Synthesis of Oligosaccharides Corresponding to Biological Repeating Units of *Shigella flexneri* Variant Y Polysaccharide. Part 1. Overall Strategy, Synthesis of a Key Trisaccharide Intermediate, and Synthesis of a Pentasaccharide

B. Mario Pinto* and David G. Morissette
Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6
David R. Bundle*
Division of Biological Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR6

The overall strategy for the synthesis of penta- up to octa-saccharides, representing the biological repeating unit of the *Shigella flexneri* serogroup Y lipopolysaccharide, is described. The key intermediate, the common terminal trisaccharide, α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*(1 ⟶ 3)-α-L-Rha*p*, has been synthesised by a series of Königs–Knorr reactions. A selectively protected rhamnose intermediate has been developed for the synthesis of this trisaccharide as its allyl glycoside. Allyl α-L-rhamnopyranoside was converted into the corresponding 2-*O*-benzoyl-4-*O*-benzyl derivative *via* a 2,3-orthobenzoate. Königs–Knorr reaction between this partially blocked rhamnoside and 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl chloride afforded the blocked disaccharide. Selective transesterification of the 2′-*O*-acetyl group in the presence of the 2-*O*-benzoate yielded the disaccharide, selectively deblocked at the C-2′ position. Reaction with the same rhamnopyranosyl chloride gave the fully blocked trisaccharide. Deallylation, followed by treatment with *NN*-dimethyl(chloromethylene)ammonium chloride, then gave the corresponding trisaccharide chloride. In conjunction with the disaccharide methyl 2-*O*-(2′-acetamido-4′,6′-*O*-benzylidene-2′-deoxy-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside, the synthesis of the blocked pentasaccharide was accomplished. Transesterification, followed by hydrogenolysis in aqueous acetic acid, afforded the pure pentasaccharide hapten, α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*-(1 ⟶ 3)-α-L-Rha*p*-(1 ⟶ 3)-β-D-Glc*p*NAc-(1 ⟶ 2)-α-L-Rha*p*, as its methyl glycoside, for use in binding studies and n.m.r. studies.

During the last three years, a large number of monoclonal antibodies that bind the *Shigella flexneri* variant Y antigen have been generated. This is a lipopolysaccharide *O*-antigen with a tetrasaccharide repeating unit.[1] Three of the four possible biological repeating units of this *O*-chain have been synthesised.[2] The synthetic compounds, which were intended for inhibition studies to map the antibody combining site, have also been used in n.m.r. studies to elucidate the conformation of the *O*-antigen in solution.[3] This study formed the basis of a recent elucidation, by n.m.r. spectroscopy, of the biological repeating unit of the *O*-antigen.[4] Oligosaccharide fragments produced by phage-associated *endo*-rhamnosidase were isolated and, from their ^{1}H n.m.r. spectra, the sequence of sugar units could be determined using the data of reference 3. The three oligosaccharides isolated were tetra-, octa-, and deca-saccharides, with the following structures.

Tetrasaccharide:

α-L-Rha*p*-(1 ⟶ 3)-β-D-Glc*p*NAc-(1 ⟶ 2)-
C D
α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*
A B

Octasaccharide:

[α-L-Rha*p*-(1 ⟶ 3)-β-D-Glc*p*NAc-(1 ⟶ 2)-
C D
α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha-(1)]$_2$
A B

Decasaccharide:

α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*-(1 ⟶ 3)-α-L-Rha*p*-(1 ⟶ 3)-
A B ↑ C
(sites of enzymic cleavage)

β-D-Glc*p*NAc-(1 ⟶ 2)-α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*-(1 ⟶ 3)-
D A B ↑
α-L-Rha*p*-(1 ⟶ 3)-β-D-Glc*p*NAc-(1 ⟶ 2)-
C D
α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*
A B

The decasaccharide represents the non-reducing terminus of the bacterial *O*-chains and, therefore, the distal portions most accessible to antibodies.

Oligosaccharides obtained by phage-mediated hydrolysis and by synthetic methods were linked to protein, and the monoclonal antibodies produced[5] were screened by ELISA against this panel of antigens. Of those IgG monoclonals most suitable for binding studies, one bound the decasaccharide antigen but not the terminal tetrasaccharide sequence ABCD nor the phage-derived tetra- or octa-saccharide.[5] The combining site of this antibody must require chain end-sequences larger than four saccharides and it is of interest to determine the lower size limit of the antigenic determinant. Based on Kabat's studies with dextrans,[6] it is expected that this limit lies between penta- and octa-saccharides. Since the phage-associated *endo*-rhamnosidase could not provide the appropriate size and sequence of oligosaccharide, we propose to use synthesis for this purpose. These oligosaccharides will also provide haptens useful for binding studies and eventually for *X*-ray crystallographic studies of the corresponding antibodies.

The block syntheses of penta- up to octa-saccharides, corresponding to the biological repeating unit of *Shigella flexneri* Y, have been designed.

Retrosynthetic analysis indicates that the following disconnections would be most advantageous for the synthesis of the parent octasaccharide.

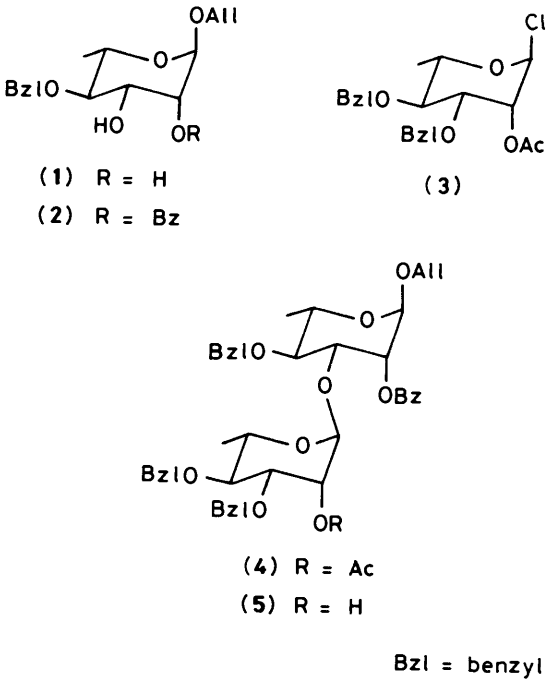
α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*-(1 ⟶ 3)-α-L-Rha*p*-(1 ⟶ 3)≃
β-D-Glc*p*NAc-(1 ⟶ 2)≃α-L-Rhap-(1 ⟶ 2)-α-L-(1 ⟶ 3)-
α-L-Rha*p*-(1 ⟶ 3)≃β-D-Glc*p*NAc-X

