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Standardized intermediates: Synthesis of model bacterial *O*-antigens. A regio-/ stereoselective synthesis of 1,2 -*trans* disaccharides as allyl glycosides suitable for chain extension

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The synthesis of α-L-Rhap- (1→3)-4-*O*- Me-α-L-Rhap; α-L-Rhap - (1→6) - 2, 3-di-*O*-Me- α-D-Glcp and β-D-Glcp-(1→3) -4-*O*-Me-α-L-Rhap, the three chemically modified spacer armed disaccharide fragments related to bacterial *O*-lipopolysaccharides (*lps*) have been reported in the form of allyl glycosides for conjugation to protein. Allyl 4-*O*-Me-α-L-Rhap, allyl 2,3-di-*O*-Me- α-D-Glcp, 2,3,4-tri-*O*-acetyl-α- L-Rhap trichloroacetimidate, 2,3,4-tri-*O*-acetyl- α-L-rhamnopyranosyl chloride and 2,3,4,6-tetra- *O*-acetyl-α-D-Glcp trichloroacetimidate have been used as glycosyl intermediates. Stereoselectivity in the formation of 1,2 - *trans* linked glycosidic bonds is governed by the *O*-2 acyl group in the glycosyl donor and the regioselectivity leaves margin for further chain extension. Such compounds are expected to be useful in the specificity studies of an antibody raised against related antigen.

The increasing awareness of the biological significance of oligosaccharides related to bacterial *O-lps* has stimulated remarkable progress in carbohydrate synthesis in recent years[1]. The availability of a general procedure for the synthesis of oligosaccharides and neoglycoconjugates (NGCs) is of paramount importance since it would allow many biologically and clinically active substances such as antigens to be readily available. For example, such saccharides could function as antigens to produce antibodies that may potentially serve as diagnostic markers. These saccharides could also serve as vaccines[2] that would induce an immune response. The synthesis of oligosaccharides constituting the repeating units of these polysaccharide building blocks, is a worthwhile synthetic challenge since these structures may act as antigenic determinants which are valuable markers of bacterial infection[3].

The immunodominant regions of bacterial *O*-antigens have been synthesized in the form of allyl glycosides in order to allow the coupling to various carrier molecules to give NGCs. These NGCs can then be used for building artificial membranes or neoglycoproteins[1]. Although a plethora of synthetic approaches for *O*-glycosylation have been described in variable degrees of anomeric selectivity[4]. Activated derivatives such as trichloroacetimidates[5] and halo sugars[6] have been found to react in a highly stereocontrolled manner. This is due to kinetic and thermodynamic stereoelectronic effects and *O*-acyl group at *C*-2, the stereoselectivity of this reaction is further secured.

The present paper describes the synthesis of unique 6-deoxyhexose diglycosyl allyl glycosides as sugar epitopes in order to investigate serological cross reactions between pathogenic bacteria and antibodies prepared against artificial carbohydrate antigens. It also deals with the problems of glycosidic bond formation, the regio-and stereoselectivities as well as various reactivities of donors and acceptors which depend in part on the effect of protecting groups, neighbouring group participation, through space steric interactions and amphiphilic properties. All of which make the generalizations of the glycosidation reactions rather difficult.

