Recl. Trav. Chim. Pays-Bas **108**, 374–383 (1989) 0165–0513/89/10374–10$3.00

Syntheses of tri- and tetrasaccharide fragments of the capsular polysaccharide of *Streptococcus pneumoniae* type 23F

A. M. P. van Steijn, M. Jetten, J. P. Kamerling and J. F. G. Vliegenthart

Department of Bio-Organic Chemistry, Utrecht University, Transitorium III, P.O. Box 80.075, NL-3508 TB Utrecht, The Netherlands
(Received April 24th, 1989)

Abstract. The syntheses of two trisaccharides, being fragments of the capsular polysaccharide of *Streptococcus pneumoniae* type 23F (3-OPO_3^{2-})-β-D-Glc*p*-(1–4)-[α-L-Rha*p*-(1–2)]-β-D-Gal*p*-(1-OCH_3) (**1**), α-L-Rha*p*-(1–2)-β-D-Gal*p*-(1–4)-β-L-Rha*p*-(1-OCH_3) (**2**) and the repeating unit (3-OPO_3^{2-})-β-D--Glc*p*-(1–4)-[α-L-Rha*p*-(1–2)]-β-D-Gal*p*-(1–4)-β-L-Rha*p*-(1-OCH_3) (**3**), are presented.

Introduction

The current vaccine Pneumovax© 23 against pneumococcal diseases contains isolated capsular polysaccharides from 23 species of *Streptococcus pneumoniae*[1]. Although of medical importance, disadvantages of this vaccine are associated with the non-immunogenicity of polysaccharides in newborns and the inherent problems with induction of immunological memory. These observations have stimulated the search for synthetic vaccines based on oligosaccharide conjugates[2] (neoglycoproteins/neoglycolipids), having better clinical features. To establish the oligosaccharide determinant with the highest immunogenicity, a series of oligosaccharides of growing complexity, which can be tested in inhibition experiments, have to be synthesized. After selection of the most promising structure, this compound can be prepared in a suitable conjugated form for further immunological studies. Here, we focus attention on the capsular polysaccharide of *S. pneumoniae* serotype 23F, one of the constituents of the current vaccine, and the syntheses is described of tri- and tetrasaccharides **1**, **2** and **3**, being elements of the reported structure **4A**[3] of polysaccharide 23F

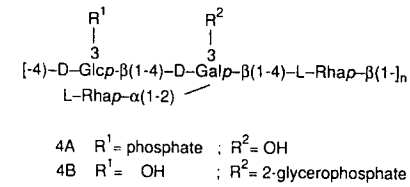
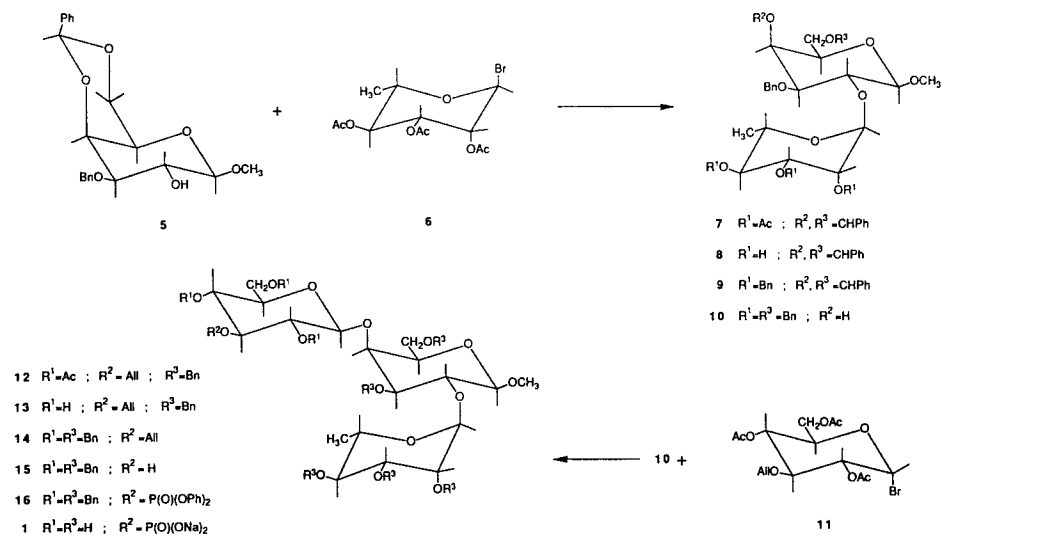


Fig. 1. Structure of the repeating unit of the capsular polysaccharide of S. pneumoniae *type 23F;* **4A**[3], **4B**[4].



Scheme 1

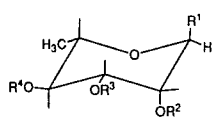
(Fig. 1). It has to be noted that, after we had completed the preparation of **1–3**, a revised structure **4B** (Fig. 1) was published[4]. This latter finding has prompted further synthetic studies of fragments of polysaccharide 23F.

Results and discussion

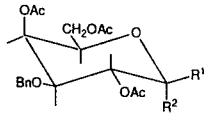
For the synthesis of the trisaccharide element **1**, the monosaccharide synthons **5**, **6** and **11** were chosen (Scheme 1). Benzylidenation of methyl 3-*O*-benzyl-β-D-galactopyranoside[5] with α,α-dimethoxytoluene in the presence of *p*-toluenesulfonic acid gave **5** (96%). Coupling of **5** with 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide **6** in nitromethane/toluene, using mercuric cyanide as a promoter, yielded the crystalline disaccharide **7** (78%). In the glycosylation reaction, the use of more than 1 equivalent of mercuric cyanide relative to **6**[6] is critical, since lower amounts resulted in a loss of the benzylidene group during work-up. Compound **7** was deacetylated (→ **8**, 99%) and benzylated (→ **9**, 80%). In the deacetylation step, the neutralisation was carried out via washing with water, since the use of Dowex-50 (H^+) resin led to loss of the benzylidene group. Regioselective reductive opening of the 4,6-*O*-benzylidene ring of **9** with borane–trimethylamine complex and aluminium(III) chloride in tetrahydrofuran[7] gave **10** (78%). We found that the ring opening proceeded much faster when crystalline **9** was used, instead of the corresponding syrup. Condensation of **10** with 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl bromide (**11**)[8] in benzene/nitromethane, in the presence of mercuric cyanide as catalyst, afforded the trimer fragment **12** (88%). Using **11** as glycosyl donor and mercuric bromide or silver triflate as promoters, or ethyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-1-thio-β-D-glucopyranoside as glycosyl donor and methyl triflate[9,10] as a catalyst, only low yields of **12** were obtained. Deacetylation of **12** (→ **13**), followed by benzylation (→ **14**, 83%), deallylation using potassium *tert*-butoxide/hydrochloric acid–acetone[11] (→ **15**, 38%) and diphenylphosphorylation with diphenyl phosphorochloridate in the presence of 4-(dimethylamino)pyridine[12] afforded **16** (90%). Finally, **16** was debenzylated and dephenylated by catalytic hydrogenolysis over Pd/C and PtO_2, respectively, yielding, after work-up, the disodium salt of trisaccharide **1** (41%). The structure of this trisaccharide was verified by 2D ^1H NMR spectroscopy (COSY and HOHAHA) and the ^1H NMR data are presented in Table I. To mimic the β-anomeric configuration of the L-rhamnose residue in the polysaccharide backbone, the synthesized oligosaccharides **2** and **3** terminate on a methyl β-L-rhamnopyranoside unit. The selected procedure for the preparation of a suitable synthon for this unit involves the condensation of a bromide-activated L-rhamnopyranosyl residue with a non-participating group at C-2 as glycosyl donor and methanol, in the presence of silver silicate[13]. In our strategy, use has been made of the ethylthio group at the anomeric centre, which, in a later stage, can be converted into a bromide. Tetra-*O*-acetyl-α-L-rhamnopyranose[6] (**17**) (Scheme 2) was converted with ethanethiol in the presence of zinc chloride[14] into the α-thioglycoside **18** (44%), which was deacetylated (→ **19**), isopropylidenated with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid (→ **20**, 98%), allylated (→ **21**, 98%), deisopropylidenated using aqueous 45% acetic acid (→ **22**, 97%) and benzylated to give **23** (97%).

