Strategies for the Synthesis of Branched Oligosaccharides of the *Shigella flexneri* 5a, 5b, and Variant X Serogroups Employing a Multifunctional Rhamnose Precursor†

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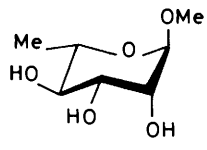
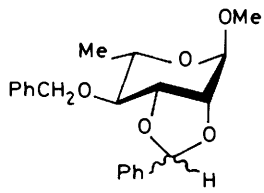
Allylation of methyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**4**) using allyl trichloroacetimidate under mildly acidic conditions provides the multifunctional rhamnose derivative (**7**). Glycosylation of the vicinal O-2 and O-3 positions of this derivative in either sequence permitted the synthesis, in good yield, of a branched trisaccharide (**24**) corresponding to a crucial portion of the *Shigella flexneri* variant X O-antigen. The flexibility of the derivative (**7**) was further demonstrated by the synthesis of a tetrasaccharide (**36**) containing the branch point of the *S. flexneri* serogroup 5a antigen. Attempts to synthesize the pentasaccharide (**39**) corresponding to the branched *S. flexneri* serogroup 5b antigen were hampered by the low yields and poor stereospecificity of the α-glucosylation reactions.

Studies on the synthesis of repeating units of the complex, linear polysaccharide which is the O-antigen of *Shigella flexneri* variant Y were recently reviewed.[1] Conformational studies by ^1H and ^{13}C n.m.r. spectroscopy, which have led to a model describing short range features of this polysaccharide antigen, were also detailed.[1,2] The variant Y polysaccharide has the simplest repeating unit (Figure 1) of all *S. flexneri* O-antigens[3,4] and for this reason was studied first. The serogroup 5a and the variant X polysaccharides are created by branching with single α-D-glucosyl residues at either of the O-3 positions on the contiguous rhamnose units *a* and *b* (Figure 1). Serogroup 5b polysaccharide possesses both branching glucosyl residues[4] (Figure 1). The synthesis of the Y-antigenic oligosaccharides has provided evidence essential to the elucidation of the biological repeating unit of the *S. flexneri* O-antigen[5] and in order to study further these three additional serogroup polysaccharides (5a, 5b, X), synthetic strategies were developed to permit the synthesis of antigenic determinants of tetra- and penta-saccharide size.

A key intermediate in earlier work was 3,4-di-*O*-benzyl-1,2-*O*-methoxyethylidene-β-L-rhamnopyranose.[6] This orthoester was readily converted to 2-*O*-acetyl-3,4,-di-*O*-benzyl-α-L-rhamnopyranosyl chloride, a glycosyl donor derivative well suited for high yield glycosylation steps. Subsequent deacetylation at O-2 of this residue permits the facile conversion of the new chain-end residue into a glycosyl acceptor for chain extension reactions. The presence of a persistent blocking group at O-3 of this rhamnose derivative renders it unsuitable for synthesis



(1)



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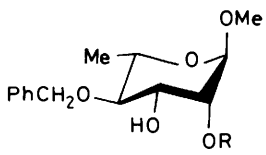
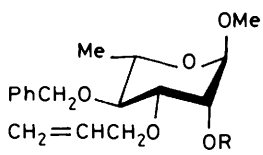
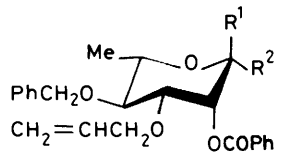


(3) R = H
(4) R = Bz
(5) R = Ac



(6) R = Ac
(7) R = Bz
(8) R = H



(9) R^1 = OAc, R^2 = H
(10) R^1 = H, R^2 = OAc
(11) R^1 = Cl, R^2 = H

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{2)α-L-Rha*p*(1 → 2)α-L-Rha*p*(1 → 3)α-L-Rha*p*(1 → 3)β-D-GlcNAc*p*(1}
a *b* *c* *d*
S. flexneri Variant Y polysaccharide

{2)[α-D-Glc*p*(1 → 3)]α-L-Rha*p*-(1 → 2)-α-L-Rha*p*-(1 → 3)-α-L-Rha*p*(1 →3)-β-D-GlcNAc*p*(1}
S. flexneri Variant X polysaccharide

{2)α-L-Rha*p*-(1 → 2)[α-D-Glc*p*(1 → 3)]α-L-Rha*p*(1 → 3)-α-L-Rha*p*(1 → 3)-β-D-GlcNAc*p*(1}
S. flexneri 5a polysaccharide

{2)[α-D-Glc*p*(1 → 3)]α-L-Rha*p*-(1 → 2)-[α-D-Glc*p*(1 → 3)]α-L-Rha*p*(1 → 3)-α-L-Rha*p*-(1 → 3)-β-D-GlcNAc*p*(1}
S. flexneri 5b polysaccharide

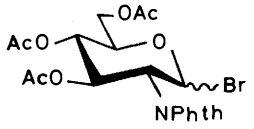
Figure 1

involving branch points such as those present in the 5a, 5b, and X repeating units (Figure 1). For such syntheses it was necessary to choose a rhamnose intermediate, which under ideal circumstances could fulfill the role of glycosyl donor and acceptor. Furthermore, the protecting groups for O-3 and O-2 should permit glycosylation at either of these positions and in either sequence, O-2 prior to O-3, or *vice versa*. Thus a persistent blocking group such as benzyl ether was required for O-4 and to direct α-glycosylation reactions, a participating group such as benzoate or acetate at O-2 was indicated. An O-3 ether group was desirable in order to maintain the reactivity of the O-2 position and a base-stable allyl ether at O-3 would then provide for the duality of the deprotection sought. Glycosides (**6**) or (**7**) were considered to fulfill this role. Transesterification would provide an intermediate (**8**) selectively protected for chain extension at O-2, followed by allyl group removal for the introduction of an O-3 branch point. Since the allyl group could be selectively cleaved in the presence of benzyl ether and ester groups, the reverse sequence of glycosylation and deprotection could also be utilized. This capability was desirable since in earlier, unpublished work[7] we had found that the order of glycosylation at vicinal centres could be crucial to the success and yields of these reactions.

Introduction of an allyl ether to a selectively protected rhamnopyranoside such as (**4**) or (**5**) by conventional chemistry employing basic conditions[8] would cleave base labile substituents and in order to prepare compounds (**6**) or (**7**) it was essential to use allyl trichloroacetimidate, which permits allylation under acid catalysis.[9] Methyl α-L-rhamnopyranoside (**1**) may be converted in three steps into the crystalline 4-*O*-benzyl ether[10] (**3**) and subsequent orthoester formation followed by regioselective opening, provides either the benzoate[11] (**4**) or the acetate (**5**). An alternative route to (**4**) proceeds by way of the 2,3-*O*-benzylidene derivative of (**1**) which is not isolated but benzylated to give the diastereoisomers (**2**).[12] Reaction with triphenylcarbenium tetrafluoroborate[13] under anhydrous conditions, followed by an aqueous work-up and chromatography to remove salts, yields the benzoate (**4**). Although this procedure provides (**4**) in one less step, the sequence *via* (**3**) was the most practical, in our hands, for the large scale (>10 g) work. Introduction of an allyl ether to the glycosides (**4**) or (**5**) without affecting the ester group at O-2 was achieved in good yield (85%) by reaction with allyl trichloroacetimidate.[9]

In order to convert the fully protected rhamnopyranosides (**6**) and (**7**), or the corresponding moiety present in an oligosaccharide into a glycosyl acceptor, the O-2 ester may be selectively cleaved to give (**8**) or a related glycoside unit. Alternatively the O-3 allyl ether may be cleaved leaving the acetate and ether groups intact. Prior to employing (**7**) as a glycosyl donor, activation at C-1 was necessary, and direct conversion of (**7**) into a rhamnopyranosyl halide (**11**) or conversion into an intermediate which undergoes facile transformation to (**11**) were the routes investigated. Reaction of the methyl glycoside (**7**) with dichloromethyl methyl ether[14] gave the halide (**11**) but only under conditions which resulted in some loss of the 4-*O*-benzyl group. Controlled acetolysis of (**7**) gave a mixture of the anomeric acetates (**9**) and (**10**), and these reacted with dichloromethyl methyl ether to give (**11**) quantitatively after 15 min. Although the bromo analogue of (**11**) may be prepared in an analogous fashion with dibromomethyl methyl ether or bromotrimethylsilane[15] it was not as stable as the chloride and decomposed under glycosylation conditions. Thus the glycoside (**8**) and halide (**11**) were the key intermediates for the synthesis of the branched *S. flexneri* oligosaccharide structures and both were readily prepared in high yield reactions from a single derivative, either (**7**) or (**6**), in which an acetate replaced the benzoate of (**7**).

As α-glycosylation of a derivative such as (**4**) followed by transesterification and attempted glycosylation at O-2 were previously unsuccessful,[7] it was desirable to reverse the order of glycosylation at positions O-3 and O-2. Reaction of (**8**) with (**12**) gave the disaccharide (**15**) in 89% yield using silver trifluoromethanesulphonate–2,4,6-trimethylpyridine[16] in dichloromethane. Two routes were then investigated, either the disaccharide (**16**) in which the glucosamine residue carried a phthalimido group or the disaccharide (**18**), the acetamido analogue of (**16**), were glucosylated by tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**13**) using mercuric bromide as the heavy metal catalyst. The phthalimido derivative (**16**) gave the target trisaccharide (**20**) in only 33% overall yield, as a 3:2 α/β mixture, and starting disaccharide (**16**) was recovered in 62%



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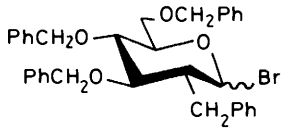

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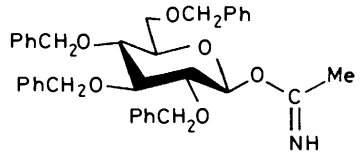