X = $O[CH_2]_8CO_2Me$

The disconnections ensure that the common terminal trisaccharide, α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*-(1 ⟶ 3)-α-L-Rha*p*, can be used in the syntheses of all of the desired oligosaccharides. In conjunction with an allyl 2-deoxy-2-phthalimido-β-D-glucopyranoside unit, and the disaccharide units β-D-Glc*p*NAc-(1 ⟶ 2)-α-L-Rha*p*-OAll and α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*-OAll, the synthesis of large terminal oligosaccharides should be possible. The salient features of the proposed syntheses are the use of allyl glycosides throughout, the generation of the glycosyl halides (the glycosyl donors) under mild conditions, and the selective removal of the acetate protecting group in the presence of the benzoate ester to yield the glycosyl acceptors. Thus, the use of allyl glycosides should permit their easy conversion into the corresponding hemiacetals *via* iridium(I)- or rhodium(I)-catalysed isomerisation to the prop-1-enyl glycosides[7,8] and subsequent hydrolysis.[9] The hemiacetals could in turn be converted under mild conditions into the corresponding glycosyl chlorides or bromides by use of Vilsmeier–Haack reagents.[10] The glycosyl halides could then be used for block oligosaccharide syntheses or for the attachment of the linking arm[11] which permits covalent coupling to protein.[12]

We report here the elaboration of the key trisaccharide intermediate and also the synthesis of a pentasaccharide, as its methyl glycoside, for use as a hapten in binding studies and n.m.r. studies.

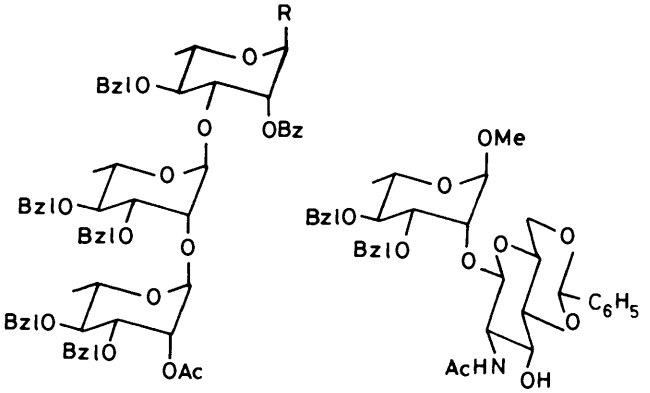
The partially blocked monosaccharide, allyl 4-*O*-benzyl-α-L-rhamnopyranoside (**1**),[13] obtained from L-rhamnose in three steps, was the starting point for the syntheses reported here. Conversion of diol (**1**) into the 2-*O*-benzoyl derivative (**2**) followed a procedure reported previously by Josephson and Bundle.[14] Reaction of compound (**1**) with trimethyl orthobenzoate gave a 2,3-orthobenzoate which was opened stereoselectively in aqueous acetic acid to provide the selectively protected monosaccharide (**2**). This unit possesses the necessary persistent blocking group at 0—4 and a participating group at 0—2 to direct subsequent α-glycosylation reactions. Königs–Knorr reaction of compound (**2**) with 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl chloride (**3**) (obtained from 3,4-di-*O*-benzyl-1,2-*O*-methoxyethylidene-β-L-rhamnopyranose, as described previously[14]) using silver trifluoromethanesulphonate and 1,1,3,3-tetramethylurea[15] afforded the disaccharide (**4**) in 64% yield. Selective removal of the 2′-*O*-acetyl group in the presence of the 2-*O*-benzoate was then necessary in order to provide the glycosyl acceptor for chain-extension reactions. This transformation was effected by treatment of disaccharide (**4**) with 0.6M-methanolic hydrogen chloride,[16] giving the disaccharide (**5**) in 72% yield, after chromatography. When the disaccharide (**5**) was treated with the rhamnopyranosyl chloride (**3**), as described above, the trisaccharide (**6**) was obtained as a syrup in 61% yield. The trisaccharide (**6**) represents the key intermediate in the proposed syntheses since it can serve both as glycosyl acceptor and glycosyl donor. In the present study, we describe its use as a glycosyl donor for the elaboration of a pentasaccharide comprising the sequence ABCDA. Thus, rhodium(I)-catalysed isomerisation[8] of the allyl glycoside to the prop-1-enyl glycoside and subsequent hydrolysis[9] afforded the hemiacetal (**7**). The glycosyl donor, namely the rhamnopyranosyl chloride (**8**), was then readily obtained by reaction of compound (**7**) with the Vilsmeier–Haack reagent *NN*-dimethyl(chloromethylene)ammonium chloride.[10] The selectively protected disaccharide (**9**) to be used as a glycosyl acceptor in the synthesis of the pentasaccharide was next prepared in an analogous manner to that described[17] for the



corresponding 8-methoxycarbonyloctyl glycoside. The methyl glycoside was chosen for convenience since the pentasaccharide was required only as a hapten suitable for inhibition studies. Reaction of chloride (**8**) with glycoside (**9**) promoted by silver trifluoromethanesulphonate and 1,1,3,3-tetramethylurea[15] in dichloromethane solution afforded the desired α-linked pentasaccharide (**10**) as a glass in 68% yield. The protected pentasaccharide (**10**) was transesterified and the product hydrogenolysed in the presence of palladium–charcoal in aqueous acetic acid. The crude pentasaccharide thus obtained was purified by chromatography on silica gel. The product was analytically pure and its spectral data were consistent with the expected structure (**11**).

