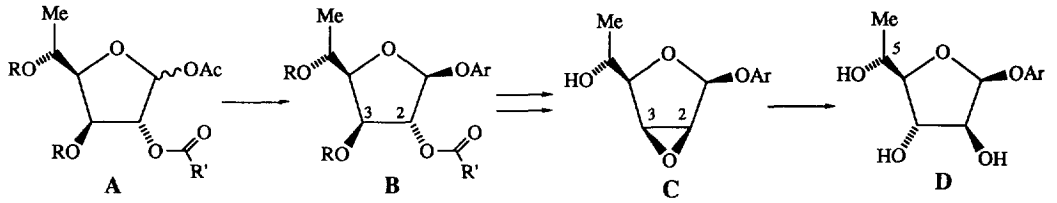
In any approach to the total synthesis of Hygromycin A and analogues, one stereochemical issue which requires particular attention concerns the stereoselective synthesis of the β-*cis* glycosidic link between the sugar residue and the central cinnamate unit (2-methylcaffeic acid in Hygromycin A itself).[9] In

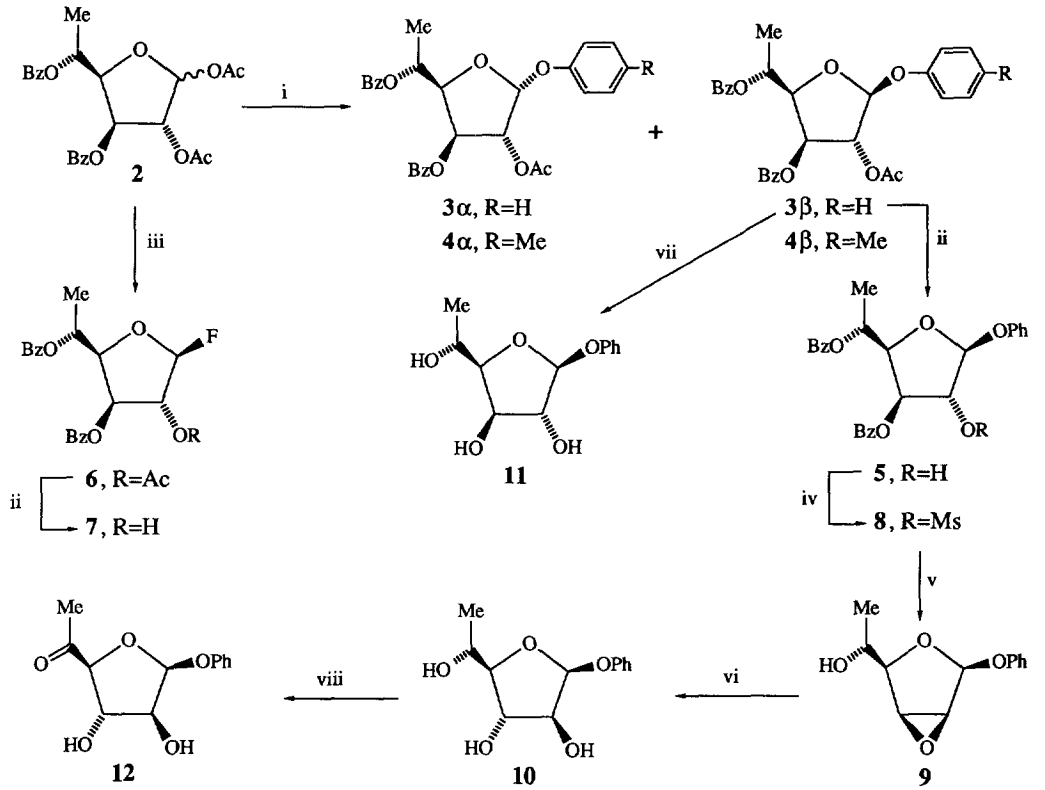
the one reported total synthesis of Hygromycin A (**1**),[10] the glycosidic link was made by Mitsunobu coupling of a carbohydrate hemiacetal of correct configuration, with *O*-2 protected as a benzyl ether, with a suitable phenol (3-benzyloxy-4-hydroxybenzaldehyde). However, this method of coupling gave virtually no stereocontrol (β:α, 5:4). We considered an alternative approach (Scheme 1) in which a precursor **A** of D-*gluco*-configuration, and with *O*-2 acylated, undergoes glycosylation with a phenol to give an aryl glycoside in which the 1,2-*trans*-product **B** should predominate due to intramolecular participation by the *O*-acyl group.[9] Subsequently, the stereochemistry at both C-2 and C-3 could be inverted *via* the formation of an epoxide of β-D-*manno*-configuration (**C**), since hydrolysis of such an oxirane should occur by regioselective attack of hydroxide ion at C-3 to give a product **D** of β-D-*altro*-stereochemistry.[11,12] We also envisaged that compounds of type **D** could be selectively oxidised at C-5 by use of the Jones reagent without the need for elaborate protective sequences, as reported from Kiely's laboratory for similar substrates.[13]



Scheme 1

The applicability of this approach was first investigated with phenol and *p*-cresol as aglycones (Scheme 2). The 6-deoxy-D-glucofuranose derivative **2** is readily available from 1,2-*O*-isopropylidene-α-D-glucofuranose by reduction of the 6-*O*-tosyl derivative with $LiAlH_4$.[14] Reaction of **2** with phenol or *p*-cresol in the presence of $SnCl_4$ in toluene[15] gave the glycosides **3** and **4** in moderate yield, but with a somewhat disappointing degree of stereocontrol (β:α~2:1). The anomers were however separable by column chromatography. Other reported conditions for the preparation of aryl glycosides[16] gave inferior yields with no improvement in stereoselectivity. The anomeric configurations of **3α**, **4α**, **3β** and **4β**, and other similar compounds described below, were clear from n.m.r. data. In the ^1H-spectra, the α-anomers displayed H-1 as a doublet (*J*~4.5 Hz) whilst the β-anomers, in which H-1 and H-2 are oriented *trans*-, showed the signals for H-1 as singlets.[17] In ^{13}C- spectra, the α-anomers, in which the substituents at C-1 and C-2 are *cis*, showed the signals for C-1 at higher field than was observed for the corresponding β-anomer (for **3α**, δ 98.4; for **3β**, δ 103.7).[18]

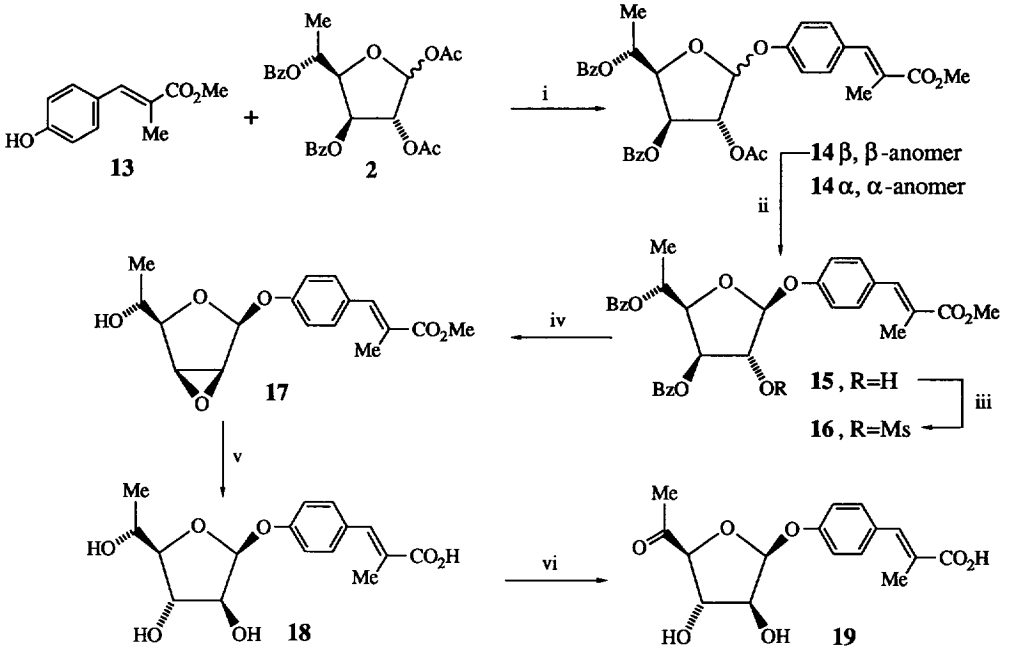
Initial attempts at selective deacetylation of **3β** under various conditions[19] were accompanied by varying degrees of concomitant debenzoylation. However, alcohol **5** could be obtained in 78% yield when **3β** was treated with 1 equivalent of sodium phenoxide and 1 equivalent of phenol in ethanol. These conditions were arrived at as a result of parallel studies on the possible use of glycosyl fluoride **6** [from **2** and pyridinium poly(hydrogen fluoride)[20]] as a potential glycosylating agent. It has been reported that treatment of tetra-*O*-acetyl-β-D-glucofuranosyl fluoride with a large excess of sodium phenoxide in ethanol gives a high yield of phenyl β-D-glucofuranoside, with the α-1,2-epoxide as a presumed intermediate.[21] It was hoped that in the case of **6**, debenzoylation might be avoided by the use of the minimum amount of reagent for deacetylation, epoxide formation, and epoxide opening, i.e. 1 equivalent each of PhONa and PhOH. In fact, these conditions did not convert **6** to **5**, but gave only clean deacetylation to yield **7**. Deacetylation also resulted when **3β** was treated in this way. We also observed that when a mixture of **3α** and **3β** was treated with NaOPh/PhOH in EtOH for 30 min, the β-anomer was cleanly deacetylated, whilst the α-anomer remained essentially unchanged. The alcohol **5** could then be easily separated from acetate **3α** by chromatography.



Scheme 2. i, PhOH or *p*-cresol, $SnCl_4$, toluene; ii, NaOPh, PhOH (1:1), EtOH, 30 min; iii, pyridinium poly(HF), toluene; iv, MsCl, C_5H_5N; v, NaOMe (1.5 eq.), MeOH, 30 min; vi, NaOH aq, reflux, 1.5 h; vii, NaOMe (cat.), MeOH, 1h; viii, CrO_3, H_2SO_4, acetone.

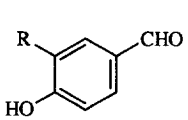
Alcohol **5** could be converted to mesylate **8** in high yield, and this upon treatment with NaOMe/MeOH gave the D-*manno*-epoxide **9** in 90% yield. When **9** was heated under reflux with aqueous NaOH solution, the D-*altro*-triol **10** was obtained as a crystalline solid. The stereostructure of **10** was supported by spectroscopic data ($J_{1,2}$ 4.4 Hz; C-1, δ 101.2) and by the synthesis of D-*gluco*-triol **11** ($J_{1,2}$ ~ 0; C-1, δ 108.2) by deacylation of **3β**. Selective oxidation of **10** with Jones' reagent proved successful and the 5-keto-compound **12** was obtained in 60% yield.

With the general approach validated, we wished to prepare an analogue containing *p*-hydroxy-2-methyl-cinnamic acid as the aglycone. Attempts to oxidise the benzylic methyl group of **4β** using ceric ammonium nitrate, a reaction used in the total synthesis of hygromycin,[10] were unsuccessful, as were attempts to condense **2** with *p*-hydroxybenzaldehyde. Thus the enoate **13** (Scheme 3) was prepared by a Wittig reaction; the *E*-isomer **13** was the major product, but small amounts of the *Z*-isomer were also formed. The two could be readily distinguished both by n.O.e. measurements and by the deshielded position of the alkene proton in **13**. Condensation of **13** with **2** in the presence of $SnCl_4$ gave **14β** and **14α** in a ratio of 2.4:1 (total yield 55%). The β-anomer could be separated by chromatography, and deacetylated to give **15** (85%) using PhONa-PhOH in ethanol. The conversion of glucoside **15** to altroside **18** ($J_{1,2}$ 4.3 Hz; C-1, δ 101.0) was carried out (Scheme 3) as in the simpler model series, and again selective oxidation was possible to give the keto-compound **19**.

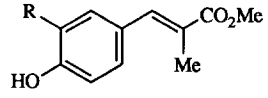


Scheme 3. i, $SnCl_4$, CH_2Cl_2; ii, NaOPh, PhOH (1:1), EtOH, 30 min; iii, MsCl, C_5H_5N; iv, NaOMe (1.1 eq.), MeOH, 50 min; v, NaOH aq, reflux, 3h; vi, CrO_3, H_2SO_4, acetone.