Results and Discussion

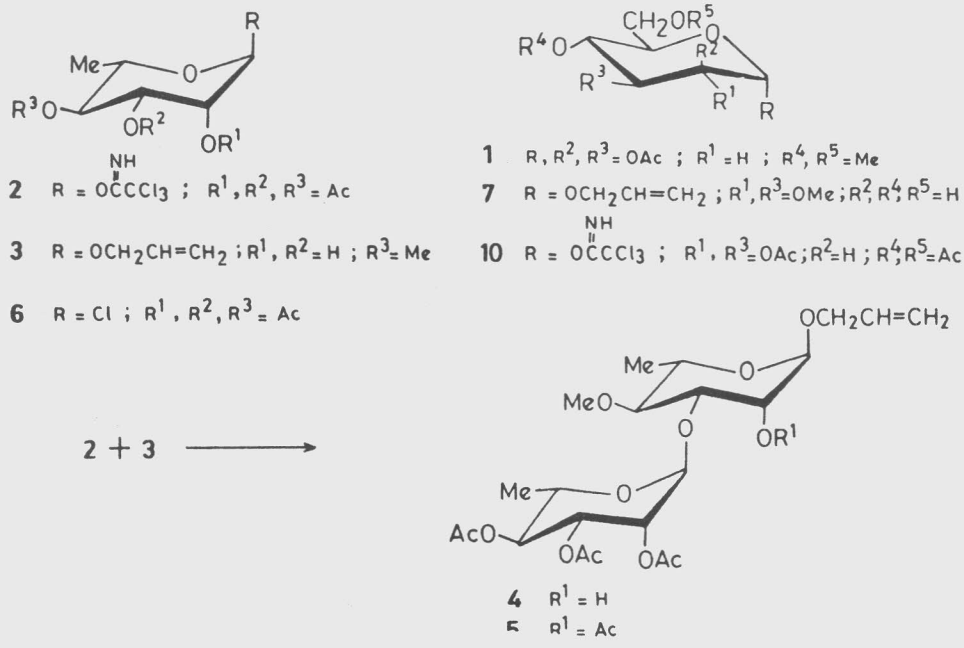
The synthesis of allyl 3-*O*-(2,3,4-tri-*O*-acetyl-α-L- rhamnopyranosyl)-4-*O*-methyl-α-L- rhamnopyranoside **4**, allyl 6-*O*-(2,3,4-tri-*O*-acetyl-α- L- rhamnopyranosyl)- 2,3-di-*O*-methyl-α-D-glucopyranoside **8** and allyl 3-*O*- (2,3,4,6-tetra-*O*-acetyl- β-D-glucopyranosyl) - 4 - *O*-methyl - α -L-rhamnopyranoside **11**, the three disaccharide fragments, which

are the object of this synthetic work are exclusively glycosides of 1,2-*trans* type. Each disaccharide has been synthesized as an allyl glycoside to allow for subsequent covalent attachment to a protein[1]. This necessitates the formation of two stereospecific glycosidic linkages in each disaccharide consistent with those portions of the *lps* corresponding to the artificial antigen. Deallylation[7] of the diglycoside followed by activation of the anomeric center[8] should also permit conversion into a glycosyl donor for chain extension reactions.

The strategy envisaged for the chemically modified disaccharide fragment, α - L-Rhap - (1→3) - α -L- Rhap, existing as a terminal disaccharide fragment of the repeating unit [(→2)-α- L-Rhap- (1→3)-α-L- Rhap (1→3)-β-D-GlcpNAc- (1→2)-α-L-Rhap →1] of the *lps O*-antigen of the bacterium *S. flexneri*[3], involved condensation of peracetylated rhamnopyranosyl trichloroacetimidate **2** [12] with 2,3-*cis*-diol **3**[1] using Lewis acid catalyst such as boron trifluoride etherate yielding the desired α-L- (1→3) linked disaccharide **4** stereo- and regioselectively in 60% yield. No additional products corresponding to the 1→2 linked disaccharide and/or trisaccharide were detected on TLC. The participating ester group at *C*-2 in the rhamnosyl donor governed the stereoselectivity of the reaction giving 1,2 - *trans* α- linked disaccharide exclusively. The 400 MHz ^{1}H NMR spectrum of compound **4** confirmed an α-mannosidic linkage by exhibiting two expected singlets for two anomeric protons at δ 4.72 and 5. 08. The presence of four singlets due to three protons each at δ 2.04, 210, 2.19 and 3.48 could be attributed to three acetoxy and one methoxy groups respectively in **4** besides the two secondary methyl doublets (6 Hz each) of 6-deoxymannose appearing at 1.16 and 1.24. The allylic methyne proton appeared as a multiplet in the region of δ 5.77-5.88 and allylic methylene protons in the region 4.96-5.04.

The nature and size of the linkage in **4** could be ascertained as 1→3 linked disaccharide and not 1→2 since the peracetylated derivative **5** of **4** showed a downfield shifting of H-2 methyne proton from δ 3.90 to 5.35 besides an additional acetoxy singlet of three protons which appeared in the ^{1}H NMR spectrum of **5**. The ability of an equatorially oriented hydroxyl group at *C*-3 in **4** to participate as a nucleophile could be explained due to lesser crowded environment while the axial hydroxyl group at *C*-2 is more sterically encumbered[13] (Scheme I).