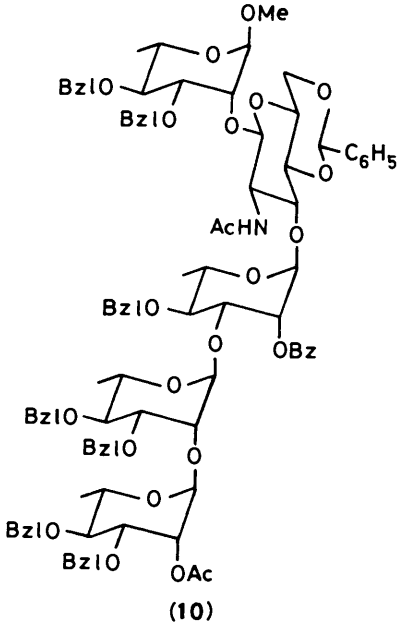
The structures assigned were in accord with their ^{13}C and ^{1}H n.m.r. data. Chemical-shift assignments were made by comparison of data[3,14,17–22] on related compounds and also by comparison of data within the present series of compounds. Anomeric purity and configuration of the di, tri, and pentasaccharides were confirmed by means of the ^{1}H and ^{13}C n.m.r. spectral data. In particular, the one-bond $^{1}J_{^{13}C\text{-}H}$ coupling constants for the anomeric carbons were diagnostic[23] of the anticipated α-linked rhamnose residues and the β-linked *N*-acetylglucosamine residue. The chemical-shift data, for the most part, are unexceptional. However, ^{13}C n.m.r. data for the deblocked pentasaccharide (**11**) are worthy of note. The assignments were made by use of the data [after correction (−0.65 p.p.m.) for the different reference used in this work] reported[3] for the comparative models, α-L-Rha*p*-(1 ⟶ 2)-α-L-Rha*p*-(1 ⟶ 3)-α-L-Rha*p*, and β-D-Glc*p*NAc-(1 ⟶ 2)-α-L-Rha*p*, and the *Shigella flexneri* Y polysaccharide. The close correlation of the chemical-shift data for the pentasaccharide (**11**) and the polysaccharide indicate similar conformations in solution for these two molecules.

As a final point of interest, we comment on the immunochemical studies with pentasaccharide (**11**) currently in progress. The compound is being tested in inhibition experiments with monoclonal antibodies and polyclonal sera raised against the Y-polysaccharide. Preliminary results with one monoclonal antibody indicate that the ABCDA sequence exhibits greater binding activity than either of the two tetrasaccharide



(6) R = OAll
(7) R = OH
(8) R = Cl

(9)



(10)

sequences, ABCD or BCDA. Further studies with other monoclonal antibodies are in progress in an attempt to delineate the features of the antigen surface of importance in the antibody–antigen interaction.

Experimental

General.—M.p.s were determined on a Fisher–Johns melting-point apparatus and are uncorrected. ^{1}H N.m.r. (400.13 MHz) and ^{13}C n.m.r. (100.6 MHz) spectra were recorded on a Bruker WM-400 n.m.r. spectrometer. Spectra were measured in deuteriochloroform unless otherwise stated. Chemical shifts are given in p.p.m. downfield from $SiMe_4$. For those spectra measured in deuterium oxide, chemical shifts are given in p.p.m. downfield from $Me_3Si[CH_2]_3SO_3Na$. Chemical shifts and coupling constants were obtained from a first-order analysis of the spectra. Optical rotations were measured on a Perkin-Elmer P22 spectropolarimeter.

Analytical t.l.c. was performed on pre-coated glass plates with Merck silica gel 60F-254 as the adsorbent. The developed plates were air-dried, exposed to u.v. light and/or sprayed with 10% sulphuric acid in ethanol, and heated at 150 °C. Medium-pressure column chromatography was performed according to a published procedure.[24] High-performance liquid chromatography (h.p.l.c.) was performed at 4 MPa on a Waters Associates Prep LC/system 500 instrument with two Prep PAK-500 silica gel normal-phase columns and a refractive-index detector.

Solvents were distilled before use and were dried, as necessary, by literature procedures. Work-up of solutions involved evaporation under reduced pressure at below 40 °C.

Reactions performed under nitrogen were carried out in deoxygenated solvents. Transfers under nitrogen were effected by means of standard Schlenck-tube techniques.

Allyl 2-O-*Benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**2**).—Allyl alcohol (400 cm^3) containing trifluoromethanesulphonic acid (4 cm^3) was stirred at reflux with L-rhamnose monohydrate (50 g, 0.27 mol) for *ca.* 3 h. After having cooled, the reaction mixture was neutralised with triethylamine (10 cm^3), filtered, and concentrated. Co-distillation with toluene (3 × 100 cm^3) left the residual, crude allyl α-L-rhamnopyranoside, which was dried over phosphorus pentaoxide in a desiccator for *ca.* 1 h. The residue was dissolved in a mixture of dry acetone (300 cm^3) and 2,2-dimethoxypropane (100 cm^3) containing toluene-*p*-sulphonic acid (PTSA) (500 mg), and the solution was stirred for 1 h at room temperature. Triethylamine (3 cm^3) was added and the reaction mixture was concentrated to afford a syrup which was dried (P_2O_5). The resulting syrup was dissolved in dry, freshly distilled *NN*-dimethylformamide (DMF) (300 cm^3) and the solution was added slowly to a stirred suspension of sodium hydride (16 g) in DMF (100 cm^3). Benzyl bromide (45 cm^3, 0.38 mol) was then added dropwise to the reaction mixture. After 20 h at room temperature, t.l.c. [hexane–ethyl acetate (2:1)] indicated complete reaction of the alcohol. Methanol (50 cm^3) was added slowly to the stirred suspension and after 2 h the reaction mixture was poured into cold water (1 500 cm^3). Extraction with ethyl acetate (3 × 200 cm^3) and concentration of the extracts gave a residue which was dissolved in ethanol (400 cm^3) containing 0.5M-hydrochloric acid (400 cm^3). Hydrolysis of the acetal was complete after 1 h at reflux, as indicated by t.l.c. [hexane–ethyl acetate (2:1)]. The mixture was neutralised with solid potassium hydrogen carbonate, filtered, and then extracted with dichloromethane (3 × 200 cm^3). The extracts were concentrated to give a syrup which was dissolved in ethyl acetate (60 cm^3) and applied to a short column of silica gel. Elution with hexane–ethyl acetate (3:1) gave allyl 4-*O*-benzyl-α-L-rhamnopyranoside (**1**) (36.3 g, 46%). An analytically pure sample was obtained as white prisms from dichloromethane–hexane, m.p. 66.0—67.5 °C (lit.,[13] 68—70 °C); $[\alpha]_D^{25}$ −75.2° (*c* 1.0 in CH_2Cl_2) [lit.,[13] −71.5° (*c* 1 in $CHCl_3$)]; δ_C 18.0 (C-6), 67.4 (C-5), 67.9 (C-2), 71.2 ($CH_2CH{=}CH_2$), 71.6 (C-3), 75.0 (CH_2Ph), 81.6 (C-4), 98.7 ($^1J_{^{13}C-H}$ 169 Hz, C-1), 117.3 ($CH{=}CH_2$), 133.8 ($CH{=}CH_2$), and 127.9, 128.0, 128.5, and 138.4 (Ar) (Found: C, 65.1; H, 7.6. Calc. for $C_{16}H_{22}O_5$: C, 65.31; H, 7.48%).