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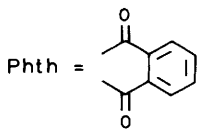
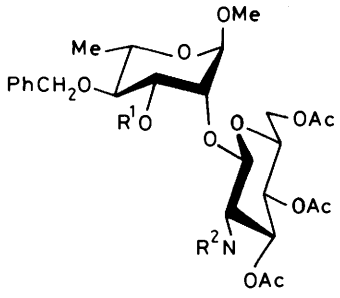
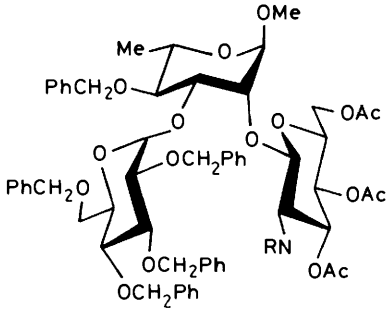


yield. Glucosylation of the acetamido derivative (**18**) gave the branched trisaccharide (**21**) as a 2:1 α/β mixture, in 87% overall yield. By comparison, the glycosyl imidate[17] (**14**) reacted with (**18**) to give a 3:2 α/β mixture of the trisaccharide in 34% yield. Thus by reversing the order of glycosylation at O-3 and O-2 of the rhamnoside (**7**), the trisaccharide (**21**) could be prepared in an acceptable yield, provided that the amino sugar was protected as the acetamido derivative. Previous unsuccessful attempts[7] to synthesize (**21**) by glucosylation at O-3 followed by reaction with (**12**) presumably failed due to the steric bulk of the glycosyl donor and the relatively low reactivity of the O-2 position.[18]

In order to deprotect selectively the disaccharide (**15**) to give (**16**) or the disaccharide (**18**) *via* (**17**), deallylation was performed on derivatives (**15**) and (**17**). The catalyst employed, tris(triphenylphosphine)rhodium(I) chloride, gave (**16**) in 85% yield but in the case of (**17**) both (**18**) (72%) and its propyl ether (**19**) (14%) were isolated from the selective deprotection step. The rhodium catalyst is known to effect this outcome in some instances.[19] Glucosyl bromide (**13**) was prepared by treatment of tetra-*O*-benzyl-D-glucose with (bromomethylene)dimethyliminium bromide prepared *in situ* from oxalyl bromide and a catalytic amount of *N*,*N*-dimethylformamide (DMF) [*cf.* Iversen and Bundle[14]]. The product was isolated by freeze-drying and treated immediately with (**16**) or (**18**). Hydrogenolysis of the fully protected trisaccharide (**21**) which contained some of the β-linked glucose isomer, gave (**22**) in 91% yield contaminated by the β-glucose isomer. Due to similar chromatographic mobilities the α- and β-isomers could not be resolved and acetylation of (**22**) followed by column chromatography of (**23**), also failed to remove the contaminating

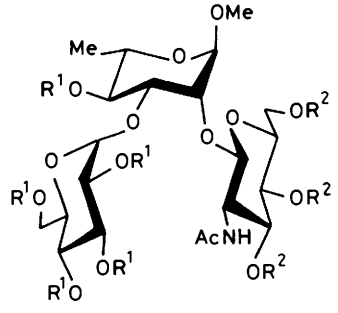


(15) $R^1 = CH_2CH=CH_2$, R^2 = Phth
(16) R^1 = H, R^2 = Phth
(17) $R^1 = CH_2CH=CH_2$, R^2 = Ac, H
(18) R^1 = H, R^2 = Ac, H
(19) $R^1 = (CH_2)_2Me$, R^2 = Ac, H



(20) R = Phth
(21) R = Ac, H

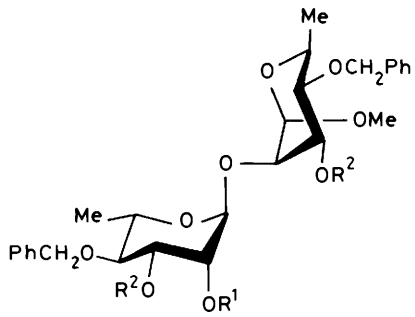
β-isomer, which was finally separated from the deblocked trisaccharide (**24**), after transesterification of (**23**) and column chromatography.



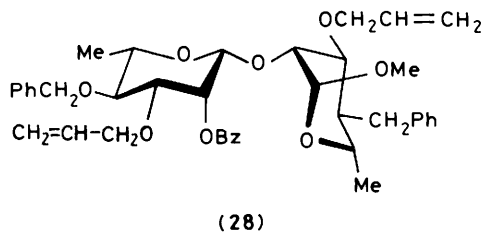
(22) R^1 = H, R^2 = Ac
(23) $R^1 = R^2$, Ac
(24) $R^1 = R^2$ = H

Observations from this trisaccharide synthesis had direct bearing upon the strategy adopted for the preparation of the branched tetra- and penta-saccharides of *S. flexneri* serogroups 5a and 5b. Efficient introduction of an α-glucosyl substituent at O-3 of the rhamnose unit bearing a glucosamine substituent on the vicinal O-2 position clearly dictates that the amino group be protected as an acetamido and not a phthalimido group. Also, in view of the reduced reactivity of the O-3 position of rhamose units bearing a 2-*O*-glycosyl substituent, it was considered desirable to use an active combination of glucosyl donor and heavy metal catalyst.[20] As was the case in the synthesis of the trisaccharide (**21**) these would be tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**13**) and mercuric bromide.

Synthesis of the *S. flexneri* tetrasaccharides, β-D-GlcNAc*p*-(1 → 2)-[α-D-Glc*p*-(1 → 3)]-α-L-Rha*p*-(1 → 2)-α-L-Rha*p* (Variant X) or β-D-GlcNAc*p*-(1 → 2)-α-L-Rha*p*-(1 → 2)-[α-D-Glc*p*-(1 → 3)]-α-L-Rha*p* could have envisaged the combination of the glycosyl donor (**11**) or glycosyl acceptor (**8**) with a 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnose derivative used previously in the synthesis of the *S. flexneri* variant Y structures.[1,6] However, synthesis of the branched pentasaccharide (**38**) required a combination of both monosaccharide building units (**7**) and (**11**) to yield a disaccharide such as (**25**), which could serve as an intermediate for the synthesis of branched structures, wherein both rhamnose residues carried a 3-*O*-α-D-glucopyranosyl branch point. In this paper the latter approach was adopted and the systematic synthesis of the variant X and serogroup 5a tetrasaccharides is not reported here. The following describes the attempted synthesis of the branched pentasaccharide (**38**) and an alternative route to one of the aforementioned tetrasaccharides (serogroup 5a), which arose from fortuitous reactions *en route* to the pentasaccharide.

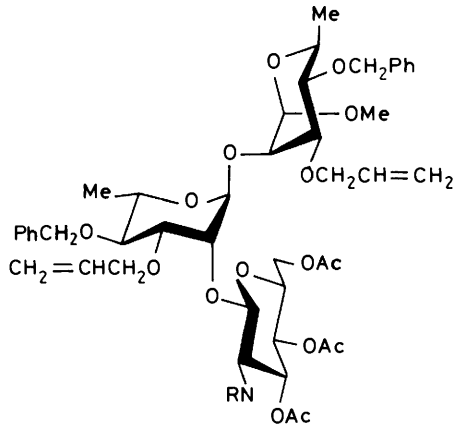


(25) R^1 = Bz, $R^2 = CH_2CH=CH_2$
(26) R^1 = Bz, R^2 = H
(27) R^1 = H, $R^2 = CH_2CH=CH_2$

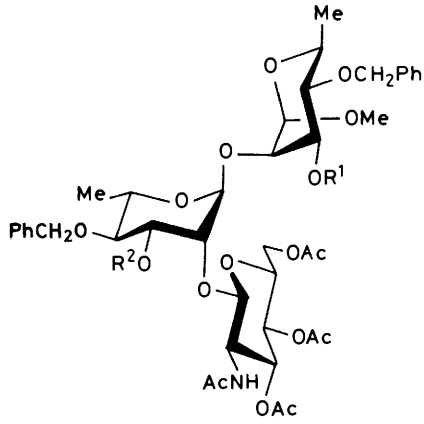


(28)

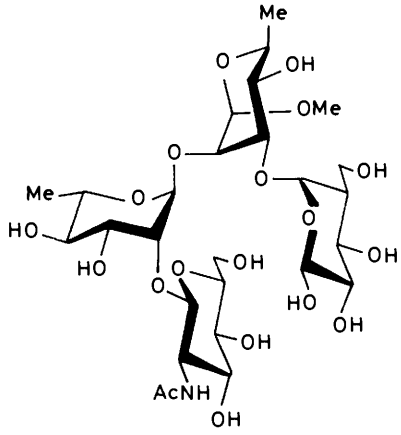
Reaction of the rhamnopyranosyl chloride (**11**) with methyl rhamnopyranoside (**8**) using either mercuric cyanide or a mixture with mercuric bromide and cyanide resulted in yields in the range 27—34% for the disaccharide (**25**). When silver trifluoromethanesulphonate and tetramethylurea[21] respectively were used as the heavy metal catalyst and acid acceptor, the yield of (**25**) increased to 78%. The β-anomer (**28**) obtained as a minor component (4.5% yield) was easily separated from (**25**) by column chromatography. The disaccharide glycoside (**25**) was selectively deprotected to give either the diol (**26**) following rhodium(I) catalysed isomerization and concomitant hydrolysis of the isoprenyl ether, or (**27**) by transesterification. This intermediate (**27**) was treated with (**12**) under standard conditions[16] to give the linear trisaccharide (**29**) in 75% yield, and 14% of recovered starting disaccharide (**27**). The



(29) R = Phth
(30) R = Ac, H



(31) $R^1 = R^2 = H$
(32) $R^1 = H$, $R^2 = CH_2CH{=}CH_2$



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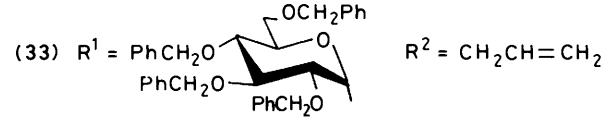
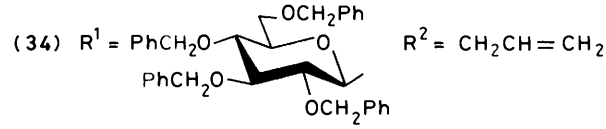
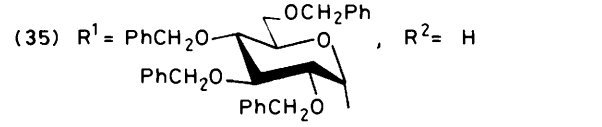


(33) R^1 = $PhCH_2O$ $PhCH_2O$ $PhCH_2O$ OCH_2Ph $R^2 = CH_2CH{=}CH_2$



(34) R^1 = $PhCH_2O$ $PhCH_2O$ OCH_2Ph OCH_2Ph $R^2 = CH_2CH{=}CH_2$



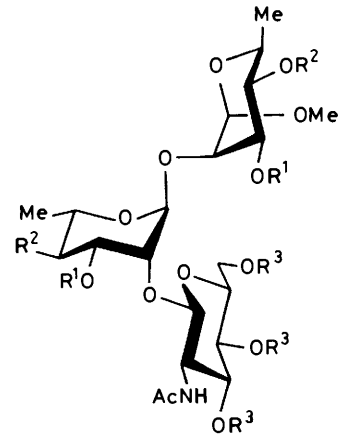
(35) R^1 = $PhCH_2O$ $PhCH_2O$ $PhCH_2O$ OCH_2Ph, R^2 = H

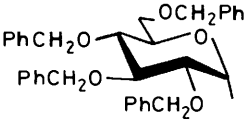
phthalimido group was readily converted into an acetamido function and allyl ether groups were removed from this trisaccharide (**30**) to give the dihydroxy derivative (**31**) in 71% yield. A mono-deallylated compound (**32**) was also obtained in 20% yield following rechromatography. This latter product was used to obtain the branched tetrasaccharide (**33**) *via* an unambiguous route.

