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Stereoselective Synthesis of α-Linked 2-Deoxysaccharides and Furanosaccharides by Use of 2-Deoxy 2-Pyridyl-1-Thio Pyrano- and Furanosides as Donors and Methyl Iodide as an Activator

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Key words: 2-Deoxy 2-pyridyl-1-thiopyranosides; 2-pyridyl-1-thiofuranosides, α-Linked 2-deoxysaccharides, Oleandrosyl-olenadroside, α-Linked furanosaccharides.

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Abstract : A practical and highly stereoselective glycosidation methodology is described, where anomeric mixture of 2-deoxy 2-pyridyl-1-thiopyranoside donors (**1-3,27**) have been coupled with several sugar alcohols (**4-8,29,31**) on activation by methyl iodide to obtain axially linked 2-deoxysaccharides (**9-17,30,32,33**). Application of this method for the synthesis of disaccharide fragment **28** of avermectin is also described. Utility of this method is also shown by use of 2-pyridyl-1-thiofuranosides (**34-36**) as donors to prepare α-linked furnaosides (**42-51**).

Introduction: α-Linked 2-deoxysaccharides are constituents of various naturally occurring antibiotics of therapeutic value[1]. Due to their significant role in conferring optimal biological activity to numerous antibiotics, their syntheses continue to command interest specially for studying structure activity relationship. Stereoselective synthesis of 1,2-cis glycopyranosides in general benefits from the non-participating C-2 neighbouring group[2] to forge the axial O-glycosidic bond; evidently the particular problem in the chemical synthesis of 2-deoxysaccharides is the missing neighbouring group which is also associated with enhanced lability. The efficient methods[3,4] so far developed involve iodo-[5] and selenoglycosylation[6] of glycals followed by reduction to obtain the α-linked 2-deoxysaccharides. 2,6-Dideoxy glycosyl fluoride[7] as a donor has also been successfully used for achieving α-selectivity; however the 2-deoxy chloro- and bromoglycosyl donors were found to be labile and have exhibited low selectivity[8]. We have recently introduced a novel method of activating 2-pyridyl 1-thioglycopyranosides which appears to be full of promise in the area of glycoside synthesis[9]. We report here that the so-called "methyl iodide activation procedure of pyridyl thioglycosides" is the method of choice also for the synthesis of α-linked 2-deoxysaccharides and furanosaccharides. Thiophillic metal and proton mediated glycosidation of 2-deoxy 2-pyridyl-1-thioglycosides have earlier resulted in the formation of anomeric mixture[10].

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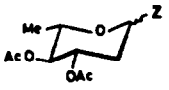
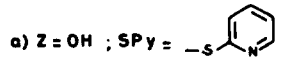
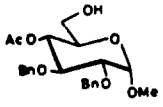
Results and Discussion: 2-Deoxy 2-pyridyl 1-thioglycosyl donors **1-3** and **27** required for glycosylations are easily accessible either by 1,2-addition of 2-mercaptopyridine to substituted glycals[11] or from the reaction of 2-deoxyglycosides with 2,2'-dithiodipyridyl/nBu_3P[10a]. Donors **1-3,27** were found to be highly stable and possessed a very long shelf life, which merits their use over other conventional donors such as glycosyl halides.

1 X = H , Y = OAc , Z = SPy
2 X = OAc , Y = H , Z = SPy



3 Z = SPy

a) Z = OH ; SPy = 



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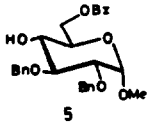

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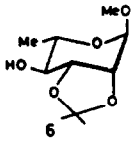

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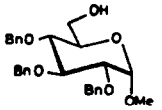

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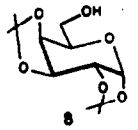

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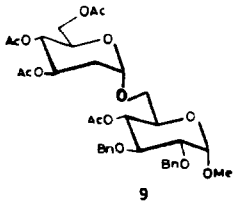

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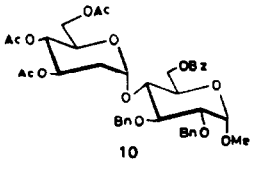

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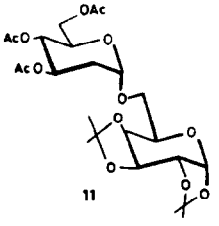

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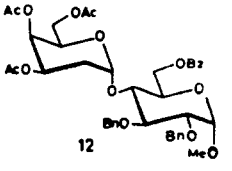

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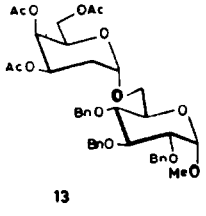

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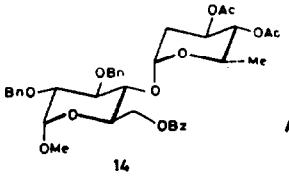

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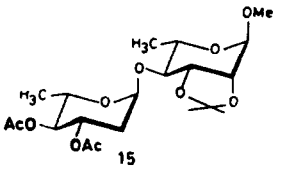

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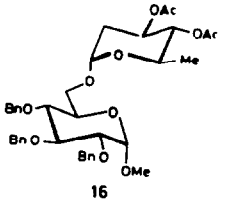

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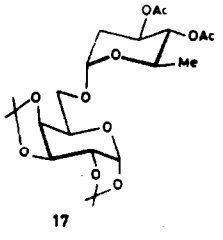

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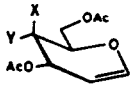
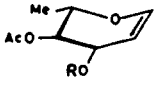


18 X = H , Y = OAc
19 X = OAc , Y = H

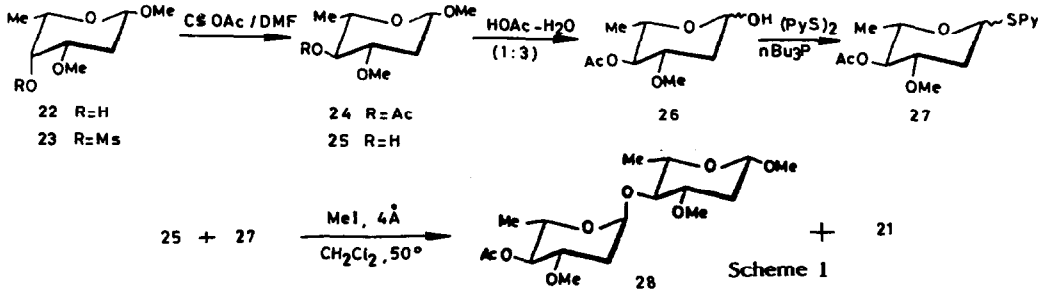


20 R = Ac
21 R = CH_3

The coupling[12] of donors **1-3** (α/β mixture) with several sugar alcohols **4-8**[23,24] having divergent reactivity and protecting groups was performed in dichloromethane at 50°C in presence of methyl iodide and molecular sieves (4 A) to obtain nine α-linked 2-deoxysaccharides (**1+4=9, 1+5=10, 1+8=11, 2+5=12, 2+7=13, 3+5=14, 3+6=15, 3+7=16, 3+8=17**) in good yields (65-87%). The diasaccharides **11** and **17** were however obtained as anomeric mixtures where the α-anomers predominated (α/β ca. 85/15, by ^{1}H-n.m.r.). The reactivity of 2-deoxy donors **1-3** and **27** was found to be higher compared to the corresponding 2-O-substituted ethers[12], the coupling reactions being complete in 16-22 h. It was also observed that during the coupling reactions 2,6-dideoxy donors **3** and **27** alone showed the formation of 1,2-elimination products **18** and **19** respectively (5-8%), which however can be recycled[11]. Tri-O-acetyl-D-glucal (**20**)[13], -D-galactal-(**21**)[14], di-O-acetyl-L-rhamnal (**18**)[15] and 3-O-methyl-4-O-acetyl- L-oleandrose (**19**) have been the sole products (80-85%) when **1-3** and **27** respectively were reacted with methyl iodide in dichloromethane (50°C) in the absence of a nucleophile. Thus, the ability to add (1,2-addition)[11] and eliminate 2-mercaptopyridine represents a new protection and deprotection procedure of glycals. Presence of traces of water resulted in the rapid hydrolysis (45°C, 2h) of the 2-pyridyl 1-thioglycosyl donors **1-3** and **26** to the corresponding 2-deoxyglycosides **1a-3a** and **27** respectively.

Formation of α-linkage at the newly formed O-glycosidic bond was established based on the ^{1}H-n.m.r. data where the H-1' appears as a doublet (J_{1e2a}=2.5-3.6 Hz); where as the corresponding β-anomer appears as a double doublet ($J_{1a,2a}$=9-11 Hz, $J_{1a,2e}$=0-1.5 Hz)[16]. The ^{13}C-n.m.r. data also supports the formation of α-linkage from the appearence of C-1' (α-anomer) at ca. δ 97.0-100.0, whereas the corresponding β-anomer at ca.δ 102.0-105.0. The 2-D, ^{1}H-^{1}H COSEY correlation spectra for the disaccharides **9, 10, 13, 14** and **16** were also obtained to assign the chemical shift and coupling constants of H-1' specially when the signals were hidden.

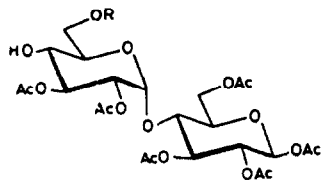
Efficacy of this methodology was also demonstrated by synthesising the disaccharide fragment **28** of the antiparasitic agent avermectin[17] (Scheme 1). D-Glucose was converted to the known methyl 2,6-dideoxy-3-O-methyl-β-L-arabinopyranoside (**22**)[18] in five steps and mesylated to obtain **23** as a crystalline compound. Reaction of **23** with CsOAC in DMF[19] at 100° gave the required S_N2 bimolecular inversion product **24**, which served as a key intermediate for the synthesis of the disaccharide **28**. Deacetylation of **24** gave the glycosyl acceptor **25**, which on further acid catalysed hydrolysis provided the glycoside **26**. **26** on reaction with 2,2'-dithiodipyridyl/nBu_3P gave the required 2-pyridylthio donor **27**[10a] (α / β, 2/3). Glycoside



Scheme 1

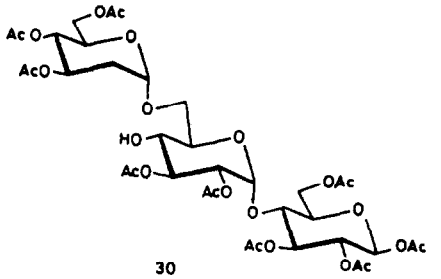
coupling of **25** with **27** in dichloromethane containing methyl iodide (20h) gave the crystalline disaccharide **28**[17] (m.p. 100-101°C, 78%) along with **19** (8%) as a by-product. Formation of α-linkage was evident[17] from the ^{1}H-n.m.r. spectrum by the appearence of H-1' as a doublet at δ 5.4 with a coupling of $J_{1'2'}$=2.8 Hz, and also from the ^{13}C-n.m.r. spectrum where C-1' appeared at δ 98.5.