The benzyl ether (**1**) was dissolved in acetonitrile (150 cm^3) containing trimethyl orthobenzoate (29 cm^3). PTSA (0.54 g) was added, and the mixture was partially concentrated under vacuum at 50 °C on a rotatory evaporator, and then stirred at room temperature for 18 h. Triethylamine (3 cm^3) was added and the mixture was concentrated to give a syrup. The syrup was dissolved in 80% aqueous acetic acid (200 cm^3) and after 5 min the solution was evaporated to dryness. The residue was chromatographed on silica gel (500 g) with hexane–ethyl acetate (3:1) as eluant to yield the *title compound* (**2**) as a clear syrup (43.5 g, 40%), $[\alpha]_D^{25}$ +5.5° (*c* 0.9 in CH_2Cl_2); δ_C 18.1 (C-6), 67.6 (C-5), 68.2 ($CH_2CH{=}CH_2$), 70.6 (C-3), 73.4 (C-2), 75.1 (CH_2Ph), 81.8 (C-4), 96.7 (C-1), 117.5 ($CH{=}CH_2$), and 133.6 ($CH{=}CH_2$); δ_H($CDCl_3$) 1.41 (3 H, d, $J_{5,6}$ 6.3 Hz, 6-H_3), 3.49 (1 H, t, $J_{3,4}$ +

α-L-Rha*p*-(1 → 2)-α-L-Rha*p*-(1 → 3)-α-L-Rha*p*-(1 → 3)-β-D-Glc*p*NAc-(1 → 2)-α-L-Rha*p*-OMe

A B C D A

(11)

$J_{4,5}$ 19 Hz, 4-H), 3.85 (1 H, m, 5-H), 4.27 (1 H, dd, $J_{2,3}$ 3.6, $J_{3,4}$ 9.5 Hz, 3-H), 4.92 (1 H, d, $J_{1,2}$ 1.8 Hz, 1-H), and 5.37 (1 H, dd, $J_{1,2}$ 1.8, $J_{2,3}$ 3.4 Hz, 2-H) (Found: C, 69.1; H, 6.6. $C_{23}H_{26}O_6$ requires C, 69.35; H, 6.53%).

Allyl 3-O-(2′-O-*Acetyl*-3′,4′-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*)-2-O-*benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**4**).—A mixture of allyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**2**) (4.55 g, 11.4 mmol), 1,1,3,3-tetramethylurea (11.2 cm^3, 0.09 mol), silver trifluoromethanesulphonate (7.43 g, 28.3 mmol), and 4A molecular sieves in anhydrous dichloromethane (15 cm^3) was stirred under nitrogen for 0.5 h. The mixture was cooled to −78 °C and a solution of 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl chloride (**3**)[14] (8.56 g, 20 mmol) in anhydrous dichloromethane (15 cm^3), previously stirred with 4A molecular sieves for 0.5 h under N_2 and then cooled to −78 °C, was added by means of a cannula under N_2. The flask was rinsed with additional portions of dichloromethane (3 × 5 cm^3) and the contents were transferred as before. The mixture was allowed to warm gradually to room temperature and was stirred for 72 h. The solids were removed by filtration and the filtrate was washed successively with aqueous sodium hydrogen carbonate and aqueous sodium chloride. The organic layer was dried (Na_2SO_4) and concentrated to give a syrup that was chromatographed by h.p.l.c. with hexane–ethyl acetate (3.5:1) as eluant. The *title compound* (**4**) was obtained as a clear syrup (5.4 g, 64%); $[\alpha]_D^{25}$ +5.1° (*c* 1.0 in CH_2Cl_2); δ_C 17.7, 18.0 (C-6 and 6′), 20.9 ($OCOCH_3$), 96.3 ($^1J_{^{13}C-H}$ 171 Hz, C-1), 99.4 ($^1J_{^{13}C-H}$ 171 Hz, C-1′), 117.4 ($CH_2CH{=}CH_2$), 165.7, 170.0 (CO), and 67.8, 68.2, 68.6, 69.3, 71.7, 72.7, 74.5, 75.4, 77.4, 77.5, 79.7, and 80.5 (remaining carbons); δ_H 1.16 (3 H, d, $J_{5',6'}$ 6.1 Hz, 6′-H_3), 1.35 (3 H, d, $J_{5,6}$ 6.1 Hz, 6-H_3), 2.10 (3 H, s, OCOMe), 3.37 (1 H, t, $J_{3,4} + J_{4,5}$ 19 Hz, 4-H), 3.59 (1 H, t, $J_{3',4'} + J_{4',5'}$ 19 Hz, 4′-H), 3.80 (2 H, m, 5- and 5′-H), 3.80 (1 H, dd, $J_{2',3'}$ 3.2, $J_{3',4'}$ 9.3 Hz, 3′-H), 4.28 (1 H, dd, $J_{2,3}$ 3.3, $J_{3,4}$ 9.5 Hz, 3-H), 4.92 (1 H, d, $J_{1,2}$ 1.8 Hz, 1-H), 5.07 (1 H, d, $J_{1',2'}$ 1.8 Hz 1′-H), and 5.39 (2 H, m, 2- and 2′-H) (Found: C, 70.7; H, 6.7. $C_{45}H_{50}O_{11}$ requires C, 70.50; H, 6.53%).