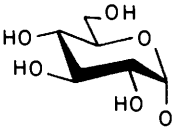
The identity of the monoallylated intermediate (**32**) was established by ^{13}C n.m.r. of spectroscopy of this product and the related compounds (**17**), (**25**), (**27**), and (**30**). For compounds (**25**), (**27**), and (**30**), it is seen that the olefinic carbon atom belonging to the allyl group attached to the terminal rhamnose residue has a characteristic chemical shift of 116.6—116.8 p.p.m. The same atom of the allyl group of the non-terminal rhamnose unit [compounds (**25**), (**27**) and (**30**)] has a chemical shift of 117.6—118.1 p.p.m. Therefore the monoallylated product (**32**) is readily identified as such by the presence of the single resonances for the olefinic and allylic carbon atoms at δ 117.6 and 134.9 p.p.m. That this allyl group is present on the non-terminal rhamnose unit is required by the chemical shift of the olefinic carbon atom and also by the chemical shift of the rhamnose C-2 and C-3 resonances. In compounds lacking the allyl group, the value for C-2 shifts to lower field whilst the shift of the C-3 atom moves to higher field, *cf.* compounds (**25**)—(**27**), (**30**) and (**31**).

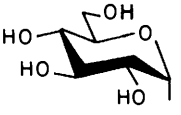
Tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**13**) was treated with the monohydroxy trisaccharide (**32**) in the presence of mercuric bromide and 4Å molecular sieves. Chromatography of the products gave the tetrasaccharide (**33**) (36%), trisaccharide starting material (15%), and the β-linked tetrasaccharide (**34**) (7%). Complete deprotection of (**33**) by first removing the allyl group to yield (**35**) followed by hydrogenolysis and transesterification gave the tetrasaccharide glycoside (**36**), a component of the *S. flexneri* serogroup 5a repeating unit.

Two possibilities were thus available for the synthesis of the serogroup 5b pentasaccharide (**38**). Glycosylation of the dihydroxy trisaccharide intermediate (**31**) could yield the pentasaccharide (**37**) directly or the de-allylated tetrasaccharide (**35**) could be subjected to a further α-glucosylation reaction to provide (**37**). The trisaccharide (**31**) was treated with glucosyl bromide (**13**) (5 mol) using mercuric bromide and molecular sieves as the promoter and acid scavenger. A complex mixture of products was obtained from which the tetrasaccharide (**35**) was isolated. Material of higher R_F corresponding to a mixture of pentasaccharides was identified and separated. However, complete resolution of this mixture by a combination of column chromatography and preparative t.l.c. proved impossible. Glycosylation of the tetrasaccharide (**35**) by comparison gave the desired pentasaccharide, contaminated by the β-linked isomer, in 39% yield. In this reaction the glycosyl bromide (**13**) was used in conjunction with silver perchlorate and silver carbonate as the promoter and acid acceptor. Hydrogenolysis of (**37**) and its β-isomer followed by extensive chromatography gave the partially acetylated pentasaccharide (**39**) *ca.* 80% pure as judged by t.l.c. and n.m.r. spectroscopy. A final transesterification gave the deblocked pentasaccharide (**38**)



(37) R^1 =  R^2 = CH_2Ph, R^3 = Ac

(38) R^1 =  R^2 = H, R^3 = Ac

(39) R^1 =  R^2 = R^3 = H

corresponding to a portion of the *S. flexneri* 5b repeating unit. The pentasaccharide compounds (**37**)—(**39**) could not be obtained analytically pure without resort to extensive chromatography, and although ^1H n.m.r. spectroscopy at 500 MHz indicated that the products were better than 80% pure, further investigation of the α-glucosylation reactions is required. In particular it would seem that the lower yields and reduced stereospecificity of α-glucosylation observed here and by others,[22,23] will require a sequential approach to synthesis of (**37**), rather than the simultaneous glycosylation of two hydroxy groups as present in trisaccharide (**31**). In this regard the use of a second multifunctional rhamnose derivative similar to (**6**) and (**7**) but with an alternative protecting group at O-3 is under investigation.

Experimental

The general methods and materials employed in this work were similar to those described in the preceding paper and in earlier work from this laboratory.[24] Hexane refers to a mixture of hexanes available commercially under the name Skellysolve B from Getty Refining and Marketing Co., Tulsa, Oklahoma. ^{13}C N.m.r. spectra were recorded at 20 MHz, and chemical shifts are expressed relative to internal tetramethylsilane for solutions in [^2H]chloroform or [$^2H_4$]methanol, and relative to external tetramethylsilane for solutions in deuterium oxide. Chemical shift assignments were made by analogy with the literature, where this was relevant and otherwise by analogy with model compounds. ^1H N.m.r. spectra were recorded at 79.9 MHz except for compound (**39**). These data were recorded at 500 MHz with a Bruker AM-500 spectrometer.

Methyl 2-O-*Benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**4**).—*Method A.* A solution of methyl 4-*O*-benzyl-α-L-rhamnopyranoside (**3**)[10] (5.0 g, 18.6 mmol) in anhydrous DMF (35 cm^3) and trimethyl orthobenzoate (4.1 g, 22.3 mmol) containing toluene-*p*-sulphonic acid (50 mg) was heated at 50 °C for 1 h. After the addition of triethylamine (1 cm^3) the solution was evaporated and treated with 80% aqueous acetic acid. The rearrangement of the orthoester to the title compound was complete after 30 min and the solution was evaporated and immediately purified by preparative h.p.l.c. with hexane–ethyl acetate (3:1) as the eluant to give the benzoate (**4**) (5.13 g, 74%).

Method B. A solution of methyl (2,3*R*,*S*)-4-*O*-benzyl-2,3,-*O*-benzylidene-α-L-rhamnopyranoside (**2**)[12] (0.9 g, 2.53 mmol) in anhydrous acetonitrile (50 cm^3) was treated with triphenylcarbenium tetrafluoroborate (1.08 g, 3.16 mmol) under an atmosphere of dry nitrogen. After 24 h the reaction mixture was poured into aqueous sodium hydrogen carbonate and extracted with dichloromethane, dried, and evaporated to a syrup. Purification by preparative h.p.l.c. with hexane–ethyl acetate (3:1) as the eluant gave the *benzoate* (**4**) (707 mg, 75%) as a syrup (Found: C, 67.9; H, 6.55. $C_{21}H_{24}O_6$ requires C, 67.7; H, 6.50%); $[\alpha]_D$ 24.5° (*c* 0.36 in dichloromethane); δ_H (C_6D_6) 1.40 (3 H, d, $J_{5,6}$ 5.9 Hz, 6-H_3), 3.04 (3 H, s, OMe), 3.59 (br dd, $J_{4,5}$ 9.2 $J_{3,4}$ 8.8 Hz, 4-H), 3.89 (dq, $J_{4,5}$ 9.2, $J_{5,6}$ 5.9 Hz 5-H), 4.29 (br ddd, $J_{3,4}$ 8.8 $J_{2,3}$ 3.5 Hz, 3-H), 4.59 (d, J_{AB} 11.4 Hz, $PhCH_AH_B$), 4.71 (d, $J_{1,2}$ 1.6 Hz, 1-H), 4.91 (d, $PhCH_AH_B$), 5.57 (1 H, dd, $J_{2,3}$ 3.5 $J_{1,2}$ 1.6 Hz, 2-H), 6.91—7.21 (8 H, m, ArH), and 8.01—8.24 (2 H, m, ArH).

Methyl 2-O-*Acetyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**5**).—A solution of (**3**) (1.0 g, 3.71 mmol) in anhydrous DMF (20 cm^3), triethyl orthoacetate (0.82 cm^3, 4.45 mmol), and toluene-*p*-sulphonic acid (20 mg) was kept at 50 °C for 40 min. After the addition of triethylamine (0.5 cm^3), the solution was evaporated and the resulting syrup dissolved in aqueous 80% acetic acid (10 cm^3). After 10 min the solution was evaporated and immediately purified on a silica gel column with hexane–ethyl acetate (2:1) as eluant. The *title compound* (**5**) (70%) was obtained as a homogeneous syrup $[\alpha]_D^{24}$ −39.8° (*c* 2.4, in dichloromethane) (Found: C, 61.7; H, 7.05. $C_{16}H_{22}O_6$ requires C, 61.9; H, 7.15%). The ^1H n.m.r. spectrum was similar to that of (**4**), δ_H (C_6D_6) 1.81 (s, 3 H, MeCO) and 5.34 (dd, 1 H, $J_{2,3}$ 3.6 Hz, 2-H).