Saccharide coupling was also performed by use of disaccharide acceptors **29** and **31**. Thus reaction of **29**[20] with the donor **1** gave the trisaccharide **30**, likewise the coupling of donor **3** with acceptors **29**[21] and **31**[22] respectively was also carried out to obtain the corresponding α-linked trisaccharides **32** and **33** by this methodology.



29 R = H

31 R = Bz



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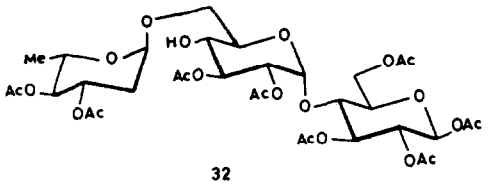

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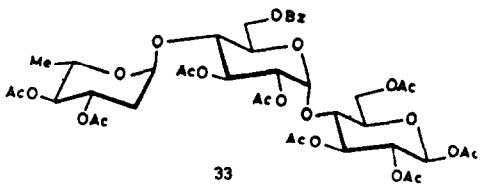
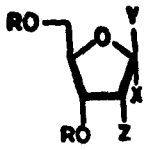


33

Synthesis of α-linked furanosaccharides[25,26] was also carried out successfully by this methodology. The furanosyl donors per O-benzyl 2-pyridyl-1-thio-β-D-ribofuranoside (**34**), 2-pyridyl 3,5-di-O-benzoyl-1-thio-2-deoxy-α/β-D-ribofuranoside (**35**) and 2-pyridyl 2,3:5,6-di-O-isopropylidene-1-thio-β-D-mannofuranoside (**36**) as stable glycosyl donors were prepared from D-ribose, 2-deoxy-D-ribose and D-mannose respectively. Accordingly 2,3,5-tri-O-benzoyl-α-D-ribofuranosyl-bromide (**37**)[27] was treated with 2-mercaptopyridine in presence of K_2CO_3 in toluene-acetone to give 2-pyridyl 2,3,5-tri-O-benzoyl-1-thio-β-D-ribofuranoside (**38**), which on debenzoylation and subsequent benzylation afforded the donor **34**. Similarly, methyl 2-deoxy-α/β-D-ribofuranoside[28] was benzoylated to give **39**, and subsequently hydrolysed with aq. AcOH to furnish the reducing sugar **40**. Reaction of **40** with 2,2'-dipyridyl disulphide/n-Bu_3P in CH_2Cl_2 afforded **35**. The mannofuranosyl donor **36** was prepared in one step from the known 2,3:5,6-di-O-isopropylidene-β-D-mannofuranoside (**41**)[29] on reaction with 2,2'-dipyridyldisulphide. The furanosyl donors **34-36** have been characterised fully from the spectral data. In the ^{1}H NMR spectrum of **34**, H-1 appeared at δ 6.23 as a doublet ($J_{1,2}$=3.3 Hz) while H-1 in compound **36** resonated at δ 5.8 as a doublet ($J_{1,2}$=3.7 Hz) whereas **35**, obtained as anomeric mixture (α/β 1/1) was indicated from the ^{1}H NMR spectrum where H-1 (β) appeared at δ 6.17 (dd, $J_{1,2}$=5.5 Hz) and



34 X = H, Y = 2-S-Py, Z = OBn, R = Bn ;

35. X/Y = 2-S-Py, Z = H, R = Bz

36. X = H, Y = 2-S-Py

41. X = H, Y = OH

37 X = Br, Y = H, Z = OBz, R = Bz

38. X = H, Y = 2-S-Py, Z = OBz, R = Bz

39 X = Z = H, R = Bz, Y = OCH_3

40. X / Y = OH, Z = H, R = Bz

42 Y = H, Z = OBn, R = Bn, X = a

43 Y = H, Z = OBn, R = Bn, X = b

44 Y = H, Z = OBn, R = Bn, X = c

45 Y, Z = H, R = Bz, X = a

46 Y, Z = H, R = Bz, X = b

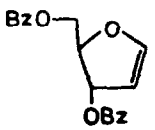
47 Y, Z = H, R = Bz, X = c

48 Y, Z = H, R = Bz, X = d

49 Y = H, X = a

50. Y = H, X = b

51 Y = H, X = c



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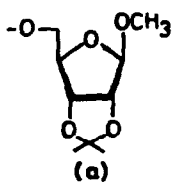

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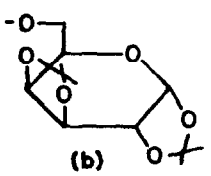

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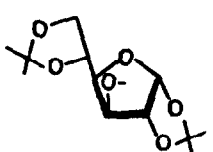

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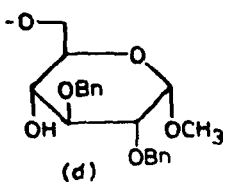

(d)

H-1 (α) at δ 6.55 as a triplet ($J_{1,2}$=4.0 Hz) together integrating for one proton. **34-36** have been found to be highly stable indefinetely at room temperature, they were subjected to glycosidation reaction with a variety of sugar alcohols (**a-d**) in CH_2Cl_2, using methyl iodide as activator to afford α-linked furanosaccharides **42-51**[12].

Thus, glycosidation of **34** and **36** with acceptors such as methyl 2,3-O-isopropylidene-β-D-ribofuranoside (**a**)[30], 1,2:3,4-di-O-isopropylidene-D-galactopyranoside (**b**)[14] and 1,2:5,6-di-O-isopropylidene-α-D-glucofuranoside (**c**)[9] gave the α-ribofuranodisaccharides **42-44** and **49-51** respectively. Likewise, donor **35** on reaction with **a,b,c** and methyl 2,3-di-O-benzyl-α-D-glucopyranoside (**d**)[31] furnished the 2-deoxyribofuranodisaccharides (**45-48**) respectively, along with 1,4-anhydro-2-deoxy-3,5-di-O-benzoyl-D-erythro-pent-1-enitol (**52**)[32] in small amount (6-9%).

Structures of the furanodisaccharides **42-51** have been fully characterised from the ^{1}H, ^{13}C-NMR and optical rotation. In the ^{1}H-NMR spectra of ribodisaccharides **42-44**, H-1' from the newly formed glycoside linkage, appeared at δ 5.05, 5.15 and 5.16 respectively as doublets ($J_{1',2'}$ = 4.6 Hz), while C-1' in ^{13}C-NMR resonated at ca. δ102.0 that are characteristic of α-linked ribofuranosides[33]. Similarly, the manno-disaccharides (**49-51**) exhibited H-1' at δ 5.07, 4.95 and 5.31 respectively as singlets in ^{1}H-NMR, while C-1' resonated at ca. δ 106.6 in the ^{13}C-NMR. The H-1' signals of the 2-deoxyribosaccharides (**45-48**) in ^{1}H-NMR spectra appeared at δ 5.15, 5.23, 5.30 and 5.15 as broad singlets, while C-1' in ^{13}C-NMR was indicated at ca. δ97.7. In the ^{1}H-NMR spectrum of the by-product **52**, the chemical shift for H-1 appeared at δ6.65 as a doublet ($J_{1,2}$=5.4 Hz) while H-2 signal resonated at δ 5.10 as a double doublet ($J_{2,3}$=4.4 Hz) indicating the presence of cyclic enol ether[32] in **52**.

This method of glycosylation offers considerable variation in the use of the donor and acceptor. Stability, easy preparation of the donors and their use as anomeric mixture makes this method very attractive and practical.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. NMR spectra (^{1}H and ^{13}C) were recorded for solutions in $CDCl_3$ (internal Me_4Si) on Varian 200 Gemini spectrometer (^{1}H-200 MHz, ^{13}C-50 MHz) or Varian MSL 300 (^{1}H-300 MHz, ^{13}C-75 MHz). Optical rotations were measured on a JASCO DIP 360 or 370 polarimeter using sodium vapor lamp. Chromatographic purifications were done with silica gel (60-120 mesh, Acme) while flash chromatography on silica gel (finer than 200 mesh, Acme). TLC was performed on silica gel 60 F_{254} (Merck) with detection by spraying a solution of 2% phosphomolybdic acid, 1% $Ce_2SO_4 \cdot 4H_2O$ in 20% aq. H_2SO_4 and heating the plates at 130°. All the reactions were carried out in anhydrous solvents unless otherwise stated. Typical experimental procedures as described earlier[12] have been followed.

2-Deoxy-3,4,6-tri-O-acetyl-α/ β-D-glucopyranoside (1a) - ^{1}H-n.m.r. (80 MHz, δ in ppm, J in Hz):1.7-1.9 (ddd, 1H, $J_{1,2a}$=3.1, $J_{2a,3}$=12.9, $J_{2,2gem}$=16.6, H-2a), 2.02, 2.08, 2.1 (3s, 9H, 3xOCOCH_3), 2.2-2.35 (ddd, 1H, $J_{1,2e}$=1.0, $J_{2e,3}$=5.3, H-2e), 3.65 (br.s, 1H, OH), 4.0-4.4 (m, 3H, H-5,6,6), 4.9-5.1 (m, 2H, H-1,4), 5.4 (m, 1H, H-3).