Allyl 2-O-*Benzoyl*-4-O-*benzyl*-3-O-(3′,4′-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* (**5**).—A solution of the disaccharide (**4**) (4.6 g, 6.0 mmol) in methanolic HCl (50 cm^3) [prepared by treating anhydrous methanol (50 cm^3) with acetyl chloride (2 cm^3)] was kept at room temperature for 48 h, after which t.l.c. [hexane–ethyl acetate (2:1)] indicated that the starting material had been consumed. The mixture was neutralised by addition of Rexyn 201 OH^- resin, the resin was removed by filtration, and the filtrate was concentrated to give a syrup. The product was dissolved in dichloromethane and the solution was washed with aqueous sodium chloride and dried (Na_2SO_4). Evaporation of the solvent gave a syrup that was chromatographed with hexane–ethyl acetate (2:1) as eluant. The *title compound* (**5**) was obtained as a clear syrup (3.14 g, 72%); $[\alpha]_D^{25}$ −8.0° (*c* 0.3 in CH_2Cl_2); δ_C 17.7, 18.0 (C-6 and -6′), 96.4 (C-1), 101.3 (C-1′), 117.4 ($CH_2CH{=}CH_2$), 165.7 (CO), 67.8 and 68.3 (2 C), and 69.2, 72.0, 73.0, 74.5, 75.3, 77.7, 79.5, 79.8, and 80.6 (remaining carbons); δ_H 1.16 (3 H, d, $J_{5',6'}$ 6.1 Hz, 6′-H_3), 1.34 (3 H, d, $J_{5,6}$ 6.1 Hz, 6-H_3), 3.38 (1 H, t, $J_{3,4} + J_{4,5}$ 19 Hz, 4-H), 3.57 (1 H, t, $J_{3',4'} + J_{4',5'}$ 19 Hz 4′-H), 3.69 (1 H, dd, $J_{2',3'}$ 3.1, $J_{3',4'}$ 9.1 Hz, 3′-H), 3.77 and 3.83 (2 × 1 H, 2 m, 5- and 5′-H), 3.90 (1 H, m, 2′-H), 4.27 (1 H, dd, $J_{2,3}$ 3.3, $J_{3,4}$ 9.5 Hz, 3-H), 4.92 (1 H, d, $J_{1,2}$ 1.8 Hz, 1-H), 5.11 (1 H, d, $J_{1',2'}$ 1.8 Hz, 1′-H), and 5.41 (1 H, dd, $J_{1,2}$ 1.8, $J_{2,3}$ 3.3 Hz, 2-H) (Found: C, 71.1; H, 6.8. $C_{43}H_{48}O_{10}$ requires C, 71.27; H, 6.63%).

Allyl 3-O-[2′-O-(2″-O-*Acetyl*-3″,4″-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*)-3′,4′-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*]-2-O-*benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**6**).—A mixture of the disaccharide (**5**) (2.28 g, 3.15 mmol), silver trifluoromethanesulphonate (1.64 g, 6.25 mmol), 1,1,3,3-tetramethylurea (2.5 cm^3, 20.1 mmol), and 4A molecular sieves in anhydrous dichloromethane (10 cm^3) was stirred under N_2 and cooled to −78 °C. A solution of 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl chloride (**3**)[14] (2.52 g, 5.89 mmol) in anhydrous dichloromethane (10 cm^3), previously stirred with 4A molecular sieves for 0.5 h under N_2 and cooled to −78 °C, was added by means of a cannula under N_2. The flask was rinsed with additional portions of dichloromethane (2 × 3 cm^3) and the contents were transferred as before. The mixture was allowed to warm gradually to room temperature and was stirred for 48 h. The solids were removed by filtration and the filtrate was washed successively with aqueous sodium hydrogen carbonate and aqueous sodium chloride. The organic layer was dried (Na_2SO_4) and concentrated to give a syrup that was chromatographed with hexane–ethyl acetate (2:1) as eluant. The *title compound* (**6**) was obtained as a clear syrup (2.1 g, 61%); $[\alpha]_D^{25}$ −1.0° (*c* 1.4 in CH_2Cl_2); δ_C 17.7, 17.87, and 17.94 (C-6, -6′, and -6″), 20.9 ($OCOCH_3$), 96.3 ($^1J_{^{13}C-H}$ 170 Hz, C-1), 99.1 ($J_{^{13}C-H}$ 171 Hz, C-1″), 100.9 ($J_{^{13}C-H}$ 169 Hz, C-1′), 117.3 ($CH_2CH{=}CH_2$), 165.7 and 169.9 (CO), 67.7, 68.3, 68.9, 72.9, 75.3, 77.5, 78.3, 79.1, 79.7, 80.0, and 80.1 (other CH), and 68.2, 71.7, 72.1, 74.3, 75.16, and 75.23 ($PhCH_2$); δ_H 1.08, 1.23, and 1.27 (3 × 3 H, 3 d, *J* 6.1 Hz, 6-, 6′-, and 6″-H_3), 2.12 (3 H, s, OCOMe), 3.35 and 3.39 (2 × 1 H, 2 t, $J_{AX} + J_{BX} \simeq 19$ Hz, 4- and 4″-H), 3.54 (1 H, t, $J_{3',4'} + J_{4',5'}$ 19.5 Hz, 4′-H), 3.69 (1 H, m, 5″-H), 3.73 (1 H, dd, $J_{2',3'}$ 3.0, $J_{3',4'}$ 9.5 Hz, 3′-H), 3.80 (2 H, m, 5- and 5′-H), 3.89 (1 H, t, $J_{1',2'} + J_{2',3'}$ 6 Hz, 2′-H), 3.93 (1 H, dd, $J_{2'',3''}$ 3.5, $J_{3'',4''}$ 9.25 Hz, 3″-H), 4.21 (1 H, dd, $J_{2,3}$ 3.5, $J_{3,4}$ 9.4 Hz, 3-H), 4.91 (2 H, m, 1- and 1′-H), 5.01 (1 H, d, $J_{1'',2''}$ 1.5 Hz, 1″-H), 5.38 (1 H, dd, $J_{1,2}$ 1.8, $J_{2,3}$ 3.1 Hz, 2-H), and 5.49 (1 H, dd, $J_{1'',2''}$ 1.8, $J_{2'',3''}$ 3.1 Hz, 2″-H) (Found: C, 71.25; H, 6.6. $C_{65}H_{72}O_{15}$ requires C, 71.43; H, 6.59%).

3-O-[2′-O-(2″-O-*Acetyl*-3″,4″-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*)-3′,4′-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*]-2-O-*benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranose* (**7**).—Tris(triphenylphosphine)rhodium(I) chloride (29.2 mg, 0.031 mmol) was added to a solution of the allyl glycoside (**6**) (0.615 g, 0.564 mmol) in ethanol–water (9:1) (30 cm^3) and the mixture was heated at reflux for 18 h under nitrogen. The solvent was removed to give a residue that was dissolved in ethyl acetate, and the solution was filtered through a short column of silica gel. Removal of solvent gave a syrup that was identified as being the prop-1-enyl glycoside; δ_C 12.2 ($CH{=}CHCH_3$), 17.8, 17.9, and 18.0 (C-6, -6′, and -6″), 21.0 ($OCOCH_3$), 96.4 (C-1), 99.2 (C-1″), 101.0 (C-1′), 104.9 ($CH{=}CHCH_3$), 142.4 ($CH{=}CHCH_3$), 165.8 and 169.9 (CO), and 68.3, 68.4, 69.0, 69.1, 71.8, 72.2, 72.4, 74.4, 75.2, 75.3, 75.5, 77.6, 78.1, 79.2, 79.8, 80.0, and 80.1 (remaining carbons); δ_H 1.10, 1.24, and 1.28 (3 × 3 H, 3 d, *J* 6.1 Hz, 6-, 6′-, and 6″-H_3), 1.57 (3 H, dd, *J* 6.8 and 1.5 Hz, CH=CHMe), 2.14 (3