Methyl 3-O-*Allyl*-2-O-*benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**7**).—Trifluoromethanesulphonic acid (2 cm^3) was added dropwise over 5 min to a stirred solution of compound (**4**) (11.0 g, 29.5 mmol) in carbon tetrachloride (20 cm^3), cyclohexane (85 cm^3) and allyl trichloroacetimidate[9] (12.0 g, 59 mmol). After 18 h at room temperature, the solution was filtered and the residue washed with dichloromethane. Triethylamine was added to the filtrate, which was then concentrated. Non-carbohydrate material was removed by crystallization from hexane–ethyl acetate (3:1). The concentrated filtrate was purified by preparative h.p.l.c. with hexane–ethyl acetate (10:1) as eluant. The *title compound* (**7**) 10.5 g (86.1%) was obtained as a homogeneous syrup $[\alpha]_D^{24}$ 22.1° (*c* 1.3, in dichloromethane) (Found: C, 69.65; H, 6.85. $C_{24}H_{28}O_6$ requires C, 69.9; H, 6.85%); δ_H (C_6D_6) 1.45 (d, 3 H, $J_{5,6}$ 5.8 Hz, 6-H_3), 3.08 (s, 3 H, OMe), 3.73 (dd, 1 H, $J_{4,5}$ 9.0, $J_{3,4}$ 9.0 Hz, 4-H), 3.96 (dq, 1 H, $J_{5,6}$ 5.8 Hz 5-H), 4.14 (dd, 1 H, $J_{3,4}$ 9.0, $J_{2,3}$ 3.3 Hz, 3-H), 4.74 (d, 1 H, $J_{1,2}$ 1.8 Hz, 1-H), 5.84 (dd, $J_{2,3}$ 3.3, $J_{1,2}$ 1.8 Hz, 2-H), and 5.85 (m, CH_2=C*H*CH_2O); δ_C ($CDCl_3$) 134.8 (CH_2=*C*HCH$_2$O), 117.1 (*C*H_2=CHCH$_2$O), 98.8 (C-1), 80.1 (C-4), 77.8 (C-3), 75.4 (*C*H_2Ph), 70.6 (CH_2=CH*C*H$_2$O), 69.7 (C-2), 67.6 (C-5), 54.9 (OMe), and 18.2 (C-6).

Methyl 2-O-*Acetyl*-3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**6**).—Methyl 2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside[10] (15.2 g, 56.4 mmol) was acetylated at C-2 as described for the preparation of compound (**5**). Crude compound (**5**) without chromatographic purification was allylated in the manner described for the synthesis of (**7**), using 2 mol equiv. of allyl trichloroacetimidate[9] per mol equiv. of (**5**). Purification by h.p.l.c. as described for (**7**) gave (**6**) as a syrup (16.14 g, 81.6%) $[\alpha]_D^{24}$ −39.7° (*c* 1.8, in dichloromethane) (Found: C, 64.9; H, 7.3. $C_{19}H_{26}O_6$ requires C, 65.1, H, 7.5%). The proton spectrum was similar to that of (**7**) with the notable exceptions δ_H (C_6H_6) 1.83 (s, 3 H, MeCO) and 5.54 (dd, $J_{2,3}$ 3.1 Hz, 2-H); δ_C ($CDCl_3$). 134.7 (CH_2=*C*HCH$_2$O), 117.0 (*C*H$_2$=CHCH$_2$O), 98.6 (C-1), 80.0 (C-4), 77.5 (C-3), 75.3 (Ph*C*H$_2$), 70.6 (O*C*H$_2$CH=CH$_2$), 69.1 (C-2), 67.5 (C-5), 54.7 (OMe), 20.9 (OCO*Me*), and 17.9 (C-6).

Methyl 3-O-*Allyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**8**).—*Method A.* A solution of the 2-benzoate (**7**) (1.77 g, 4.29 mmol) in methanol (20 cm^3) was left for 18 h at room temperature following the addition of sodium in methanol 1% w/v, 1 cm^3. The solution was deionized (Rexyn 101-H$^+$), evaporated, and purified on a silica gel column using hexane–ethyl acetate (3:1) as the eluant. Pure compound (**8**) 1.22 g (80.4%) was obtained as a homogeneous syrup.

Method B. A solution of the 2-acetate (**6**) (8.36 g, 23.8 mmol) in methanol (150 cm^3) was treated with methanolic sodium methoxide and the mixture was worked up in the usual manner. The *title compound* (**8**), 5.86 g (80%) obtained after chromatography was a syrup $[\alpha]_D^{24}$ −72.3° (*c* 1.0, in dichloromethane) (Found: C, 66.05; H, 8.0. $C_{17}H_{24}O_5$ requires C, 66.2; H, 7.85%); δ_C ($CDCl_3$), 134.6 (CH_2=*C*HCH$_2$O), 117.4 (*C*H$_2$=CHCH$_2$O), 100.1 (C-1), 79.9 (C-4), 79.6 (C-3), 75.3 (Ph*C*H$_2$), 70.9 (CH_2=CH*C*H$_2$O), 68.6 (C-2), 67.1 (C-5), 54.7 (OMe), and 17.9 (C-6).

1-O-*Acetyl*-3-O-*allyl*-2-O-*benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranose* (**9**) *and* -β-L-*rhamnopyranose* (**10**).—A solution of the methyl rhamnoside (**7**) (4.17 g, 9.74 mmol) in a mixture of acetic anhydride–acetic acid–conc. sulphuric acid (100:40:1) 60 cm^3; was kept at 20 °C for 25 min and then poured into aqueous potassium carbonate (10% w/v; 200 cm^3). After 30 min the suspension was extracted with dichloromethane (2 × 300 cm^3). The combined organic layers were washed with water, dried ($MgSO_4$) evaporated, and co-distilled with toluene. Chromatography on silica gel using hexane–ethyl acetate as the eluant and gave (**9**) and (**10**) as a mixture (3.36 g, 78.3%). Chromatography of a 1 g sample gave pure (**9**) (701 mg) as a syrup, $[\alpha]_D^{24}$ 2.2° (*c* 1.6, in dichloromethane) (Found: C, 67.9; H, 6.3. $C_{25}H_{28}O_7$ requires C, 68.2; H, 6.4%); δ_H (C_6D_6) 1.63 (s, 3 H, MeCO), 5.79 (dd, 1 H, $J_{2,3}$ 3.1, $J_{1,2}$ 2.0 Hz, 2-H), and 6.53 (d, 1 H, $J_{1,2}$ 2.0 Hz, 1-H); δ_C ($CDCl_3$) 134.5 (CH_2=*C*HCH$_2$O), 117.3 (*C*H$_2$=OHCH$_2$O), 91.2 (C-1), 79.5 (C-4), 77.4 (C-3), 75.6 ($C_6H_5CH_2$), 70.8 (CH_2=CH*C*H$_2$O), 70.0 (C-5), 68.5 (C-2), 20.9 (*Me*OCO), and 18.2 (C-6). The β-anomer (59 mg) crystallized from ethyl acetate and hexane, m.p. 59—61 °C, $[\alpha]_D^{24}$ 52.4° (*c* 1.1, in dichloromethane) (Found: C, 68.3; H, 6.5%); δ_H (C_6D_6), 1.57 (s, 3H, MeCO), 5.82—5.90 (m, 2 H, 1-H, 2-H); δ_C ($CDCl_3$) 134.2 (CH_2=*C*HCH$_2$O), 117.6 (*C*H$_2$=CHCH$_2$O), 91.4 (C-1), 79.6 (C-4), 79.3 (C-3), 75.4 ($C_6H_5CH_2$), 72.7 (C-5), 70.6 (CH_2=CH*C*H$_2$O), 68.4 (C-2), 20.8 (*Me*OCO), and 18.1 (C-6).

3-O-*Allyl*-2-O-*benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranosyl Chloride* (**11**).—A solution of the anomeric acetates (**9**) and (**10**) (2.44 g, 5.5 mmol) in dry dichloromethane (5 cm^3) was stirred with dichloromethyl methyl ether (0.53 cm^3, 5.8 mmol) and a catalytic amount of zinc bromide (20 mg) under an atmosphere of dry nitrogen. After 15 min the solution was freeze-dried, taken up in dry dichloromethane (5 cm^3), filtered through cotton wool, and freeze-dried (2.3 g, 100%). The syrup was homogeneous by t.l.c. and existed exclusively as the α-anomer. The material was characterized by ^{1}H n.m.r. spectroscopy and used immediately; δ_H (C_6D_6), 1.31 (d, 3 H, $J_{5,6}$ 6.1 Hz, 6-H$_3$), 3.66 (dd, 1 H, $J_{4,5}$ 9.4, $J_{3,4}$ 9.3 Hz, 4-H), 4.24 (dq, $J_{4,5}$ 9.4, $J_{5,6}$ 6.1 Hz 5-H), 4.31 (dd, $J_{3,4}$ 9.3, $J_{2,3}$ 3.2 Hz, 3-H), 5.80 (ddt, 1 H, CH_2=C*H*CH$_2$O), 5.83 (dd, 1 H, $J_{2,3}$ 3.2, $J_{1,2}$ 1.7 Hz, 2-H), 5.99 (d, 1 H, $J_{1,2}$ 1.7 Hz, 1-H), 7.09—7.34 (m, 8 H, ArH), and 8.13—8.36 (m, 2 H, ArH).

2,3,4,6-*Tetra*-O-*benzyl*-α-D-*glucopyranosyl Bromide* (**13**).—A solution of 2,3,4,6-tetra-*O*-benzylglucose (224 mg, 0.4 mmol) in anhydrous dichloromethane (2 cm^3) containing DMF (0.1 cm^3) was treated with oxalyl bromide (0.055 cm^3) for 20 min at room temperature. Freeze-drying gave a slightly yellow syrup (**13**), which contained a small amount of starting material; δ_C ($CDCl_3$), 91.9 (C-1), 82.2 (C-3), 79.7 (C-2), 76.1 (C-4), 75.8, 75.3, 73.5 (4 C, $C_6H_5CH_2$), 72.8 (C-5), and 67.8 (C-6).