Table I 500-MHz ^1H NMR data of the title compounds **1**, **2** *and* **3**.

Residue	Proton (J)	In ppm (H_2) for					
		1		**2**		**3**	
Rha β	H-1 ($J_{1,2}$)			4.544	(<0.5)	4.544	(<0.5)
	H-2 ($J_{2,3}$)			3.928	(3.2)	3.927	(3.3)
	H-3 ($J_{3,4}$)			3.75	(9.5)	3.771	(9.5)
	H-4 ($J_{4,5}$)			3.711	(9.5)	3.676	(9.5)
	H-5 ($J_{5,6}$)			3.447	(6.3)	3.446	(6.2)
	H-6			1.266		1.353	
	OCH_3			3.516		3.513	
Gal β	H-1 ($J_{1,2}$)	4.401	(7.8)	4.816	(7.8)	4.847	(7.9)
	H-2 ($J_{2,3}$)	3.602	(9.7)	3.555	(9.7)	3.627	(9.7)
	H-3 ($J_{3,4}$)	3.808	(3.3)	3.75	(3.4)	3.837	(3.1)
	H-4 ($J_{4,5}$)	4.176	(<1)	3.900	(<1)	4.179	(<1)
	H-5 ($J_{5,6a}$)	3.699	(~6)	3.622	(4.8)	n.d.	(n.d.)
	H-6a ($J_{6a,6b}$)	3.86–	(n.d.)	3.82–	(n.d.)	n.d.	(n.d.)
	H-6b ($J_{5,6b}$)	–3.79	(~6)	–3.72	(8.3)	n.d.	(n.d.)
	OCH_3	3.564					
Rha α	H-1 ($J_{1,2}$)	5.006	(1.7)	5.085	(1.8)	5.101	(1.4)
	H-2 ($J_{2,3}$)	4.036	(3.4)	4.053	(3.4)	4.052	(3.4)
	H-3 ($J_{3,4}$)	3.756	(9.8)	3.779	(9.7)	3.785	(9.7)
	H-4 ($J_{4,5}$)	3.444	(9.8)	3.469	(9.7)	3.467	(9.7)
	H-5 ($J_{5,6}$)	3.90	(6.3)	4.090	(6.3)	4.070	(6.3)
	H-6	1.271		1.185		1.266	
Glc β	H-1 ($J_{1,2}$)	4.700	(8.0)			4.714	(8.0)
	H-2 ($J_{2,3}$)	3.46	(~8)			3.49	(~8)
	H-3 ($J_{3,4}$)	3.987	(~8)			3.992	(~8)
	H-4 ($J_{4,5}$)	3.50	(n.d.)			3.53	(n.d.)
	H-5 ($J_{5,6a}$)	3.49	(n.d.)			3.51	(1.8)
	H-6a ($J_{6a,6b}$)	3.73	(n.d.)			3.895	(–12.3)
	H-6b ($J_{5,6b}$)	3.91	(n.d.)			3.732	(5.2)
	($J_{3,p}$)		(~8)				(~8)



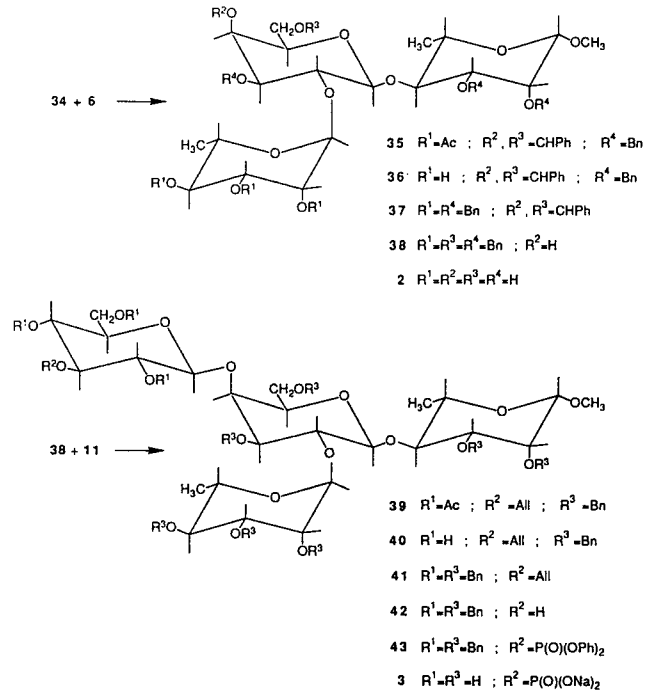
17 R^1 = OAc ; R^2 = R^3 = R^4 = Ac
18 R^1 = SEt ; R^2 = R^3 = R^4 = Ac
19 R^1 = SEt ; R^2 = R^3 = R^4 = H
20 R^1 = SEt ; R^2, R^3 = $C(Me)_2$; R^4 = H
21 R^1 = SEt ; R^2, R^3 = $C(Me)_2$; R^4 = All
22 R^1 = SEt ; R^2 = R^3 = H ; R^4 = All
23 R^1 = SEt ; R^2 = R^3 = Bn ; R^4 = All