As part of our study on the 1,2 - *trans* glycosidation reactions, the synthesis of α-mannosyldisaccharides was performed as it has special importance in relation to a class of glycoproteins[9]. Besides, the well recognized difficulty in β-mannoside synthesis, the α-selective formation of mannosidic linkages in



Scheme I

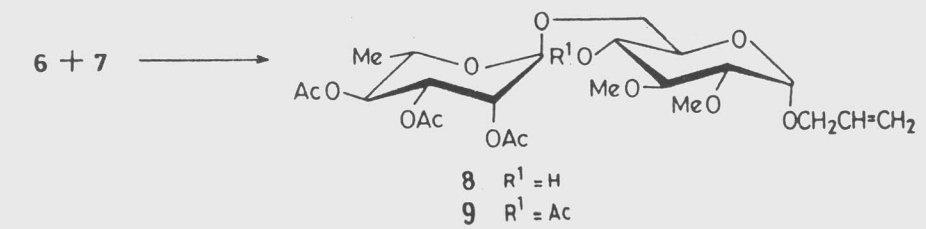
α-D-Manp- (1→3)-α-L-Rhap is also not necessarily straightforward. The initial stage of the synthesis required the mannosyl derivatives which would function as glycosyl donor upon activation, thus providing mannose at the non-reducing terminus. Thus, 2,3-di-*O*-acetyl-4,6-di-*O*-methyl- D-mannosyl chloride [synthesised from 1,2,3 tri-*O*-acetyl - 4, 6 - di-*O*-methyl-α-D-mannopyranose **1**] and **3**[2] upon condensation in the presence of silver triflate failed to afford the desired disaccharide. Also, when the former glycosyl donor was changed to peracetylated mannosyl imidate[10] and coupled with various 2,3-*cis*-diols of allyl α-L-Rhap[1] in the presence of boron trifluoride etherate, it failed to react. However, when mannose was replaced to the recducing terminal and 6-dexoymannose at the non-reducing terminal for the synthesis of α-L-Rhap- (1→3)- α-D-Manp, the corresponding disaccharide was obtained in appreciable yield[11].

For the synthesis of the terminal disaccharide fragement, α-L-Rhap-(1→6)-α- D-Glcp, of the *O* 4 specific polysaccharide from *E.coli O*4: K52[14] whose structure has been established as [→2)- α-L-Rhap-(1→6) - α- D- Glcp- (1→3)- α-L-FucpNAc- (1→3) β-D-GlcpNAc (1→], donor **6**[15] was condensed with 4,6-diol **7** [11] using 1:1 silver triflate tetramethylurea at -78°C yielding regio- and stereospecifically. the desired α- (1→6) linked disaccharide **8** in 72.5% yield. The glycosidic linkage formed in this process was produced by the reaction of *C*-6 hydroxyl group in the sugar alcohol (*su-OH*) in accordance with its order of reactivity as the reactivity of various hydroxyl groups present in *su-OH* decreases in the order *C*-6 > *C*-3 > *C*-2 > *C*-4.[16] The product was 1,2 - *trans* linked and this could be attributed to the *C*-2 ester participation[6]. The α-linkage of the diglycosyl moiety was confirmed by a singlet at δ 4.81 for H-1. Also another anomeric proton, derived from glycosyl accepter, appeared as a doublet (*J* = 3 Hz) at δ 5.02. The three acetoxy substituents were evident by singlets of three protons each at δ 1.99, 2.06 and 2.17 and a doublet with *J* = 6 Hz for secondary methyl at 1.23 was attributed to 6- deoxymannose. The two *O*-methyl substituents appeared as two singlets of three protons each at δ 3.49 and 3.64. Allylic methyne protons and allylic methylene protons appeared as a multiplet in the regions δ 5.94-6.03 and 5.26-5.38, respectively. The -OCH_2 of allyl group appeared in the region δ 3.90-3.98.