In order to prepare glycosides incorporating the additional phenolic oxygen function found in Hygromycin A, we first investigated the reactions of **2**, under Lewis acid catalysis, with the aglycones **20**,[22] vanillin (**21**), and 3-acetoxy-4-hydroxybenzaldehyde (**22**),[23] but no glycosides could be isolated from any of these reactions under a variety of conditions. Experiments with 4-hydroxy-3-methylbenzaldehyde (**23**) and with 4-hydroxy-3-nitrobenzaldehyde (**24**) were equally unrewarding. The three 2-methyl-cinnamates **25**, **26**, and **27**, containing substituents of varying electron demand, were prepared by Wittig reactions, but attempted condensations of these with **2** under Lewis acid-catalysed conditions were also unsuccessful. Given the fact that the simpler phenol **13** reacted satisfactorily, it can be concluded that the lack of reactivity in the case of the more substituted compounds is primarily steric in origin.[24]



20, R=OBn
21, R=OMe
22, R=OAc
23, R=Me
24, R=NO_2

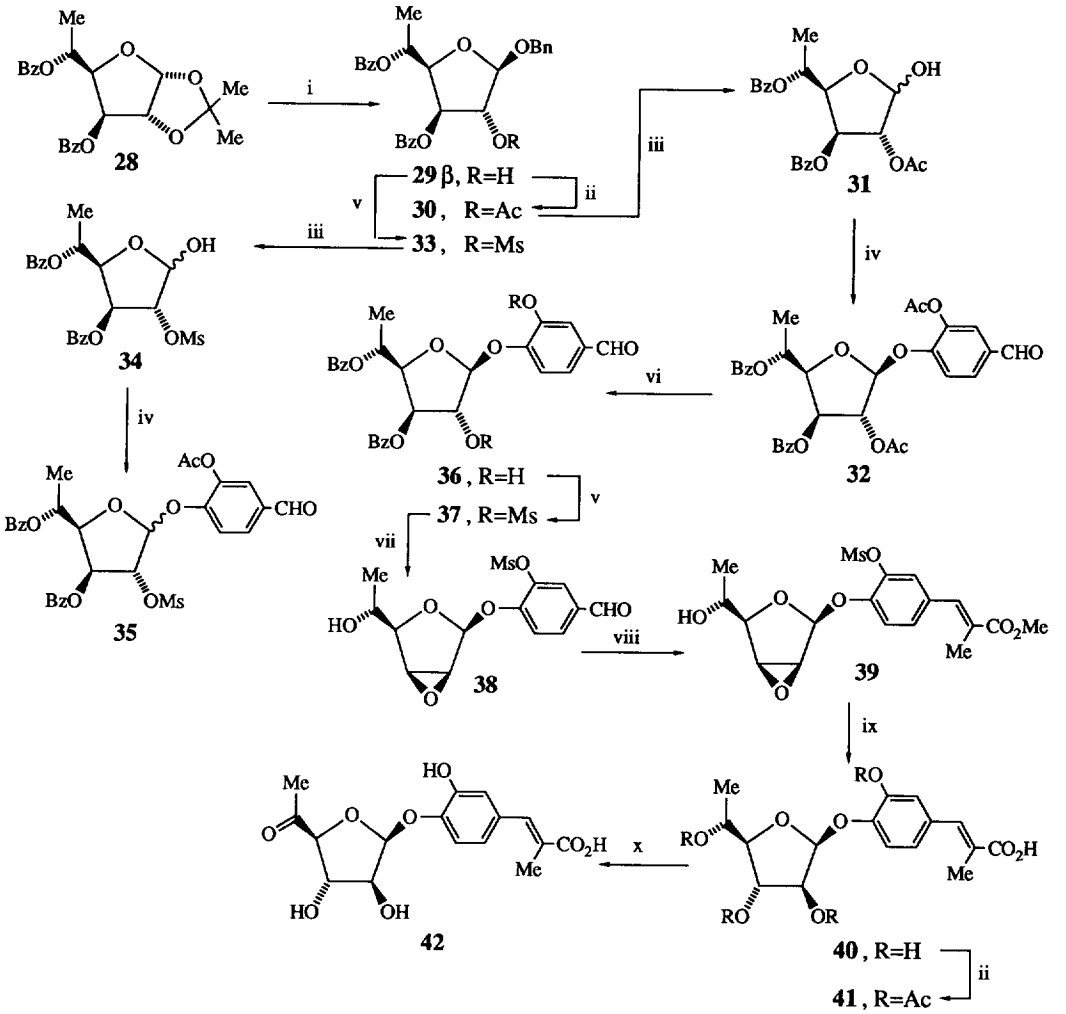


25, R=OMe
26, R=Me
27, R=NO_2

We therefore considered the use of Mitsunobu coupling[25] to produce the glycosidic link, as in Ogawa's synthesis of Hygromycin A,[10] but with the use of a potentially participatory acetyl substituent at *O*-2. There seems to be very limited evidence as to whether *O*-acyl participation can influence the stereochemistry of glycosylations using the Mitsunobu reaction, although Grynkiewicz has reported that glycosylation of phenol with 2,3,4,6-tetra-*O*-acetyl-D-mannopyranose under Mitsunobu conditions gave only the α-glycoside, a result that could reflect steric factors rather than intramoleuclar participation.[26]

Since attempts to deacetylate **2** selectively at the anomeric position did not proceed well, the isopropylidene derivative **28** (the immediate precursor of **2**) was treated with benzyl alcohol under acidic

conditions to give glycoside **29β** (74%), together with some of the α-anomer (Scheme 4). Conventional acetylation gave **30**, and hydrogenolysis produced **31** in good yield.[27] Reaction of **31** with 3-acetoxy-4-hydroxybenzaldehyde (**22**) in the presence of Ph_3P and diethyl azodicarboxylate gave a moderate yield of the β-anomer **32**; the α-anomer could not be detected amongst the products.



Scheme 4. i, BnOH, HCl; ii, Ac_2O, C_5H_5N; iii, H_2, Pd/C, 1 atm.; iv, **22**, Ph_3P, DEAD, THF; v, MsCl, C_5H_5N; vi, NaOPh, PhOH (1:1), EtOH, 80 min; vii, NaOMe, MeOH; viii, $Ph_3PC(Me)CO_2Me$, CH_2Cl_2; ix, NaOH aq, reflux, 4h; x, CrO_3, H_2SO_4, acetone.

We were also interested in finding whether the presence of a mesylate at *O*-2, as required in the later steps of the sequence, would exert any directing effect, either for steric or electronic reasons. Thus **29β** was converted *via* **33** to **34** (Scheme 4); reaction of **34** with **22** under Mitsunobu conditions gave glycoside **35** (43%), but as a 2:3 mixture of anomers.

The diacetyl derivative **32** could be cleanly deacetylated to give the phenolic alcohol **36** using phenoxide and phenol. Mesylation and epoxide formation proceeded in good yield to give **38**. It was

anticipated that the phenolic mesylate function would undergo hydrolysis under the conditions used for epoxide opening. Therefore, the epoxide **38** was firstly subjected to a Wittig reaction to give **39** (86%), which upon heating under reflux with aqueous sodium hydroxide solution gave the fully-deprotected hydroxyacid **40**, characterized further as the tetra-*O*-acetyl derivative **41**. The selective oxidation of **40** was again possible, to give the keto-compound **42**, which constitutes the complete 'left' and 'central' portions of Hygromycin A (**1**).

EXPERIMENTAL

I.R. spectra were recorded on a Perkin-Elmer FT-IR 1600 instrument. Mass spectrometry was performed using an updated VG-MS 9 spectrometer. NMR spectra were recorded on Perkin-Elmer WP 80 and Perkin-Elmer WP 200 SY spectrometers. All proton spectra were run at 200 MHz and carbon at 50 MHz, using $CDCl_3$ as solvent, unless otherwise stated. Coupling constants are quoted in Hz.

Specific rotations were performed on a Bendix-NPL 143D automatic polarimeter (path length 1 cm); units for $[\alpha]_D$ -values are 10^{-1} deg cm^2 g^{-1}. Melting points were determined using an Electrothermal MK II melting point apparatus and are uncorrected.

Reactions were monitored by t.l.c. on pre-coated aluminium backed plates, Kieselgel HF_{254} type 60 (Merck). Detection was effected using u.v. light or 5% aqueous ammonium molybdate solution to which concentrated sulfuric acid had been added. Column chromatography was carried out using Sorbsil C60 40/60H (Prolabo); an external pressure was applied to the top of the columns. Light petroleum refers to material of boiling range 60-80 °C.

Phenyl 2-O-*acetyl*-3,5-*di*-O-*benzoyl*-6-*deoxy*-α-D-*glucofuranoside* (**3α**), and the β-*isomer* (**3β**). - Stannic chloride (1.7 g, 6.0 mmol) was added dropwise to an ice-cooled solution of 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-D-glucofuranose (**2**)[14] (2.475 g, 5.43 mmol) and phenol (614.4 mg, 6.54 mmol) in dry toluene (25 cm^3). After 15 h the reaction mixture was diluted with toluene (25 cm^3) and washed with aqueous NaOH solution (2M, 25 cm^3) and then with water until neutral. The extracts were dried (Na_2SO_4), filtered and reduced *in vacuo* to give a syrup. Chromatography on silica, with ethyl acetate-toluene (1:20) as eluent gave firstly the α-anomer **3α** (449.7 mg, 17%) as a thick syrup; $[\alpha]_D$ +77.3 (*c* 0.88 in $CHCl_3$); ν_{max} (KBr) 3000, 1733, 1717, 1599 and 1495 cm^{-1}; δ_H 1.41 (3H, d, $J_{6,5}$ 6.2, H-6), 2.3 (3H, s, OAc), 4.59 (1H, dd, $J_{4,3}$ 6.2, $J_{4,5}$ 7.8, H-4), 5.24 (1H, t, *J* 4.8, H-2), 5.35 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 7.7, H-5), 5.89 (1H, d, $J_{1,2}$ 4.6, H-1), 6.01 (1H, dd, $J_{3,4}$ 6.1, $J_{3,2}$ 5.0, H-3), 7-7.9 (15H, m, Ar); δ_C 17.2 (C-6), 20.5 ($COCH_3$), 68.8 (C-5), 74.6, 77.0 and 78.0 (C-2, C-3 and C-4), 98.4 (C-1), 117.3, 122.9, 128.1-129.7 (7 signals), 132.8, 133.3, 156.7, 165.2 and 165.3 (*C*OBz) and 170.1 ($COCH_3$); *m/z* (EI) 379 (M - PhO)$^+$, 275 (M - PhO - $PhCO_2H$)$^+$ and 94 (PhOH)$^+$ (Found: C, 68.3; H, 5.6%. $C_{28}H_{26}O_8$ requires C, 68.55; H, 5.35%).

Further elution gave the β-anomer **3β** (804.6 mg, 30%) as a thick syrup; $[\alpha]_D$ -172.5 (*c* 1.09 in $CHCl_3$); ν_{max} (KBr) 2995, 1754, 1725, 1600 and 1497 cm^{-1}; δ_H 1.35 (3H,d, $J_{6,5}$ 6.2, H-6), 2.1 (3H, s, OAc), 4.63 (1H, dd, $J_{4,3}$ 5.5, $J_{4,5}$ 8.6, H-4), 5.39 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.6, H-5), 5.40 (1H, d, $J_{2,3}$ 1.3, H-2), 5.67 (1H, s, H-1), 5.73 (1H, dd, $J_{3,4}$ 5.4, $J_{3,2}$ 1.2, H-3), 7-8 (15H, m, Ar); δ_C 17.8 (C-6), 20.7 ($COCH_3$), 69.3 (C-5), 74.4, 80.7 and 83.3 (C-2, C-3 and C-4), 103.7 (C-1), 116.4, 122.3, 128.1-129.8 (7 signals), 132.7, 133.3, 156.4, 165.1 and 169.2; *m/z* (EI) 379 (M - PhO)$^+$, 275 (M - PhO - $PhCO_2H$)$^+$ and 94 (PhOH)$^+$ (Found: C, 68.9; H, 5.2%. $C_{28}H_{26}O_8$ requires C, 68.55; H, 5.35%).