2-Deoxy-3,4,6-tri-O-acetyl-α/β-D-galactopyranoside (2a) - ^{1}H-n.m.r. (80 MHz, δ in ppm, J in Hz):1.6-2.3 (m, 2H, H-2, hidden), 1.91, 2.02, 2.1 (3s, 9H, OCOC$\underline{H_3}$x3), 3.24 (br.s, 1H, OH), 3.9-4.2 (m, 3H, H-5,6,6), 4.38 (dd, 0.5H, $J_{1,2a}$=8.0, $J_{1,2e}$=1.5, H-1β), 4.8 (m, 0.5H, H-1,α), 5.1-5.35 (m, 1H, H-1).

2,6-Dideoxy-3,4-di-O-acetyl-α/β-L-rhamnopyranoside (3a) - ^{1}H-n.m.r. (80 MHz, δ in ppm, J in Hz):1.1-1.2 (d, 3H, $J_{5,6}$=6.1 Hz, H-6), 1.8-2.25 (m, 2H, H-2), 2.05, 2.08, 2.1, 2.18 (4s, 6H, OCOC$\underline{H_3}$), 4.0-4.2 (m, 1H, H-5), 4.25-5.25 (m, 2.5H, H-3,4 and H-1α), 5.45 (m, 0.5H, H-1β).

Methyl 6-O-(3,4,6-tri-O-acetyl-2-deoxy- α-D-arabinohexopyranosyl)-4-O-acetyl-2,3-di-O-benzyl-α-D-glucopyranoside (9): Coupling of donor **1**[11] (0.4 g, 1.06 mmol) with the acceptor **4**[22] (0.44 g, 1.1 mmol) (22 h) afforded **16** (0.44 g, 68%) as a syrup after column chromatographic purification (SiO_2, hexane/ethyl acetate 4/1). $[\alpha]_D$ + 65° (c 0.4, $CHCl_3$). ^{1}H-n.m.r. (300 MHz, δ in ppm, J in Hz): 1.8 (ddd, 1H, $J_{1',2'a}$=3.6, $J_{2'a3'}$=11.5, $J_{2',2'}$=16.7, H-2' ax), 1.90, 1.99, 2.03, 2.04 (4s, 12H, OCOC$\underline{H_3}$ x 4), 2.25 (ddd, 1H, $J_{1'2e'}$=1.2, $J_{2'e3'}$=5.4, H-2' eq), 3.45 (s, 3H, OC$\underline{H_3}$), 3.4-4.4 (m, 8H, H-2,3,5,5',6,6'), 4.5-5.0 (m, 9H, H-1,4,1',3',4' and O$\underline{CH_2}$Phx2), 4.85 (br.s, 1H, H-1' signal hidden, assigned from 2D, COSEY, 'H-'H correlation spectrum), 5.25 (ddd, 1H, $J_{2'e,3}$=5.4, $J_{2a,3'}$=9.5, $J_{3',4'}$=11.4, H-3'), 7.2-7.4 (m, 10H, aromatic); ^{13}C-n.m.r. (75 MHz) (δ in ppm): 20.4, 20.5, 20.6 (4q, OCO$\underline{CH_3}$x4), 34.6 (t, C-2'), 55.1 (q, OCH_3), 62.1, 66.3 (t, O$\underline{CH_2}$Ph), 96.5 (d, C-1), 97.7 (d, C-1'), 127.0-139.0 (aromatic), 169.5, 169.6, 170.4 (4s, O$\underline{CO}$CH$_3$x4). Anal Calcd. for $C_{35}H_{44}O_{14}$: C, 61.03; H, 6.44. Found: C, 60.96; H, 6.39%.

Methyl 4-O-(3,4,6-tri-O-acetyl-2-deoxy- α-D-arabino-hexopyranosyl)-6-O-benzoyl-2,3-di-O-benzyl-α-D-glucopyranoside (10) - Coupling of donor **1** (0.42 g, 1.1 mmol) with the acceptor **5**[21] (0.58 g, 1.2 mmol) for 30 h afforded **10** (0.56 g, 68%) as a syrup after chromatographic purification (SiO_2, hexane/ethyl acetate 9/2), $[\alpha]_D$ + 61° (c 0.63, $CHCl_3$), ^{1}H-n.m.r. (300 MHz) (δ in ppm, J in Hz): 1.67 (ddd, 1H, $J_{1'2'a}$=3.9, $J_{2'a,3}$=11.7, $J_{2',2'}$=16.9, H-2' ax), 1.9, 2.0, 2.01 (3s, 9H, OCOC$\underline{H_3}$x3), 1.98-2.04 (1H, hidden, H-2' eq), 3.4 (s, 3H, OCH_3), 3.71 (dd, 1H, $J_{3,4}$=8.8, $J_{4,5}$=9.0, H-4), 3.8 (dd, 1H, $J_{1,2}$=3.5, $J_{2,3}$=9.6, H-2), 3.85-4.1 (m, 5H, H-3,5,6, 5',6'), 4.28 (dd, 1H, $J_{6,6'}$=12.5, $J_{5,6}$=4.0, H-6 or 6'), 4.43 (dd, 1H, $J_{6',6'}$=11.5, H-6 or 6'), 4.5-4.8 (m, 4H, H-1, O$\underline{CH_2}$Ph), 4.92 (dd, 1H, $J_{3',4'}$=9.6, $J_{4',5'}$=9.8, H-4'), 5.05 (d, 1H, OCH_2Ph), 5.25 (ddd, 1H, $J_{2'e3'}$=5.1, $J_{2'a3}$=9.4, $J_{3',4'}$=11.6, H-3'), 5.48 (br.d, 1H, $J_{1'2'a}$=2.78, H-1'), 7.3-8.1 (m, 15H, aromatic). ^{13}C-n.m.r. (75 MHz) (δ in ppm) : 20.4, 20.5, 20.7 (3q, OCO$\underline{CH_3}$x3), 35.0 (t, C-2'), 55.1 (q, OCH_3), 62.1, 63.7 (t, OCH_2Ph), 68.1, 68.6, 68.9, 69.0, 77.1, 80.1, 81.62 (7d, C-2,3,4,5, 3',4',5'), 73.0, 75.4 (2t, C-6,6'), 97.5 (d, C-1), 127.0-139.0 (aromatic), 166.0, 169.6, 169.9, 170.4 (4s, O$\underline{CO}$CH$_3$x3, O$\underline{CO}$Ph). Anal. Calcd. for $C_{40}H_{46}O_{14}$: C, 63.99; H, 6.18. Found: C, 63.87; H, 6.09%.

1,2:3,4-Di-O-isopropylidene-6-O-(3,4,6-tri-O-acetyl-(2-deoxy- α / β-D-arabinohexopyranosyl)-α-D-galactopyranoside (11) - Coupling of **1** (0.4 g, 1.06 mmol) with the acceptor **8**[13b] (0.3 g, 1.16 mmol) for 18 h gave the 2-deoxysaccharide **11** (0.49 g, 88%) (α/β) as a syrup after column chromatographic purification (SiO_2, hexane/ethyl acetate, 4/1), $[\alpha]_D$ + 10.4° (c 1.0, CH_3OH), ^{1}H-n.m.r. (90 MHz) (α/β, 85/15) (δ in ppm, J in Hz):1.26x2, 1.62x2 (2s, 12H, $O_2C\underline{Me}_2$x2), 1.71-1.85 (m, 1H, H-2' ax), 1.92-2.05 (3s, 9H, OCO$\underline{CH_3}$x3), 2.10-2.33 (m, 1H, H-2' eq), 3.33-5.42 (m, 12H, H-2,3,4,5,6,1',3',4',5',6'), 5.5 (d, 1H, $J_{1,2}$=5.0, H-1); ^{13}C-n.m.r. (22.63 MHz) (δ in ppm)

(α/β): 20.5x2, 20.7 (3q, OCO$\underline{C}H_3$x3), 24.3, 24.8, 25.9x2 (4q, $O_2\underline{C}Me_2$x2), 34.9 (t, C-2'), 36.0 (t, C-2' isomer), 62.4, 66.3 (2t, C-6,6'), 68.0, 69.2, 69.6, 70.5, 70.7, 71.0 (7d, C-2,3,4,5,3',4',5'), 96.3 (d, C-1), 97.0 (d, C-1'), 100.0 (d, C-1' β anomer), 108.5, 109.3 (2s, $O_2\underline{C}Me_2$x2), 169.8, 170.0, 170.5 (3s, O$\underline{C}OCH_3$x3). Anal. Calcd. for $C_{24}H_{36}O_{13}$: C, 54.13; H, 6.81. Found: C, 54.07; H, 6.79%.

Methyl 4-O-(3,4,6-tri-O-acetyl-2-deoxy- α-D-lyxo-hexopyranosyl)-6-O-benzyol-2,3-di-O-benzyl-α-D-glucopyranoside (12) - Coupling of **2**[11] (0.44 g, 1.06 mmol) with the acceptor **5**[21] (0.56 g, 1.17 mmol) for 24 h afforded **12** (0.51 g, 68%) as a syrup after chromatographic purification (SiO_2, benzene/ethyl acetate, 4/1), $[\alpha]_D$ + 76° (c 1.1, $CHCl_3$), ^{1}H-n.m.r. (300 MHz) (δ in ppm, J in Hz):1.9-2.05 (m, 2H, H-2'ax, 2'eq), 1.96, 1.97, 2.08 (3s, 9H, OCO$\underline{CH_3}$x3), 3.38 (s, 3H, O$\underline{CH_3}$), 3.54 (dd, 1H, $J_{1,2}$=3.5, $J_{2,3}$=9.6, H-2), 3.72 (dd, 1H, $J_{3,4}$=9.7, $J_{4,5}$=9.9, H-4), 3.9-4.05 (m, 5H, H-5,6,6'), 4.26 (m, 1H, H-5'), 4.42 (dd, 1H, $J_{3',4'}$=5.0, $J_{4',5'}$=12.0, H-4'), 4.6-4.8 (m, 8H, H-1, 3, OCH_2Phx1.5), 5.1 (d, 1H, OCH_2Ph), 5.3 (ddd, 1H, $J_{2'a,3'}$=7.5, $J_{2',e3'}$= 3.0, $J_{3',4'}$=5.0, H-3'), 5.5 (d, 1H, $J_{1'2'a}$=3.0, H-1'), 7.2-8.0 (m, 15H, aromatic); ^{13}C-n.m.r. (75 MHz) (δ in ppm) : 20.4, 20.5, 20.7 (3q, OCO$\underline{C}H_3$x3), 30.4 (t, C-2'), 55.2 (q, OCH_3), 65.8, 66.4, 67.6, 68.3, 77.2, 80.2, 81.6 (7d, C-2,3,4,5,3',4',5'), 62.1, 63.8, 73.1, 75.5 (4t, C-6,6' and O$\underline{C}H_2$Phx2), 97.6 (d, C-1), 99.7 (d, C-1'), 127.0-139.0 (aromatic), 166.0, 169.8, 170.0, 170.3 (4s, O$\underline{C}OCH_3$x3, O$\underline{C}$OPh). Anal. Calcd. for $C_{40}H_{46}O_{14}$: C, 63.99; H, 6.18. Found: C, 63.87; H, 6.08%.