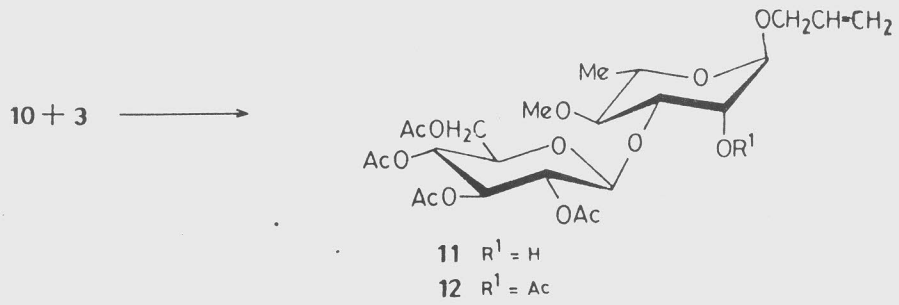
The nature of the linkage (1→6) in the rhamnosyl glucoside **8** was further confirmed by performing conventional acetylation giving *O*-4 acetylated product **9**, which was evident by its ^{1}H NMR spectrum showing a downfield shift of H-4 ring proton from δ 3.44 to 4.78 and an additonal singlet of three protons for *O*-acetyl group confirming that the disaccharide **8** was 1→6 linkage and not 1→4 (Scheme II).

The synthesis of the terminal disaccharide fragment, β-D-Glcp-(1→3)-α- L-Rhap, of the *lps* from *M. linda*[17] involved condensation of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate **10**[18] with the rhamnosyl acceptor **3**[1] using boron trifluoride etherate as an activator giving the 1,2-*trans*-β-(1→3) linked disaccharide as allyl 3-*O*- (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-*O*-methyl-α-L -rhamnopyranoside **11** in 77% yield, in a stereo-and regioselective fashion. The formation of β-glycosidic linkage in **11** was confirmed by an anomeric doublet (8 Hz) at δ 4.66 besides the H-1 singlet of α-rhamnosyl unit at 4.75 in its ^{1}H NMR spectrum. The four acetoxy substituents were evident by the appearance of singlets of three protons each at δ1.96, 1.98, 2.00 and 2.02 besides a doublet (6 Hz) and a singlet of three protons each at 1.23 and 3.38 for Me-6 of 6-deoxymannose and *O*-methyl substituent, respectively.

The ^{1}H NMR spectrum of the peracetylated derivative **12** of compound **11** gave an additional acetoxy singlet of three protons and a downfield shift of H-2 ring proton to δ 5.15 from 3.98 thereby confirming that the glycosidic linkage in **12** was indeed β (Scheme III).



Scheme II



Scheme III

Experimental Section

General. General procedures were same as reported earlier[1]. ^{1}H NMR spectra were recorded on a 400 MHz (Bruker) spectrometer in $CDCl_3$ with TMS as internal standard. 4Å molecular sieves were activated and K_2CO_3 was dried by heating to approximately 400°C in a muffle furnace and cooled to room temperature in a desicator over P_2O_5 under vacuum. All glycosidation reactions were carried out under N_2 atmosphere. Optical rotations were determined on Perkin-Elmer 241 and Jasco Dip 181 polarimeters in chloroform at ambient temperature.

1,2,3 - Tri-*O*-acetyl-4,6-di-*O*-methyl-α-D-mannopyranose 1. A solution of conc. sulphuric acid (13μL) in acetic acid (1.0 mL) was added dropwise over a period of 5 min to a solution of methyl 4,6-di-*O*-methyl- α-D mannopyranoside[19] (850 mg, 4.12 mmoles) in Ac_2O (4.0 mL) at 0°C. The mixture was stirred for 30 min at room temperature, then poured into a stirred mixture of dichloromethane (5 mL) and ice-cold saturated aqueous K_2CO_3 and the resuling mixture stirred for 30 min at room temperature. The organic and aqueous layers were extracted with dichloromethane (30 mL). The dichloromethane fractions were combined and washed successively with saturated aq. potassium carbonate and water, dried, filtered and concentrated. The residual syrup was filtered by column chromatography (9:1 light petroleum-ethyl acetate) to give **1** (900 mg. 65%) as a viscous syrup, [α]D+56.38° (*c* 0.63); ^{1}H NMR : δ 2.05, 2.12, 2.14 (3s, 9H, 3AcO), 3.42, 3.48 (2s, 6H, 2MeO), 3.60-3.75 (m, 4H, H-4 to H-6), 5.21-5.26 (m, 2H, H-2, H-3), 6.05 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1) (Found: C, 50.13; H, 6.58. $C_{14}H_{22}O_9$ requires C, 50.29; H, 6.63%).