4-*Methylphenyl* 2-O-*acetyl*-3,5-*di*-O-*benzoyl*-6-*deoxy*-α-D-*glucofuranoside* (**4α**), and the β-*isomer* (**4β**).- Stannic chloride (112 mg, 0.43 mmol) was added to an ice-cooled solution of 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-D-glucofuranose (**2**) (196.1 mg, 0.43 mmol) and 4-methylphenol (46.4 mg, 0.43 mmol) in dry toluene (15 cm^3). The mixture was allowed to stir at RT for 2 hours. The reaction was partitioned between

aqueous NaOH (0.5 M, 40 cm^3) and dichloromethane (3 x 25 cm^3). The combined organic extracts were then washed with water until neutral, dried (Na_2SO_4), filtered and reduced *in vacuo* to give a syrup. Chromatography on silica, with ethyl acetate-toluene (1:19) as eluent produced firstly the α-anomer **4α** (41.2 mg, 19 %) as a syrup; $[\alpha]_D$ +89.4 (*c* 0.71 in $CHCl_3$); ν_{max} (film) 2989, 1731, 1602, 1586 and 1490 cm^{-1}; δ_H 1.49 (3H, d, $J_{6,5}$ 6.2, H-6), 2.17 (3H, s, OAc), 2.35 (3H, s, Me), 4.66 (1H, dd, $J_{4,3}$ 6.2, $J_{4,5}$ 7.7, H-4), 5.32 (1H, t, *J* 4.9, H-2), 5.43 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 7.8, H-5), 5.96 (1H, d, $J_{1,2}$ 4.5, H-1), 6.09 (1H, dd, $J_{3,4}$ 6.1, $J_{3,2}$ 5.0, H-3), 7-7.9 (14H, m, Ar); δ_C 17.2 (C-6), 20.5 (CO*Me*), 21.4 (Me), 68.9 (C-5), 74.7, 77.6 and 78.0 (C-2, C-3 and C-4), 98.3 (C-1), 118.1, 123.7, 128.1-129.7 (6 signals), 132.8, 133.3, 139.6, 156.7, 165.2 and 165.3 (*C*OBz), and 170.1 (*C*OMe) ; *m/z* (EI) 397 (M - $MeC_6H_4O)^+$, 153 (M - MeC_6H_4O - 2 $PhCO_2H)^+$ and 108 $(MeC_6H_4OH)^+$; (Found: C, 68.6; H, 5.5 %; $C_{29}H_{28}O_8$ requires C, 69.02; H, 5.60%).

Further elution of the column gave the β-anomer **4β** (80.2 mg, 37%) as a syrup; $[\alpha]_D$ -173.9 (*c* 0.77 in $CHCl_3$); ν_{max} (film) 2992, 1755, 1731, 1602 and 1490 cm^{-1}; δ_H 1.41 (3H, d, $J_{6,5}$ 6.2, H-6), 2.17 (3H, s, OAc), 2.35 (3H, s, Me), 4.71 (1H, dd, $J_{4,3}$ 5.5, $J_{4,5}$ 8.6, H-4), 5.48 (1H, bs, H-2), 5.49 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.7, H-5), 5.73 (1H, s, H-1), 5.80 (1H, dd, $J_{3,4}$ 5.5, $J_{3,2}$ 1.3, H-3), 7-8 (14H, m, Ar); δ_C 17.8 (C-6), 20.6 (CO*Me*), 21.4 (Me), 69.3 (C-5), 74.4, 80.7 and 83.2 (C-2, C-3 and C-4), 103.7 (C-1), 113.2, 117.2, 123.1, 128.0-129.8 (6 signals), 132.7, 133.2, 139.6, 156.4, 165.1 (*C*OBz), and 169.2 (*C*OMe); *m/z* (EI) 397 (M - $MeC_6H_4O)^+$, 215 (M - MeC_6H_4O - CH_3CO_2H - $PhCO_2H)^+$ and 108 $(MeC_6H_4OH)^+$ (Found: C, 68.9; H, 5.2 %. $C_{29}H_{28}O_8$ requires C, 69.02; H, 5.60%).

Phenyl 3,5-*di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranoside* (**5**).- A solution of sodium ethoxide in ethanol (1.01 M, 220 ml, 0.22 mmol) was added to a solution of phenol (42.5 mg, 0.45 mmol) in ethanol (10 cm^3). The mixture was stirred at RT for 20 min, after which a solution of acetate **3β** (107.3 mg, 0.22 mmol) in ethanol (10 cm^3) was added. After 30 min, t.l.c. (ethyl acetate-toluene 1:4) indicated all the starting material had been consumed. The reaction mixture was added to aqueous NaOH (2 M, 30 cm^3), and extracted using dichloromethane (3 x 30 cm^3). The combined extracts were washed with water until neutral, dried (Na_2SO_4), filtered, and reduced *in vacuo* to give a thick syrup, which was chromatographed on silica, with ethyl acetate-toluene (3:17) as eluent to give the monoalcohol **5** (76.3 mg, 78%) as a glass; $[\alpha]_D$ -235.9 (*c* 0.98 in $CHCl_3$); ν_{max} (film) 3457, 2935, 1722, 1600 and 1494 cm^{-1}; δ_H 1.45 (3H, d, $J_{6,5}$ 6.2, H-6), 3.8 (1H, s, OH), 4.61 (1H, bs, H-2), 4.76 (1H, dd, $J_{4,3}$ 5.3, $J_{4,5}$ 8.5, H-4), 5.51 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.5 H-5), 5.58 (1H, dd, $J_{3,4}$ 5.2, $J_{3,2}$ 1.4, H-3), 5.75 (1H, s, H-1), 7-8 (15H, m, Ar); δ_C 17.8 (C-6), 69.4 (C-5), 77.9, 80.1 and 82.6 (C-2, C-3 and C-4), 105.7 (C-1), 116.3, 122.0, 128.1-130.0 (7 signals), 132.8, 133.4, 156.5, 165.3 and 166.4 (*C*OBz); *m/z* (EI) 355 (M - PhO)$^+$, 233 (M - PhO - $PhCO_2H)^+$ and 94 $(PhOH)^+$ [Found: MH^+ (FAB) 449.1635; $C_{26}H_{25}O_7$ requires 449.1600].

2-O-*Acetyl*-3,5-*di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranosyl fluoride* (**6**).- Pyridinium poly(hydrogen fluoride) (4 cm^3) was added dropwise to an ice cooled solution of 1,2-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-D-glucofuranoside (**2**) (1.142 g, 2.5 mmol) in dry toluene (5 cm^3). The mixture was left to stand at 0 °C for 5 h. Ether (10 cm^3) and sat. KI solution (30 cm^3) were added to the reaction mixture which was then extracted with a mixture of ether and hexane (3:1, 3 x 30 cm^3). The combined extracts were then washed with sat. KI solution (30 cm^3), sat. Na_2CO_3 solution (30 cm^3) and brine (30 cm^3), dried (Na_2SO_4), filtered and reduced *in vacuo* to give white solid. Recrystallisation from ethanol gave the fluoride (**6**) (0.26 g, 30%) as white needles, m.p. 140-142°C; $[\alpha]_D$ -87.8 (*c* 0.98 in $CHCl_3$); ν_{max} (KBr) 3004, 1727, 1711, 1600 and 1451 cm^{-1}; δ_H 1.56 (3H,d, $J_{6,5}$ 6.2, H-6), 2.16 (3H, s, OAc), 4.74 (1H, dt, $J_{4,3}$ 5.5, $J_{4,5}$ 8.4, $J_{4,F}$ 5.5, H-4), 5.34 (1H, t, $J_{2,F}$4.3, H-2), 5.50 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.4, H-5), 5.78 (1H, d, $J_{3,4}$ 5.3, H-3), 5.80 (1H, d, $J_{1,F}$ 61.6, H-1),7.2 -8 .0 (10H, m, Ar); δ_C 17.6 (C-6), 20.5 ($COCH_3$), 68.9 (C-5), 73.0, 79.6 (d, J_{CF} 36.1) and 84.9 (C-2, C-3 and C-4), 111.7 (d, J_{CF} 229.5, C-1), 128.1-133.4 (7 signals), 164.8, 165.0 and 168.9; δ_F (188 MHz, $CDCl_3$) -119.2 (dt, $J_{F,H1}$ 61.6, $J_{F,H2}$ 5.0, $J_{F,H4}$ 5.0); *m/z* (EI) 379 (M -F)$^+$, 372 (M -

$CH_3CO_2H)^+$ and 294 (M - $PhCO_2H)^+$ (Found C, 63.7; H, 5.2; F, 4.7%. $C_{22}H_{21}O_7F$ requires C, 63.44; H, 5.09; F, 4.57%).

3,5-*Di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranosyl fluoride* (**7**).- A solution of sodium ethoxide in ethanol (0.99 M, 250 ml, 0.25 mmol) was added to a solution of phenol (48.0 mg, 0.51 mmol) in ethanol (3 cm^3). The mixture was stirred at RT for 20 min, after which a solution of 2-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-β-D-glucofuranosyl fluoride (**6**) (99.9 mg, 0.24 mmol) in ethanol (3 cm^3) was added. After 30 min, the reaction mixture was added to aqueous NaOH (2 M, 30 cm^3), and extracted with dichloromethane (3 x 30 cm^3). The combined extracts were washed with water until neutral, dried (Na_2SO_4), filtered, and reduced *in vacuo* to give a thick syrup, which was chromatographed on silica, with ethyl acetate-toluene (7:93) as eluent to give **7** (50.3 mg, 56%) as a syrup; $[\alpha]_D$ -54.3 (*c* 1.01 in $CHCl_3$); ν_{max} (KBr) 3004, 1727, 1711, 1600 and 1451 cm^{-1} ; δ_H 1.59 (3H,d, $J_{6,5}$ 6.2, H-6), 2.16 (3H, s, OAc), 3.88 (1H,s, OH), 4.49 (1H, d, $J_{2,F}$4.5, H-2), 4.81 (1H, dt, $J_{4,3}$ 5.6, $J_{4,5}$ 8.2, $J_{4,F}$ 5.5, H-4), 5.56 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.2, H-5), 5.58 (1H, d, $J_{3,4}$ 5.9, H-3), 5.79 (1H, d, $J_{1,F}$ 63.2, H-1),7.2 -8 0 (10H, m, Ar); δ_C 17.7 (C-6), 65.8 (C-5), 76.3, 79.0 (d, J_{CF} 32.7) and 84.5 (C-2, C-3 and C-4), 113.9 (d, J_{CF} 226.2, C-1), 128.2-133.5 (8 signals), 165.4 and 166.2; δ_F (188 MHz, $CDCl_3$) -120.1 (dt, $J_{F,H1}$ 63.2, $J_{F,H2}$ 5.4, $J_{F,H4}$ 5.4); m/z (EI) 355 (M - F)$^+$, 252 (M - $PhCO_2H)^+$ and 234 (M - $PhCO_2H$ - $H_2O)^+$.

Phenyl 3,5-*di*-O-*benzoyl*-6-*deoxy*-2-O-*mesyl*-β-D-*glucofuranoside* (**8**). - Methanesulfonyl chloride (59.6 mg, 0.52 mmol) was added dropwise to an ice-cooled solution of the alcohol **5** (147.7 mg, 0.33 mmol) in dry pyridine (5 cm^3).The reaction mixture was stirred at RT for 2 h, when t.l.c. (ethyl acetate-toluene 1:19) indicated that the reaction was complete. The mixture was partitioned between water (40 cm^3) and chloroform (3 x 25 cm^3). The combined extracts were washed successively with dilute sulfuric acid (1 M, 25 cm^3), sat. $NaHCO_3$ solution (25 cm^3) and water (25 cm^3), dried (Na_2SO_4), filtered and reduced *in vacuo* to give the 2-*O*-mesyl derivative **8** (155.4mg, 90%) as a white foam; $[\alpha]_D$ -149.7 (*c* 1.02 in $CHCl_3$); ν_{max} (KBr) 2950, 1724, 1600 and 1495 cm^{-1}; δ_H 1.37 (3H, d, $J_{6,5}$ 6.2, H-6), 3.17 (3H, s, SO_3Me), 4.68 (1H, dd, $J_{4,3}$ 5.6, $J_{4,5}$ 8.6, H-4), 5.26 (1H, d, $J_{2,3}$ 1.4, H-2), 5.46 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.7, H-5), 5.65 (1H, dd, $J_{3,4}$ 5.5, $J_{3,2}$ 1.4, H-3), 5.86 (1H, s, H-1), 6.9-7.9 (15H, m, Ar); δ_C 17.8 (C-6), 38.4 (SO_3CH_3), 69.1 (C-5), 74.7, 82.8 and 85.1 (C-2, C-3 and C-4), 103.6 (C-1), 116.4, 122.7, 128.1-129.8 (5 signals), 132.8, 133.6, 155.9, 165.1 and 165.6 (*C*OBz); *m/z* (EI) 433 (M - PhO)$^+$, 189 (M - PhO - 2 $PhCO_2H)^+$ and 94 (PhOH)$^+$ [Found: MH$^+$ (FAB) 527.1344. $C_{27}H_{27}O_9S$ requires 527.1376].