Methyl 6-O-(3,4,6-tri-O-acetyl-2-deoxy-α-D-lyxo-hexopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (13) - Coupling of donor **2**[11] (0.4 g, 1.06 mmol) with the glycosyl acceptor **7**[23] (0.55 g, 1.17 mmol) for 20 h gave **13** (0.56 g, 71%, as a colourless syrup after work-up and chromatographic purification (SiO_2, hexane/ethyl acetate, 7/3), $[\alpha]_D$ +86° (c 0.18, $CHCl_3$), ^{1}H-n.m.r. (300 MHz), (δ in ppm. J in Hz): 1.90 (ddd, 1H, $J_{1',2'a}$ = 2.8, $J_{2'a,3'}$ = 6.0, $J_{2',2'}$ = 13.0, H-2'ax), 1.95, 1.98, 2.12 (3s, 9H, OCO$\underline{CH_3}$x3), 2.0 (dd, 1H, H-2' eq, hidden), 3.4 (s, 3H, OCH_3), 3.48 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.48, H-4), 3.52 (dd, 1H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.6, H-2), 3.6 (d, 1H, H-6), 3.78 (m, 2H, H-6,6'), 3.95-4.05 (m, 3H, H-3,5,6'), 4.6-5.0 (m, 8H, H-1,5', OCH_2Phx3), 5.05 (d, 1H, H-1'), 5.21-5.30 (m, 2H, H-3',4'), 7.25 -7.38 (m, 15H, aromatic); ^{13}C-n.m.r (75 MHz), (δ in ppm):20.5, 20.6x2 (3q, OCO$\underline{C}H_3$x3), 29.9 (t, C-2'), 54.9 (q, OCH_3), 62.2x2, 73.1, 74.7, 75.5 (5t, C-6,6', OCH_2Phx3), 66.0, 66.5, 66.6, 69.6, 77.8, 79.9, 81.9 (7d, C-2,3,4,5,3',4',5'), 97.4 (d, C-1), 97.7 (d, C-1'), 127.0-139.0 (aromatic), 169.8, 170.1, 170.2 (3s, O$\underline{C}OCH_3$x3). Anal Calcd. for $C_{40}H_{48}O_{13}$: C, 65.20; H, 5.88. Found: C, 65.11; H, 5.78%.

Methyl 4-O-(3,4-di-O-acetyl-2,6-dideoxy-α -L-arabinohexopyranosyl)-6-O-benzoyl-2,3-di-O-benzyl-α-D-glucopyranoside (14) - Saccharide coupling of donor **3**[11] (0.41 g, 1.25 mmol) with the acceptor **5** (0.66 g, 1.38 mmol) for 28 h afforded **14** ().34 g, 66%) as a syrup after chromatographic purification (SiO_2, hexane/ethyl acetate, 4/1), $[\alpha]_D$ -28° (c 0.8, $CHCl_3$); ^{1}H-n.m.r. (300 MHz) (δ in ppm, J in Hz): 0.8 (d, 3H, $J_{5',6'}$ = 6.5, H-6'), 1.75 (ddd, 1H, $J_{1',2'a}$ = 3.5, $J_{2'a,3'}$ = 11.0, $J_{2',2'}$ = 13.0, H-2'ax), 2.0x2 (2s, 6H, OCO$\underline{CH_3}$ x 2), 2.2 (ddd, 1H, $J_{1',2e}$ = 0.9, $J_{2'e,3'}$ = 5.0, H-2'e), 3.4 (s, 3H, OCH_3), 3.6 (dd, 1H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.4, H-2), 3.75 (dd, 1H, $J_{3,4}$ = 9.7, H-3), 3.8-4.35 (m, 4H, H-4,5,6,5'), 4.5-4.8 (m, 6H, H-1,6,4', OCH_2Phx1.5), 5.05 (br.s, 1H, $J_{1',2'a}$ = 3.5, H-1'), 5.1 (d, 1H, OCH_2Ph), 5.25 (ddd, 1H, H-3'), 7.3-8.2 (m, 15H, aromatic). ^{13}C-n.m.r. (75 MHz) (δ in ppm) : 17.2 (q, C-6'), 20.6, 20.8 (2q, OCO$\underline{CH_3}$x2), 35.4 (t, C-2'),

55.2 (q, OCH_3), 63.2, 73.2, 75.5 (3t, C-6, $O\underline{C}H_2Phx2$), 96.8 (d, C-1), 97.7 (d, C-1'), 127.0-138.0 (aromatic), 165.9, 169.8, 170.0 (3s, $O\underline{C}OCH_3x2$, $O\underline{C}OPh$). Anal. Calcd. for $C_{38}H_{44}O_{12}$: C, 65.88; H, 6.40. Found: C, 65.84; H, 6.36%.

Methyl 4-O-(3,4-di-O-acetyl-2,6-dideoxy- α -L-arabino-hexopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside (15) - Coupling of the donor **3** (0.38 g, 1.2 mmol) with the acceptor **6**[24] (0.29 g, 1.3 mmol) for 18 h gave **15** (0.41 g, 81%) as a colourless syrup, after column chromatographic purification (SiO_2, hexane/ethyl acetate, 4/1), $[\alpha]_D$ -121° (c 1.0, $CHCl_3$), ^{1}H-n.m.r. (300 MHz) (δ in ppm, J in Hz); 1.17 (d, 3H, $J_{5,6}$ = 6.28, H-6), 1.31 (d, 3H, $J_{5,6'}$ = 6.24, H-6'), 1.33, 1.54 (2s, 6H, $O_2C\underline{Me}_2$), 1.8 (ddd, 1H, $J_{1',2'a}$ = 3.1, $J_{2'a,3}$ = 12.9,, $J_{2',2'}$ = 16.6, H-2' ax), 2.01, 2.05 (2s, 6H, $OCO\underline{CH}_3$ x 2), 2.22 (ddd, 1H, $J_{2'e,3}$ = 5.3, $J_{2'e,1'}$ = 1.0, H-2'e), 3.38 (s, 3H, OCH_3), 3.47 (m, 1H, H-4), 3.67-3.85 (m, 2H, H-5,5'), 4.08 (dd, 1H, $J_{1,2}$ = 0.58, $J_{2,3}$ = 5.6, H-2); 4.16 (dd, 1H, $J_{3,4}$ = 7.1, H-3), 4.73 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.6, H-4'), 4.85 (d, 1H, H-1), 5.18 (ddd, 1H, H-3'), 5.49 (dd, 1H, $J_{1',2'a}$ = 3.1, $J_{1',2e}$ = 1.0, H-1'). ^{13}C-n.m.r. (22.63 MHz) (δ in ppm); 17.5, 18.1 (2q, C-6,6'), 20.7, 20.9 (2q, $OCOCH_3x2$), 26.3, 27.9 (2q, $O_2C\underline{Me}_2$), 35.6 (t, C-2'), 54.7 (q, OCH_3), 64.0, 66.2, 69.1, 75.0, 76.2, 77.3, 78.8 (7d, C-2,3,4,5,3',4',5'), 95.3 (d, C-1), 98.3 (d, C-1'), 109.5 (s, $O_2\underline{C}Me_2$), 170.1 (2s, $O\underline{C}OCH_3x2$). Anal. Calcd. for $C_{20}H_{32}O_{10}$; C, 55.54; H, 7.45. Found: C, 55.48; H, 7.32%.

Methyl 6-O-(3,4-di-O-acetyl-2,6-dideoxy- α -L-arabinohexopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (16) - Coupling of donor **3** (0.4 g, 1.25 mmol) with the acceptor **7**[23] (0.64 g, 1.38 mmol) for 24 h gave **21** (0.6 g, 74%) as a syrup after column chromatographic purification (SiO_2, hexane/ethyl acetate 9/1), $[\alpha]_D$ - 18° (c 1.0, $CHCl_3$), ^{1}H-n.m.r. (300 MHz) (δ in ppm, J in Hz) : 1.12 (d, 3H, $J_{5',6'}$ = 6.5, H-6'), 1.7 (ddd, 1H, $J_{1',2'a}$ = 3.6, $J_{2'a,3'}$ = 11.0, $J_{2',2'}$ = 13.0, H-2'a), 2.0, 2.1 (2s, 6H, $OCO\underline{CH}_3x2$), 2.22 (ddd, 1H, $J_{2'e,3'}$ = 5.3, H-2'e), 3.4 (s, 3H, OCH_3), 3.48-3.51 (m, 3H, H-3,5,5'), 3.7-4.1 (m, 4H, H-3,4,6), 4.5-5.1 (m, 9H, H-1,1',4' and $O\underline{C}H_2Phx3$), 5.25 (ddd, 1H, $J_{2'e,3'}$ = 2.0, $J_{3',4'}$ = 11.7, H-3'), 7.2-7.4 (m, 15H, aromatic); ^{13}C-n.m.r. (75 MHz) (δ in ppm): 17.8 (q, C-6'), 20.7, 20.9 (2q, $OCO\underline{C}H_3x2$), 35.2 t, C-2'), 55.1 (q, OCH_3), 66.3, 73.3, 74.9, 75.6 (4t, C-6, $O\underline{C}H_2Phx3$), 65.5, 69.0, 69.9, 74.8, 77.8, 80.2, 82.4 (7d, C-2,3,4,5, 3',4',5'), 96.9 (d, C-1), 97.9 (d, C-1'), 127.0-139.0 (aromatic), 170.0, 170.6 (2s, $O\underline{C}OCH_3x2$). Anal. Calcd. for $C_{38}H_{47}O_{11}$: C, 67.14; H, 6.96. Found: C, 67.09; H, 6.87%.