27 R^1 = OCH_3 ; R^2 = H
28 R^1, R^2 = H, OAc
29 R^1, R^2 = H, OH
30 R^1 = H ; R^2 = $OCNHCCl_3$

Scheme 2

For the synthesis of disaccharide derivative **32** (Scheme 3), compound **23** was converted into two suitable aglycons, namely **24** and **26**. Deallylation of **23** under the conditions mentioned above afforded **24** (87%). Treatment of **23** with methanol in the presence of cupric bromide/tetrabutylammonium bromide and silver silicate as a promoter yielded the methyl β-L-rhamnopyranoside derivative **25β** (45%; ^{1}H NMR, $J_{1,2}$ ~0 Hz, H-5 δ 3.271 ppm[15]) and the α-analogue **25α** (26%; ^{1}H NMR, $J_{1,2}$ 1.8 Hz, H-5 δ 3.615 ppm)[15]. The bromide salts take care for the *in situ* generation of the derivatized rhamnosyl bromide[16], leaving the allyl group intact. Conversion of the ethylthio group into a bromide using bromine gave several spots on TLC, probably due to the bromination of the allyl group. Deallylation of **25β** under the usual conditions gave **26**. In both condensation reactions, glycosyl donor **30** (Scheme 2) was used, prepared from methyl 3-*O*-benzyl-β-D-galactopyranoside[5] by acetylation (→ **27**, 70%), acetolysis of the anomeric methyl group using 2% sulfuric acid in acetic anhydride (→ **28**), removal of the anomeric acetyl group with hydrazine acetate[18] (→ **29**) and treatment with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene to give **30** in an overall yield of 71%. When sodium hydride[19] was used as a base for the imidation of **29**, the yield of **30** was only 41%.

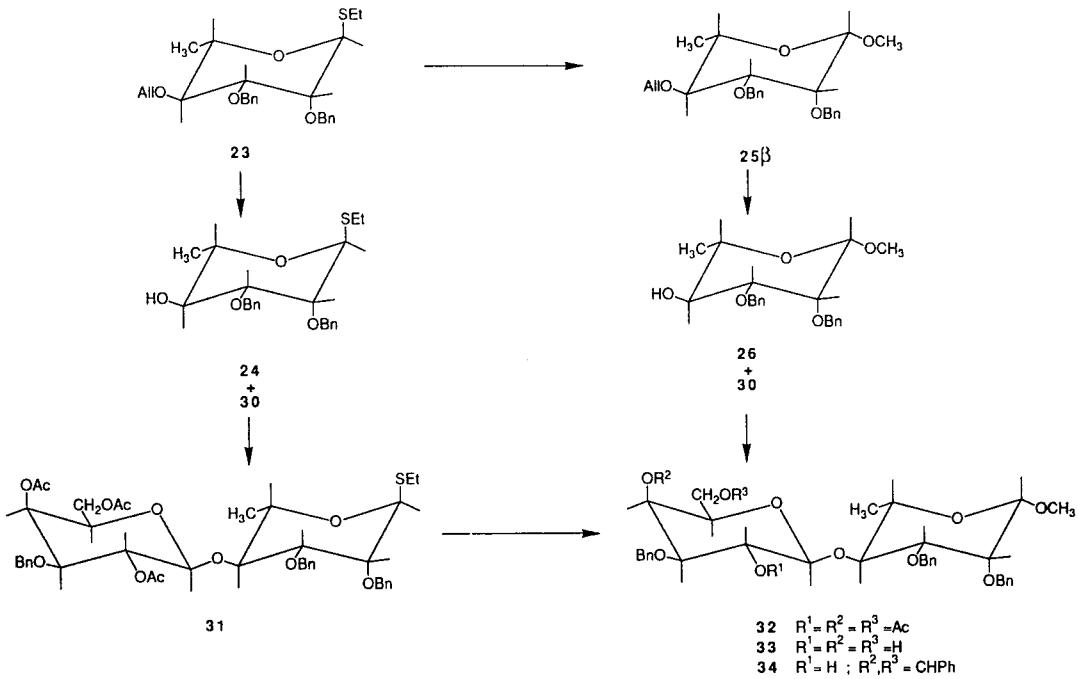


35 R^1=Ac ; R^2, R^3 =CHPh ; R^4 =Bn
36 R^1=H ; R^2, R^3 =CHPh ; R^4 =Bn
37 R^1=R^4=Bn ; R^2, R^3=CHPh
38 R^1=R^3=R^4=Bn ; R^2=H
2 R^1=R^2=R^3=R^4=H

39 R^1=Ac ; R^2 =All ; R^3 =Bn
40 R^1=H ; R^2 =All ; R^3 =Bn
41 R^1=R^3=Bn ; R^2 =All
42 R^1=R^3=Bn ; R^2 =H
43 R^1=R^3=Bn ; R^2 =P(O)(OPh)$_2$
3 R^1=R^3 =H ; R^2 =P(O)(ONa)$_2$

Scheme 4

Glycosylation of aglycon **24** with **30** in dichloromethane using trimethylsilyl triflate as catalyst at −30°C afforded **31** (81%) which was treated with bromine[17], followed by condensation with methanol in the presence of silver silicate to give **32β** (71%; ^{1}H NMR, $J_{1,2}$ ~0 Hz, H-5 δ 3.304 ppm)[15] and **32α** (8%; ^{1}H NMR, $J_{1,2}$ 1.5 Hz, H-5 δ 3.612 ppm)[15]. It is evident that in this case the anomeric specificity is quite different from that obtained in the preparation of **25**. Condensation of the thio aglycon **24** with a bromide, prepared from **27**, in nitromethane/toluene with mercuric bromide as a promoter gave disaccharide **31** in 30% yield. Glycosylation of aglycon **26** with **30**, under the same conditions as mentioned above for the condensation of **24** and **30**, yielded **32β** (87%). Compound **32β** was deacetylated (→ **33**), benzylidenated (→ **34**, 79%) and coupled with 2,3,4-tri-*O*-ace-



23
25β
24 + 30
26 + 30
31

32 R^1= R^2 = R^3 =Ac
33 R^1= R^2 = R^3 =H
34 R^1= H ; R^2,R^3 = CHPh

Scheme 3

tyl-α-L-rhamnopyranosyl bromide **6**[6] in dichloromethane, in the presence of mercuric bromide/mercuric cyanide (1:1) as promoter, to give trisaccharide derivative **35** (79%) (Scheme 4).

Deacetylation of **35** (→**36**, 99%) and catalytic debenzylation and debenzylidenation by hydrogenolysis over Pd/C gave trisaccharide **2** (89%). The unprotected trisaccharide **2** thus formed was analyzed by 2D ^{1}H NMR spectroscopy (COSY) and the ^{1}H NMR data are presented in Table I.

For the synthesis of tetrasaccharide **3**, the same strategy was followed as for trisaccharide **1**. Compound **36** was benzylated (→**37**, 97%) and selective opening of the 4,6-*O*-benzylidene ring of **37** with borane–trimethylamine complex as reducing agent and aluminium(III) chloride in tetrahydrofuran[7] gave **38** (86%), having a free OH-4 group on the galactose residue. Condensation of **38** (Scheme 4) with 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl bromide[8] **11** in dichloromethane, using mercuric bromide as a promoter, afforded tetrasaccharide derivative **39** (75%). It should be mentioned that glycosylation of **38** with **11** in the presence of mercuric cyanide under various reaction conditions (temperature, solvent) failed. Deacetylation of **39** yielded **40**, which was benzylated (→**41**, 88%) and deallylated (→**42**, 59%) under the conditions mentioned above. Finally, compound **42** was diphenylphosphorylated (→**43**, 86%) and debenzylated/dephenylated as described for **16**, yielding **3** (95%). For ^{1}H NMR data obtained from 2D ^{1}H NMR experiments, see Table I and Figs. 2 and 3.