Phenyl 2,3-*anhydro*-6-*deoxy*-β-D-*mannofuranoside* (**9**). - Sodium methoxide (16.5 mg, 0.3 mmol) was added to a solution of phenyl 3,5-di-*O*-benzoyl-6-deoxy-2-*O*-mesyl-β-D-glucofuranoside (**8**) (114.1 mg, 0.22 mmol) in methanol (5 cm^3). After 30 min t.l.c. (ethyl acetate-toluene 1:1) indicated that the reaction had proceeded to completion.The mixture was neutralised using dilute hydrochloric acid (2 M) and evaporated to dryness. Chromatography on silica, with ethyl acetate-toluene (1:1) as eluent gave a white solid which was recrystallized from ether-light petroleum to give the epoxide **9** (43.2 mg, 90%), m.p. 99-100°C; $[\alpha]_D$ -139.9 (*c* 1.07, $CHCl_3$); ν_{max} (KBr) 3332, 2950 and 1592 cm^{-1}; δ_H 1.31 (3H, d, $J_{6,5}$ 6.3, H-6), 2.27 (1H, bs, OH), 3.81 (1H, d, $J_{4,5}$ 6.4, H-4), 3.91 (2H, s, H-2 and H-3), 4.08 (1H, quin, *J* 6.4, H-5), 5.55 (1H, s, H-1), 6.9-7.4 (5H,m, Ar); δ_C 20.7 (C-6), 54.5 and 56.0 (C-2 and C-3), 66.7 (C-5), 81.3 (C-4), 101.2 (C-1), 116.5, 122.5, 129.4 and 157.2; *m/z* (EI) 222 (M)$^+$, 127 (M - OPh)$^+$ and 94 (PhOH)$^+$ (Found C, 65.2; H, 6.4%. $C_{12}H_{14}O_4$ requires C, 64.84; H, 6.35%).

Phenyl 6-*deoxy*-β-D-*altrofuranoside* (**10**).- The epoxide **9** (203.1 mg, 0.91 mmol) in aqueous NaOH (1 M, 25 cm^3) was heated under reflux for 90 min. The reaction was neutralised using dilute hydrochloric acid (2 M) and the mixture evaporated to dryness. Chromatography on silica, with ethyl acetate as eluent gave a white solid. Recrystallisation from ethyl acetate-light petrol gave the D-*altro*- product **10** (132.9 mg, 60%), m.p.

114-115 °C; $[\alpha]_D$ -98.6 (*c* 1.06 in MeOH); ν_{max} (KBr) 3405, 2929 and 1599 cm^{-1}; δ_H (200 MHz, CD_3OD) 1.31 (3H, d, $J_{6,5}$ 6.3, H-6), 3.56 (1H, t, *J* 6.2, H-4), 3.65 (1H, quin, *J* 6.2, H-5), 4.03 (1H, dd, $J_{2,3}$ 7.8, $J_{2,1}$ 4.4, H-2), 4.14 (1H, dd, $J_{3,2}$ 7.8, $J_{3,4}$ 6.0, H-3), 5.42 (1H, d, $J_{1,2}$ 4.4, H-1), 6.9-7.4 (5H, m, Ph); δ_C (50 MHz, CD_3OD) 19.1 (C-6), 70.1 (C-5), 77.4, 79.2 and 88.0 (C-2, C-3 and C-4), 101.2 (C-1), 117.8, 123.1, 130.4 and 158.6; *m/z* (EI) 240 $(M)^+$, 147 $(M - PhO)^+$ and 94 $(PhOH)^+$ [Found: M^+ (EI) 240.0987. $C_{12}H_{16}O_5$ requires 240.0998].

Phenyl 6-deoxy-β-D-glucofuranoside (**11**).- Sodium methoxide (5 mg, 0.09 mmol) was added with stirring to a solution of phenyl 2-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-β-D-glucofuranoside (**3β**) (120.1 mg, 0.25 mmol) in methanol (25 cm^3). After 1 h, the mixture was neutralised with dilute hydrochloric acid (2 M) and evaporated to dryness. Chromatography on silica, with ethyl acetate as eluent gave the triol **11** (44.2 mg, 75%) as a glass; $[\alpha]_D$ -18.2 (*c* 0.88 in MeOH); ν_{max} (KBr) 3334, 2932 and 1588 cm^{-1}; δ_H (200 MHz, CD_3OD) 1.21 (3H, d, $J_{6,5}$ 6.0, H-6), 3.96 (1H, dd, $J_{4,3}$ 4.4, $J_{4,5}$ 8.3, H-4), 4.06 (1H, dq, $J_{5,6}$ 6.0, $J_{5,4}$ 8.3, H-5), 4.23 (1H, dd, $J_{3,2}$ 1.4, $J_{3,4}$ 4.3, H-3), 4.27 (1H, bs, H-2), 5.48 (1H, s, H-1), 6.9-7.3 (5H, m, Ph); δ_C (50 MHz, CD_3OD) 20.7 (C-6), 67.3 (C-5), 77.4, 82.8, 87.7 (C-2, C-3 and C-4), 108.2 (C-1), 117.6, 122.9, 130.4 and 158.5; *m/z* (EI) 240 $(M)^+$, 147 $(M - PhO)^+$ and 94 $(PhOH)^+$ [Found: M^+ (EI) 240.0982. $C_{12}H_{16}O_5$ requires 240.0998].

Phenyl 6-deoxy-5-keto-β-D-arabino-hexofuranoside (**12**).- Chromic acid [0.1 ml, 0.27 mmol, from a solution of CrO_3 (2.7g) in conc. H_2SO_4 (2.3 cm^3) made up to 10 cm^3 with water], was added to a solution of phenyl 6-deoxy-β-D-altrofuranoside (**10**) (63.8 mg, 0.27 mmol) in acetone (10 cm^3) cooled in an acetone/CO_2 bath, and which had been degassed by bubbling N_2 through it for 15 min. The reaction temperature was allowed to rise to -5 °C. After 45 min, t.l.c. (ethyl acetate-toluene 9:1) indicated complete reaction.The mixture was partitioned between water (20 cm^3) and ethyl acetate (3 x 15 cm^3). The combined extracts were washed with sat. $NaHCO_3$ solution (15 cm^3) and water (15 cm^3), dried (Na_2SO_4), filtered, and reduced *in vacuo* to give a white crystalline solid. Recrystallisation from ether-light petroleum gave the 5-keto product **12** (38 mg, 60%), m.p. 121-123°C; $[\alpha]_D$ -107.1 (*c* 0.98 in MeOH); ν_{max} (KBr) 3445, 2928, 1712 (C=O) and 1596 cm^{-1}; δ_H (200 MHz, CD_3OD) 2.05 (3H, s, H-6), 4.15 (1H, dd, $J_{2,3}$ 7.1, $J_{2,1}$ 4.2, H-2), 4.19 (1H,d, $J_{4,3}$ 6.1, H-4), 4.37 (1H, dd, $J_{3,2}$ 7.1, $J_{3,4}$ 6.1, H-3), 5.66 (1H, d, $J_{1,2}$ 4.2, H-1), 6.9-7.4 (5H, m, Ph); δ_C (50 MHz, CD_3OD) 26.2 (C-6), 77.6, 78.4 and 88.4 (C-2, C-3 and C-4), 102.1 (C-1), 117.7, 123.4, 130.5, 158.5 and 210.4 (C-5); *m/z* (EI) 238 $(M)^+$, 145 $(M - PhO)^+$ and 94 $(PhOH)^+$ (Found C, 60.9; H, 5.6%. $C_{12}H_{14}O_5$ requires C, 60.48; H, 5.93%).

4[(E)-2-*(Methoxycarbonyl)*-1-*propen*-1-*yl*]*phenol* (**13**) and the (Z)-*isomer* - A solution of $Ph_3PC(Me)CO_2Me$ (29.1 g, 83.6 mmol) in dry THF (50 cm^3) was added to a solution of 4-hydroxybenzaldehyde (10.2 g, 83.6 mmol) in dry THF (50 cm^3). After 4 h, t.l.c. (ethyl acetate-toluene, 3:7) indicated that most of the aldehyde had been consumed.The reaction mixture was reduced *in vacuo* to give a crude syrup. Chromatography on silica, with ethyl acetate-toluene (3:7) as eluent gave firstly a white solid, which on recrystallisation from ether-light petrol gave the *E*-alkenoate **13** (11.4g, 71 %), m.p. 101-103 °C; ν_{max} (KBr) 3414, 2953, 1675, 1604 and 1581 cm^{-1} ; δ_H 2.12 (3H, d, Me), 3.82 (3H, s, CO_2Me), 6.32 (1H, bs, OH), 6.90 (2H, m, Ar), 7.34 (2H, m, Ar), 7.65 (1H, bs, CH); δ_C 14.0 (Me), 52.1 (CO_2Me), 115.5, 125.8, 128.3, 131.6, 139.1 (CH), 156.3 and 169.9 (CO_2Me); *m/z* (EI) 192 $(M)^+$, 161 $(M - OCH_3)^+$ and 133 $(M - CO_2Me)^+$ (Found: C, 68.76; H, 6.59%. $C_{11}H_{12}O_3$ requires C, 68.73; H, 6.59%).

Further elution of the column gave another solid, which on recrystallisation from ether-light petroleum gave the *Z*-isomer (0.6g, 4%), m.p. 74-76 °C; ν_{max} (KBr) 3320, 2942, 1685, 1605 and 1586 cm^{-1} ; δ_H 2.11 (3H, d, *J* 1.4, Me), 3.72 (3H, s, CO_2Me), 6.15 (1H, bs, OH), 6.65 (1H, bs, CH), 6.72 (2H, m, Ar), 7.13 (2H, m, Ar); δ_C 21.5 (Me), 51.9 (CO_2Me), 115.2, 127.2, 128.4, 129.8, 135.5 (CH), 155.8 and 170.9

(CO_2Me); *m/z* (EI) 192 $(M)^+$, 161 $(M - OMe)^+$ and 133 $(M - CO_2Me)^+$ (Found: C, 68.53; H, 6.39%. $C_{11}H_{12}O_3$ requires C, 68.73; H, 6.59%).

4-[(E)-2-*(Methoxycarbonyl)*-1-*propen*-1-*yl*]*phenyl* 2-O-*acetyl*-3,5-*di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranoside* (**14β**), and the α-*isomer* (**14α**) - Stannic chloride (512 mg, 1.96 mmol) was added to a solution of 1,2-di-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-D-glucofuranose (**2**) (894.3 mg, 1.96 mmol) and the (E)-alkene **13** (376.0 mg, 1.96 mmol) in dry dichloromethane (25 cm^3) cooled in acetone-dry ice, and the mixture was allowed to warm to RT. After 15h, the reaction mixture was diluted with dichloromethane (25 cm^3) and washed with dilute aqueous NaOH (2 M, 25 cm^3), and then with water until neutral. The dried extracts were filtered and reduced *in vacuo* to give a syrup. Chromatography on silica, with ethyl acetate-toluene (1:24) as eluent produced firstly the α-isomer **14α** (189.7 mg, 16.5%) as a thick syrup; $[\alpha]_D$ +97.5 (*c* 1.6 in $CHCl_3$); ν_{max} (film) 3059, 2948, 1724, 1601 and 1509 cm^{-1}; δ_H 1.48 (3H, d, $J_{6,5}$ 6.3, H-6), 2.12 (3H, d, *J* 1.4, Me), 2.16 (3H, s, OAc), 3.8 (3H, s, CO_2Me), 4.65 (1H, dd, $J_{4,3}$ 6.3, $J_{4,5}$ 7.7, H-4), 5.32 (1H, t, *J* 4.8, H-2), 5.42 (1H, dq, $J_{5,6}$ 6.3, $J_{5,4}$ 7.7, H-5), 6.0 (1H, d, $J_{1,2}$ 4.6, H-1), 6.08 (1H, dd, $J_{3,4}$ 6.1, $J_{3,2}$ 5.1, H-3), 7.6 (1H, m, CH), 7-7.9 (15H, m, Ar); δ_C 14.0 (Me), 17.1 (C-6), 20.4 (CO*Me*), 51.9 (CO_2Me), 68.8 (C-5), 74.5, 77.6 and 78.2 (C-2, C-3 and C-4), 98.1 (C-1), 117.0, 127.2-131.2 (8 signals), 132.8, 133.3, 138.2 (CH), 156.6, 165.1 and 165.3 (*C*OBz), 169.1 (*C*OMe) and 170.1 (CO_2Me), ; *m/z* (EI) 379 $[M - OC_6H_4CHC(Me)CO_2Me]^+$, 153 $[M - OC_6H_4CHC(Me)CO_2Me - 2PhCO_2H]^+$ and 192 $[HOC_6H_4CHC(Me)CO_2Me]^+$ [Found: MH^+ (FAB) 589.2046. $C_{33}H_{33}O_{10}$ requires 589.2074].