1,2,3,4-Di-O-isopropylidene-6-O-(3,4-di-O-acetyl-2,6-dideoxy- α -L-arabino-hexopyranosyl)-α-D-galactopyranoside (17) - Coupling of the donor **3** (0.4 g, 1.25 mmol) with the acceptor **8**[13b] (0.35 g, 1.38 mmol) for 16 h afforded **17** (0.49 g, 86%) as a colourless syrup (SiO_2, hexane/ethyl acetate, 4/1), $[\alpha]_D$ - 103° (c 1.26, $CHCl_3$), ^{1}H-n.m.r. (300 MHz, δ in ppm, J in Hz), (85/15 α/β) : 1.16 (d, 2.55 H, $J_{5',6'}$ = 6.2, H-6'), 1.21 (d, 0.45H, H-6'), 1.34x2 (s, 6H, $O_2C\underline{Me}_2$), 1.44, 1.56 (2s, 6H, O_2Me_2), 1.77 (ddd, 1H, $J_{1,2'a}$ = 3.2, $J_{2'a,3'}$ = 9.6, $J_{2',2'}$ = 13.3, H-2'a), 2.00, 2.04 (2s, 6H, $OCOCH_3x2$), 2.24 (ddd, 1H, $J_{1,2'e}$ = 1.4, $J_{2'e,3'}$ = 5.0, H-2'e), 3.5-4.7 (m, 7H, H-2,3,4,5,6,5'), 4.73 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.6, H-4'), 4.95 (d, H-1'), 5.25 (ddd, 1H, H-3'), 5.5 (d, 1H, $J_{1,2}$ = 5.0, H-1), ^{13}C-n.m.r. (22.63 MHz) (δ in ppm) : 17.4 (q, C-6'), 17.6 (q, C-6' anomer), 20.7, 20.9, 24.5, 25.0, 26.1x2 (6q, $OCO\underline{CH}_3x2$, $O_2C\underline{Me}_2x2$), 35.4 (t, C-2), 65.5 (t, C-6), 65.7, 67.0, 69.3, 70.9x2, 71.2, 75.1 (7d, C-2,3,4,5,3',4',5'), 96.4 (d, C-1), 96.9 (d, C-1',α), 100.0 (d, C-1'β), 108.7, 109.3 (2s, $O_2\underline{C}Me_2x2$), 170.2, 170.3 (2s, $O\underline{C}OCH_3x2$). Anal. Calcd. for $C_{22}H_{34}O_{11}$: C, 55.68; H, 7.22. Found: C, 55.59; H, 7.20%.

Synthesis of tri-O-acetyl-D-glucal (18) - D-galactal (19), 2,6-dideoxy-3,4-di-O-acetyl-L-rhamnal (20) and 2,6-dideoxy-3-O-methyl-4-O-acetyl-L-rhamnal (21). - Substrates **1-3** and **26** (2 mmol) were reacted with methyl iodide (0.1 ml) in dry dichloromethane (7 ml) at reflux for 6 h. After completion of the reaction more dichloromethane (50 ml) was added, the organic phase was washed with 1% $Na_2S_2O_3$, 1% cold aq. KOH and water. The organic phase was separated, dried (Na_2SO_4) and evaporated to obtain the corresponding glycals **18-21** (80-85%). **(21).** - ^{1}H-n.m.r. (90 MHz, δ in ppm, J in Hz):1.16 (d, 3H, $J_{5,6}$ = 6.2, H-6), 2.02 (s, 3H, $OCOC\underline{H}_3$), 3.36 (s, 3H, OCH_3), 3.65-3.72 (m, 1H, H-3), 3.96 (dq, 1H, $J_{4,5}$ = 5.6, H-5), 4.72 (dd, 1H, $J_{1,2}$ = 7.4, $J_{2,3}$ = 2.6, H-2), 4.94 (dd, 1H, H-4), 6.24 (dd, 1H, $J_{1,3}$ = 0.9, H-1).

Methyl 2,6-dideoxy-3-O-methyl-4-O-methanesulfonyl-β-L-lyxo-hexopyranoside (23) - To a solution of **22**[18] (1.49 g, 7.82 mmol) in dry pyridine (12 ml) was added at 0°C methanesulfonyl chloride (0.72 ml, 8.72 mmol) and stirred at room temperature for 1 h and diluted with dichloromethane (100 ml), organic phase was washed with water, 2% cold aq. HCl, saturated $NaHCO_3$, water, dried (Na_2SO_4) and concentrated to obtain **23** (1.6 g, 80%) as crystals, m.p. 93° C. $[\alpha]_D$ +9.9° (c 0.53, $CHCl_3$), ^{1}H-n.m.r. (90 MHz) (δ in ppm, J in Hz) : 1.35 (d, 3H, $J_{5,6}$ = 6.0, H-6), 1.5-2.2 (m, 2H, H-2,2), 3.13 (s, 3H, $SO_2C\underline{H}_3$), 3.1-3.7 (m, 2H, H-3,5), 3.44-3.5 (s, 6H, OCH_3x2), 4.4 (dd, 1H, $J_{1,2a}$ = 10, $J_{1,2e}$ = 2, H-1), 4.8 (d, 1H, $J_{3,4}$ = $J_{4,5}$ = 3.0, H-4), ^{13}C-n.m.r. (22.63 MHz) (δ in ppm):17.0 (q, C-6), 31.9 (t, C-2), 38.9 (q, $SO_2\underline{C}H_3$), 56.2, 56.4 (2q, OCH_3x2), 69.2, 76.8, 78.0 (d, C-3,4,5), 100.9 (d, C-1); Anal. calcd. for $C_9H_{18}O_6S$: C, 42.50; H, 7.13. Found: C, 42.39; H, 7.15%.

Methyl 2,6-dideoxy-3-O-methyl-4-O-acetyl-β-L-arabino-hexopyranoside (24). - To a solution of CsOAc[19] (0.99 g, 5.19 mmol) in dry DMF (5 ml) was added **23** (1.19 g, 4.33 mmol) in dry DMF (5 ml). The reaction mixture was heated to 100°C for 26 h under nitrogen atmosphere. After completion of the reaction it was cooled and diluted with water (250 ml) and extracted into dichloromethane/ethyl ether (1/3). The organic phase was washed with 5% aq. HCl (10 ml), water, brine, dried over Na_2SO_4 and the solvent removed to obtain **24** (0.61 g, 72%) as a syrup, after filtration over a bed of silica gel (hexane/ethyl acetate, 2/1), $[\alpha]_D$ +79° (c 1.0, $CHCl_3$), ^{1}H-n.m.r. (90 MHz)(δ in ppm, J in Hz):1.18 (d, 3H, $J_{5,6}$ = 6.0, H-6), 1.7-2.15 (m, 2H, H-2), 2.05 (s, 3H, $OCOC\underline{H}_3$), 3.3, 3.4 (2s, 6H, OCH_3x2), 3.2-3.5 (m, 2H, H-3,5, signals hidden), 4.3 (dd, 1H, $J_{1,2e}$ = 2.0, $J_{1,2q}$ = 10.0, H-1), 4.6 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 10.0, H-4), ^{13}C-n.m.r. (22.63 MHz) (δ in ppm) : 17.6 (q, C-6), 20.9 (q, $OCO\underline{C}H_3$), 35.9 (t, C-2), 56.3, 56.4 (q, OCH_3x2), 70.1, 75.8, 78.0 (3d, C-3,4,5), 100.7 (d, C-1), 170.1 (s, $O\underline{C}OCH_3$). Anal. calcd. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.3. Found: C, 55.1; H, 8.25%.

Methyl 2,6-dideoxy-3-O-methyl-β-L-arabino-hexopyranoside (25).- To a solution of **24** (2.2 g, 10.1 mmol) in anhydrous methanol (20 ml) was added sodium metal (20 mg) and left at room temperature for 6 h. The reaction mixture was neutralized with amberlite H^+ resin (IR 120), resin was filtered off and methanol evaporated to obtain **25** (1.79 g, 98%) as colourless crystals, m.p. 69-70°C. $[\alpha]_D$ +39.7° (c 0.5, $CHCl_3$), ^{1}H-n.m.r. (90 MHz) (δ in ppm, J in Hz), 1.3 (d, 3H, $J_{5,6}$ = 6.0, H-6), 2.12-2.4 (m, 2H, H-2), 3.05-3.3 (m, 3H, H-3,4,5), 3.35, 3.40 (2s, 6H, OCH_3x2), 4.3 (dd, 1H, $J_{1,2e}$ = 2.0, $J_{1,2a}$ = 10.0, H-1), ^{13}C-n.m.r. (22.63 MHz)(δ in ppm): 17.4 (q, C-6), 34.7 (t, C-2), 60.0x2 (2q, OCH_3x2), 70.4, 74.3, 79.4 (d, C-3,4,5), 90.0 (d, C-1).

Anal. calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.42; H, 9.07%.

2,6-Dideoxy-3-O-methyl-4-O-acetyl- α/β -L-arabino-hexopyranoside (26)[10a].- A solution of **24** (1.0 g, 4.9 mmol) and acetic acid/water (3/1, 20 ml) was heated to 60°C for 6 h. Water was co-distilled with toluene several times and the resulting residue was filtered on a bed of silica gel (hexane/ethyl acetate, 2/1) to give **26** (0.58 g, 79%) as a syrup.