Allyl 3-*O*-(2,3,4-tri-*O*-acetyl-α-L- rhamnopyranosyl) -4-*O*-methyl-α- L- rhamnopyranoside 4: To a stirred and cooled (0°C) mixture of **3**[1] (1.0 g, 4.58 mmoles), **2**[12] (2.71 g, 6.23 mmoles) and powdered molecular sieves (4 Å, 500 mg) in CH_2Cl_2 (5 mL) was added boron trifluoride etherate (0.7 ml, 1.25 meq) and the reaction mixture stirred overnight at room temperature. The mixtre was filtered through Celite and the pad washed with dichloromethane. The combined filtrate and washings were concentrated, and column chromatography of the residue (8:2 light petroleum:ethyl acetate) afforded **4** (1.41 g, 60%) as a viscous syrup, [α]D- 13.15°(*c* 0.38); ^{1}H NMR : δ 1.16, 1.24 (2d, 6H, $J_{5,6}$= 6Hz, Me-6, Me-6′), 2.04, 2.10, 2.19 (3s, 9H, 3AcO), 3.12 (t, 1H, $J_{3,4,5}$= 8Hz, H-4), 3.48 (s, 3H, MeO), 3.54-3.58 (m, 1H, H5), 3.84 (dd, 1H, $J_{2,3}$=3.5 Hz, $J_{3,4}$=8Hz,H-3), 3.88-3.96 (m, 2H, -OC*H*$_2$CH=CH$_2$, H-2),4.04-4.12 (m, 2H, -OC*H*$_2$CH = CH$_2$, H- 5′), 4.72 (s, 1H, H-1), 4.96-5.04 (m, 2H, -OCH$_2$CH=C*H*$_2$), 5.08 (s, 1H, H-1′), 5.15-5.24 (m, 2H, H-2′, H- 4′), 5.30 (dd, 1H, $J_{2,3}$ = 3Hz, $J_{3,4}$= 8Hz, H- 3′), 5.77-5.88 (m, 1H, -OCH$_2$C*H*=CH$_2$) (Found : C, 53. 68; H, 6.79. $C_{22}H_{34}O_{12}$ requires C, 53.87; H, 6.98%).

Allyl 2-*O*-acetyl - 3 - O - (2,3,4 - tri - *O* - acetyl -α-L-rhamnopyranosyl)- 4 - *O* - methyl - α - L - rhamnopyranoside 5. Acetic anhydride (5 mL) was added to **4** (lg, 2.04 mmoles) in pyridine (5 mL) at room temperature and the solution stirred overnight. The mixture was concentrated by co- evaporation of toluene under reduced pressure. Column chromatography of the residue with light petroleum-ethyl acetate (9.5 : 0.5) gave **5** (1.0 g, 92%) as a viscous syrup, [α]$_D$- 32°(*c* 0.18); ^{1}H NMR : δ 1.10 (d, 6H, $J_{5,6}$=6Hz, Me-6, Me-6′), 1.94, 2.06, 2.14, 2.18 (4s, 12H, 4AcO), 3.28 (t, 1H, $J_{3,4,5}$= 8 Hz, H-4), 3.55 (s, 3H, MeO), 3.60 -3.68 (m, 1H, H-5), 3.98 (dd, 1H, $J_{2,3}$ =3Hz, $J_{3,4}$ = 8 Hz, H-3), 4.08 - 4.18 (m, 2H, -OC*H*$_2$CH = CH$_2$,H- 5′), 4.28 (dd, 1H, *J* =6 Hz, *J*= 12Hz, -OC*H*$_2$CH =CH$_2$), 4.73 (d, 1H, $J_{1,2}$= 1.5 Hz, H-1), 5.12 (d, 1H, $J_{1,2}$ = 1.2Hz, H- 1′), 5.14-5.18 (m, 4H, - OCH$_2$CH=C*H*$_2$, H- 2′, H- 4′), 5.28 (dd, 1H, $J_{2,3}$=3Hz, $J_{3,4}$=8Hz, H- 3′), 5.35 (dd,

1H, $J_{1,2}$=1 Hz, $J_{2,3}$= 3Hz, H-2), 5.78-5.92 (m, 1H, -OCH_2CH = CH_2), (Found : C, 54.00; H, 6.68. $C_{24}H_{36}O_{13}$ requires C, 54. 13; H, 6.81%).