Further elution gave the β-isomer **14β** (442.9 mg, 38%) as a thick syrup; $[\alpha]_D$ -69.2 (*c* 1.48 in $CHCl_3$); ν_{max} (film) 3063, 2950, 1755, 1729, 1603 and 1509 cm^{-1} ; δ_H 1.42 (3H, d, $J_{6,5}$ 6.2, H-6), 2.14 (1H, d, *J* 1.4, Me), 2.17 (3H, s, OAc), 3.80 (3H,s, CO_2Me), 4.72 (1H, dd, $J_{4,3}$ 5.4, $J_{4,5}$ 8.5, H-4), 5.46 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.5, H-5), 5.48 (1H, d, $J_{2,3}$ 1.1, H-2), 5.75 (1H, s, H-1), 5.80 (1H, dd, $J_{3,4}$ 5.4, $J_{3,2}$ 1.2, H-3), 7.6 (1H, m, CH), 7-8 (14H, m, Ar); δ_C 14.0 (Me), 17.8 (C-6), 20.7 (CO*Me*), 51.9 (CO_2Me), 69.1 (C-5), 74.3, 80.6 and 83.5 (C-2, C-3 and C-4), 103.5 (C-1), 116.2, 126.9-130.1 (8 signals), 131.3, 132.8,133.3, 138.3 (CH), 156.3, 165.0 and 165.1 (*C*OBz), and 169.2 (CO_2Me); *m/z* (EI) 379 $[M - OC_6H_4CHC(Me)CO_2Me]^+$, 153 $[M - OC_6H_4CHC(Me)CO_2Me - 2PhCO_2H]^+$ and 192 $[HOC_6H_4CHC(Me)CO_2Me]^+$ [Found: MNa^+ (FAB) 611.1864. $C_{33}H_{32}O_{10}Na$ requires 611.1893].

4-[(E)-2-*(Methoxycarbonyl)*-1-*propen*-1-*yl*]*phenyl* 3,5-*di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranoside* (**15**) - A solution of sodium ethoxide in ethanol (0.91 M, 473 ml, 0.43 mmol) was added to a solution of phenol (78.4 mg, 0.83 mmol) in ethanol (5 cm^3). After 15 min, a solution of β-anomer **14β** (254.2 mg, 0.43 mmol) in ethanol (10 cm^3) was added. After 45 min, t.l.c. (ethyl acetate-toluene 3:17) indicated the starting material had been consumed. The reaction mixture was partitioned between aqueous NaOH (2 M, 30 cm^3) and dichloromethane (3 x 30 cm^3). The combined extracts were washed with water until neutral, dried, filtered, and evaporated to give a thick syrup. Chromatography on silica, with ethyl acetate-toluene (3:17) as eluent gave the 2-hydroxy-compound **15** (200 mg, 85%) as a glass, $[\alpha]_D$ -189.2 (*c* 1.02 in $CHCl_3$); ν_{max} (film) 3445, 2951, 1715, 1603 and 1509 cm^{-1} ; δ_H 1.44 (3H, d, $J_{6,5}$ 6.2, H-6), 2.13 (1H,d, *J* 1.4, Me), 3.80 (3H, s, CO_2Me), 4.62 (1H, bs, H-2), 4.77 (1H, dd, $J_{4,3}$ 5.2, $J_{4,5}$ 8.4, H-4), 5.50 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.4, H-5), 5.57 (1H, dd, $J_{3,4}$ 5.2, $J_{3,2}$ 1.4, H-3), 5.76 (1H, s, H-1), 7.6 (1H, m, CH), 7-8 (14H, m, Ar); δ_C 14.0 (Me), 17.8 (C-6), 52.0 (CO_2Me), 69.3 (C-5), 77.6, 79.8 and 82.9 (C-2, C-3 and C-4), 105.5 (C-1), 116.1, 126.6, 128.1-129.9 (6 signals), 131.3, 132.8, 133.4, 138.6 (CH), 156.5, 165.4 and 166.3 (*C*OBz) and 169.5 (CO_2Me); *m/z* (FAB) 547 $(M)^+$, 355 $[M - OC_6H_4CHC(Me)CO_2Me]^+$, 233 $[M - OC_6H_4CHC(Me)CO_2Me - PhCO_2H]^+$ and 192 $[OC_6H_4CHC(Me)CO_2Me]^+$.

4-[(E)-2-*(Methoxycarbonyl)*-1-*propen*-1-*yl*]*phenyl* 3,5-*di*-O-*benzoyl*-6-*deoxy*-2-O-*mesyl*-β-D-*glucofuranoside* (**16**).- Methanesulfonyl chloride (59.6 mg, 0.52 mmol) was added to an ice-cooled solution of alcohol **15** (90.8 mg, 0.17 mmol) in dry pyridine (5 cm^3). After 15 h, when t.l.c. (ethyl acetate-toluene,

1:19) indicated the reaction was complete, the mixture was partitioned between water (30 cm^3) and dichloromethane (3 x 20 cm^3). The combined extracts were washed successively with dilute sulfuric acid (1 M, 20 cm^3), sat. $NaHCO_3$ solution (20 cm^3) and water (20 cm^3), dried (Na_2SO_4), filtered and reduced *in vacuo* to give the 2-*O*-mesyl compound **16** (91.3 mg, 88%) as a glass, $[\alpha]_D$ -114.8 (*c* 0.92 in $CHCl_3$); ν_{max} (film) 2951, 1714, 1603 and 1509 cm^{-1} ; δ_H 1.43 (3H, d, $J_{6,5}$ 6.2, H-6), 2.15 (1H, d, *J* 1.4, Me), 3.25 (3H, s, SO_2Me), 3.80 (3H, s, CO_2Me), 4.75 (1H, dd, $J_{4,3}$ 5.5, $J_{4,5}$ 8.6, H-4), 5.33 (1H, d, $J_{2,3}$ 1.3, H-2), 5.52 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.6, H-5), 5.71 (1H,dd, $J_{3,4}$ 5.5, $J_{3,2}$ 1.3, H-3), 5.94 (1H, s, H-1), 7.65 (1H, m, C*H*), 7-8 (14H, m, Ar); δ_C 14.0 (Me) 17.7 (C-6), 38.3 (SO_2Me), 51.9 (CO_2*Me*), 68.9 (C-5), 74.7, 83.0 and 84.9 (C-2, C-3 and C-4), 103.4 (C-1), 116.2, 127.1, 128.1-130.4 (6 signals), 131.3, 132.8, 133.6, 138.1 (CH), 155.8, 165.1 and 165.5 (*C*OBz), and 169.1 (*C*O_2Me); *m/z* (FAB) 624 $(M)^+$, and 433 [M - $OC_6H_4CHC(Me)$ $CO_2Me]^+$ [Found: MH^+ (FAB) 625.1752. $C_{32}H_{33}O_{11}S$ requires 625.1744].

4-[(*E*)-2-*(Methoxycarbonyl)*-1-*propen*-1-*yl*]*phenyl* 2,3-*anhydro*-6-*deoxy*-β-D-*mannofuranoside* **(17)**. -Sodium methoxide (34.5 mg, 0.64 mmol) was added to a solution of the mesylate **16** (364.0 mg, 0.58 mmol) in methanol (20 cm^3). After 50 min, t.l.c. (ethyl acetate-toluene, 1:4) indicated that the reaction was complete. The mixture was neutralised with dil. HCl (2 M) and evaporated to dryness. Chromatography on silica, with ethyl acetate-toluene (1:1) as eluent and recrystallisation from ether-light petroleum gave epoxide **17** (144.9 mg, 78 %), m.p. 101-103 °C, $[\alpha]_D$ -112.2 (*c* 0.90 in $CHCl_3$); ν_{max} (KBr) 3460, 2924, 1708 and 1604 cm^{-1}; δ_H 1.31 (3H, d, $J_{6,5}$ 6.3, H-6), 2.10 (3H, d, *J* 1.4, Me), 2.25 (1H, bs, OH), 3.79 (3H, s, CO_2Me), 3.82 (1H, d, $J_{4,5}$ 6.5, H-4), 3.93 (2H, s, H-2 and H-3), 4.08 (1H, quin, *J* 6.4, H-5), 5.61 (1H, s, H-1), 7.0-7.4 (4H, m, Ar), 7.6 (1H, bs, CH); δ_C 14.0 (Me), 20.2 (C-6), 52.0 (CO_2*Me*), 54.6 and 56.0 (C-2 and C-3), 66.7 (C-5), 81.5 (C-4), 100.0 (C-1), 116.3, 126.9, 130.2, 131.2, 138.4 (CH), 157.2 and 169.3 (*C*O_2Me); *m/z* (EI) 320 $(M)^+$, 192 $[HOC_6H_4CHC(Me)CO_2Me]^+$ and 129 [M- $OC_6H_4CHC(Me)CO_2Me]^+$ (Found: C, 64.0; H, 6.3. $C_{17}H_{20}O_6$ requires C, 63.72; H, 6.30%).

4-[(E)-2-*Carboxy*-1-*propen*-1-*yl*]*phenyl* 6-*deoxy*-β-D-*altrofuranoside* **(18)**. -The epoxide **17** (50.4 mg, 0.16 mmol) was added to aqueous NaOH solution (1M, 5 cm^3). The mixture was heated under reflux for 3 h. The mixture was neutralised using Amberlite IR-120 (H^+), filtered and evaporated to dryness. Chromatography on silica, with ethyl acetate as eluent, followed by recrystallisation from ethyl acetate-light petroleum gave the altroside **18** (26 mg, 51%), m.p. 114-115°C; $[\alpha]_D$ -198.4 (*c* 0.63 in MeOH); ν_{max} (KBr) 3339, 2930 and 1684 cm^{-1}; δ_H (200 MHz, CD_3OD) 1.08 (3H, d, $J_{6,5}$ 6.1, H-6), 2.09 (3H, d, *J* 1.4, Me), 3.67 (1H, t, *J* 5.9, H-4), 3.74 (1H, quin, *J* 6.0, H-5), 4.15 (1H, dd, $J_{2,3}$ 7.8, $J_{2,1}$ 4.3, H-2), 4.24 (1H, dd, $J_{3,2}$ 7.8, $J_{3,4}$ 5.9, H-3), 5.58 (1H, d, $J_{1,2}$ 4.3, H-1), 7.0-7.4 (4H, m, Ar), 7.62 (1H, bs, CH); δ_C (50 MHz, CD_3OD) 14.2 (Me), 19.0 (C-6), 70.0 (C-5), 77.3, 79.1 and 88.1 (C-2, C-3 and C-4), 101.0 (C-1), 117.6, 128.0, 131.1, 132.3, 139.7 (CH), 158.6 and 172.3 (CO_2H); *m/z* (EI) 132 $[M\text{-}OC_6H_4CHC(Me)CO_2H]^+$ and 178 $[HOC_6H_4CHC(Me)CO_2H]^+$ [Found: MH^+ (FAB) 325.1307. $C_{16}H_{21}O_7$ requires 325.1287].

4-[(E)-2-*Carboxy*-1-*propen*-1-*yl*]*phenyl* 6-*deoxy*-5-*keto*-β–D-arabino-*hexofuranoside* **(19)**. -Chromic acid [0.113 cm^3, 0.3 mmol, from a solution of CrO_3 (2.7g) in conc. H_2SO_4 (2.3 cm^3), made up to 10 cm^3 with water], was added to a solution of the triol **18** (98.1 mg, 0.30 mmol) in acetone (10 cm^3) cooled in dry ice-acetone, which had been degassed by bubbling N_2 through it for about 15 min. The reaction temperature was allowed to rise to -5 °C. After 55 min, t.l.c (ethyl acetate) indicated complete reaction. Water (20 cm^3) was added, and the mixture was extracted with ethyl acetate (6 x 15 cm^3). The combined extracts were washed with sat. $NaHCO_3$ solution (15 cm^3) and water (15 cm^3), dried filtered, and reduced *in vacuo* to give a white solid which was crystallised from ether-light petroleum to give the 5-keto compound **19** (53.3 mg, 52%), m.p. 154-156 °C; $[\alpha]_D$ -260.8 (*c* 0.40 in MeOH); ν_{max} (KBr) 3236, 2942, 1708 (C=O), 1691, 1603 cm^{-1}; δ_H (200 MHz, CD_3OD) 2.07 (3H, s, H-6), 2.09 (1H, d, *J* 1.4, Me), 4.17 (1H, dd, $J_{2,3}$ 7.1,$J_{2,1}$ 4.3, H-2), 4.20 (1H, d, $J_{4,3}$ 6.1, H-4), 4.36 (1H, dd, $J_{3,2}$ 7.1, $J_{3,4}$ 6.2, H-3), 5.72 (1H, d, $J_{1,2}$ 4.3, H-1), 7.1-7.5

(4H, m, Ar), 7.65 (1H, bs, CH); δ_C (50 MHz, CD_3OD) 14.2 (Me), 26.2 (C-6), 77.6, 78.5 and 88.6 (C-2, C-3 and C-4), 102.0 (C-1), 117.6, 128.3, 131.1, 132.4, 139.6 (CH), 158.6, 172.2 (CO_2H) and 210.1(C-5); *m/z* (EI) 145 [M- $OC_6H_4CHC(Me)CO_2H]^+$ and 178 $[HOC_6H_4CHC(Me)CO_2H]^+$ [Found: MH^+ (FAB) 323.1101. $C_{16}H_{19}O_7$ requires 323.1131].