Methyl 2-O-(3,4,6-*tri*-O-*Acetyl*-2-*deoxy*-2-*phthalimido*-β-D-*glucopyranosyl*)-3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**15**).—A solution of the glucosyl bromide (**12**) (2.42 g, 5.0 mmol) in anhydrous dichloromethane (30 cm^3) was added dropwise with stirring to a cooled (−70 °C) solution of the hydroxy derivative (**8**) (1.05 g, 3.41 mmol) in dichloromethane (10 cm^3) containing silver trifluoromethanesulphonate (1.31 g, 5.1 mmol) and 2,4,6-trimethylpyridine (0.67 cm^3, 5.1 mmol). The reaction was allowed to warm to 20 °C during several h and after 18 h additional catalyst and base were added, since unchanged hydroxy compound (**8**) was present. The reaction was left for a further 18 h when the mixture was finally filtered through Celite and the residue washed with dichloromethane. Triethylamine (2 cm^3) was added to the filtrate and the concentrated residue was eluted from a silica gel column with hexane–ethyl acetate (2:1). The *title compound* (**15**) (2.21 g, 89%) was obtained as a syrup, $[\alpha]_D^{24}$ 3.6° (*c* 1.5, in dichloromethane) (Found: C, 61.3; H, 6.2; N, 2.0. $C_{37}H_{44}NO_{14}$ requires C, 61.15; H, 6.1; N, 1.9%); δ_C ($CDCl_3$) 134.8 (CH_2=*C*HCH$_2$O), 117.3 (*C*H$_2$=CH-CH$_2$O), 99.9 (2 C, C-1, C-1′), 80.4 (C-4), 78.4 (2 C, C-2, C-3), 74.8 (Ph*C*H$_2$), 71.6 (C-4′), 71.5 (CH_2=CH*C*H$_2$O), 70.2 (C-3′), 69.3 (C-5′), 67.6 (C-5), 62.1 (C-6′), 54.6 (OMe), 54.5 (C-2′), 20.5, 20.6 (*Me*OCO), and 17.4 (C-6).

Methyl 2-O-(3,4,6-*Tri*-O-*acetyl*-2-*deoxy*-2-*phthalimido*-β-D-*glucopyranosyl*)-4-O-*benzyl*-α-L-*rhamnopyranoside* (**16**).—A solution of the blocked disaccharide (**15**) (189 mg, 0.26 mmol) in ethanol–water (20 cm^3, 9:1) containing tris(triphenylphosphine)rhodium(I) chloride (20 mg) was refluxed for 4 h, evaporated, taken up in ethyl acetate, and filtered through a micro-silica gel column. The concentrated filtrate in acetone (2 cm^3) was stirred with mercuric oxide (60 mg) and a solution of mercuric chloride in acetone–water [0.7 cm^3 of an 8.2% (w/v) solution in acetone–water 10:1 (v/v)]. After 15 min the reaction was filtered through Celite, the concentrated filtrates dissolved in ether (10 cm^3) and extracted with aqueous potassium iodide. The aqueous phase was back extracted with ether (10 cm^3) and the combined ether-soluble materials were chromatographed on silica gel with hexane–ethyl acetate (1:1) as the eluant to yield (**16**) (152 mg, 85%) $[\alpha]_D^{24}$ −20.0° (*c* 0.4, in dichloromethane) (Found: C, 59.35; H, 5.85; N, 2.0. $C_{34}H_{40}NO_{14}$ requires C, 59.45; H, 5.85; N, 2.05%); δ_C ($CDCl_3$) 100.2 (C-1), 99.9 (C-1′), 81.9 (C-4), 80.3 (C-5), 79.9 (C-2′), 74.9 (Ph*C*H$_2$), 71.6 (C-4′), 70.9 (C-3), 70.4 (C-3′), 69.2 (C-5′), 62.1 (C-6′), 54.6 (2 C, C-2′ and OMe), 20.7, 20.6, 20.5 (*Me*OCO), and 17.8 (C-6).

Methyl 2-O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**17**).—The fully blocked disaccharide (**15**) (2.04 g, 2.81 mmol) was deacetylated in dry methanol (20 cm^3) containing sodium methoxide, according to a published method for a related compound.[25] Following neutralization and concentration, the residue in ethanol (50 cm^3) containing hydrazine hydrate (0.9 cm^3 of an 85% aqueous solution was heated at reflux for 2 h. The solution was cooled, evaporated, and the residue acetylated with acetic anhydride (15 cm^3) in pyridine (30 cm^3). The product was worked up in the usual manner and chromatographed on silica gel with hexane–ethyl acetate (1:1) as the eluant. The main fraction (1.45 g, 81%) crystallized, m.p. 163 °C (from ethyl acetate–hexane), $[\alpha]_D^{24}$ −17.7° (*c* 1.7, in dichloromethane) (Found: C, 58.4; H, 6.85; N, 2.35. $C_{31}H_{43}NO_{13}$ requires C, 58.4; H, 6.8; N, 2.2%); δ_C ($CDCl_3$) 134.8 (CH_2=*C*HCH$_2$O), 117.6 (*C*H$_2$=CHCH$_2$O), 102.5 ($^1J_{^{13}C,^1H}$ 161 Hz, C-1′), 99.9 ($^1J_{^{13}C,^1H}$ 170 Hz, C-1), 80.4 (C-4), 79.4 (C-3), 77.5 (C-2), 75.2 (Ph*C*H$_2$), 73.0 (C-5′), 71.7 (2 C, CH_2=CH*C*H$_2$O and C-3′), 68.8 (C-4′), 67.6 (C-5), 62.2 (C-6′), 54.5 (2 C, OMe and C-2′), 23.4 (*Me*CONH), 20.6 (3 C, *Me*COO), and 17.8 (C-6).

Methyl 2-O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-4-O-*benzyl*-α-L-*rhamnopyranoside* (**18**) *and Methyl* 2-O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-4-O-*benzyl*-3-O-*propyl*-α-L-*rhamnopyranoside* (**19**).—A solution of the fully protected disaccharide (**17**) (1.30 g, 2.04 mmol) in ethanol–water (9:1, 50 cm^3) containing tris(triphenylphosphine)rhodium(I) chloride (30 mg) was gently refluxed for 4 h, evaporated, taken up in ethyl acetate and filtered through a micro silica gel column. The filtrate was evaporated and dissolved in acetone (5 cm^3). Mercury(II) oxide (433 mg, 2 mmol) and mercury(II) chloride [6.6. cm^3 of an 8.2% w/v solution in acetone–water 10:1 (v/v)] was added to the isopropenyl ether in acetone, and the mixture was stirred for 30 min and filtered through Celite. Ether was added to the concentrated filtrates and extracted with aqueous potassium iodide. Back extraction of the aqueous phase with ether, followed by concentration of the ether extracts gave a mixture that was separated by silica gel column chromatography with ethyl acetate–hexane [2:1 (v/v)] as the eluant. The *de-allylated disaccharide* (**18**) (870 mg, 72%) crystallized (from ethyl acetate–hexane), m.p. 147—147.5 °C $[\alpha]_D^{24}$ −25.9° (*c* 0.5, in dichloromethane) (Found: C, 56.2; H, 6.55; N, 2.45. $C_{28}H_{39}NO_{13}$ requires C, 56.25; H, 6.55; N, 2.35%). The propyl ether (**19**) (180 mg, 14%) was also obtained as a crystalline side product m.p. 144.5—145.5 °C (Found: C, 58.05; H, 7.15; N, 2.25. $C_{31}H_{45}$ requires C, 58.2; H, 7.05; N, 2.2%). The de-allylated disaccharide (**18**) had δ_C ($CDCl_3$) 102.9 (C-1′, $^1J_{^{13}C,^1H}$ 161 Hz), 99.8 (C-1, $^1J_{^{13}C,^1H}$ 170 Hz), 81.9 (C-4), 80.6 (C-2), 74.9 (Ph*C*H$_2$), 72.9 (C-5′), 71.8 (C-3′), 71.4 (C-3), 68.9 (C-4′), 67.1 (C-5), 62.3 (C-6′), 54.8 (C-2′), 54.5 (OMe), 23.3 (*Me*CONH), 20.5, 20.7 (3 C, Me), and 17.9 (C-6). The ^{13}C n.m.r. spectrum of (**19**) was similar to that of (**18**) with the important additions δ_C ($CDCl_3$) 73.5 (OCH$_2$CH$_2$Me), 23.7 (OCH$_2$*C*HMe), 10.7 (OCH$_2$CH$_2$*Me*).

Methyl 4-O-*Benzyl*-2-O-(3,4,6-*tri*-O-*acetyl*-2-*deoxy*-2-*phthalimido*-β-D-*glucopyranosyl*)-3-O-(2,3,4,6-*tetra*-*O*-*benzyl*-α/β-D-*glucopyranosyl*)-α-L-*rhamnopyranoside* (**20**).—A stirred solution of the disaccharide (**16**) (95 mg, 0.138 mmol) in anhydrous dichloromethane (3 cm^3) containing 4Å molecular sieves and mercury(II) bromide (162 mg, 0.45 mmol) was treated with a solution of the tetra-*O*-benzylglucosyl bromide (**13**) (prepared from 224 mg of the tetra-*O*-benzylglucose) dissolved in anhydrous dichloromethane (6 cm^3). After 48 h at 20 °C well dried mercury(II) bromide (100 mg) was added to the reaction, which was then left for a further 24 h. After filtration and addition of triethylamine (0.2 cm^3), the product was chromatographed on silica gel with hexane–ethyl acetate [in a stepped gradient of 2:1 and 1:1 (v/v), each containing 0.1% triethylamine]. The 3:2 mixture of α/β-glucose anomers (**20**) (50 mg, 30%) was obtained as a syrup together with recovered starting material (59 mg, 62%) (Found: C, 67.4; H, 6.3; N, 1.2. $C_{68}H_{74}NO_{19}$ requires C, 67.55; H, 6.15; N, 1.15%); δ_C (CD_3OD) 101.4 (2 C, C-1′, C-1″β), 100.2 (C-1), 99.0 (C-1″α).

Methyl 2-O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-4-O-*benzyl*-3-O-(2,3,4,6-*tetra*-O-*benzyl*-α/β-D-*glucopyranosyl*)-α-L-*rhamnopyranoside* (**21**).—A solution of glucosyl bromide (**13**), prepared from tetra-*O*-benzylglucose (362 mg, 0.67 mmol) dissolved in dichloromethane (320 cm^3) was added dropwise to a stirred solution of the disaccharide (**18**) (200 mg, 0.335 mmol) in dichloromethane (5 cm^3) containing 4Å molecular sieves and mercury(II) bromide (144 mg, 0.4 mmol). Further mercury(II) bromide (140 mg) and molecular sieves were added after 18 h and the reaction allowed to proceed for a further 4 h. The reaction mixture was worked up and chromatographed in the manner described for compound (**20**). A 2:1 mixture of the α/β glucose linked trisaccharide (**21**) (328 mg, 87%) was obtained from column chromatography (Found: C, 66.35; H, 6.7; H, 1.35. $C_{62}H_{75}NO_{18}$ requires C, 66.45; H, 6.55; N, 1.25%); δ_C ($CDCl_3$), 103.5 (C-1″β), 102.9 (C-1′), 99.9 (C-1), and 94.5 (C-1″α).