H, s, OCOMe), 3.37 (1 H, t, $J_{3,4}$ + $J_{4,5}$ 19 Hz, 4-H), 3.42 (1 H, t, $J_{3'',4''}$ + $J_{4'',5''}$ 19 Hz, 4''-H), 3.55 (1 H, t, $J_{3',4'}$ + $J_{4',5'}$ 19 Hz, 4'-H), 3.68 (1 H, m, 5''-H), 3.73 (1 H, dd, $J_{2',3'}$ 2.9, $J_{3',4'}$ 9.3 Hz, 3'-H), 3.82 (2 H, m, 5- and 5'-H), 3.91 (1 H, dd, $J_{1'',2''}$ 1.8, $J_{2'',3''}$ 2.6 Hz, 2''-H), 3.94 (1 H, dd, $J_{2'',3''}$ 3.25, $J_{3'',4''}$ 9.2 Hz, 3''-H), 4.23 (1 H, dd, $J_{2,3}$ 3.25, $J_{3,4}$ 9.5 Hz, 3-H), 4.92 (1 H, br s, 1'-H), 5.03 (1 H, d, $J_{1'',2''}$ 1.5 Hz, 1''-H), 5.11 (1 H, d, $J_{1',2'}$ 1.8 Hz, 1-H), 5.15 (1 H, m, CH=C*H*Me), 5.40 (1 H, dd, $J_{1,2}$ 1.8, $J_{2,3}$ 3.3 Hz, 2-H), 5.51 (1 H, dd, $J_{1'',2''}$ 1.8, $J_{2'',3''}$ 3.3 Hz, 2''-H), and 6.16 (1 H, m, C*H*=CHMe).

The syrup was dissolved in 90% aqueous acetone (30 cm^3) and the solution was stirred while yellow mercury(II) oxide (0.122 g, 0.563 mmol) was added, followed by the dropwise addition, during 2 min, of a solution of mercury(II) chloride (1.50 ml of an 8.2% solution; 0.452 mmol) in acetone–water (10:1), followed by the dropwise addition of 90% aqueous acetone (20 cm^3) during 2 min. The mixture was stirred for 2.5 h, the solvent was evaporated off, and the resulting syrup dissolved in ethyl acetate. Following filtration through Celite, the filtrate was washed successively with saturated aqueous potassium iodide (2×), aqueous sodium thiosulphate (2×), and water (2×). The organic layer was dried (Na_2SO_4), the solvent was removed, and the residue was dissolved in ethyl acetate and the solution filtered through a short column of silica gel. The filtrate was concentrated and the residue was purified by chromatography with hexane–ethyl acetate (3:1) as eluant to give pure deallylated trisaccharide (**7**) (0.533 g, 90%); δ_C(α-anomer) 17.7, 17.9, and 18.1 (C-6, -6', and -6''), 21.1 ($OCOCH_3$), 91.7 (C-1), 99.2 (C-1''), 100.8 (C-1'), and 165.8 and 170.0 (CO).

3-O-[2'-O-(2''-O-*Acetyl*-3'',4''-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*)-3',4'-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*]-2-O-*benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranosyl Chloride* (**8**).—Oxalyl chloride (0.2 cm^3, 2.29 mmol) was added to a stirred solution of DMF (0.2 cm^3, 2.58 mmol) in anhydrous dichloromethane (2 cm^3) and the mixture was kept under nitrogen for 5 min. The solvent was evaporated off under reduced pressure and the white salt was dried for 0.75 h. The *NN*-dimethyl(chloromethylene)-ammonium chloride was then dissolved in anhydrous dichloromethane) (2 cm^3) and a solution of the hemiacetal (**7**) (0.476 g, 0.452 mmol) in anhydrous dichloromethane (3 cm^3) was transferred to the flask under nitrogen by means of a double-tipped needle. The flask was rinsed with an additional portion (3 cm^3) of solvent and the contents were transferred as before. The mixture was stirred under nitrogen for 3.5 h, at which time the reaction was quenched by addition of cold aqueous sodium hydrogen carbonate (15 cm^3). The organic layer was diluted with dichloromethane, then washed successively with aqueous sodium hydrogen carbonate and aqueous sodium chloride, and dried over anhydrous potassium carbonate. Evaporation of the solvent gave the glycosyl chloride (**8**) as a light yellow syrup (0.479 g, 99%). The compound was dried *in vacuo* and used directly in glycosylation reactions; δ_C(α-anomer) 17.7, 17.8, and 17.9 (C-6, -6', and -6''), 21.1 ($OCOCH_3$), 89.6 (C-1), 99.3 (C-1''), 101.1 (C-1'), and 165.5 and 170.0 (CO).

Methyl 2-O-(2'-*Acetamido*-4',6'-O-*benzylidene*-2'-*deoxy*-β-D-*glucopyranosyl*)-3,4-*di*-O-*benzyl*-α-L-*rhamnopyranoside* (**9**).—The *title compound* (**9**) was prepared in an analogous manner to that described[17] for the corresponding 8-methoxycarbonyloctyl glycoside and was obtained as a syrup, $[\alpha]_D^{24}$ −54.5° (*c* 0.5 in CH_2Cl_2); δ_C 17.8 (C-6), 22.3 ($NHCOCH_3$), 54.6 (OCH_3), 60.0 (C-2'), 66.7 (C-5), 67.5 (C-6'), 68.5 ($PhCH_2$), 73.9 (C-5'), 74.6 (C-3'), 75.6 ($PhCH_2$), 78.8 (C-2), 80.6 (C-3), 81.4 (C-4'), 81.45 (C-4), 99.8 (C-1), 101.9 (PhCH), 103.4 (C-1'), and 173.4 (CO); δ_H 1.37 (3 H, d, $J_{5,6}$ 6.2 Hz, 6-H_3), 3.37 (3 H, s, OMe), 3.40 (2 H, m, 4- and 5'-H), 3.61 (1 H, t, $J_{3',4'}$ + $J_{4',5'}$ 19 Hz, 4'-H), 3.65—3.76 (3 H, complex m, 2'-, 3'-, and 5-H), 3.80 (1 H, t, $w_{\frac{1}{2}}$ 21 Hz, 6'-H_a), 4.35 (1 H, dd, $J_{5',6b'}$ 5.0, $J_{6a',6b'}$ 10.5 Hz, 6'-H_6), 4.48 (1 H, d, $J_{1'',2''}$ 8.1 Hz, 1'-H), 4.71 (1 H, d, $J_{1,2}$ 1.0 Hz, 1-H), and 5.58 (1 H, s, PhC*H*) (Found: C, 66.3; H, 6.7; N, 2.4. $C_{36}H_{43}NO_{10}$ requires C, 66.55; H, 6.67; N, 2.16%).