Allyl 6-*O*-(2,3,4-tri-*O*-acetyl-α-L- rhamnopyranosyl)- 2,3-di-*O*-methyl-α-D- glucopyranoside 8. A solution of *su*-OH such as allyl 2,3-di-*O*- methyl-α-D- glucopyranoside **7**[11] (900 mg, 3.62 mmoles), silver triflate (1.52 g, 5.91 mmoles), tetramethylurea (0.7 mL, 5.91 mmoles) and molecular sieves (500 mg) in dry dichloromethane (10 mL) was stirred under nitrogen for 0.5 hr. The mixture was cooled to -78°C and a solution of donor **6** [15] (1.23 g, 3.98 mmoles) in dry dichloromethane (5 mL), previously stirred for 0.5 hr under nitrogen atmosphere at -78°C was added to the acceptor flask and stirring continued for 72 hr at room temperature. The mixture was filtered through Celite and then washed with aq. $NaHCO_3$ and water, dried, filtered and concentrated. The residue was chromatographed over silica gel using 7:3 light petroleum-ethyl acetate as eluent to give **8** (1.36 g, 73%) as a viscous syrup, $[\alpha]_D$- 20°(*c* 0.2); ^{1}H NMR: δ 1.23 (d, 3H, $J_{5,6}$ =6Hz, Me-6′), 1.99, 2.06, 2.17 (3s, 9H, 3AcO), 3.26 (dd, 1H, $J_{2,3}$=6Hz, $J_{3,4}$=8Hz, H-3), 3.40-3.48 (m, 1H, H-4), 3.49 (s, 3H, MeO), 3.60 (m, 1H, H-2), 3.64 (s, 3H, MeO), 3.64-3.84 (m, 2H, H-5, H-5′), 3.90-3.98 (m, 2H, -OCH_2CH = CH_2), 4.07-4.17 (m, 1H, H-6′), 4.20- 4.28 (m, 1H, H-6), 4.81 (s, 1H, H-1′), 5.02 (d, 1H, $J_{1,2}$= 3Hz, H-1), 5.04 -5.14 (m, 1H, H-4′), 5.24 (dd, 1H, $J_{1,2}$= 1Hz, $J_{2,3}$= 3 Hz, H-2′), 5.26 - 5.38 (m, 2H, -OCH_2CH =CH_2), 5.38 (dd, 1H, $J_{2,3}$ = 2Hz, $J_{3,4}$ = 6 Hz, H- 3′), 5.94-6.03 (m, 1H - OCH_2CH = CH_2) (Found : C, 53.00; H, 6.90. $C_{23}H_{36}O_{13}$ requires C, 53.07; H, 6.97%).

Allyl 4-*O*-acetyl-6-*O*-(2,3,4 - tri - *O* - acetyl - α - L-rhamnopyranosyl) -2,3-di-*O*-methyl-α-D- glucopyranoside 9. Conventional acetylation of compound **8** (lg, 1.92 mmoles) with 1:1 pyridine- acetic anhydride (10 mL) gave a 4-*O*-acetylated product as in the case of **5**. Column chromatography of the residue with 8:2 light petroleum-ethyl acetate gave **9** (900 mg, 83%) as a viscous syrup, $[\alpha]_D$+11.5°C(*c* 0.17); ^{1}H NMR : δ 1.20 (d, 3H, $J_{5,6}$ = 6Hz, Me-6′), 2.00, 2.06, 2.16, 2.19 (4s, 12H, 4AcO) 3.30 (dd, 1H, $J_{2,3}$ - 6Hz, $J_{3,4}$ = 8Hz, H-3), 3.52, 3.54 (2s, 6H, 2MeO), 3.54-3.60 (m, 1H, H-5), 3.62 - 3.69 (m, 2H, H-2, H-5′), 3.88-3.97 (m, 2H, -OCH_2CH = CH_2), 4.17-4.20 (m, 1H, H-6), 4.28-4.35 (m, 1H, H- 6′), 4.78 (dd, 1H, $J_{3,4}$) -6Hz, $J_{4,5}$ - 8Hz, H-4), 5.03 (d, 1H, $J_{1,2}$ = 3Hz, H-1), 5.08 (s, 1H, H- 1′), 5.12- 5.20 (m, 1H, H-4′), 5.26 (dd, 1H, $J_{1,2}$ = 1Hz, $J_{2,3}$ -3Hz, H-2 ′), 5.28-5.40 (m, 3H, -OCH_2CH = CH_2, H- 3′), 5.92-6.00 (m, 1H, -OCH_2CH = CH_2) (Found : C 53.32; H, 6.65. $C_{22}H_{38}O_{14}$ requires C, 53.37; H, 6.80%).