Methyl 2-O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-3-O-(α/β-D-*glucopyranosyl*)-α-L-*rhamnopyranoside* (**22**).—A solution of the trisaccharide (**21**) (310 mg, 0.277 mmol) in ethanol (60 cm^3) was hydrogenated for 48 h with 10% palladium-on-charcoal (300 mg) as the catalyst. After filtration and evaporation the crude syrup was chromatographed on silica gel using ethyl acetate–methanol–water (7:2:1 v/v/v) as the eluant. Separation of the anomers was poor and a second column yielded a fraction enriched in the α-anomer (**21**) (103 mg, 56%). Total recovery of both α- and β-anomers was 168 mg (91%); δ_C (CD_3OD) 103.9 (C-1″β), 103.4 (C-1′), 101.6 (C-1), and 96.1 (C-1″α).

Methyl 2-O-(2-*Acetamido*-2-*deoxy*-β-D-*glucopyranosyl*)-3-O-α-D-*glucopyranosyl*-α-L-*rhamnopyranoside* (**24**).—The partially blocked trisaccharide (**22**) (103 mg, 0.154 mmol) was acetylated with pyridine (5 cm^3) and acetic anhydride (3 cm^3) at 4 °C for 18 h. Evaporation, co-distillation with toluene, and chromatography on silica gel using ethyl acetate–hexane (4:1 v/v) as the eluant gave the peracetylated trisaccharide (**23**) (122 mg, 90%) which was contaminated with the isomeric β-D-glucose linked trisaccharide. Catalytic transesterification of (**23**) in absolute methanol (10 cm^3) to which 2% sodium methoxide solution (1 cm^3) was added gave crude compound (**24**). After de-ionization with Rexyn 101-(H^+) resin, chromatography on silica gel, with ethyl acetate–methanol–water 6:3:1 (v/v/v) as eluant gave first a fraction containing both the β- and α-glucose trisaccharides. The more mobile β-isomer eluted first but was not sufficiently pure for characterisation. Pure *trisaccharide* (**24**) (39 mg, 52%) eluted in the later fractions, $[\alpha]_D^{22}$ 43.0° (*c* 0.5, methanol) (Found: C, 46.3; H, 7.0; N, 2.7. $C_{21}H_{37}NO_{15}$ requires C, 46.4; H, 6.9; N, 2.6%); δ_C (D_2O) 103.0 (C-1′), 101.0 (C-1), 95.8 (C-1″), 77.1, 76.9, 75.4, 75.1, 74.8, 74.2, 72.6, 72.4, 70.9, 70.5, 69.9, 61.8, 61.4, 56.8, 55.9, 23.8, 17.9.

Methyl 2-O-(3-O-*Allyl*-2-O-*benzoyl*-4-O-*benzyl*-α-L-*rhamnopyranosyl*)-3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**25**).—A solution of freshly prepared rhamnopyranosyl chloride (**11**) (2.3 g, 5.5 mmol) in dichloromethane (35 cm^3) was added dropwise to a stirred solution of the 2-hydroxyrhamnose

derivative (**8**) (862 mg, 2.8 mmol) in dichloromethane (10 cm^3) containing tetramethylurea (1.75 cm^3, 14.5 mmol) and silver trifluoromethanesulphonate (1.12 g, 4.36 mmol) at −70 °C. The reaction mixture was held at −70 °C for 3 h and then allowed to warm slowly to room temperature overnight. It was then filtered through a pad of Celite, washed with dichloromethane, evaporated and immediate chromatography on silica gel (hexane–ethyl acetate 4:1 as the eluant) to yield (**25**) (1.50 g, 78%) as a syrupy product, $[\alpha]_D^{24}$ −9.0° (*c* 0.6, in dichloromethane) (Found: C, 69.8; H, 7.2. $C_{40}H_{48}O_{10}$ requires C, 69.75; H, 7.0%); δ_C ($CDCl_3$) 134.8 (CH_2=*C*HCH$_2$O), 117.1, 116.6 (*C*H$_2$=CHCH$_2$O), 99.9 (C-1, $^1J_{C,H}$ 169 Hz), 99.1 (C-1′, $^1J_{C,H}$ 172 Hz), 80.1 (C-4), 79.9 (C-4′), 79.4 (C-3), 77.5 (C-3′), 75.4, 75.2 (Ph*C*H$_2$), 74.3 (C-2), 70.9 (O*C*H$_2$CH=CH$_2$), 70.7 (OCH$_2$CH=*C*H$_2$), 69.7 (C-2′), 68.3 (C-5′), 67.8 (C-5), 54.6 (OMe), 18.2 (C-6), and 18.0 (C-6′).

A small amount of the isomeric β linked disaccharide (**28**) (85 mg, 4.5%) was obtained as a pure syrup, $[\alpha]_D$ 56.0° (*c* 0.7 in dichloromethane) (Found: C, 69.4; H, 7.1. $C_{40}H_{48}O_{10}$ requires C, 69.75; H, 7.0%); δ_C ($CDCl_3$) 135.5, 134.6 (CH_2=*C*HCH$_2$O), 117.5, 115.8 (*C*H$_2$=CHCH$_2$O), 98.4 (C-1, $^1J_{C,H}$ 167 Hz), 96.5 (C-1′, $^1J_{C,H}$ 157 Hz), 79.9 (3 C, C-3, C-4, C-4′), 78.1 (C-3′), 75.5 (Ph*C*H$_2$), 74.7 (Ph*C*H$_2$-), 71.9 (C-2), 71.7 (C-5′), 70.4 (O*C*H$_2$CH=CH$_2$), 69.8 (OCH$_2$CH=*C*H$_2$), 69.2 (C-2′), 67.9 (C-5), 54.7 (OMe), 18.2 (C-6), and 18.0 (C-6′).

Methyl 2-O-(2-O-*Benzoyl*-4-*benzyl*-α-L-*rhamnopyranosyl*)-4-O-*benzyl*-α-L-*rhamnopyranoside* (**26**).—A solution of the blocked disaccharide (**25**) (1.45 g, 2.1 mmol) in ethanol (16 cm^3) and water (4 cm^3) containing tris(triphenylphosphine)rhodium(I) chloride (50 mg) was maintained at 80 °C for 4.5 h, evaporated and taken up in ethyl acetate (10 cm^3). This solution was run through a small column of silica gel (20 g) and the combined ethyl acetate fractions from the column were evaporated and the resultant syrup chromatographed on silica gel using hexane and ethyl acetate as the eluant. The dihydroxy compound (**26**) (816 mg, 64%) was obtained as a homogeneous syrup, $[\alpha]_D^{24}$ −10.8° (*c* 1.0, in dichloromethane) (Found: C, 66.95; H, 6.7. $C_{34}H_{40}O_{10}$ requires C, 67.1; H, 6.6%); δ_C ($CDCl_3$) 99.6 (C-1′), 82.1 (C-4), 81.6 (C-4′), 78.9 (C-2), 75.2, 75.1 (Ph*C*H$_2$), 73.3 (C-2′), 71.4 (C-3), 70.5 (C-3′), 68.2 (C-5′), 67.3 (C-5), 54.8 (OMe), 18.4 (C-6′), and 18.0 (C-6).

Methyl 2-O-(3-O-*Allyl*-4-O-*benzyl*-α-L-*rhamnopyranosyl*)-3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**27**).—A solution of the disaccharide (**25**) (3.1 g, 4.5 mmol) in methanol was treated with methanolic sodium methoxide solution 2% (w/v) for 96 h at 5 °C. The solution was de-ionized with Rexyn 101-H^+ ion-exchange resin. Subsequent chromatography using hexane and ethyl acetate (1:1) as the eluant gave (**27**) (2.25 g, 86%) as a syrup $[\alpha]_D^{24}$ −41.8° (*c* 3.1, in dichloromethane) (Found: C, 67.9; H, 7.5. $C_{33}H_{44}O_9$ requires C, 67.8; H, 7.5%); δ_C($CDCl_3$), 134.9 (CH_2=*C*HCH$_2$O), 117.2, 116.8 (*C*H$_2$=CHCH$_2$O), 100.8 (C-1′, $^1J_{C,H}$ 168 Hz), 100.1 (C-1, $^1J_{C,H}$ 172 Hz), 80.1 (C-4, C-4′), 79.6 (C-3′), 79.4 (C-3), 75.3, 75.2 (Ph*C*H$_2$O), 74.3 (C-2), 71.0 (2 C, CH_2=CH*C*H$_2$O), 68.8 (C-2′), 68.0 (C-5′), 67.8 (C-5), 54.6 (OMe), 18.1 (C-6′), and 18.0 (C-6).

Methyl O-3,4,6-*Tri*-O-*acetyl*-2-*deoxy*-2-*deoxy*-2-*phthalimido*-β-D-*glucopyranosyl*)-(1 → 2)-O-(3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranosyl*)-(1 → 2)-3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**29**). A solution of the tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide (2.25 g, 4.5 mmol) in dry dichloromethane (30 cm^3) was added dropwise with stirring to a cooled (−70 °C) solution of the selectively deprotected disaccharide (**27**) (1.76 g, 3.01 mmol) in dry dichloromethane (25 cm^3) containing 4Å molecular sieves, 2,4,6-trimethylpyridine (0.66 cm^3, 5.0 mmol) and silver trifluoromethanesulphonate (1.29 g, 5.0 mmol). The reaction was maintained at −70 °C for 2 h and then allowed to warm to 20 °C over 16 h. 2,4,6-Trimethylpyridine (0.33 cm^3) was added followed by silver trifluoromethanesulphonate (640 mg) and stirring was continued for 24 h. Filtration through Celite, evaporation, and chromatography on silica gel using hexane–ethyl acetate (1:1) as the eluant gave (**29**) (1.81 g, 60%), and (**27**) (247 mg, 14%). Repeated chromatography of the mixed fractions provided a further quantity of (**29**) (458 mg, total yield 75%), $[\alpha]_D^{24}$ 3.6° (*c* 1.4, in dichloromethane) (Found: C, 63.35; H, 6.5; N, 1.53. $C_{53}H_{63}NO_{18}$ requires C, 63.5; H, 6.3; N, 1.4%); δ_C ($CDCl_3$), 135.1, 134.9 (CH_2=*C*HCH$_2$O), 133.9 (Phth), 117.6, 116.6 (*C*H$_2$=CHCH$_2$O), 100.8 (C-1′), 99.9 (2 C, C-1, C-1″), 80.6 (C-4′), 80.1 (C-4), 79.2 (C-3), 78.6 (C-3′), 78.0 (C-2′), 75.0 (2 C, Ph*C*H$_2$O), 74.9 (C-2), 71.9 (CH_2=CH*C*H$_2$O), 71.5 (C-4″), 70.8 (CH_2=CH*C*H$_2$O), 70.2 (C-3″), 69.1 (C-5″), 68.4 (C-5′), 67.5 (C-5), 62.0 (C-6″), 54.6 (OMe), 20.6 (*Me*CO), 18.0 (C-6), and 17.7 (C-6′).