Experimental

General procedures

^{1}H NMR spectra were recorded at 60 MHz using a Varian 360, at 360 MHz using a Bruker HX 360 or at 500 MHz using a Bruker AM 500 apparatus at 25°C. Two-dimensional double-quantum filtered ^{1}H–^{1}H correlation spectra (2D DQF ^{1}H–^{1}H COSY) were recorded in the phase-sensitive mode[21] and two-dimensional homonuclear Hartmann–Hahn spectra (2D HOHAHA) with a 120 ms MLEV-17 mixing sequence[22]. ^{13}C NMR spectra were recorded at 50 MHz using a Bruker WP-200 spectrometer at 25°C. Chemical shifts (δ) are given in ppm relative to internal Me_4Si ($CDCl_3$) or internal 3-(trimethylsilyl)-1-propanesulfonate (D_2O; indirectly to internal acetone, δ 2.225) for ^{1}H, and to internal Me_4Si ($CDCl_3$; indirectly to $CDCl_3$, δ 76.9) and external Me_4Si (D_2O; indirectly to internal acetone, δ 31.55) for ^{13}C data. Column chromatography was performed on Kieselgel 60 (Merck, <230 mesh) and the fractions were monitored by TLC, performed on Kieselgel 60 F_{254} (Merck). Detection was effected by charring with sulfuric acid and examination under UV light. Optical rotations were measured at 20°C using a Perkin Elmer 241 polarimeter and a 10-cm 1-ml cell. Melting points were determined using a Mettler FP 51 instrument. In the work-up procedures, washings were carried out three times with appropriate quantities of water and aqueous sodium hydrogencarbonate unless indicated otherwise. Evaporations were conducted under reduced pressure at 40°C. All solvents were distilled from appropriate drying agents.

Methyl 3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranoside (**5**)

To a solution of methyl 3-*O*-benzyl-β-D-galactopyranoside[5] (6.27 g, 22.08 mmol) in α,α-dimethoxytoluene (30 ml) was added *p*-toluenesulfonic acid monohydrate (200 mg). After 15 min at room temperature, the mixture was diluted with dichloromethane (750 ml), neutralised with solid sodium hydrogen carbonate and washed with water. The organic layer was dried ($MgSO_4$) and concentrated. Crystallisation from ethanol gave **5** (6.21 g, 76%), m.p. 195°C, $[\alpha]_D$ +55.3° (*c* 1, chloroform). The mother liquor was purified by column chromatography (dichloromethane/ethyl acetate 9/1, v/v) yielding an additional amount of **5** (1.68 g, 20%), R_f 0.26 (dichloromethane/ethyl acetate 9/1, v/v). Anal. calcd. for $C_{21}H_{24}O_6$ (372.42): C 67.7, H 6.5; found: C 67.6, H 6.5%. NMR data ($CDCl_3$): ^{13}C, δ 137.9 and 128.8–126.2 ($C_6H_5CH_2O$ and C_6H_5CH), 103.7 (C-1), 101.0 (C_6H_5CH), 71.3 ($C_6H_5CH_2O$), 69.1 (C-6), 79.1, 72.9, 69.8 and 66.5 (C-2–C-5), 56.8 (OCH_3); ^{1}H, δ 7.543–7.296 (m, 10H, $C_6H_5CH_2O$ and C_6H_5CH), 5.465 (s, 1H, C_6H_5CH), 4.779 and 4.729 (2d, 2H, $C_6H_5CH_2O$), 4.333 (dd, 1H, H-6b), 4.246 (d, 1H, H-1), 4.147 (bd, 1H, H-4), 4.042 (dd, 1H, H-6a), 3.995 (m, 1H, H-2), 3.578 (s, 3H, OCH_3), 3.503 (dd, 1H, H-3), 3.387 (m, 1H,

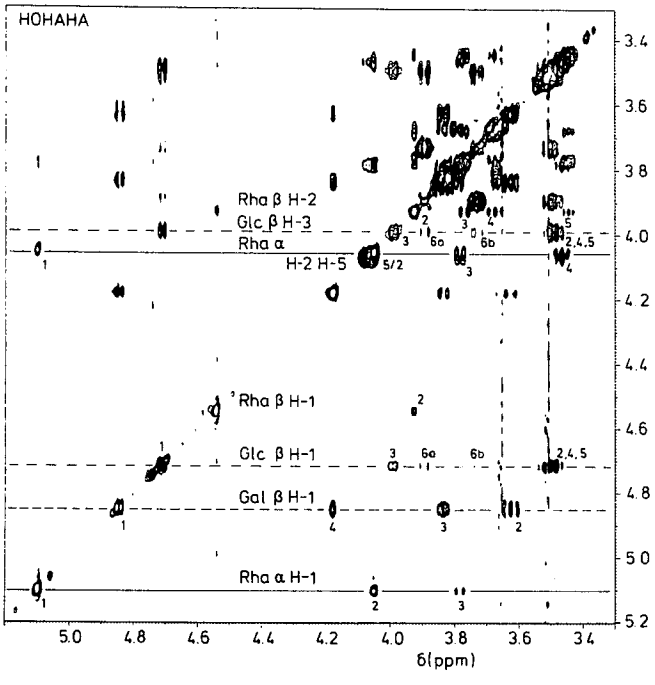


Fig. 2. 500 MHz 2D Homonuclear Hartmann–Hahn spectrum (region 3.3–5.2 ppm) of **3**. *The lines in the spectrum indicate scalar coupled networks for the respective residues (Rha β ·····; Gal β– — —; Rha α ———; Glc β – · – · –).*

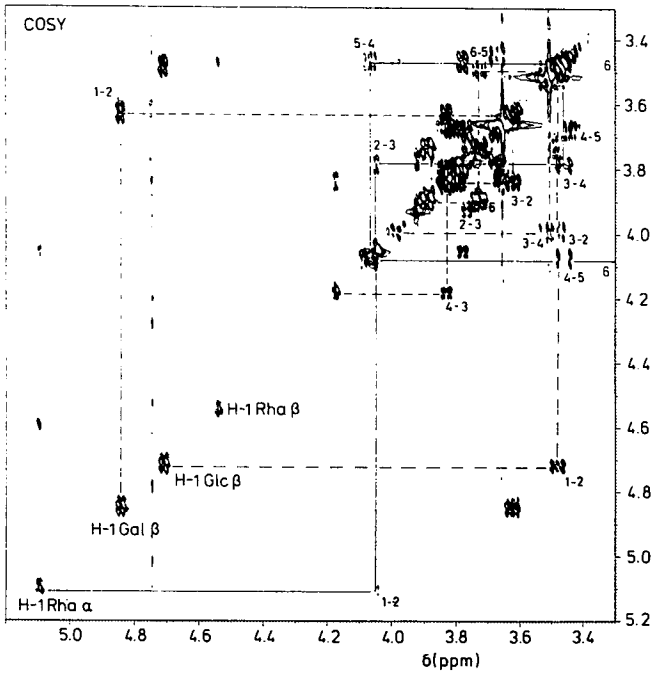


Fig. 3. 500 MHz 2D ^{1}H–^{1}H double-quantum-filtered shift-correlation spectrum (region 3.3–5.2 ppm) of **3**. *The lines in the spectrum indicate the spin connections for the respective residues (Rha β ·····; Gal β– — —; Rha α ———; Glc β – · – · –).*