Methyl 4-O-(4'-O-acetyl-α-L-oleandrosyl)-β-L-oleandroside (28).- In a single neck round bottom flask (10 ml) were taken **27** (0.31 g, 1.00 mmol), **25** (0.16 g, 1.1 mmol) and molecular sieves (4A) (0.3 g) in 5 ml dichloromethane containing 3% methyl iodide and was reacted at 50° for 2h to obtain after column chromatography (SiO_2, hexane/ethyl acetate, 2/1), **19** (6%) and **28** (0.22 g, 78%) as a crystalline solid, m.p. 100-101°C. $[\alpha]_D$ -37° (c 1.0, $CHCl_3$), ^{1}H-n.m.r. (300 MHz) (δ in ppm, J in Hz) : 1.13 (d, 3H, $J_{5',6'}$ = 6.3, H-6), 1.34 (d, 3H, $J_{5,6}$ = 6.1, H-6'), 1.44 (ddd, 1H, $J_{1,2a}$ = 9.5, $J_{2,3}$ = 11.0, $J_{2,2}$ = 13.0, H-2a), 1.66 (ddd, 1H, $J_{1',2'}$ = 2.8, $J_{2',3'}$ = 10.8, $J_{2',2'}$ = 13.0, H-2'a), 2.11 (s, 3H, $OCOCH_3$), 2.24-2.37 (m, 2H, H-2e,2'e), 3.2 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4, H-4), 3.25-3.33 (m, 2H, H-3,3', hidden), 3.35x2 (2s, 6H, OCH_3x2), 3.49 (s, 3H, OCH_3), 3.56 (dq, 1H, H-5), 3.84 (dq, 1H, $J_{4',5'}$ = 9.87, H-5'), 4.34 (dd, 1H, H-1), 4.66 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.8, H-4'), 5.4 (d, 1H, H-1'); ^{13}C-n.m.r. (22.63 MHz) (δ in ppm); 17.5, 18.6 (2q, C-6,6'), 35.3, 35.9 (2t, C-2,2'), 56.4, 56.9 (2q, OCH_3x2), 66.7, 71.0, 75.8, 76.5, 80.6, 81.7(6d, C-3,4,5,3',4',5'), 98.5 (d, C-1'), 100.8 (d, C-1), 170.2 (s, $OCOCH_3$). Anal. calcd. for $C_{17}H_{30}O_8$: C, 54.34; H, 8.34. Found: C, 54.29; H, 8.26%.

O-(3,4,6-Tri-O-acetyl-2-deoxy-α -D-arabino-hexopyranosyl-)-(1-6)-O-(2,3-di-O-acetyl-α -D-glucopyranosyl)-(1-4)-1,2,3,6-tetra-O-acetyl-β -D-glucopyranoside (30).- Coupling of **1** (0.4 g, 1.06 mmol) with the saccharide acceptor **29**[20] (0.6 g, 1.16 mmol) for 31 h gave the α-linked 2-deoxy trisaccharide **30** (0.56 g, 63%) as a white foam after column chromatographic purification (SiO_2, hexane/ethyl acetate, 1/2), m.p. 100-102°C, $[\alpha]_D$ +66° (c 1.18, $CHCl_3$); ^{1}H-n.m.r. (300 MHz) (δ in ppm, J in Hz):1.19 (ddd, 1H, $J_{1'',2''a}$ = 3.6, $J_{2''a,3''}$ = 12.0, $J_{2'',2''}$ = 15.4, H-2"a), 2.0-2.15 (9s, 27H, $OCOCH_3$x9), 2.3 (dd, 1H, $J_{1'',2''e}$ = 0.42, $J_{2''e,3''}$ = 5.5, H-2"e), 3.55-4.5 (m, 11H, H-2,3,4,5,6,2',3',4',5',5"), 5.01 (brs, 1H, H-1"), 4.7-5.4 (m, 6H, H-1',6',3",6"), 5.78 (d, 1H, $J_{1,2}$ = 8.2, H-1), ^{13}C-n.m.r. (75 MHz) (δ in ppm): 20.3x3, 20.4x3, 20.5x3 (9q, $OCOCH_3$x9), 34.6 (t, C-2"), 62.3, 62.6, 64.9 (3t, C-6',6",6"'), 67.7, 68.4, 68.7, 69.4, 70.0, 70.8, 71.8, 72.2, 72.3, 75.1 (11d, C-2,3,4,5,2',3',4',5',3",4",5"), 91.1 (d, C-1'), 95.7 (d, C-1), 96.9 (d, C-1"), 168.6, 169.3, 169.7, 169.8, 169.9, 170.3x2, 170.7, 171.1 (9s, $OCOCH_3$x9); Anal. calcd. for $C_{36}H_{50}O_{24}$: C, 49.88; H, 5.89. Found: C, 49.74; H, 5.79%.

O-(3,4-Di-Oacetyl-2,6-dideoxy-α -L-arabino-hexopyranosyl)-(1-6)-(2,3-di-O-acetyl-α -D-glucopyranosyl)-(1-4)-1,2,3,4-tetra-O-acetyl-β -D-glucopyranoside (32).- Coupling of the donor **3** (0.44 g, 1.36 mmol) with the acceptor **29** (0.89 g, 1.49 mmol) for 25 h gave **32** (0.68 g, 71%) after column chromatographic purification (SiO_2, hexane/ethyl acetate, 1/1) as a foam, m.p. 85-87°C, $[\alpha]_D$ -4.8° (c 1.12, $CHCl_3$); ^{1}H-n.m.r. (300 MHz) (δ in ppm, J in Hz):1.25 (d, 3H, $J_{5'',6''}$ = 6.4, H-6"), 1.85 (ddd, 1H, $J_{1'',2''a}$ = 3.6, $J_{2''a,3''}$ = 11.0, $J_{2'',2''}$ = 13.0, H-2"a), 2.1-2.25 (8s, 24H, $OCOCH_3$x8), 2.3 (ddd, 1H, $J_{1'',2''e}$ = 0.9, $J_{2''e,3''}$ = 5.3, H-$_{2''e}$), 3.6-4.0 (m, 6H, H-2,5,2',4',5',5"), 4.1 (dd, 1H, $J_{3,4}$=$J_{4,5}$ = 9.6, H-4), 4.2-4.85 (m, 4H, H-3,6,3',6'), 4.9 (d, 1H, H-1"), 5.1 (dd, 1H, $J_{3'',4''}$ = 8.0, $J_{4'',5''}$ = 9.0, H-4"), 5.2-5.5 (m, 4H, H-6,1',6',3"), 5.8 (d, 1H, $J_{1,2}$ = 8.2, H-1); ^{13}C-

n.m.r. (75 MHz)(δ in ppm): 17.2 (q, C-6"), 20.2, 20.3, 20.5x6 (8q, OCOCH$_3$x8), 34.7 (t, C-2"), 62.6, 65.6x2, 68.8x2, 70.1, 70.8, 71.6, 72.2x2, 73.2, 74.5, 78.1 (13d, C-2,3,4,5,6,2',3',4',5',6',3",-4",5"), 91.2 (d, C-1'), 95.8 (d, C-1), 97.2 (d, C-1"), 169.0-171.5 (8s, OCOCH$_3$x8). Anal. calcd. for $C_{34}H_{48}O_{22}$: C, 50.49; H, 5.98. Found: C, 50.41; H, 5.88%.

O-(3,4-Di-O-acetyl-2,6-dideoxy- α -L-arabino-hexopyranosyl)-(1-4)-(2,3-di-O-acetyl-6-O-benzoyl- α -D-glucopyranosyl)-(1-4)-1,2,3,6-tetra-O-acetyl- α -D-glucopyranoside (33).- Coupling of **3** (0.42 g, 1.39 mmol) with the disaccharide acceptor **31**[21] (0.98 g, 1.41 mmol) in dry dichloromethane at 50° for 36 h gave the 2-deoxytrisaccharide **33** (0.74 g, 66%) as a colourless foam, m.p. 103-105°C, $[\alpha]_D$ +11.4° (c 0.98, $CHCl_3$), ^{1}H-n.m.r. (300 MHz)(δ in ppm, J in Hz):1.1 (d, 3H, H-6"), 1.75 (m, 1H, H-2"e), 2.0-2.22 (8s, 25H, OCOCH$_3$x8, H-2"e hidden), 3.8-4.3 (m, 6H, H-2,4,5,2',4',5'), 4.4-4.8 (m, 4H, H-3,6,3',6'), 4.9-5.55 (m, 6H, H-6,1',6',1",3",4"), 5.75 (d, 1H, $J_{1,2}$ = 9.2, H-1), 7.4-8.1 (m, 5H, aromatic); ^{13}C-n.m.r. (75 MHz)(δ in ppm):17.3 (q, C-6"), 20.5x2, 20.6x2, 20.7x4 (7q, OCOCH$_3$x8), 36.0 (t, C-2"), 62.2, 62.3, 67.0, 68.3, 69.8, 70.3, 70.5, 70.9, 72.6, 73.0, 74.3, 75.2, 75.3 (11d, 2t, C-2,3,4,5,6,2',3',4',5',6',3",4",5"), 91.2 (d, C-1'), 95.8 (d, C-1), 98.6 (d, C-1"), 128.5, 129.6 (aromatic), 168.7-170.0 (8s, OCOCH$_3$x7, OCOPh). Anal. calcd. for $C_{41}H_{52}O_{23}$: C, 53.94; H, 5.74. Found: C, 53.89; H, 5.71%.