Methyl O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-(1 → 2)-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranosyl*)-(1 → 2)-3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**30**).—A solution of the blocked trisaccharide (**29**) (1.6 g, 1.6 mmol) in dry methanol (50 cm^3) containing a solution of sodium in methanol [1 cm^3; 2% (w/v)] was kept at 4 °C for 18 h. Deionization with Rexyn 101-H^+ ion-exchange resin followed by concentration gave a syrup, which was dissolved in ethanol (80 cm^3) and refluxed with hydrazine hydrate (1 cm^3 of an 85% aqueous solution) for 3 h. Evaporation and co-distillation with toluene gave a crude product which was acetylated in pyridine (40 cm^3) and acetic anhydride (20 cm^3) at 4 °C for 16 h. Evaporation and co-distillation gave the crude product, which was chromatographed on silica gel using hexane–ethyl acetate (1:1) as the eluant. The pure trisaccharide (**30**) (1.07 g, 73%) showed $[\alpha]_D^{22}$ −14.7° (*c* 0.1, in dichloromethane) (Found: C, 61.6; H, 6.8; N, 1.6. $C_{47}H_{63}NO_{17}$ requires C, 61.8; H, 6.95; N, 1.55%); δ_C ($CDCl_3$) 135.0, 134.7 (CH_2=*C*HCH$_2$O), 118.1, 116.7 (*C*H$_2$=CHCH$_2$O), 102.7 (C-1″), 100.8 (C-1′), 99.1 (C-1), 81.1 (C-4′), 80.2 (C-4), 79.3 (C-3), 79.2 (C-3′), 77.8 (C-2′), 75.5 (Ph*C*H$_2$O), 75.1 (2 C, C-2, Ph*C*H$_2$O), 73.4 (C-5″), 72.3 (CH_2=CH*C*H$_2$O), 72.0 (C-3″), 70.9 (CH_2=CH*C*H$_2$O), 68.4 (2 C, C-4″, C-5′), 67.5 (C-5), 62.0 (C-6″), 54.6 (2 C, C-2″, OMe), 25.3 (*Me*CONH), 20.7, 20.6 (*Me*CO$_2$), 18.1 (C-6), and 17.8 (C-6′).

Methyl O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-(1 → 2)-O-(4-O-*benzyl*-α-L-*rhamnopyranosyl*)-(1 → 2)-4-O-*benzyl*-α-L-*rhamnopyranoside* (**31**) *and Methyl* O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-(1 → 2)-O-(3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranosyl*)-(1 → 2)-4-O-*benzyl*-α-L-*rhamnopyranoside* (**32**).—A solution of the trisaccharide (**30**) (1.06 g, 1.16 mmol) in ethanol–water (9:1 v/v; 20 cm^3) containing tris(triphenylphosphine)rhodium(I) chloride (45 mg) was gently refluxed for 13 h. After cooling, the mixture was filtered through Celite and washed with ethanol. The combined filtrates were evaporated, the residue dissolved in acetone and filtered through a small amount of silica gel. Following evaporation of the filtrate the resulting syrup was dissolved in acetone–water (10:1 v/v; 11 cm^3) and the solution stirred with mercuric oxide (1.0 g, 4.6 mmol) and a solution of mercuric chloride in acetone–water [15.5 cm^3 of an 8.2% (w/v) solution in acetone–water 10:1 (v/v)]. After 1 h the mixture was filtered through Celite and washed with acetone. The combined filtrates were evaporated, the residue dissolved in ether, and the organic solution extracted with aqueous potassium iodide solution. The syrup obtained on evaporation of the ether was chromatographed on silica gel using a solvent gradient beginning with ethyl acetate–hexane (2:1 v/v) and finishing with ethyl acetate. Two fractions were obtained, first a mono-allylated compound followed by the diol (**31**) (686 mg, 71%),

$[\alpha]_D^{24}$ −21.2° (*c* 1.0, in dichloromethane) (Found: C, 59.2; H, 6.55; N, 1.8. $C_{41}H_{55}NO_{17}$ requires C, 59.05; H, 6.65; N, 1.7%); δ_C ($CDCl_3$) 102.6 (C-1″), 101.4 (C-1′), 99.6 (C-1), 82.0 (C-4), 81.9 (C-4′), 80.5 (C-2′), 80.0 (C-2), 75.0, 74.6 (Ph*C*H_2O), 72.9 (C-5″), 71.9 (C-3″), 71.1 (2 C, C-3, C-3′), 68.9 (C-4″), 67.9 (C-5′), 67.0 (C-5), 62.2 (C-6″), 54.7 (OMe), 54.5 (C-2″), 23.2 (*Me*CONH), 20.7, 20.6 (*Me*CO_2), 18.1 (C-6), and 17.8 (C-6′).

The first fraction was rechromatographed on silica gel with ethyl acetate–hexane (5:2 v/v) as the eluant and pure monodeallylated trisaccharide (**32**) (202 mg, 20%) $[\alpha]_D^{24}$ −25.0° (*c* 0.5, in dichloromethane) was obtained as a homogeneous syrup (Found: C, 60.2; H, 6.65; N, 1.7. $C_{44}H_{59}NO_{17}$ requires C, 60.45; H, 6.8; N, 1.6%); δ_C ($CDCl_3$), 134.9 (CH_2=*C*HCH_2O), 117.6 (*C*H_2=$CHCH_2O$), 102.5 (C-1″), 101.5 (C-1′), 99.6 (C-1), 81.8 (C-4), 80.7 (C-4′), 79.5 (C-3′), 78.9 (C-2), 77.8 (C-2′), 75.4, 74.5 (Ph*C*H_2O), 72.9 (C-5″), 71.9 (2 C, CH_2=CH*C*H_2O, C-3″), 71.0 (C-3), 68.6 (C-5′), 68.4 (C-4″), 66.8 (C-5), 62.0 (C-6″), 54.7 (2 C, OMe, C-2″), 23.4 (*Me*CONH), 20.7, 20.6 (*Me*CO), 18.1 (C-6), and 17.8 (C-6′).

*Methyl O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-*D*-glucopyranosyl)-(1 → 2)-O-(3-O-allyl-4-O-benzyl-*α*-*L*-rhamnopyranosyl)-(1 → 2)-O-[(2,3,4,6-tetra-*O*-benzyl-*α*-*D*-glucopyranosyl)-(1 → 3)]-4-O-benzyl-*α*-*L*-rhamnopyranoside* (**33**) *and Methyl* O-(2-*Acetamido*-3,4,6-*tri*-O-*acetyl*-2-*deoxy*-β-D-*glucopyranosyl*)-(1 → 2)-O-(3-O-*allyl*-4-O-*benzyl*-α-L-*rhamnopyranosyl*)-(1 → 2)-O-[(2,3,4,6-*tetra*-O-*benzyl*-β-D-*glucopyranosyl*)-(1 → 3)]-4-O-*benzyl*-α-L-*rhamnopyranoside* (**34**).—A solution of tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**13**) (235 mg, 0.44 mmol) in dry dichloromethane (4 cm^3) was added to a stirred solution of the monohydroxy trisaccharide (**32**) (190 mg, 0.22 mmol) in dichloromethane (5 cm^3) containing 4Å molecular sieves (0.3 g) and mercuric bromide (180 mg, 0.5 mmol). The mixture was stirred overnight and then filtered through a pad of Celite, concentrated, and chromatographed on silica gel using hexane–ethyl acetate (1:2 v/v) as the eluant. Two fractions containing a mixture of α or β linked tetrasaccharides (**33**) and (**34**) and pure (**33**) (45 mg) were obtained together with starting trisaccharide (**32**) (29 mg, 15%). The impure tetrasaccharides were purified by preparative t.l.c. (hexane–ethyl acetate 1:1, developed four times) to give (**34**) (20 mg; 7%) and a further 65 mg of (**33**) (total 110 mg; 36%), $[\alpha]_D^{24}$ 11.3° (*c*, 1.3, in dichloromethane) (Found: C, 66.95; H, 6.75; N, 1.05. $C_{78}H_{93}NO_{22}$ requires C, 67.1; H, 6.7; N, 1.0%); δ_C ($CDCl_3$) 134.6 (CH_2=*C*HCH_2O), 117.9 (*C*H_2=$CHCH_2O$), 101.8 (C-1″), 99.6 (C-1), 99.6 (C-1′), 93.7 (C-1‴), 82.1, 80.7, 79.9, 79.7, 78.5, 77.8, 77.0, 75.3 (3 C), 74.9, 74.4, 73.4, 73.3, 73.2, 72.4, 72.0, 70.3, 68.4, 68.3 (2 C), 68.0, 61.9, 54.8, 23.5, 20.7, 20.6, 18.1, and 17.9. The β-linked tetrasaccharide (**34**) $[\alpha]_D$ −1.0° (*c* 0.5, in dichloromethane) had δ_C ($CDCl_3$) 103.4 (C-1‴), 102.3 (C-1″), 100.7 (C-1′), and 99.7 (C-1).