Methyl 2-O-(2'-*Acetamido*-3'-O-{3''-O-[2'''-O-(2''''-O-*acetyl*-3'''',4''''-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*)-3''',4'''-*di*-O-*benzyl*-α-L-*rhamnopyranosyl*]-2''-O-*benzoyl*-4''-O-*benzyl*-α-L-*rhamnopyranosyl*}-4',6'-O-*benzylidene*-2'-*deoxy*-β-D-*glucopyranosyl*)-3,4-*di*-O-*benzyl*-α-L-*rhamnopyranoside* (**10**).—A mixture of methyl 2-O-(2'-acetamido-4',6'-*O*-benzylidene-2'-deoxy-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**9**) (0.24 g, 0.37 mmol), silver trifluoromethanesulphonate (0.47 g, 1.83 mmol), 1,1,3,3-tetramethylurea (0.22 cm^3, 1.84 mmol), and 4A molecular sieves in anhydrous dichloromethane (3 cm^3) was stirred under nitrogen for 0.5 h. The mixture was cooled to −78 °C and a solution of the glycosyl chloride (**8**) (1.28 g, 1.20 mmol) in anhydrous dichloromethane (3 cm^3), previously stirred with 4A molecular sieves for 0.5 h under nitrogen and cooled to −78 °C, was added by means of a double-tipped needle under N_2. The flask was rinsed with additional portions of solvent (2 × 2 cm^3) and the contents were transferred as before. The mixture was stirred for 66 h while being allowed to warm gradually to room temperature. The solids were removed by filtration and the filtrate was washed successively with aqueous sodium hydrogen carbonate (2×), aqueous sodium chloride, and water, and dried (Na_2SO_4). Evaporation of the solvent afforded a syrup that was chromatographed with hexane–ethyl acetate (2.5:1) as eluant. The *title compound* (**10**) was obtained as a clear glass (0.446 g, 68%); $[\alpha]_D^{24}$ −12.0° (*c* 1.4 in CH_2Cl_2); δ_C 17.2, 17.6, 17.8, and 17.9 (C-6, -6'', -6''', and -6''''), 21.0 ($OCOCH_3$), 23.3 ($NHCOCH_3$), 54.4 (OCH_3), 97.4 (C-1''), 98.8 (C-1''''), 100.0 (C-1), 100.6 (C-1'''), 101.6 and 101.7 (C-1', PhCH), and 165.7, 169.9, and 171.3 (CO); δ_H 0.73 (3 H, d, *J* 6.1 Hz, 6''-H_3), 1.04 and 1.25 (2 × 3 H, 2 d, *J* 6.1 Hz, 6'''- and 6''''-H_3), 1.36 (3 H, d, *J* 6.1 Hz, 6-H_3), 1.89 (3 H, s, NHCOMe), 2.13 (3 H, s, OCOMe), 3.33 (3 H, s, OMe), 3.34, 3.40, 3.41, and 3.42 (4 × 1 H, 4 t, J_{AX} + J_{BX} ≃ 19 Hz, 4-, 4''-, 4'''-, and 4''''-H), 3.73 (1 H, dd, $J_{2'''',3''''}$ 3.0, $J_{3'''',4''''}$ 9.2 Hz, 3'''-H), 3.96 (1 H, dd, $J_{2'''',3''''}$ 3.2, $J_{3'''',4''''}$ 9.4 Hz, 3''''-H), 4.13 (1 H, dd, $J_{2'',3''}$ 3.2, $J_{3'',4''}$ 9.2 Hz, 3''-H), 4.70 (1 H, d, $J_{1'',2''}$ 1.8 Hz, 1''-H), 4.88 (1 H, d, $J_{1,2}$ 1.8 Hz, 1-H), 4.93 and 4.97 (2 × 1 H, 2 d, *J* 1.8 Hz, 1'''- and 1''''-H), 5.05 (1 H, d, $J_{1',2'}$ 8.1 Hz, 1'-H), 5.25 (1 H, dd, $J_{1'',2''}$ 1.8, $J_{2'',3''}$ 3.2 Hz, 2''-H), 5.49 (1 H, dd, $J_{1'''',2''''}$ 1.8 Hz, $J_{2'''',3''''}$ 3.0 Hz, 2''''-H), and 5.50 (1 H, s, PhC*H*) (Found: C, 69.55; H, 6.8; N, 1.0. $C_{98}H_{109}NO_{24}$ requires C, 69.86; H, 6.52; N, 0.83%).

A mixture of the hemiacetals (**7**) (0.79 g, 0.751 mmol) was recovered and recycled.

Methyl 2-O-(2'-*Acetamido*-2'-*deoxy*-3'-O-{3''-O-[2'''-O-(α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranosyl*]-α-L-*rhamnopyranosyl*}-β-D-*glucopyranosyl*)-α-L-*rhamnopyranoside* (**11**).—A solution of the pentasaccharide (**10**) (0.243 g, 0.140 mmol) in methanol–dichloromethane (4:1) (50 cm^3) at 0 °C was treated with a solution of sodium methoxide in methanol (10 cm^3; 0.9M) at 0 °C and the mixture was allowed to warm to room temperature. The mixture was stirred for 24 h and then neutralised by addition of Rexyn 101 (H^+) resin. The resin was removed by filtration and the filtrate was concentrated to give a syrup. The syrup was dissolved in dichloromethane and the solution was dried (Na_2SO_4). Removal of the solvent yielded a syrup that was chromatographed with hexane–ethyl acetate (2:1) as eluant to give a syrup; this product was dissolved in 80% aqueous acetic acid and hydrogenolysed over 10% palladium–carbon (0.3 g) at a hydrogen pressure of 45 p.s.i. for 5 days. The mixture was filtered through Celite and the filtrate was evaporated to dryness. Chromatography with ethyl acetate–