H-5), 2.458 (d, 1H, HO-2), $J_{1,2}$ 7.7, $J_{2,3}$ 9.7, $J_{3,4}$ 3.6, $J_{4,5} < 1$, $J_{5,6b}$ 1.9, $J_{5,6a}$ 1.6 and $J_{6a,6b}$ −12.4 Hz.

Methyl 3-O-benzyl-4,6-O-benzylidene-2-O-(2,3,4-tri-O-acetyl-α-L--rhamnopyranosyl)-β-D-galactopyranoside (7)

A mixture of **5** (1.02 g, 2.74 mmol) and mercuric cyanide (2.32 g, 9.18 mmol) in nitromethane (20 ml)/toluene (20 ml) was concentrated until 20 ml of the solvent had been distilled off at atmospheric pressure. Powdered molecular sieves (4 Å, 10 g) were added and the mixture was stirred for 1 h at room temperature under argon. 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl bromide **6**[6] (1.64 g, 4.64 mmol) dissolved in freshly distilled nitromethane/toluene (4 ml) was added, followed by a second portion (830 mg, 2.35 mmol) after 1 h. After 3 h, TLC (dichloromethane/ethyl acetate 9/1, v/v) showed all the starting aglycon had disappeared. The mixture was then diluted with dichloromethane (300 ml), filtered, washed with aqueous 5% potassium iodide (3 × 75 ml) and water, dried ($MgSO_4$), and concentrated. Crystallisation from ethanol gave **7** (1.38 g, 78%), m.p. 199°C, $[\alpha]_D$ −8.2° (*c* 1, chloroform), R_f 0.60 (dichloromethane/ethyl acetate 9/1, v/v). Anal. calcd. for $C_{33}H_{40}O_{13}$ (644.67): C 61.5, H 6.2; found: C 61.3, H 6.2%. NMR data ($CDCl_3$): ^{13}C, δ 170.0 ($COCH_3$), 137.8 and 128.8–126.6 ($C_6H_5CH_2O$ and C_6H_5CH), 102.2 (C-1), 101.0 (C_6H_5CH), 98.3 (C-1′), 71.3 ($C_6H_5CH_2O$), 80.1, 74.2, 72.7, 71.0, 69.6, 69.3 and 66.2 (2 ×) (C-2–C-5 and C-2′–C-5′), 69.1 (C-6), 56.1 (OCH_3), 20.7 ($COCH_3$), 16.9 (C-6′); ^1H, δ 7.536–7.298 (m, 10H, $C_6H_5CH_2O$ and C_6H_5CH), 5.448 (s, 1H, C_6H_5CH), 5.372 (dd, 1H, H-2′), 5.271 (dd, 1H, H-3′), 5.182 (d, 1H, H-1′), 5.064 (t, 1H, H-4′), 4.657 (s, 2H, $C_6H_5CH_2O$), 4.315 (dd, 1H, H-6a), 4.301 (d, 1H, H-1), 4.221 (m, 1H, H-5′), 4.093 (bd, 1H, H-4), 4.020 (dd, 1H, H-6b), 4.002 (dd, 1H, H-2), 3.582 (dd, 1H, H-3), 3.534 (s, 3H, OCH_3), 3.348 (m, 1H, H-5), 2.091, 2.057 and 2.002 (3s, each 3H, $COCH_3$), 1.183 (d, 3H, H-6′), $J_{1,2}$ 7.8, $J_{2,3}$ 9.6, $J_{3,4}$ 3.6, $J_{4,5} < 1$, $J_{5,6a}$ 1.6, $J_{5,6b}$ 1.8, $J_{6a,6b}$ −12.6, $J_{1',2'}$ 1.8, $J_{2',3'}$ 3.4, $J_{3',4'} = J_{4',5'}$ 10.0 and $J_{5',6'}$ 6.3 Hz.

Methyl 3-O-benzyl-4,6-O-benzylidene-2-O-(2,3,4-tri-O-benzyl-α-L--rhamnopyranosyl)-β-D-galactopyranoside (9)

To a solution of **7** (4.50 g, 6.99 mmol) in dichloromethane (20 ml) and methanol (10 ml) was added solid sodium methoxide (pH 9). After stirring overnight, the solution was diluted with dichloromethane (750 ml), washed with water (5 × 75 ml), dried ($MgSO_4$) and concentrated, yielding **8** (3.61 g, 99%). To a mixture of **8** (3.61 g, 6.97 mmol) and powdered potassium hydroxide (4.7 g, 83.9 mmol) in dry dimethylformamide (40 ml) was added benzyl bromide (9.3 ml, 52.3 mmol) at 0°C. The mixture was stirred overnight at room temperature, methanol was added and the solution was diluted with dichloromethane (750 ml), filtered, washed with water, dried ($MgSO_4$) and concentrated. Column chromatography (petroleum ether [b.p. 40/60]/ethyl acetate 1/1, v/v) of the residue gave **9** (4.40 g, 80%), m.p. 147°C (from ethanol), $[\alpha]_D$ +17.8° (*c* 1, chloroform), R_f 0.76 (petroleum ether [b.p. 40/60]/ethyl acetate 1/1, v/v). Anal. calcd. for $C_{48}H_{52}O_{10}$ (788.93): C 73.1, H 6.6; found: C 73.1, H 6.6%. NMR data ($CDCl_3$): ^{13}C, δ 138.6–137.6 and 128.6–126.2 ($C_6H_5CH_2O$ and C_6H_5CH), 102.3 (C-1), 100.8 (C_6H_5CH), 98.7 (C-1′), 80.4, 79.9 (3 ×), 74.6, 72.3, 67.9 (C-2–C-5, C-2′–C-5′), 75.1, 71.7, 71.6 and 70.6 (4 $C_6H_5CH_2O$), 68.9 (C-6), 55.9 (OCH_3), 17.5 (C-6′); ^1H, δ 7.186–7.540 (m, 25H, 4 $C_6H_5CH_2O$ and C_6H_5CH), 5.429 (s, 1H, C_6H_5CH), 5.223 (d, 1H, H-1′), 4.921, 4.647, 4.609, 4.602, 4.554 (2 ×), 4.498 and 4.448 (8d, 8H, 4 $C_6H_5CH_2O$), 4.287 (dd, 1H, H-6a), 4.200 (d, 1H, H-1), 4.090 (bd, 1H, H-4), 4.020 (m, 1H, H-5′), 4.007–3.059 (m, 2H, H-2 and H-6b), 3.829 (dd, 1H, H-3′), 3.789 (dd, 1H, H-2′), 3.621 (t, 1H, H-4′), 3.499 (s, 3H, OCH_3), 3.461 (dd, 1H, H-3), 3.281 (m, 1H, H-5), 1.314 (d, 3H, H-6′), $J_{1,2}$ 7.8, $J_{2,3}$ 9.5, $J_{3,4}$ 3.6, $J_{4,5} < 1$, $J_{5,6a}$ 1.4, $J_{6a,6b}$ −12.3, $J_{1',2'}$ 1.7, $J_{2',3'}$ 3.1, $J_{3',4'} = J_{4',5'}$ 9.5 and $J_{5',6'}$ 6.2 Hz.