3-Acetoxy-4-hydroxybenzaldehyde (**22**). - A solution of acetic anhydride (0.736 g, 7.22 mmol) in ether (40 cm^3) was added to a solution of 3,4-dihydroxybenzaldehyde (0.996g, 7.22 mmol) and NaOH (0.29 g, 7.22 mmol) in water (100 cm^3). The mixture was shaken vigorously for 10 min. The organic layer was washed with water until neutral, dried, filtered and evaporated to give a crude syrup. Chromatography on silica with ethyl acetate-toluene (3:17) as eluent gave a white powder. Recrystallisation from ether-light petrol gave the monoacetylated product **22** (0.654 g, 50%), m.p. 87-89°C; ν_{max} (KBr) 3171, 1773, 1671 and 1575 cm^{-1}; δ_H (200 MHz, CD_3OD) 2.00 (3H, s, Ac), 6.90 (1H, d, *J* 8), 7.30 (2H, m), 9.67 (1H, s, CHO); δ_C (50 MHz, CD_3OD) 20.5 (CO*Me*), 115.5, 116.3, 126.4, 130.8, 147.1, 153.6, 173.5 (*C*OMe) and 193.1 (CHO); *m/z* (EI) 180 $(M)^+$ and 138 $(M - COCH_3)^+$ (Found: C, 59.7; H, 4.3%. $C_9H_8O_4$ requires C, 59.99; H, 4.48%).

4-[(E)-2-(*Methoxycarbonyl*)-1-*propen*-1-*yl*]-3-*methoxyphenol* (**25**). - A solution of vanillin (0.995g, 7.3 mmol) in dry THF (25 cm^3) was added dropwise to a solution of phosphorane $Ph_3PC(Me)CO_2Me$ (2.64 g, 7.6 mmol) in THF (25 cm^3). This mixture was left to stir at RT for 4h, and then evaporated to give a white solid. Chromatography on silica with ethyl acetate-toluene (1:9) as eluent, produced **25** (1.164 g, 72%), m.p. 73-75°C; ν_{max} (KBr) 3452, 2966, 1685 and 1588 cm^{-1}; δ_H 2.13 (3H, d, Me), 3.80 (3H, s, CO_2Me), 3.88 (3H, s, OMe), 5.90 (1H, bs, OH), 6.9-7.0 (3H, m, Ar), 7.63 (1H, bs, CH); d_C 14.1, 52.0, 55.9, 112.4, 114.4, 123.8, 126.1, 128.2, 139.0, 146.3, 146.3 and 169.4; *m/z* 222 (M^+), 191 $(M - OCH_3)^+$ and 162 $(M - CO_2Me)$ (Found: C, 64.8; H, 6.5% . $C_{12}H_{14}O_4$ requires C, 64.84; H, 6.35%).

4-[(E)-2-(*Methoxycarbonyl*)-1-*propen*-1-*yl*]-3-*methylphenol* (**26**). - 4-Hydroxy-3-methylphenol (1.102 g, 8.1 mmol) and $Ph_3PC(Me)CO_2Me$ (2.92 g, 8.4 mmol) were processed as described in the preparation of **25.** Recrystalisation from dichloromethane-light petroleum gave **26** (1.12 g, 67%) as needles, m.p. 100-102 °C; ν_{max} (KBr) 3328, 2927, 1666 and 1597 cm^{-1}; δ_H 2.13 (3H, d, Me), 2.25 (3H, s, Me), 3.80 (3H, s, CO_2Me), 6.20 (1H, bs, OH), 6.82 (1H, d, *J* 8, Ar), 7.18 (2H, m, Ar), 7.61 (1H, bs, CH); δ_C 14.0, 15.8, 52.1, 114.9, 124.1, 125.4, 128.2, 129.0, 133.0, 139.4, 154.6 and 170.0; *m/z* 206 (M^+), 175 $(M - OCH_3)^+$ and 146 $(M - CO_2Me)$; (Found C, 69.9; H, 6.9%. $C_{12}H_{14}O_3$ requires C, 69.87; H, 6.85%).

4-[(E)-2-(*Methoxycarbonyl*)-1-*propen*-1-*yl*]-3-*nitrophenol* (**27**). - A solution of 4-hydroxy-3-nitrobenzaldehyde (1.02g, 6.1 mmol) in dry THF (25 cm^3) was added dropwise to a solution of $Ph_3PC(Me)CO_2Me$ (2.31 g, 6.6 mmol) in THF (25 cm^3). The mixture stirred at RT for 17 h, by which time t.l.c (ethyl acetate-toluene 1:3) showed that most of the aldehyde had been consumed. The crude mixture was reduced *in vacuo* to give a thick syrup. Chromatography on silica using ethyl acetate-toluene (3:20) as eluent, gave olefin **27** (1.128g, 78%) as a yellow crystalline solid, m.p. 95-96°C; ν_{max} (KBr) 3290, 2951, 1703, 1619 and 1568 cm^{-1} ; δ_H 2.13 (3H, d, Me), 3.82 (3H, s, CO_2Me), 7.15 (1H, d, *J* 8, Ar), 7.58 (1H, bs, CH), 7.63 (1H, dd, *J* 8, 2, Ar), 8.14 (1H, d, *J* 2, Ar); δ_C 14.0, 52.2, 120.1, 125.8, 128.4, 129.5, 133.4, 135.7, 138.5, 154.7 and 168.5; m/z 237 (M^+), 206 $(M - OCH_3)^+$ and 178 $(M-CO_2Me)$ (Found: C, 55.5; H, 4.8; N, 5.8%. $C_{11}H_{11}NO_5$ requires C, 55.68; H, 4.68; N, 5.91%)

Benzyl 3,5-*di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranoside* (**29**β), and the α-*anomer*. - 3,5-Di-*O*-benzoyl-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**28**) (2.014 g, 4.86 mmol) was dissolved in benzyl alcohol (30 cm^3), through which dry HCl gas had been passed, with ice-cooling, for 1 min. The reaction mixture was left to stir until all the starting material had been consumed, and then partitioned between water (200 cm^3) and dichloromethane (3 x 50 cm^3) . The extracts were washed with sat. $NaHCO_3$ solution until neutral, then

with water (100 cm^3), dried (Na_2SO_4), filtered, and reduced *in vacuo* to give a syrup. Chromatography on silica, with ethyl acetate-toluene (3:17) as eluent produced firstly the α-anomer (**29α**) (0.28 g, 12%) as a syrup; $[\alpha]_D$ -23.1 (*c* 1.43 in $CHCl_3$); ν_{max} (film) 3502, 3063, 2935, 1724, 1602 and 1495 cm^{-1}; δ_H 1.48 (3H, d, $J_{6,5}$ 6.2, H-6), 2.90 (1H, bs, OH), 4.35 (1H, t, *J* 4.3, H-2), 4.53 (1H, dd, $J_{4,3}$ 5.6, $J_{4,5}$ 7.7, H-4), 4.70 and 4.91 (each 1H, d, *J* 11.8, PhCH_2), 5.28 (1H, d, $J_{1,2}$ 4.6, H-1), 5.39 (1H, dq, $J_{5,6}$ 6.3, $J_{5,4}$ 7.7, H-5), 5.62 (1H, dd, $J_{3,4}$ 5.6, $J_{3,2}$ 4.0, H-3), 7.2-7.9 (15H, m, Ar); δ_C 17.3 (C-6), 68.9 and 70.3 (CH_2 and C-5), 77.1, 78.4 and 78.7 (C-2, C-3 and C-4), 99.9 (C-1), 128.1-130.0 (8 signals), 132.8, 133.2, 137.0, 165.3 and 165.8 (*C*OBz); *m/z* (FAB) 463 $(MH)^+$, 355 $(M - OBn)^+$, and 91 $(Bn)^+$ (Found: C, 70.4; H, 5.3%. $C_{27}H_{26}O_7$ requires C, 70.12; H, 5.67%).

Further elution produced the β-isomer (**29β**) (1.653 g, 74%) as a syrup; $[\alpha]_D$ -57.8 (*c* 1.80 in $CHCl_3$); ν_{max} (film) 3458, 3063, 2988, 1722, 1601 and 1493 cm^{-1}; δ_H 1.55 (3H, d, $J_{6,5}$ 6.2, H-6), 3.4 (1H, bs, OH), 4.38 (1H, bs, H-2), 4.54 and 4.86 (each 1H, d, *J* 11.6, PhCH_2), 4.68 (1H, dd, $J_{4,3}$ 5.2, $J_{4,5}$ 8.5, H-4), 5.18 (1H, s, H-1), 5.48 (1H, dd, $J_{3,4}$ 5.1 $J_{3,2}$ 1.4, H-3), 5.51 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.6, H-5), 7.2-7.9 (15H, m, Ar); δ_C 17.9 (C-6), 69.5 and 69.8 (CH_2 and C-5), 77.9, 79.9 and 82.0 (C-2, C-3 and C-4), 107.3 (C-1), 127.7-130.1 (9 signals), 132.8, 133.2, 137.4, 165.4 and 166.3 (*C*OBz); *m/z* (FAB) 463 $(MH)^+$, 355 $(M - OBn)^+$, 341 $(MH - PhCO_2H)^+$, and 91 (Bn). [Found: MNa^+ (FAB) 485.1584. $C_{27}H_{26}O_7Na$ requires 485.1576].

Benzyl 2-O-*acetyl*-3,5-*di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranoside* (**30**). - Acetic anhydride (59.6 mg, 0.52 mmol) was added to an ice-cooled solution of alcohol **29β** (147.7 mg, 0.33 mmol) in dry pyridine (5 cm^3). The reaction mixture was stirred at RT for 2 h, when t.l.c. (ethyl acetate-toluene 1:9) showed that the reaction had gone to completion. The mixture was partitioned between water (40 cm^3) and chloroform (3 x 25 cm^3). The combined extracts were washed successively with dilute sulfuric acid (1M, 25 cm^3), sat. $NaHCO_3$ solution (25 cm^3), and water (25 cm^3), dried (Na_2SO_4), filtered and reduced *in vacuo* to give the *O*-acetyl compound (140.2 mg, 87%) as a thick syrup; $[\alpha]_D$ -94.0 (*c* 1.08 in $CHCl_3$); ν_{max} (film) 3063, 2992, 1728, 1602 and 1495 cm^{-1}; δ_H 1.54 (3H, d, $J_{6,5}$ 6.2, H-6), 2.13 (3H, s, Ac), 4.59 and 4.68 (each 1H, d, *J* 11.8, PhCH_2), 4.63 (1H, dd, $J_{4,3}$ 5.3, $J_{4,5}$ 8.7, H-4), 5.18 (1H, s, H-1), 5.27 (1H, bs, H-2), 5.45 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.7, H-5), 5.72 (1H, dd, $J_{3,4}$ 5.6, $J_{3,2}$ 1.0, H-3), 7.2-7.8 (15H, m, Ar); δ_C 17.9 (C-6), 20.7 (CO*Me*), 69.3 and 69.7 (CH_2 and C-5), 74.2, 80.5 and 82.9 (C-2, C-3 and C-4), 105.2 (C-1), 127.8-129.8 (6 signals), 132.7, 133.1, 137.2, 165.1 and 165.2 (*C*OBz), and 169.2 (*C*OMe); *m/z* (FAB) 505 $(MH)^+$, 397 $(M - BnO)^+$, and 91 $(Bn)^+$. (Found: C, 69.3; H, 5.3%. $C_{29}H_{28}O_8$ requires C, 69.02; H, 5.60%).