methanol–water (6:3:1) as eluant afforded pure *pentasaccharide* (**11**) as an amorphous white solid (0.08 g, 70%); $[\alpha]_D^{24}$ −80.2° (*c* 0.4 in water); $\delta_C(D_2O)$ 16.6 (C-6′′), 16.8 (3 C, C-6, -6′′′, and -6′′′′), 22.4 ($NHCOCH_3$), 55.0 (OCH_3), 55.8 (C-2′), 60.9 (C-6′), 68.5 (C-5′′′), 68.7 (C-5), 69.1 (C-5′′), 69.3 (C-4′ and -5′′′′), 70.1 (C-3), 70.19, 70.23, and 70.3 (C-3′′′, -2′′′′, and -3′′′′), 70.7 (C-2′′), 71.8 (C-4′′), 72.2 (C-4′′′′), 72.3 (C-4′′′), 72.5 (C-4), 76.1 (C-5′), 77.4 (C-3′′), 78.2 (C-2′′′), 78.6 (C-2), 81.6 (C-3′), 99.9 ($^1J_{^{13}C-H}$ 172 Hz, C-1), 101.0 ($^1J_{^{13}C-H}$ 169 Hz, C-1′′′), 101.4 ($^1J_{^{13}C-H}$ 166 Hz, C-1′′), 102.2 ($^1J_{^{13}C-H}$ 161 Hz, C-1′), 102.4 ($^1J_{^{13}C-H}$ 167 Hz, C-1′′′′), and 174.5 (CO); δ_H (D_2O; 340 K), 1.10, 1.12, and 1.13 (3 × 3 H, 3 d, *J* 6.3 Hz, 6-, 6′′-, and 6′′′′-H_3), 1.17 (3 H, d, $J_{5''',6'''}$ 6.2 Hz, 6′′′-H_3), 1.91 (3 H, s, NHCOMe), 3.24 (3 H, s, OMe), 3.08—3.95 (complex m, ring hydrogens), 4.59 (1 H, d, $J_{1',2'}$ 8.5 Hz, 1′-H), 4.69 (1 H, d, $J_{1,2}$ 1.4 Hz, 1-H), 4.72 (1 H, d, $J_{1'',2''}$ 1.4 Hz, 1′′-H), 4.83 (1 H, d, $J_{1'''',2''''}$ 1.6 Hz, 1′′′′-H), and 5.01 (1 H, d, $J_{1''',2'''}$ 1.4 Hz, 1′′′-H) (Found: C, 48.0; H, 7.2; N, 1.6. $C_{33}H_{57}NO_{22}$ requires C, 48.35; H, 7.01; N, 1.71%).

Acknowledgements

We are grateful to J. Christ for technical assistance, Simon Fraser University and the B. C. Health Care Research Foundation for financial support in the form of grants (to B. M. P), and the National Research Council of Canada for support (to D. R. B.).

References

1 L. Kenne, B. Lindberg, K. Petersson, E. Katzenellenbogen, and E. Romanowska, *Carbohydr. Res.*, 1977, **56**, 363.
2 D. R. Bundle, M. A. J. Gidney, S. Josephson, and H.-P. Wessel, *ACS Symp. Ser.*, 1983, **231**, 49, and references therein; see also N. E. Byramova, Y. E. Tsvetkov, L. V. Backinowsky, and N. K. Kochetkov, *Carbohydr. Res.*, 1985, **137**, C8.
3 K. Bock, S. Josephson, and D. R. Bundle, *J. Chem. Soc., Perkin Trans. 2*, 1982, 59.
4 N. I. A. Carlin, A. A. Lindberg, K. Bock, and D. R. Bundle, *Eur. J. Biochem.*, 1984, **139**, 189.
5 N. I. A. Carlin, A. A. Lindberg, M. A. J. Gidney, and D. R. Bundle, unpublished results.
6 E. A. Kabat, 1961, in 'Experimental Immunochemistry,' eds. E. A. Kabat and M. M. Mayer, 2nd edn., Charles C. Thomas, Springfield, Ill., p. 241.
7 J. J. Oltvoort, C. A. A. van Boeckel, J. H. de Koning, and J. H. van Boom, *Synthesis*, 1981, 305; D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1978, 694.
8 E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1973, **38**, 3224.
9 R. Gigg and C. D. Warren, *J. Chem. Soc. C*, 1968, 1903.
10 H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, 1959, **42**, 1653; T. Iversen and D. R. Bundle, *Carbohydr. Res.*, 1982, **103**, 29; R. U. Lemieux, S. Z. Abbas, and B. Y. Chung, *Can. J. Chem.*, 1982, **60**, 58.
11 R. U. Lemieux, D. R. Bundle, and D. A. Baker, *J. Am. Chem. Soc.*, 1975, **97**, 4076; R. U. Lemieux, D. A. Baker, and D. R. Bundle, *Can. J. Biochem.*, 1977, **55**, 507.
12 B. M. Pinto and D. R. Bundle, *Carbohydr. Res.*, 1983, **124**, 313.
13 R. Gigg, S. Payne, and R. Conant, *J. Carbohydr. Chem.*, 1983, **2**, 207.
14 S. Josephson and D. R. Bundle, *J. Chem. Soc., Perkin Trans. 1*, 1980, 297.
15 S. Hanessian and J. Banoub, *Carbohydr. Res.*, 1977, **53**, 13.
16 N. E. Byramova, M. V. Ovchinnikov, L. V. Backinowsky, and N. K. Kochetkov, *Carbohydr. Res.*, 1983, **124**, C8.
17 D. R. Bundle and S. Josephson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2736.
18 A. Liptak, P. Nanasi, and A. Neszmelyi, *Tetrahedron*, 1980, **36**, 1261; V. Pozsgay and A. Neszmelyi, *Carbohydr. Res.*, 1980, **80**, 196.
19 H.-P. Wessel and D. R. Bundle, *Carbohydr. Res.*, 1983, **124**, 301.
20 D. R. Bundle and S. Josephson, *Can. J. Chem.*, 1979, **57**, 662.
21 S. Josephson and D. R. Bundle, *Can. J. Chem.*, 1979, **57**, 3073.
22 D. R. Bundle and S. Josephson, *Carbohydr. Res.*, 1980, **80**, 75.
23 K. Bock and C. Pedersen, *J. Chem. Soc., Perkin Trans. 2*, 1974, 293; K. Bock and C. Pedersen, *Acta Chem. Scand., Ser. B*, 1975, **29**, 258.
24 D. R. Bundle, T. Iversen, and S. Josephson, *Int. Lab.*, 1980, 21.

Received 17*th September* 1985; *Paper* 5/1604