Methyl 3,6-di-O-benzyl-2-O-(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (10)

To a solution of crystalline **9** (1.01 g, 1.26 mmol) in freshly distilled tetrahydrofuran (20 ml) were added borane–trimethylamine complex (0.56 g, 7.68 mmol) and powdered molecular sieves (4 Å, 10 g). After stirring for 1 h, aluminium(III) chloride (1.07 g, 8.02 mmol) was added and TLC (dichloromethane/ethyl acetate 9/1, v/v) showed the ring opening to be complete within 5 min (**10**, R_f 0.32). The mixture was filtered over celite, diluted with dichloromethane (300 ml), washed with 1 M sulfuric acid (3 × 50 ml), water, aqueous 5% sodium hydrogen carbonate, water, dried ($MgSO_4$) and concentrated. Purification of the residue by column chromatography (dichloromethane/ethyl acetate 85/15, v/v) gave **10** as a syrup (0.80 g, 78%), $[\alpha]_D$ −9.8° (*c* 1, chloroform). Anal. calcd. for $C_{48}H_{54}O_{10}$ (790.95): C 72.9, H 6.9; found C 72.9, H 7.0%. NMR data ($CDCl_3$): ^{13}C, δ 138.5–137.2 and 128.2–127.1 ($C_6H_5CH_2O$), 102.5 (C-1), 98.7 (C-1′), 81.4, 80.2, 79.8, 75.1, 73.7, 73.3, 67.9, 65.5 (C-2–C-5, C-2′–C-5′), 74.9, 72.7, 72.0, 71.7, 70.8 (5 $C_6H_5CH_2O$), 68.9 (C-6), 56.3 (OCH_3), 17.4 (C-6′); ^1H, δ 7.334–7.206 (m, 25H, 5 $C_6H_5CH_2O$), 5.191 (d, 1H, H-1′), 4.448–4.929 (m, 10H, 5 $C_6H_5CH_2O$), 4.141 (d, 1H, H-1), 3.985 (m, 1H, H-5′), 3.620 (t, 1H, H-4′), 3.483 (s, 3H, OCH_3), 3.419 (dd, 1H, H-3), 2.354 (d, 1H, HO-4), 1.290 (d, 3H, H-6′), $J_{1,2}$ 7.7, $J_{2,3}$ 9.4, $J_{3,4}$ 3.1, $J_{1',2'}$ 1.8, $J_{3',4'} = J_{4',5'}$ 9.3 and $J_{5',6'}$ 6.3 Hz.

Methyl 3,6-di-O-benzyl-4-O-(2,4,6-tri-O-acetyl-3-O-allyl-β-D-glucopyranosyl)-2-O-(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (12)

To a solution of **10** (240 mg, 0.30 mmol) in benzene/nitromethane (1/1, 7 ml) was added mercuric cyanide (231 mg, 0.91 mmol). After *ca.* 2 ml of the solvent had been distilled off, the mixture was cooled to 45°C and 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl bromide (**11**)[8] (293 mg, 0.72 mmol) was added. The mixture was stirred at 45°C until the aglycon (R_f 0.46, dichloromethane/ethyl acetate 85/15, v/v) had disappeared (6 h). It was then worked up as described for **7**. The crude product was purified by column chromatography (dichloromethane/ethyl acetate 85/15, v/v) affording **12** (297 mg, 88%), $[\alpha]_D$ −5.8° (*c* 1, chloroform), R_f 0.57 (dichloromethane/ethyl acetate 85/15, v/v). Anal. calcd. for $C_{63}H_{74}O_{18}$ (1119.27): C 67.6, H 6.7; found: C 67.6, H 6.7%. NMR data ($CDCl_3$): ^{13}C, δ 170.3 ($COCH_3$), 138.5 and 128.3–126.8 ($C_6H_5CH_2O$), 134.1 ($H_2C{=}CH{-}CH_2O$), 116.7 ($H_2C{=}CH{-}CH_2O$), 102.2 (C-1), 100.0 (C-1″), 98.5 (C-1′), 83.2, 80.3, 80.0, 79.4, 75.5, 73.5, 72.9, 72.4, 71.6, 69.2 and 67.9 (C-2–C-5, C-2′–C-5′, C-2″–C-5″), 69.0 (C-6), 61.9 (C-6″), 55.6 (OCH_3), 20.6 (2 ×) and 20.4 (3 $COCH_3$), 17.4 (C-6′); ^1H, δ 7.407–7.241 (m, 25H, 5 $C_6H_5CH_2O$), 5.776 (m, 1H, $H_2C{=}CH{-}CH_2O$), 5.181 (d, 1H, H-1′), 5.211 and 5.143 (2 m, 2H, $H_2C{=}CH{-}CH_2O$), 4.796 (d, 1H, H-1″), 4.154 (d, 1H, H-1), 3.434 (s, 3H, OCH_3), 2.111, 2.048 and 1.970 (3 s,, each 3H, 3 $COCH_3$), 1.280 (d, 3H, H-6′), $J_{1,2}$ 7.6, $J_{1',2'}$ 1.8, $J_{5',6'}$ 6.3 and $J_{1'',2''}$ 8.0 Hz.

Methyl 3,6-di-O-benzyl-4-O-(3-O-allyl-β-D-glucopyranosyl)-2-O--(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (13)

Compound **12** (679 mg, 0.61 mmol) was suspended in dry methanol (10 ml) and sodium methoxide was added (pH 10). After stirring for 16 h, deacetylation was complete on TLC (R_f 0.63; dichloromethane/methanol 9/1, v/v) and the mixture was neutralized with DOWEX-50 (H^+) resin, filtered and concentrated. The resulting product **13** (602 mg, 0.61 mmol) was used without further purification in the next step. NMR data ($CDCl_3$): ^1H, δ 7.379–7.220 (m, 25H, 5 $C_6H_5CH_2O$), 5.981 (m, 1H, $H_2C{=}CH{-}CH_2O$), 5.314 and 5.204 (2 m, 2H, $H_2C{=}CH{-}CH_2O$), 5.117 (d, 1H, H-1′), 4.658–4.434 (m, 10H, 5 $C_6H_5CH_2O$), 4.284 (d, 1H, H-1″), 4.226 (m, 1H, $H_2C{=}CH{-}CH_2O$), 4.105 (d, 1H, H-1), 3.955 (m, 1H, H-5′), 3.456 (s, 3H, OCH_3), 2.571 (bs, 3H, 3 OH), 1.285 (d, 3H, H-6′), $J_{1,2}$ 7.7, $J_{1',2'}$ 1.7, $J_{5',6'}$ 6.3 and $J_{1'',2''}$ 7.7 Hz.