2-O-*acetyl*-3,5-*di*-O-*benzoyl*-6-*deoxy*-D-*glucofuranoside* (**31**). - The benzyl glycoside **30** (1.544 g, 3.1 mmol) dissolved in ethanol (20 cm^3) was stirred in the presence of palladium-on-carbon (5%, 1.5 g) under one atmosphere of H_2 at RT for 3 days. The catalyst was removed by filtration and the filtrate reduced *in vacuo* to give a syrup. Chromatography on silica, with ethyl acetate-toluene (3:17) as eluent gave free sugar **31** (1.015g, 80%) as a colourless syrup, α:β, 1:1; $[\alpha]_D$ -49.3 (*c* 1.08 in $CHCl_3$); ν_{max} (film) 3461, 3063, 2992, 1727, 1602 and 1492 cm^{-1}; δ_H 1.50 (3H, 2d, $J_{6,5}$ 6.2, H-6α+β), 2.14 (3H, 2s, Acα+β), 3.48 ($^1/_2$H, bd, OH), 3.67 ($^1/_2$H, bd, OH), 4.54 ($^1/_2$H, dd, $J_{4,5}$ 8.6, $J_{4,3}$ 5.0, H-4β), 4.61 ($^1/_2$H, dd, $J_{4,5}$ 7.7, $J_{4,3}$ 5.7, H-4α), 5.19 (1H, m, H-2α+β), 5.35 ($^1/_2$H, dq, $J_{5,4}$ 7.7, $J_{5,6}$ 6.2, H-5α), 5.40 ($^1/_2$H, m, H-1β), 5.51 ($^1/_2$H, dq, $J_{5,4}$ 8.6, $J_{5,6}$ 6.2, H-5β), 5.69 ($^1/_2$H, dd, $J_{3,4}$ 5.0, $J_{3,2}$ 1.1, H-3β), 5.73 ($^1/_2$H, bt, H-1α), 5.88 ($^1/_2$H, dd, $J_{3,4}$ 5.6, $J_{3,2}$ 4.1, H-3α), 7.0-8.0 (10H, m, Ar); δ_C 17.2 and 17.8 (C-6), 20.6 and 20.7 (CO*Me*), 68.9 and 69.3 (C-5), 74.5, 75.0, 77.4, 78.0, 81.1 and 82.6 (C-2, C-3 and C-4), 94.7 (C-1α), 101.0 (C-1β), 128.1-129.7 (5 signals), 132.8, 133.4, 165.0 and 165.3 (*C*OBz), 169.5 and 170.0 (*C*OMe); *m/z* (FAB) 415 $(MH)^+$, 397 $(MH - H_2O)^+$, 355 $(MH - CH_3CO_2H)^+$, and 293 $(MH - PhCO_2H)^+$ (Found: C, 63.5; H, 5.5%. $C_{22}H_{22}O_8$ requires C, 63.75; H, 5.35%).

2-Acetoxy-4-formylphenyl 2-O-*acetyl*-3,5-*di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranoside* (**32**). - A mixture of 2-*O*-acetyl-3,5-di-*O*-benzoyl-6-deoxy-D-glucofuranoside (**31**) (717.3 mg, 1.73 mmol), triphenylphosphine (465 mg, 1.77 mmol) and 3-acetoxy-4-hydroxy benzaldehyde (**22**) (320.4 mg, 1.78 mmol) was dried by evaporation three times using benzene. The mixture, dissolved in dry THF (15 cm^3) was cooled in ice while a solution of diethyl azodicarboxylate (304 mg, 1.75 mmol) in dry THF (10 cm^3) was added dropwise. The mixture was allowed to stir at RT overnight and then reduced *in vacuo* to give a syrupy residue. Chromatography on silica, with ethyl acetate-toluene (1:9) as eluent produced only the β-isomer **32** (349.3 mg, 35%) as a glass; $[\alpha]_D$ -66.9 (*c* 1.51 in $CHCl_3$); ν_{max} (film) 3063, 2992, 1728, 1602 and 1495 cm^{-1}; δ_H 1.45 (3H, d, $J_{6,5}$ 6.2, H-6), 1.92 (3H, s, Ac), 2.18 (3H, s, Ac), 4.75 (1H, dd, $J_{4,3}$ 5.3, $J_{4,5}$ 8.3, H-4), 5.44 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.7, H-5), 5.45 (1H, s, H-2), 5.77 (1H, bs, H-1), 5.72 (1H, dd, $J_{3,4}$ 5.2, $J_{3,2}$ 1.0, H-3), 7.2-7.8 (13H, m, Ar), 9.89 (1H, s, CHO); δ_C 17.7 (C-6), 20.0 (CO*Me*), 20.6 (CO*Me*), 68.9 (C-5), 73.9, 80.3 and 84.2 (C-2, C-3 and C-4), 104.3 (C-1), 116.7, 124.1, 128.1-129.8 (8 signals), 132.8, 133.5, 140.8, 153.2, 165.0 and 165.1 (*C*OBz), 168.3 and 169.0 (*C*OMe) and 189.9 (CHO); *m/z* (FAB) 599 $(MNa)^+$, 455 $(M - PhCO_2H)^+$ and 397 $[M - OC_6H_3(OCOMe)CHO]^+$.

Benzyl 3,5-*di*-O-*benzoyl*-6-*deoxy*-2-O-*mesyl*-β-D-*glucofuranoside* (**33**). - Methanesulfonyl chloride (59.6 mg, 0.52 mmol) was added to an ice-cooled solution of benzyl 3,5-di-*O*-benzoyl-6-deoxy-β-D-glucofuranoside (**29β**) (147.7 mg, 0.33 mmol) in dry pyridine (5 cm^3). The reaction mixture was stirred at RT for 2 h, by which time t.l.c. (ethyl acetate-toluene 1:9) indicated that the reaction was complete. The reaction mixture was partitioned between water (40 cm^3) and chloroform (3 x 25 cm^3). The combined extracts were washed successively with dilute sulfuric acid (1 M, 25 cm^3), sat. $NaHCO_3$ solution (25 cm^3) and water (25 cm^3), dried (Na_2SO_4), and evaporated to give mesylate **33** (155.4 mg, 90%) as a syrup; ν_{max} (film) 3063, 2992, 1728, 1602 and 1495 cm^{-1}; δ_H 1.54 (3H, d, $J_{6,5}$ 6.2, H-6), 3.15 (3H, s, SO_2Me), 4.58 and 4.87 (each 1H, d, *J* 11.6, CH_2), 4.67 (1H, dd, $J_{4,3}$ 5.4, $J_{4,5}$ 8.6, H-4), 5.12 (1H, bs, H-2), 5.39 (1H, s, H-1), 5.53 (1H, dq, $J_{5,6}$ 6.2, $J_{5,4}$ 8.7, H-5), 5.66 (1H, d, $J_{3,4}$ 4.6, H-3), 7.2-7.9 (15H, m, Ar); δ_C 17.7 (C-6), 38.2 (SO_2Me), 69.1 and 69.9 (CH_2 and C-5), 74.7, 82.2 and 85.0 (C-2, C-3 and C-4), 105.0 (C-1), 127.6-129.8 (7 signals), 132.8, 133.4, 136.7, 165.1 and 165.5 (*C*OBz); *m/z* (FAB) 541 (MH^+), 433 $(MH - BnOH)^+$ and 419 $(MH - PhCO_2H)^+$ (Found: C, 61.9; H, 5.4; S, 6.3%. $C_{29}H_{28}O_9S$ requires C, 62.21; H, 5.22; S, 5.92%).

3,5-*Di*-O-*benzoyl*-6-*deoxy*-2-O-*mesyl*-D-*glucofuranoside* (**34**). - The benzyl glycoside **33** (2.51 g, 4.65 mmol) in ethanol (150 cm^3) was hydrogenolysed in the presence of Pd/C (5%, 2 g) under one atmosphere of H_2 at RT for 4 days. The residue after filtration and evaporation was chromatographed on silica with ethyl acetate-toluene (3:17), as eluent to give **34** (1.40 g, 66%) as a syrup, α:β, 1:1; ν_{max} (film) 3471, 3064, 2938, 1724, 1602 and 1492 cm^{-1}; δ_H 1.50 (3H, 2d, $J_{6,5}$ 6.2, H-$6_{\alpha+\beta}$), 3.17 (3H, 2s, SO_2Me), 3.48 (1H, bs, OH), 4.57 ($^1/_2$H, dd, $J_{4,5}$ 8.6, $J_{4,3}$ 5.2, H-4β), 4.64 ($^1/_2$H, dd, $J_{4,5}$ 7.8, $J_{4,3}$ 5.7, H-4α), 5.05 ($^1/_2$H, bs, H-2β), 5.09 ($^1/_2$H, t, $J_{2,3}$ 4.1, H-2α), 5.38 ($^1/_2$H, dq, $J_{5,4}$ 7.7, $J_{5,6}$ 6.3, H-5α), 5.56 ($^1/_2$H, dq, $J_{5,4}$ 8.6, $J_{5,6}$ 6.2, H-5β), 5.61 ($^1/_2$H, s, H-1β), 5.64 ($^1/_2$H, dd, $J_{3,2}$ 1.1, H-3β), 5.73 ($^1/_2$H, d, $J_{1,2}$ 4.2, H-1α), 5.86 ($^1/_2$H,dd, $J_{3,4}$ 5.6, $J_{3,2}$ 4.1, H-3α), 7-8 (10H, m, Ar); δ_C 17.2 and 17.7 (C-6), 38.2 and 38.5 (SO_2Me), 68.7 and 69.2 (C-5), 74.9, 77.7, 81.8, 81.8 and 85.7 (C-2, C-3 and C-4), 94.6 (C-1α), 100.1 9 (C-1β), 128.1-129.7 (5 signals), 132.9, 133.6, 165.3, 165.4 and 165.5 (*C*OBz); *m/z* (EI) 433 $(M - OH)^+$, 328 $(M - PhCO_2H)^+$, and 232 $(M - PhCO_2H - MeSO_3H)^+$ (Found: C, 55.8; H, 5.2; S, 7.0%. $C_{21}H_{22}O_9S$ requires C, 55.99; H, 4.93; S, 7.10%).

2-Acetoxy-4-formylphenyl 3,5-*di*-O-*benzoyl*-6-*deoxy*-2-*O*-*mesyl*-D-*glucofuranoside* (**35**). - A mixture of mesylate **34** (138.4 mg, 0.31 mmol), triphenylphosphine (85.7 mg, 0.33 mmol) and 3-acetoxy-4-hydroxybenzaldehyde (**22**) (60 mg, 0.33 mmol) was evaporated to dryness three times with benzene and then

dissolved in dry THF (15 cm^3). This solution was ice-cooled and a solution of diethyl azodicarboxylate (56.2 mg, 0.32 mmol) in dry THF (5 cm^3) was added dropwise. The mixture was stirred at RT overnight and then reduced *in vacuo* to give a syrupy residue. Chromatography in silica, with ethyl acetate-toluene (1:9) produced glycoside **35** (80.6 mg, 43%) as a glassy anomeric mixture; ν_{max} (film) 3063, 2992, 1728, 1602 and 1495 cm^{-1}; δ_H 1.45 (3H, m, H-6), 1.81 ($^6/_5$H, s, Ac), 2.35 ($^9/_5$H, s, Ac), 3.09 ($^6/_5$H, s, Ms), 3.23 ($^9/_5$H, s, Ms), 4.65 ($^2/_5$H, t, *J* 7.0 H-4), 4.79 ($^3/_5$H, dd, *J* 5.4, 8.2, H-4), 5.32 (1H, m, H-2), 5.46 (1H, m, H-5), 5.71 ($^3/_5$H, dd, J 1, 5.2, H-3), 5.89 ($^7/_5$H, m, H-1+ H-3), 7.2-8.0 (13H, m, Ar), 9.88 (1H, d, 2 CHO); d_C 16.9 and 17.6 (C-6), 19.9 and 20.5 (CO*Me*), 38.3 and 38.4 (SO_2*Me*), 68.6 and 68.7 (C-5), 74.0, 74.4, 78.3, 80.3 and 83.7, 84.5 (C-2, C-3 and C-4), 97.4 and 104.0 (C-1), 116.0, 116.4, 123.9, 124.0, 128.2-133.8 (13 signals), 140.7, 141.3, 152.6 (2 signals), 165.0, 165.4, 168.2 and 168.7 (*C*OBz), and 189.8 (CHO); *m/z* (FAB) 634 $(MNa)^+$, 455 $(M - PhCO_2H)^+$ and 433 $(M - OC_6H_3(OCOMe)CHO)^+$.

2-*Hydroxy*-4-*formylphenyl* 3,5-*di*-O-*benzoyl*-6-*deoxy*-β-D-*glucofuranoside* (**36**). - Sodium ethoxide in ethanol (1.04 M, 260 ml, 0.27 mmol) was added to a solution of phenol (52.4 mg, 0.55 mmol) in ethanol (3 cm^3). After 15 min, this was added to a solution of **32** (155.2 mg, 0.27 mmol) in ethanol (7 cm^3). After 80 min, the reaction mixture was partitioned between aqueous NaOH (2M, 30 cm^3) and dichloromethane (3 x 30 cm^3). The combined extracts were washed with water, until neutral, dried (Na_2SO_4), filtered, and reduced *in vacuo* to give a thick syrup. Chromatography on silica, with ethyl acetate-toluene (1:4) gave the diol **36** (115.3 mg, 87%) as a glass; $[\alpha]_D$ -169.7 (*c*. 0.60 in $CHCl_3$); ν_{max} (film) 3432, 3065, 2937, 1722, 1694, 1602 and 1505 cm^{-1}; δ_H 1.42 (3H, d, $J_{6,5}$ 6.2, H-6), 4.44 (1H, bs, OH), 4.73 (1H, bs, H-2), 4.80 (1H, dd, $J_{4,3}$ 5.0, $J_{4,5}$ 8.1, H-4), 5.47 (1H, dq, $J_{5,6}$ 6.3, $J_{5,4}$ 8.1 H-5), 5.58 (1H, dd, $J_{3,4}$ 5.0, $J_{3,2}$ 1.1, H-3), 5.76 (1H, s, H-1), 6.48 (1H, bs, OH), 7.0-8.0 (13H, m, Ar), 9.73 (1H, s, CHO); δ_C 17.8 (C-6), 68.9 (C-5), 76.3, 79.7 and 83.5 (C-2, C-3 and C-4), 106.3 (C-1), 114.8, 115.3, 124.0, 128.1-129.6 (6 signals), 131.8, 132.9, 133.7, 146.6, 148.8, 165.4 and 166.3 (*C*OBz) and 191.3 (CHO) ; *m/z* (FAB) 493 $(MH)^+$, 355 $[M - OC_6H_3(OH)CHO]^+$ and 233 $[M - OC_6H_3(OH)CHO - PhCO_2H]^+$ [Found: MNa^+ (FAB) 515.1307. $C_{27}H_{24}O_9Na$ requires 515.1318].