Methyl O-(2-*Acetamido*-2-*deoxy*-3,4,6-*tri*-O-*acetyl*-β-D-*glucopyranosyl*)-(1 → 2)-O-(4-O-*benzyl*-α-L-*rhamnopyranosyl*)-(1 → 2)-O-[(2,3,4,6-*tetra*-*O*-*benzyl*-α-D-*glucopyranosyl*)-(1 → 3)]-4-O-*benzyl*-α-L-*rhamnopyranoside* (**35**).—A solution of the protected tetrasaccharide (**33**) (100 mg, 71.6 μmol) in ethanol–water [20 cm^3; 9:1 (v/v)] was refluxed in the presence of tris(triphenylphosphinerhodium(I) chloride (15 mg) for 6 h. Then the mixture was evaporated and the residue taken up in ethyl acetate and filtered through a micro silica gel column. The filtrates were evaporated, dissolved in acetone (4 cm^3) and stirred with mercuric oxide (15.5 mg, 71 μmol) and a solution of mercuric chloride in acetone–water [0.24 cm^3 of an 8.2% (w/v) solution in acetone–water 10:1 (v/v)]. After 30 min the mixture was filtered through Celite, and the filtrate evaporated and the residue dissolved in ether and extracted with aqueous potassium iodide. The organic phase was evaporated and subjected to column chromatography on silica gel using ethyl acetate–hexane (2:1, v/v) as the eluant. The de-allylated tetrasaccharide (**35**) (54 mg, 56%) was obtained chromatographically pure, δ_C ($CDCl_3$), 103.2 (C-1″), 100.3 (C-1′), 99.4 (C-1), and 93.3 (C-1‴).

Methyl O-2-*Acetamido*-2-*deoxy*-β-D-*glucopyranosyl*-(1 → 2)-O-α-L-*rhamnopyranosyl*-(1 → 2)-O-[(α-D-*glucopyranosyl*)-(1 → 3)]-α-L-*rhamnopyranoside* (**36**).—A solution of the protected tetrasaccharide (**33**) (100 mg, 72 μmol) in ethanol–water (9:1 v/v; 20 cm^3) was refluxed in the presence of tris(triphenylphosphine)rhodium(I) chloride (15 mg) for 6 h. The mixture was evaporated and the residue taken up in ethyl acetate and filtered through a micro silica gel column. The filtrate was evaporated and the residue dissolved in acetone (4 cm^3) and stirred with mercuric oxide (15.5 mg, 71 μmol) and a solution of mercuric chloride in acetone–water [0.24 cm^3 of a 8.2% (w/v) solution in acetone–water 10.1 (v/v)]. After 30 min the mixture was filtered through a pad of Celite and washed with acetone. The filtrates were evaporated, dissolved in ether and extracted with aqueous potassium iodide. The organic phase was evaporated and subjected to silica gel column chromatography using ethyl acetate–hexane 2:1 as the eluant. The selectively deprotected tetrasaccharide (**35**) (54 mg, 56%) was obtained as a homogeneous product, δ_C ($CDCl_3$) 103.2 (C-1″), 100.3 (C-1′), 99.4 (C-1), 93.3 and (C-1‴). This material (45 mg, 32.3 μmol) was dissolved in ethanol and hydrogenated over 10% palladium-on-charcoal for 18 h. Filtration, evaporation and transesterification in methanol containing sodium (0.5% w/v) gave (**36**) (20 mg, 87%) after deionization, $[\alpha]_D^{24}$ 20.2° (*c* 0.3, in methanol) (Found: C, 46.9; H, 6.9; N, 2.05. $C_{27}H_{47}NO_{19}$ requires C, 47.0; H, 6.85; N, 2.05%); δ_C 103.6 (C-1″), 102.2 (C-1′), 100.7 (C-1), 95.6 (C-1‴), 79.7, 77.1, 75.9, 74.8, 74.7, 74.2, 73.5, 72.8, 72.3, 71.6, 71.2, 71.0, 70.7, 70.4, 69.7, 62.1, 61.6, 57.1, 56.2, 23.5, 18.0, and 17.8.

Methyl O-(2-*Acetamido*-2-*deoxy*-3,4,6-*tri*-O-*acetyl*-β-D-*glucopyranosyl*)-(1 → 2)-O-[(α-D-*glucopyranosyl*)-(1 → 3)]-α-L-*rhamnopyranosyl*-(1 → 2)-O-[(α-D-*glucopyranosyl*)-(1 → 3)]-α-L-*rhamnopyranoside* (**38**).—A solution of tetra-*O*-benzyl α-D-glucopyranosyl bromide (**13**) (3.20 mmol) in dry dichloromethane (25 cm^3) was added to a stirred solution of trisaccharide (**31**) (575 mg, 0.69 mmol) in dry dichloromethane (10 cm^3) containing molecular sieves (4Å) and mercuric bromide (1.26 g, 3.5 mmol). After 18 h all the starting material was consumed and the mixture was filtered through Celite, washed with dichloromethane, evaporated and the residue chromatographed on a silica gel column with hexane–ethyl acetate [1:1 (v/v)] as the eluant. Several fractions were obtained, the fastest moving of which consisted of a mixture of pentasaccharides containing α and β linked glucose residues. The tetrasaccharide (**35**) (420 mg, 50%) was also obtained as an impure fraction. Preparative t.l.c. of the pentasaccharide components with hexane–ethyl acetate (3:2, v/v) as the developing solvent gave after three developments a component (50 mg, *ca.* 4%) substantially enriched in (**37**).

The isolated and purified tetrasaccharide (**35**) (64 mg, 47 μmol) was glycosylated with tetra-*O*-benzyl glucopyranosyl bromide (**13**) (2 mol) with silver carbonate (127 mg) and silver perchlorate (13 mg) as the catalyst. The reaction mixture was worked up in the usual manner and chromatographed to give crude (**37**) (35 mg, 39%).

The combined pentasaccharide products of the two experiments (85 mg, 45 μmol) were dissolved in ethanol–toluene [60 cm^3; 2:1 (v/v)] and hydrogenated at 0.5 MPa in the presence of palladium-on-carbon. After filtration and evaporation of the solvents, the major component (**38**) (26 mg) of the two products formed, was isolated by silica gel chromatography

with ethyl acetate–methanol–water 7:2:1 (v/v/v) as the eluant. Final purification of (**38**) (15 mg, 34%) was achieved by preparative t.l.c. using the solvent employed for column chromatography, $[\alpha]_D^{24}$ 38.5° (*c* 0.7, methanol); δ_C ($CDCl_3$) 102.6 (C-1″), 102.0 (C-1′), 100.7 (C-1), 95.6 (2 C, C-1‴, C-1⁗), 62.9 (C-6″), and 61.4 (2 C, C-6‴, C-6⁗).

Methyl O-(2-*Acetamido*-2-*deoxy*-β-D-*glucopyranosyl*)-(1 → 2)-O-[(α-D-*glucopyranosyl*)-(1 → 3)]-α-L-*rhamnopyranosyl*-(1 → 2)-O-[α-D-*glucopyranosyl*)-(1 → 3)]-α-L-*rhamnopyranoside* (**39**).—A solution of the partially deblocked pentasaccharide (**38**) (14.6 mg, 15 μmol) in absolute methanol (5 cm^3) was transesterified by addition of sodium methoxide in methanol [0.2 cm^3 of a 2% (w/v) solution]. After 2 h the solution was de-ionized with Rexyn 101-H^+ resin, filtered, and concentrated to give (**39**) (13 mg), $[\alpha]_D^{24}$ 46.7 (*c* 0.6, methanol) which was not analytically pure, but by 500 MHz ^1H n.m.r. was shown to be ⩾ 85% pure; δ_C (D_2O), 102.9 (C-1″), 102.3 (C-1′), 100.7 (C-1), 95.6 (2 C, C-1‴, C-1⁗), 62.2 (C-6″), and 61.6 (2 C, C-6‴, C-6⁗).

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References

1 D. R. Bundle, M. A. J. Gidney, S. Josephson, and H.-P. Wessel, *Am. Chem. Soc. Symp. Ser.*, 1983, **231**, 49.
2 K. Bock, S. Josephson, and D. R. Bundle, *J. Chem. Soc., Perkin Trans. 2*, 1982, 59.
3 L. Kenne, B. Lindberg, K. Petersson, and E. Romanowska, *Carbohydr. Res.*, 1977, **56**, 363.
4 L. Kenne, B. Lindberg, K. Petersson, E. Katzenellenbogen, and E. Romanowska, *Eur. J. Biochem.*, 1977, **76**, 327; 1978, **91**, 279.
5 N. Carlin, A. A. Lindberg, K. Bock, and D. R. Bundle, *Eur. J. Biochem.*, 1984, **139**, 189.
6 S. Josephson and D. R. Bundle, *J. Chem. Soc., Perkin Trans. 1*, 1980, 297.
7 D. R. Bundle and S. Josephson, unpublished work.
8 J. Gigg and R. Gigg, *J. Chem. Soc.*, 1966, 82.
9 H.-P. Wessel, T. Iversen, and D. R. Bundle, *J. Chem. Soc., Perkin Trans. 1*, preceding paper.
10 A. H. Haines, *Carbohydr. Res.*, 1969, **10**, 466.
11 P. J. Garegg and H. Hultberg, *Carbohydr. Res.*, 1979, **72**, 276.
12 D. M. Clode, D. Horton, and W. Weckerle, *Carbohydr. Res.*, 1976, **49**, 305.
13 S. Jakobsen and C. Pedersen, *Acta Chem. Scand., Ser. B*, 1974, **28**, 866.
14 T. Iversen and D. R. Bundle, *Carbohydr. Res.*, 1982, **103**, 29.
15 J. Thiem and B. Meyer, *Chem. Ber.*, 1980, **113**, 3075.
16 R. U. Lemieux, T. Takeda, and B. Y. Chung, *Am. Chem. Soc., Symp. Ser.*, 1976, **39**, 90.
17 J.-R. Pougny, A. M. N. Mahmoud, N. Naulet, and P. Sinay, *Nouv. J. Chem.*, 1978, **2**, 389.
18 D. R. Bundle and S. Josephson, *Can. J. Chem.*, 1979, **57**, 662.
19 C. D. Warren and R. W. Jeanloz, *Carbohydr. Res.*, 1977, **53**, 67.
20 H. Paulsen, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 155.
21 S. Hanessian and J. Banoub, *Carbohydr. Res.*, 1977, **53**, 13.
22 R. U. Lemieux, K. B. Hendriks, R. V. Stick, and K. James, 1977, **97**, 4056.
23 D. Schwarzenbach and R. W. Jeanloz, *Carbohydr. Res.*, 1981, **90**, 193.
25 D. R. Bundle and S. Josephson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2736.
24 D. R. Bundle and S. Josephson, *Carbohydr. Res.*, 1980, **80**, 75.

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