Methyl 3,6-di-O-benzyl-4-O-(3-O-allyl-2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2-O-(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (14)

A solution of **13** (302 mg, 0.30 mmol) and benzyl bromide (2.2 ml, 18.26 mmol) in dry dimethylformamide (5 ml) was added dropwise to a suspension of sodium hydride (60 mg, 2.52 mmol) in dimethylformamide (3 ml) at 0°C. The mixture was maintained for 30 min at 0°C, followed by 15 min at room temperature. TLC then indicated the complete conversion of **13** into a product with R_f 0.55 (dichloromethane/ethyl acetate 95/5, v/v). To destroy the excess sodium hydride, methanol was added, the mixture was poured into ice-water (150 ml) and the product extracted with diethyl ether (4 × 50 ml). The organic phase was dried ($MgSO_4$) and concentrated and the residue purified by column chromatography (dichloro-

methane/ethyl acetate 95/5, v/v) yielding **14** (313 mg, 83%), $[\alpha]_D$ +9.5° (*c* 1, chloroform). Anal. calcd. for $C_{78}H_{86}O_{15}$ (1263.53): C 74.2, H 6.9; found: 74.1, H 7.0%. NMR data ($CDCl_3$): ^{13}C, δ 138.6–137.9 and 128.0–126.8 ($C_6H_5CH_2O$), 135.0 ($H_2C=CH-CH_2O$), 116.3 ($H_2C=CH-CH_2O$), 102.9 and 102.0 (C-1, C-1″), 98.4 (C-1′), 56.4 (OCH_3), 17.5 (C-6′); ^1H, δ 7.484–7.090 (m, 40H, 8 $C_6H_5CH_2O$), 5.966 (m, 1H, $H_2C=CH-CH_2O$), 5.281 and 5.161 (2 m, 2H, $H_2C=CH-CH_2O$), 5.120 (d, 1H, H-1′), 3.514 (s, 3H, OCH_3), 1.285 (d, 3H, H-6′), $J_{1',2'}$ 1.3 Hz.

Methyl 3,6-di-O-benzyl-4-O-(2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2-O-(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D-galacto-pyranoside (**15**)

A solution of **14** (267 mg, 0.21 mmol) in dry dimethylformamide (2 ml) was heated at 90°C and potassium *tert*-butoxide was added until the mixture turned black. After 1½ h, the reaction was complete on TLC and the mixture was cooled, diluted with aqueous 5% sodium chloride (50 ml). The product (R_f 0.67; dichloromethane/ethyl acetate 95/5, v/v) was then extracted with dichloromethane (3 × 25 ml). The organic layer was then dried ($MgSO_4$) and concentrated. The residue was suspended in 1 M hydrochloric acid (0.2 ml) and acetone (1.8 ml) and boiled under reflux for 2 h. The mixture was neutralised with aqueous 5% sodium hydrogen carbonate, concentrated and diluted with dichloromethane (50 ml) and water (15 ml). The organic phase was then washed with water, dried ($MgSO_4$) and concentrated. Column chromatography (dichloromethane/ethyl acetate 9/1, v/v) of the residue gave **15** (98 mg, 38%), $[\alpha]_D$ +11.9° (*c* 1, chloroform), R_f 0.45 dichloromethane/ethyl acetate 9/1, v/v). NMR data ($CDCl_3$): ^{13}C, δ 138.7–137.5 and 128.3–126.9 ($C_6H_5CH_2O$), 102.9 and 102.4 (C-1, C-1″), 98.7 (C-1′), 82.8, 81.4, 80.5, 80.0, 77.0, 76.6, 75.5 (2 ×), 74.4, 73.8, 70.9 and 68.0 (C-2–C-5, C-2′–C-5′, C-2″–C-5″), 75.1, 74.3 (2 ×), 73.4, 73.2, 72.0, 71.8, 71.7 (8 $C_6H_5CH_2O$), 70.2 and 69.2 (C-6, C-6″), 56.5 (OCH_3), 7.5 (C-6′).

Methyl 3,6-di-O-benzyl-4-O-[2,4,6-tri-O-benzyl-3-O-(diphenyl phosphoryl)-β-D-glucopyranosyl]-2-O-(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**16**)

To a solution of **15** (98 mg, 0.08 mmol) in anhydrous dichloromethane (5 ml) were added pyridine (20 µl, 0.25 mmol), 4-(dimethylamino)pyridine (31 mg, 0.25 mmol) and diphenyl phosphorochloridate (50 µl, 0.24 mmol). After 6 h stirring at room temperature, TLC showed a single spot with R_f 0.61 (dichloromethane/ethyl acetate 95/5, v/v). The mixture was then diluted with dichloromethane (50 ml), washed with 1 M hydrochloric acid (3 × 15 ml), water, aqueous 5% sodium hydrogen carbonate, water, dried ($MgSO_4$) and concentrated. Column chromatography (dichloromethane/ethyl acetate 95/5, v/v) of the residue afforded **16** (104 mg, 90%), $[\alpha]_D$ +11.2° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 150.4, 144.8, 130.7 (2 ×), 120.1 and 120.0 ($[C_6H_5O]_2P$), 138.7–137.5 and 129.3–126.9 ($C_6H_5CH_2O$), 103.0 and 102.4 (C-1, C-1″), 98.5 (C-1′), 56.5 (OCH_3), 17.5 (C-6′); ^1H, δ 7.467–7.040 (m, 50H, 8 $C_6H_5CH_2O$ and $[C_6H_5O]_2P$), 4.970 (d, 1H, H-1′), 3.954 (m, 1H, H-5′), 3.503 (s, 3H, OCH_3), 1.272 (d, 3H, H-6′), $J_{1',2'}$ 1.3, $J_{4',5'}$ 9.3 and $J_{5',6'}$ 6.2 Hz.