2-Pyridyl 2,3,5-tri-O-benzyl-1-thio-β -D-ribofuranoside (34).- Reaction of **37** (5.25 g, 10 mmol), 2-mercaptopyridine (1.33 g, 12 mmol) and K_2CO_3 (1.65 g, 12 mmol) in toluene-acetone (300 ml, 1/1) afforded **38** (4.88 g, 88% yield) as a syrup, $[\alpha]_D$ -15.6° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{31}H_{25}NO_7S$: C, 67.01; H, 4.54; N, 2.52; S, 5.77. Found: C, 66.94; H, 4.52; N, 2.50, S, 5.72%. ^{1}H-n.m.r. (200 MHz) (δin ppm, J in Hz): 4.5-4.85 (m, 3H, H-4,5,5'), 5.85-6.05 (m, 2H, H-2,3), 6.23 (d, 1H, $J_{1,2}$=3.1, H-1), 7.0-8.5 (m, 19H, ArH). Debenzylation of **38** (4.5 g, 8.1 mmol) with catalytic amount of NaOMe in methanol gave the hydroxy compound in quantitative yield. Reaction of the above crude product (1.96 g, 8.1 mmol) with NaH (0.873 g, 36.3 mmol) and benzyl bromide (3.83 ml, 32.6 mmol) in dry DMR (5 ml) afforded, after chromatographic purification (SiO_2, hexane/ethyl acetate, 6/1) **34** (3.55 g, 86% yield) as a syrup, $[\alpha]_D$ +20.9° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{31}H_{31}NO_4S$: C, 72.49; H, 6.08; N, 2.73; S, 6.24. Found: C, 72.45; H, 6.10; N, 2.69; S, 6.20%. ^{1}H-n.m.r. (200 MHz)(δ in ppm, J in Hz): 3.5-3.8 (m, 2H, H-5,5'), 4.1-4.9 (m, 9H, H-2,3,4, OCH$_2$Phx3), 6.23 (d, 1H, $J_{1,2}$=3.1, H-1), 7.0-8.5 (m, 19H, ArH).

2-Pyridyl 2,5-di-O-benzoyl-2-deoxy-1-thio-α,β -D-ribofuranoside (35).- Compound **39**[28] (3.2 g) in aq AcOH (3 ml, 1/1) containing a drop of conc. HCl was heated at 80°C for 1 h. Usual workup gave the lactol **40** in quantitative yield. **40** (2.7 g, 7.89 mmol) and 2,2'-dipyridyl disulfide (1.8 g, 8.2 mmol) in dry CH_2Cl_2 (20 ml) was treated with n-Bu_3P (2.16 ml, 8.37 mmol) at room temperature. After 30 min. the solvent was concentrated to 5 ml and purified by column chromatography (SiO_2, hexane/ethyl acetate; 6/1) to afford **35** (3 g, 87% yield, α/β; 1/1) as a syrup. Anal. Calcd. for $C_{24}H_{21}NO_5S$: C, 66.19; H, 4.86; N, 3.22; S, 9.07. Found: C, 66.14; H, 4.82; N, 3.18; S, 9.01%. ^{1}H-n.m.r. (200 MHz)(δin ppm, J in Hz)(α/β ; 1/1): 2.2-3.0 (m, 2H, H-2,2'), 3.9-4.2 (m, 1H, H-5), 4.3-4.7 (m, 2H, H-4,5'), 5.4-5.65 (m, 1H, H-3), 6.17 (dd, 0.5 H, $J_{1,2a}$=5.5, $J_{1,2e}$=4.0, H-1a), 6.55 (t, 0.5 H, $J_{1,2a}$=$J_{1,2'e}$=3.0, H-1e), 7.0-8.5 (m, 14H, ArH).

2-Pyridyl 2,3,5,6-di-O-isopropylidene-1-thio- β-D-mannofuranoside (36).- Reaction of **41**[30] (2.6 g, 10 mmol) with 2,2'-dipyridyl disulfide (3.44 g, 10.39 mmol) and n-Bu_3P (3.68 ml, 10.60 mmol) in CH_2Cl_2 and purification by column chromatography (SiO_2, hexane/ethyl acetate, 5/1) afforded **36** (2.5 g, 71% yield) exclusively as β -anomer as yellow needles, m.p. 145°, $[\alpha]_D$ -68.5° (c 0.7, $CHCl_3$). Anal. Calcd. for $C_{17}H_{23}NO_5S$: C, 57.77; H, 6.56; N, 3.96; S, 9.07. Found: C, 57.71; H, 6.52; N, 3.92; S, 9.01%. ^{1}H-n.m.r. (200 MHz) (δ in ppm, J in Hz): 1.31, 1.33, 1.38, 1.50 (4s, 12H, $O_2C\underline{Me}_2$x2), 3.6 (dd, 1H, $J_{4,5}$=8.3, $J_{3,4}$=3.7, H-4), 3.9-4.15 (m, 2H, H-6,6'), 4.35-4.55 (m, 1H, H-5), 4.80 (dd, 1H, $J_{1,2}$=3.7, $J_{2,3}$=5.0, H-2), 4.9 (dd, 1H, H-3), 5.8 (d, 1H, H-1), 6.9-8.5 (m, 4H, SPy).

Methyl 2,3-O-isopropylidene-5-O-(2,3,5-tri-O-benzyl-α-D-ribofuranosyl)-β-D-ribofuranoside (42).- Coupling of **34** (0.513 g, 1 mmol) with **a** (0.224 g, 1.1 mmol) gave **42** (0.472 g, 78% yield) as a syrup. $[\alpha]_D$ +21° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{35}H_{42}O_9$: C, 69.29; H, 6.98. Found: C, 69.25; H, 6.95%. ^{1}H-n.m.r. (200 MHz)(δ in ppm, J in Hz): 1.3, 1.5 (2s, 6H, $O_2C\underline{Me}_2$), 3.3 (s, 3H, OCH_3), 3.35-3.90, 4.30-4.90 (m, 16H, H-2,3,4,5,2',3',4',5', $OC\underline{H}_2$Phx3), 4.95 (s, 1H, H-1), 5.05 (d, 1H, $J_{1',2'}$=4.1, H-1'), 7.12-7.50 (m, 15H, ArH). ^{13}C-n.m.r. (50 MHz, δ in ppm). 24.8, 26.2 (2q, $O_2C\underline{Me}_2$), 54.6 (q, OCH_3), 69.2, 69.9, 72.2, 72.5, 73.3, 75.3, 76.4, 81.7, 82.0, 85.1x2 (6d, 5t, C-2,3,4,5,2',3',4',5', $OC\underline{H}_2$Phx3), 102.2 (d, C-1'), 109.5 (d, C-1), 112.1 (s, $O_2C\underline{Me}_2$), 126.0-139.0 (aromatic).

1,2:3,4-Di-O-isopropylidene-6-O-(2,3,5-tri-O-benzyl- α-D-ribofuranosyl)-α -D-galactopyranoside (43).- Reaction of **34** (0.513 g, 1 mmol) with **b** (0.286 g, 1.1 mmol) gave **43** (0.536 g, 81% yield) as a syrup. $[\alpha]_D$ +27.8° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{38}H_{46}O_{10}$: C, 68.86; H, 7.00. Found: C, 68.84; H, 6.98%. ^{1}H-n.m.r. (200 MHz)(δ in ppm, J in Hz): 1.30, 1.35, 1.43, 1.52 (4s, 12H, $O_2C\underline{Me}_2$x2), 3.30-4.85 (m, 17H, H-2,3,4,5,6,2',3',4',5', $OC\underline{H}_2$Phx3), 5.15 (d, 1H, $J_{1',2'}$=4.1, H-1'), 5.52 (d, 1H, $J_{1,2}$=4.9, H-1), 7.22-7.50 (m, 15H, aromatic). ^{13}C-n.m.r. (50 MHz, δ in ppm). 24.2, 24.3, 24.8x2 (4q, $O_2C\underline{Me}_2$x2), 65.8, 66.6, 69.9, 70.6x2, 70.7, 71.6, 72.2, 73.4, 75.4, 76.4, 81.5 (7d, 5t, C-2,3,4,5,6,2',3',4',5', $OC\underline{H}_2$Phx3), 96.35 (d, C-1), 102.1 (d, C-1'), 108.6, 109.0 (2s, $O_2C\underline{Me}_2$x2), 126.0-139.0 (aromatic).

1,2:5,6-Di-O-isopropylidene-3-O-(2,3,5-tri-O-benzyl-α -D-ribofuranosyl)-α -D-glucofuranoside (44).- **34** (0.513 g, 1 mmol) on reaction with **c** (0.286 g, 1.1 mmol) afforded **44** (0.443 g, 67% yield) as a syrup. $[\alpha]_D$ +35.2° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{38}H_{46}O_{10}$: C, 68.86; H, 7.00. Found: C, 68.83; H, 6.97%. ^{1}H-n.m.r. (200 MHz)(δin ppm, J in Hz): 1.31, 1.34, 1.38, 1.41 (4s, 12H, $O_2C\underline{Me}_2$x2), 3.36-4.85 (m, 17H, H-2,3,4,5,6,2',3',4',5', $OC\underline{H}_2$Phx3), 5.16 (d, 1H, $J_{1',2'}$=4.1, H-1'), 6.02 (d, 1H, $J_{1,2}$=3.85, H-1), 7.1-7.5 (m, 15H, ArH).

Methyl 2,3-O-isopropylidene-5-O-(3,5-di-O-benzoyl-2-deoxy-α -D-ribofuranosyl)-β -D-ribofuranoside (45).- **35** (0.435 g, 1 mmol) with **a** (0.224 g, 1.1 mmol) in CH_2Cl_2 (4 ml) gave **45** and **52** after chromatographic purification (SiO_2, hexane/ethyl acetate, 4/1). The first eluted was 1,4-anhydro-2-deoxy-3,5-di-O-benzoyl-**D**-erythro-pent-1-enitol **52** (0.029 g, 9% yield). ^{1}H-n.m.r. (200 MHz) (δin ppm, J in Hz): 4.3 (m, 2H, H-5), 5.1 (dd, 1H, $J_{1,2}$=5.4, $J_{2,3}$=4.4, H-2), 5.55 (m, 1H, H-4), 5.8 (t, 1H, $J_{2,3}$=$J_{3,4}$=4.4, H-3), 6.65 (d, 1H, H-1), 7.3-8.1 (m, 10H, ArH). The second eluted was **45** (0.379 g, 72% yield). $[\alpha]_D$ -115.5° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{28}H_{32}O_{10}$: C, 63.62; H, 6.10. Found: C, 63.60; H, 6.05%. ^{1}H-n.m.r. (200 MHz) (δ in ppm,

J in Hz): 1.35, 1.50 (2s, 6H, $O_2C\underline{Me}_2$), 2.1-2.7 (m, 2H, H-2'), 3.35 (s, 3H, OCH_3), 3.5-4.8 (m, 8H, H-2,3,4,5,4',5'), 5.01 (s, 1H, H-1), 5.15 (brs, 1H, H-1'), 5.4-5.6 (m, 1H, H-3'), 7.2-8.2 (m, 10H, ArH). ^{13}C-n.m.r (50 MHz)(δ in ppm): 24.6, 26.1 (2q, $O_2C\underline{Me}_2$), 31.0 (t, C-2'), 54.6 (q, $O\underline{CH}_3$), 60.9, 66.4, 68.2, 68.6x2, 81.8, 84.9, 85.0 (5d, 3t, C-2,3,4,5,2',3',4',5'), 97.7 (d, C-1), 109.4 (d, C-1), 112.2 (s, $O_2\underline{C}Me_2$), 128.0-134.0 (aromatic), 165.4, 165.8 (2s, $O\underline{C}OPh$). However a reaction of **35** with **a** in 0.4M solution of CH_2Cl_2 (2.5 ml) gave exclusively **45** in 85% yield.