Allyl 3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)- 4-*O*-methyl-α-L- rhamnopyranoside 11. A solution of acceptor **3**[1] (800 mg, 3.66 mmoles), glucosyl imidate **10**[18] (2.49 g, 5.06 mmoles) and molecular sieves (500 mg) in dry dichloromethane (10 mL) was stirred for 0.5 hr at O°C. Boron trifluoride etherate (0.56 mL, 1.25 meq) was added and the reaction mixture stirred overnight at room temperature as in the case of **4**. Column chromatography of the residue using 9.5:0.5 hexane-chloroform gave **11** (1.54 g, 76.5%) as an amorphous solid, m.p. 65 - 68°C, $[\alpha]_D$+25°(*c* 0.1); 1HNMR : δ 1.23 (d, 3H, $J_{5,6}$ =6Hz, Me-6), 1.96, 1.98, 2.00, 2.02(4s, 12H, 4AcO), 3.08 (t, 1H, $J_{3,4,5}$ = 8Hz, H- 4), 3.38 (s, 3H, MeO), 3.52-3.59 (m, 1H-H5), 3.64-3.66 (m, 1H, H- 5′), 3.78 (dd, 1H, $J_{2,3}$= 3Hz, $J_{3,4}$ = 8Hz, H-3), 3.94 (m, 1H, OcH_2CH=CH_2), 3.98(dd, 1H, $J_{1,2}$ = 1Hz, $J_{2,3}$ = 3Hz, H- 2), 4.05-4.16 (m, 1H, OCH_2CH = CH_2), 4.66 (d, 1H, $J_{1,2}$ = 8Hz, H- 1′), 4.75 (s, 1H, H-1), 4.94 - 5.01 (m, 2H, -OCH_2CH = CH_2), 5.05-5.14 (m, 5H, H-2′ to H- 4′, H- 6, H-6′), 5.81-5.93 (m, 1H, -OCH_2CH CH_2) (Found : C, 52.30; H, 6.91. $C_{24}H_{36}O_{14}$ requires C, 52.36; H6.95%).

Allyl 2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-4-*O*-methyl-α-L-rhamnopyranoside 12. Compound **11** (1 g, 1.82 mmoles) upon acetylation with pyridine:acetic anhydride (1:1) (10 mL) gave a product as in **5** which was chromatographed using light petroleum-ethyl acetate (9:1) to give **12** (800 mg, 74%) as an amorphous solid, m.p. 108-10°C, $[\alpha]_D$- 63.15°(*c* 0.2); ^{1}H NMR: δ 1.32 (d, 3H, $J_{5,6}$ =6Hz, Me-6), 1.98, 2.00, 2.02, 2.04, 2.06 (5s, 15H, 5AcO,), 3.14 (t, 1H, $J_{3,4,5}$=8Hz, H-4), 3.48 (s, 3H, MeO), 3.61-3.67 (m, 1H, H-5), 3.68-3.73 (m, 1H, H- 5′), 3.87 (dd, 1H, $J_{2,3}$= 3Hz, $J_{3,4}$= 8Hz, H-3) 4.12 (dd, 1H, *J* = 6Hz, *J* = 12Hz, -OCH_2CH=CH_2), 4.24 (dd, 1H, *J*=6Hz, *J* = 12Hz, -OCH_2CH = CH_2), 4.71 (d, 1H, $J_{1,2}$ = 8Hz, H- 1′), 4.74 (d, 1H, $J_{1,2}$ = 1.5Hz, H-1), 5.06 (t, 1H, $J_{3,4,5}$=8Hz, H- 4′), 5.15 (dd, $J_{1,2}$ = 1Hz, $J_{2,3}$=3Hz, H-2), 5.19- 5.24 (m, 2H, H-2′, H-3′), 5.26- 5.32 (m, 2H, H-6, H-6′), 5.84-5.92 (m, 1H,-OCH_2CH=CH_2) (Found : C, 52.79; H, 6.37. $C_{26}H_{38}O_{15}$ requires C, 52.87 ; H, 6.48%).

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