4-*Formyl*-2-*mesyloxyphenyl* 3,5-*di*-O-*benzoyl*-6-*deoxy*-2-O-*mesyl*-β-D-*glucofuranoside* (**37**). - Methanesulfonyl chloride (370 mg, 3.23 mmol) was added to an ice-cooled solution of diol **36** (718.4 mg, 1.46 mmol) in dry pyridine (15 cm^3). The mixture was stirred at RT overnight, when t.l.c. (ethyl acetate-toluene, 1:19) indicated complete reaction. The mixture was partitioned between water (100 cm^3) and chloroform (3 x 30 cm^3). The combined extracts were washed successively with dilute sulfuric acid (1 M, 20 cm^3), sat. $NaHCO_3$ solution (20 cm^3) and water (20 cm^3), dried (Na_2SO_4), filtered and evaporated to give dimesylate **37** (830.8 mg, 88%) as a glass; $[\alpha]_D$ -123.7 (*c* 0.76 in $CHCl_3$); ν_{max} (KBr) 3063, 2938, 1724, 1697, 1603 and 1506 cm^{-1}; δ_H 1.43 (3H, d, $J_{6,5}$ 6.2, H-6), 2.86 (3H, s, SO_2Me), 3.25 (3H, s, SO_2Me), 4.81 (1H, dd, $J_{4,3}$ 5.3, $J_{4,5}$ 8.2, H-4), 5.42 (1H, d, $J_{2,3}$ 1.1, H-2), 5.52 (1H, dq, $J_{5,6}$ 6.3, $J_{5,4}$ 8.2 H-5), 5.78 (1H, dd, $J_{3,4}$ 5.3, $J_{3,2}$ 1.3, H-3), 6.00 (1H, s, H-1), 7.1-8.0 (13H, m, Ar), 9.88 (1H, s, CHO); δ_C 17.6 (C-6), 38.3 (SO_2Me), 68.5 (C-5), 74.3, 83.9 and 84.6 (C-2, C-3 and C-4), 104.4 (C-1), 116.7, 125.0, 125.2, 128.1-130.1 (7 signals), 131.7, 133.0, 133.8, 138.8, 153.0, 165.1 and 165.4 (*C*OBz), and 189.4 (CHO) ; *m/z* (FAB) 649 $(MH)^+$ and 433 $[M - OC_6H_3(OMs)CHO]^+$ [Found: MNa^+ (FAB) 671.0862. $C_{29}H_{28}O_{13}S_2Na$ requires 671.0869].

4-*Formyl*-2-*mesyloxyphenyl* 2,3-*anhydro*-6-*deoxy*-β-D-*mannofuranoside* (**38**). - Sodium methoxide (20.5 mg, 0.40 mmol) was added to a solution of dimesylate **37** (123 mg, 0.19 mmol) in methanol (10 cm^3). After 5 h, the mixture was neutralised using Amberlite IR-120 (H^+), filtered, and evaporated to dryness. Chromatography on silica, with ethyl acetate-toluene (1:4) as eluent gave epoxide **38** (50.1 mg, 77%), m.p. 101-103°C; $[\alpha]_D$ -108.8 (*c* 0.91 in $CHCl_3$); ν_{max} (KBr) 3460, 2924, 1708 and 1604 cm^{-1}; δ_H 1.26 (3H, d, $J_{6,5}$ 6.1, H-6), 2.30 (1H, bs, OH), 3.31 (3H, s, SO_2Me), 3.89 (1H, dd, $J_{4,5}$ 6.5, $J_{4,3}$ 1.1, H-4), 3.98 (1H,

quin, *J* 6.4, H-5), 3.99 (1H, dd, $J_{3,2}$ 2.9, $J_{3,4}$ 1.1, H-3), 4.02 (1H, dd, $J_{2,3}$ 2.9, $J_{2,1}$ 0.9, H-2), 5.74 (1H, s, H-1), 7.0-7.4 (3H, m, Ar), 9.83 (1H, s, CHO); δ_C 20.2 (C-6), 38.9 (SO_2Me), 55.6 and 56.3 (C-2 and C-3), 66.6 (C-5), 82.4 (C-4), 100.1 (C-1), 116.5, 126.0, 130.0, 131.7, 139.2, 153.9 and 189.5 (CHO); *m/z* (FAB) 345 $(MH)^+$, and 129 [M - $OC_6H_3(OMs)CHO]^+$ [Found: MH^+ (FAB) 345.0605. $C_{14}H_{17}O_8S$ requires 345.0644].

2-*Mesyloxy*-4-[(E)-2-*(methoxycarbonyl)*-1-*propen*-1-*yl*]*phenyl* 2,3-*anhydro*-6-*deoxy*-β-D-*mannofuranoside* (**39**). - A solution of **38** (88.4 mg, 0.26 mmol) in dichloromethane (5 cm^3) was added dropwise to a solution of $Ph_3PC(Me)CO_2Me$ (97.5 mg, 0.28 mmol) in dichloromethane (5 cm^3). After stirring at RT for 5 h, when t.l.c. (ethyl acetate-toluene 2:8) showed that all the starting material had been consumed, the reaction mixture was evaporated to give a syrup. Chromatography on silica, with ethyl acetate-toluene (1:4) as eluent gave the Wittig product **39** (91.7 mg, 86%) as a glass; $[\alpha]_D$ -74.8 (*c* 0.78 in $CHCl_3$); ν_{max} (KBr) 3520, 2936, 1713 and 1609 cm^{-1}; δ_H 1.27 (3H, d, $J_{6,5}$ 6.3, H-6), 2.08 (3H, d, *J* 1.4, Me), 2.40 (1H, bs, OH), 3.27 (3H, s, SO_2Me), 3.78 (3H, s, CO_2Me), 3.84 (1H, dd, $J_{4,5}$ 6.6, $J_{4,3}$ 0.9, H-4), 3.94 (1H, dd, $J_{3,2}$ 2.9, $J_{3,4}$ 0.9, H-3), 3.96 (1H, m, H-5), 3.98 (1H, dd, $J_{2,3}$ 2.9, $J_{2,1}$ 0.7, H-2), 5.74 (1H, s, H-1), 7.1-7.4 (3H, m, Ar), 7.55 (1H, bs, CH); δ_C 13.9 (Me), 20.2 (C-6), 38.6 (SO_2Me), 52.1 (CO_2Me), 55.3 and 56.2 (C-2 and C-3), 66.6 (C-5), 82.1 (C-4), 100.4 (C-1), 116.7, 126.0, 128.7, 129.9, 131.2, 138.7 (CH), 148.6 and 168.8 (CO_2Me); *m/z* (FAB) 415 $(MH)^+$, 286 $[HOC_6H_3(OSO_2Me)CHC(Me)CO_2Me]^+$ and 129 [glycosyl cation]$^+$ [Found: MH^+ (FAB) 415.1084. $C_{18}H_{23}O_9S$ requires 415.1063].

2-*Hydroxy*-4[(E)-2-*carboxy*-1-*propen*-1-*yl*]*phenyl* 6-*deoxy*-β-D-*altrofuranoside* (**40**).- The epoxide **39** (76.5 mg, 0.18 mmol) in dilute aqueous NaOH (1 M, 5 cm^3) was heated under reflux for 4 h. The mixture was neutralised using Amberlite IR-120 (H^+), filtered and evaporated to dryness. The residue was chromatographed on silica, with ethyl acetate-methanol (24:1) as eluent to give the tetraol **40** (22 mg, 35%) as a glass; $[\alpha]_D$ -157.5 (*c* 0.63 in MeOH); ν_{max} (KBr) 3339, 2930 and 1684 cm^{-1}; δ_H (200 MHz, CD_3OD) 1.11 (3H, d, $J_{6,5}$ 6.1, H-6), 2.08 (3H, d, *J* 1.4, Me), 3.70 (1H, dd $J_{4,5}$ 5.1, $J_{4,3}$ 6.4, H-4), 3.74 (1H, dq, $J_{5,4}$ 5.1, $J_{5,6}$ 6.4, H-5), 4.17 (1H, dd, $J_{2,3}$ 8.0, $J_{2,1}$ 4.4, H-2), 4.30 (1H, dd, $J_{3,2}$ 8.1, $J_{3,4}$ 6.5, H-3), 5.50 (1H, d, $J_{1,2}$ 4.5, H-1), 6.89 (1H, dd, *J* 2.1, 8.4, Ar), 6.95 (1H,d, *J* 2.0, Ar), 7.14 (1H,d, *J* 8.4, Ar), 7.57 (1H,bs, CH); δ_C (50 MHz, CD_3OD) 14.2 (Me), 18.8 (C-6), 69.5 (C-5), 76.3, 79.4 and 87.8 (C-2, C-3 and C-4), 102.7 (C-1), 117.7, 118.3, 123.0, 128.2, 132.3, 139.9 (CH), 146.4, 148.5 and 172.3 (CO_2H); *m/z* (FAB) 363 $(MNa)^+$ and 147 [glycosyl cation]$^+$ [Found: MH^+ (FAB) 341.122. $C_{16}H_{21}O_8$ requires 341.1236].

2-*Acetoxy*-4-[(E)-2-*carboxy*-1-*propen*-1-*yl*]*phenyl* 2,3,5-*tri*-O-*acetyl*-6-*deoxy*-β-D-*altrofuranoside* (**41**).- Acetic anhydride (0.1 cm^3 mmol) was added to a solution of the tetraol **40** (4.0 mg) in dry pyridine (0.5 cm^3). After 4h, water (0.3 cm^3) was added and the reaction mixture stirred for 15 min. The mixture was then evaporated to dryness. Chromatography on silica, with ethyl acetate-toluene (1:19) as eluent gave the tetra-*O*-acetyl derivative **41** (2 mg, 33%); δ_H 1.13 (3H, d, $J_{6,5}$ 6.2, H-6), 1.92 (3H, s, Ac), 2.12 (9H, m, 2Ac and Me), 2.34 (3H, s, Ac), 4.01 (1H, t, *J* 6.1, H-4), 5.06 (1H, quin, *J* 6.2, H-5), 5.19 (1H,dd, $J_{2,1}$ 4.5, $J_{2,3}$ 7.4, H-2), 5.71 (1H, dd, *J* 6.0, *J* 6.3, H-3), 5.86 (1H, d, $J_{1,2}$ 4.3, H1), 7.13 (2H, m, H), 7.25 (1H, m, H), 7.68 (1H, bs, CH); *m/z* (FAB) 509 $(MH)^+$ and 273 (glycosyl cation)$^+$.

2-*Hydroxy*-4-[(E)-2-*carboxy*-1-*propen*-1-*yl*]*phenyl* 6-*deoxy*-5-*keto*-β-D-arabino-*hexofuranoside* (**42**). - Chromic acid [0.01 cm^3, 0.027 mmol, from a solution of CrO_3 (2.7g) in conc. H_2SO_4 (2.3 cm^3), made up to 10 cm^3 with water], was added to a solution of the tetraol **40** (6.0 mg, 0.018 mmol) in degassed acetone (1 cm^3), cooled in a acetone/CO_2 bath. The reaction temperature was allowed to rise to -5°C. After 75 min, t.l.c (ethyl acetate) showed the reaction had gone to completion. The residue after evaporation was chromatographed on silica, with ethyl acetate as eluent to give the 5-keto compound **42** (2.5 mg, 42%) as a

glass; δ_H (200 MHz, CD_3OD) 2.08 (3H, d, *J* 1.4, CH_3), 2.11 (3H, s, H-6), 4.19 (1H, dd, $J_{2,1}$ 4.2, $J_{2,3}$ 7.0, H-2), 4.27 (1H,d, *J* 5.9, H-4), 4.34 (1H, q, *J* 6.9, H-3), 5.64 (1H, d, $J_{1,2}$ 4.2, H-1), 6.92 (1H, dd, *J* 2.0, 8.4), 6.97 (1H, d, *J* 2.0), 7.24 (1H, d, *J* 8.4), 7.58 (1H, bs, CH); *m/z* (FAB) 361 $(MNa)^+$, 339 $(MH)^+$ and 145 (glycosyl cation)$^+$.

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