1,2:3,4-Di-O-isopropylidene-5-O-(3,5-di-O-benzoyl-2-deoxy-α-D-ribofuranosyl)-α-D-galactopyranoside (46).- Coupling of **35** (0.435 g, 1 mmol) with **b** (0.286 g, 1.1 mmol) gave **46** (0.478 g, 82% yield) as a syrup. $[\alpha]_D$ -105.7° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{31}H_{36}O_{11}$: C, 63.69; H, 6.21. Found: C, 63.66; H, 6.18%. ^{1}H-n.m.r. (200 MHz) (δ in ppm, J in Hz): 1.35, 1.40, 1.50, 1.60 (4s, 12H, $O_2C\underline{Me}_2$x2), 2.1-2.8 (m, 2H, H-2'), 3.65-4.75 (m, 9H, H-2,3,4,5,6,4',5'), 5.23 (brs, 1H, H-1'), 5.6 (d, 1H, $J_{1,2}$=5.52, H-1), 5.65-5.80 (m, 1H, H-3'), 7.3-8.2 (m, 10H, ArH). ^{13}C-n.m.r. (50 MHz) (δ in ppm): 24.4, 24.7, 25.9x2 (4q, $O_2C\underline{Me}_2$x2), 31.2 (t, C-2'), 61.1, 66.3, 66.7, 66.9, 68.6, 70.5, 70.6, 71.7 (6d, 2t, C-2,3,4,5,6,2',3',4',5'), 96.4 (d, C-1), 98.0 (d, C-1'), 108.7, 109.4 (2s, $O_2C\underline{Me}_2$x2), 126.0-134.0 (aromatic), 165.8, 166.1 (2s, $O\underline{C}OPh$x2).

1,2:5,6-Di-O-isopropylidene-3-O-(3,5-di-O-benzoyl-2-deoxy-α-D-ribofuranosyl)-α-D-glucofuranoside (47).- Coupling of **35** (0.435 g, 1 mmol) with **c** (0.286 g, 1.1 mmol) afforded **47** (0.455 g, 78% yield) as a crystalline solid, m.p. 45°, $[\alpha]_D$ -102.4° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{31}H_{36}O_{11}$: C, 63.69; H, 6.21. Found: C, 63.67; H, 6.20%. ^{1}H-n.m.r. (200 MHz)(δ in ppm, J in Hz): 1.45, 1.55, 1.65x2 (4s, 12H, $O_2C\underline{Me}_2$x2), 2.1-2.7 (m, 2H, H-2'), 3.9-4.7 (m, 9H, H-2,3,4,5,6,4',5'), 5.3 (brs, 1H, H-1'), 5.5-5.65 (m, 1H, H-3'), 5.9 (d, 1H, $J_{1,2}$=4.0, H-1), 7.3-8.2 (m, 10H, ArH). ^{13}C-n.m.r. (50 MHz) (δ in ppm): 25.3, 26.1, 26.6, 26.7, (4q, $O_2C\underline{Me}_2$x2), 30.9 (t, C-2'), 61.5, 66.5, 67.9, 68.6, 72.1, 76.3, 81.1, 81.8 (6d, 2t, C-2,3,4,5,6,3',4',5'), 94.7 (d, C-1'), 105.3 (d, C-1), 109.4, 112.0 (2s, $O_2C\underline{Me}_2$x2), 127.0-134.0 (aromatic), 165.6, 166.1 (2s, $O\underline{C}OPh$x2).

Methyl 2,3-di-O-benzyl-6-O-(3,5-di-O-benzoyl-2-deoxy-α-D-ribofuranosyl)-α-D-glucopyranoside (48).- Coupling of **35** (0.435 g, 1 mmol) with **d** (0.411 g, 1.1 mmol) gave **48** (0.502 g, 72% yield) as a syrup, $[\alpha]_D$ -70.8° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{40}H_{42}O_{11}$: C, 68.75; H, 6.06. Found: C, 68.73; H, 6.04%. ^{1}H-n.m.r. (200 MHz) (δ in ppm, J in Hz): 2.1-2.7 (m, 2H, H-2'), 3.4 (s, 3H, OCH_3), 3.5-5.1 (m, 14H, H-1,2,3,4,5,6,4',5', OCH_2Phx2), 5.15 (brs, 1H, H-1'), 5.3-5.4 (m, 1H, H-3'), 7.2-8.1 (m, 20H, ArH). ^{13}C-n.m.r. (50 MHz) (δin ppm): 30.9 (t, C-2'), 54.9 (q, OCH_3), 66.5x2, 68.2, 69.7, 70.1, 72.9, 75.1x2, 79.7, 81.3 (6d, 4t, C-2,3,4,5,6,2',4',5', OCH_2Phx2), 97.8x2 (2d, C-1,1'), 127.0-139.0 (aromatic), 165.5, 165.9 (2s, $O\underline{C}OPh$x2).

Methyl 2,3-O-isopropylidene-5-O-(2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyl)-β-D-ribofuranoside (49).- Reaction of **36** (0.353 g, 1 mmol) with **a** (0.224 g, 1.1 mmol) afforded **49** (0.356 g, 80% yield) as a syrup, $[\alpha]_D$ +10.5° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{21}H_{34}O_{10}$: C, 56.49; H, 7.68. Found: C, 56.47; H, 7.66%. ^{1}H-n.m.r. (200 MHz) (δ in ppm, J in Hz): 1.40, 1.45, 1.50, 1.52, 1.56, 1.61 (6s, 18H, $O_2C\underline{Me}_2$x3), 3.38 (s, 3H, OCH_3), 3.45-4.90 (m, 11H, H-2,3,4, 5,2',3',4',5',6'), 5.02 (s, 1H, H-1), 5.07 (s, 1H, H-1'). ^{13}C-n.m.r. (50 MHz) (δ in ppm): 21.6, 22.0, 25.2, 25.9, 28.1, 28.8 (6q, $O_2C\underline{Me}_2$x3), 55.0 (q, OCH_3), 66.0-85.0 (7d, 2t, C-2,3,4,5,2',3',4', 5',6'), 106.9 (d, C-1'), 109.2 (d, C-1), 109.3, 112.6, 112.8 (3s, $O_2\underline{C}Me_2$x3).

1,2:3,4-Di-O-isopropylidene-6-O-(2,3:5,6-di-O-isopropylidene- α -D-mannofuranosyl)- α -D-galactopyranoside (50).- Reaction of **36** (0.353 g, 1 mmol) with **b** (0.286 g, 1.1 mmol) gave **50** (0.396 g, 79% yield) as a syrup, $[\alpha]_D$ -8.82° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{24}H_{38}O_{11}$: C, 57.36; H, 7.62. Found: C, 57.34; H, 7.60%. ^{1}H-n.m.r. (200 MHz) (δ in ppm, J in Hz): 1.25x2, 1.27, 1.29, 1.37x2, 1.39, 1.46 (8s, 24H, $O_2C\underline{Me}_2$x4), 3.5-4.8 (m, 12H, H-2,3,4,5,6,2',3',4',5',6'), 4.95 (s, 1H, H-1'), 5.45 (d, 1H, $J_{1,2}$=5.0, H-1). ^{13}C-n.m.r. (50 MHz) (δ in ppm): 24.4-26.8 (8q, $O_2C\underline{Me}_2$x4), 66.0-85.0 (8d, 2t, C-2,3,4,5,6,2',3',4',5',6'), 96.2 (d, C-1), 106.6 (d, C-1'), 109.4, 109.6, 109.7, 112.4 (4s, $O_2\underline{C}Me_2$x4).

1,2:5,6-Di-O-isopropylidene-3-O-(2,3:5,6-di-O-isopropylidene-α -D-mannofuranosyl)-α -D-glucofuranoside (51).- Coupling of **36** (0.353 g, 1 mmol) with **c** (0.286 g, 1.1 mmol) afforded **51** (0.371 g, 74% yield) as a syrup, $[\alpha]_D$ +26.07° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{24}H_{38}O_{11}$: C, 57.36; H, 7.62. Found: C, 57.24; H, 7.56%. ^{1}H-n.m.r. (200 MHz) (δ in ppm, J in Hz): 1.36, 1.37, 1.38, 1.41, 1.46, 1.50x2, 1.52 (8s, 24H, $O_2C\underline{Me}_2$x4), 3.99-4.90 (m, 12H, H-2,3,4,5,6,2',3',4',5',6'), 5.31 (s, 1H, H-1'), 5.88 (d, 1H, $J_{1,2}$=3.8, H-1). ^{13}C-n.m.r. (50 MHz) (δ in ppm): 24.4, 26.1, 26.2, 26.7, 28.1, 28.7x3 (8q, $O_2C\underline{Me}_2$x4), 66.8, 67.5, 72.5, 73.2, 79.5, 80.8x2, 81.0, 83.8, 85.2 (8d, 2t, C-2,3,4,5,6,2',3',4',5',6'), 105.0 (d, C-1), 107.6 (d, C-1'), 109.0, 109.2, 111.9, 112.7 (4s, $O_2\underline{C}Me_2$x4).

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