Methyl 4-O-(3-O-disodium phosphoryl)-β-D-glucopyranosyl-2-O-α-L--rhamnopyranosyl-β-D-galactopyranoside (**1**)

A solution of **16** (41.9 mg, 28.8 µmol) in ethanol (10 ml) was hydrogenolysed using 10% Pd/C (20 mg) at 4 kg cm^{-2} for 16 h at room temperature. The catalyst was substituted by platinum oxide (20 mg) and the hydrogenolysis was continued for 16 h. After filtration and evaporation of the solvent, the residue was dissolved in water (10 ml) and treated with DOWEX-50 (Na^+) resin. After filtration and washing with dichloromethane, the water layer was lyophilised giving **1** (7.3 mg, 41%), $[\alpha]_D$ −21.9° (*c* 0.3, water). NMR data (D_2O): ^{13}C, δ 105.2, 104.0 and 102.9 (C-1, C-1′ and C-1″), 80.1, 79.9, 79.6, 76.9, 75.4, 75.0 (2 ×), 73.3 71.5 (2 ×), 70.9 and 70.1 (C-2–C-5, C-2′–C-5′, C-2″–C-5″), 62.1 (2 ×) (C-6 and C-6″), 58.4 (OCH_3), 17.7 (C-6′); ^1H, see Table I.

Ethyl 2,3,4-tri-O-acetyl-1-thio-α-L-rhamnopyranoside (**18**)

Freshly fused zinc chloride (35.9 g, 263.7 mol) and ethanethiol (49.5 ml, 659.3 mmol) were added to a stirred solution of 1,2,3,4-tetra-*O*-acetyl-α-L-rhamnopyranose **17**[6] (21.9 g, 65.9 mmol) in dry dichloromethane (150 ml) and powdered molecular sieves (4 Å, 27.5 g). After 20 min, the reaction was complete according to TLC (R_f 0.47; petroleum ether [b.p. 40/60]/ethyl acetate 3/1, v/v). The mixture as then filtered over celite, diluted with dichloromethane (1 l), washed with 1 M sulfuric acid (6 × 100 ml), water, aqueous 5% sodium hydrogencarbonate and water, dried ($MgSO_4$) and concentrated. Purification of the residue by column chromatography (petroleum ether [b.p. 0/60]/ethyl acetate 3/1, v/v) gave **18** (9.7 g, 44%), $[\alpha]_D$ −122.1° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 169.4–169.2 ($COCH_3$), 81.5 (C-1), 71.0, 70.8, 69.0 and 66.5 (C-2–C-5), 24.9 (CH_3CH_2S), 20.4, 20.2 and 20.1 (3 $COCH_3$), 16.8 (C-6), 14.4 (CH_3CH_2S); ^1H, δ 2.67 (q, 2H, CH_3CH_2S), 2.19, 2.09 and 2.01 (3 s, each 3H, 3 $COCH_3$), 1.32 (t, 3H, CH_3CH_2S), 1.25 (d, 3H, H-6).

Ethyl 2,3-O-isopropylidene-1-thio-α-L-rhamnopyranoside (**20**)

Compound **18** 9.71 g, 29.06 mmol) was suspended in dry methanol (90 ml) and sodium methoxide was added (pH 10). After stirring for 1½ h, deacetylation was complete (TLC R_f 0.53; dichloromethane/methanol 85/15, v/v) and the solution was neutralised with Dowex-50 (H^+) resin, filtered and concentrated, yielding **19**. To a solution of **19** (6.04 g, 29.02 mmol) in 2,2-dimethoxypropane (65 ml) was added *p*-toluenesulfonic acid monohydrate (500 mg). The reaction was stopped after 30 min by adding solid sodium hydrogen carbonate. The mixture was diluted with dichloromethane (600 ml) and the organic phase was washed with aqueous 5% sodium hydrogen carbonate, water, dried ($MgSO_4$) and concentrated, affording **20** as a yellow syrup (7.06 g, 98%), $[\alpha]_D$ −173.4° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 109.2 ($C(CH_3)_2$), 79.2, 78.3, 76.6, 74.9 and 65.8 (C-1–C-5), 27.9 and 26.1 ($C(CH_{3,2})$), 24.2 (CH_3CH_2S), 17.0 (C-6), 14.4 (CH_3CH_2S); ^1H, δ 5.59 (s, 1H, H-1), 1.47 and 1.56 (2 s, each 3H, $C(CH_3)_2$), 1.43 (t, 3H, CH_3CH_2S), 1.32 (d, 3H, H-6), $J_{5,6}$ 6.8 Hz.

Ethyl 4-O-allyl-2,3-O-isopropylidene-1-α-L-rhamnopyranoside (**21**)

To a solution of **20** (4.87 g, 19.62 mmol) in dry dimethylformamide (50 ml) were added powdered potassium hydroxide (4.3 g, 77.2 mmol) and allyl bromide (3.3 ml, 38.6 mmol). When TLC showed the reaction to be complete (R_f **21** 0.45; petroleum ether [b.p. 40/60]/ethyl acetate 5/1, v/v), methanol was added and the mixture was diluted with dichloromethane (500 ml), filtered, washed with water, dried ($MgSO_4$) and concentrated. Purification of the residue by column chromatography (petroleum ether [b.p. 40/60]/ethyl acetate 1/1, v/v) afforded **21** as a syrup (5.54 g, 98%), $[\alpha]_D$ −177.0° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 134.8 ($H_2C=CH-CH_2O$), 116.6 ($H_2C=CH-CH_2O$), 108.8 ($C(CH_3)_2$), 81.2, 79.3, 78.0, 76.7 and 64.9 (C-1–C-5), 71.8 ($H_2C=CH-CH_2O$), 27.8 and 26.2 ($C(CH_3)_2$), 24.1 (CH_3CH_2S), 17.5 (C-6), 14.4 (CH_3CH_2S).

Ethyl 4-O-allyl-1-thio-α-L-rhamnopyranoside (**22**)

A suspension of **21** (2.86 g, 9.92 mmol) in aqueous 45% acetic acid (30 ml) was heated at 70°C and, after 1½ h, TLC showed a complete converison of **21** (R_f 0.74; dichloromethane/acetone 9/1, v/v) into **22** (R_f 0.23). After concentration, coevaporation with toluene, ethanol and dichloromethane, compound **22** was obtained as a white amorphous solid (2.41 g, 98%), $[\alpha]_D$ −211.1° (*c* 1, chloroform), m.p. 77.6°C. Anal. calcd. for $C_{11}H_{20}O_4S$ (248.34): C 53.2, H 8.1; found: C 53.4, H 7.9%. NMR data ($CDCl_3$): ^{13}C, δ 134.6 ($H_2C=CH-CH_2O$), 117.2 ($H_2C=CH-CH_2O$), 83.6, 81.5, 72.5, 71.7 and 67.6 (C-1–C-5), 73.7 ($H_2C=CH-CH_2O$), 24.9 (CH_3CH_2S), 17.7 (C-6), 14.8 (CH_3CH_2S).

Ethyl 4-O-allyl-2,3-di-O-benzyl-1-thio-α-L-rhamnopyranoside (**23**)

To a solution of **22** (6.30 g, 25.39 mmol) in dry dimethylformamide (75 ml) were added powdered potassium hydroxide (11.8 g, 210.7 mmol) and benzyl bromide (12.3 ml, 101.6 mmol). After 2 h, TLC (petroleum ether [b.p. 40/60]/ethyl acetate 5/1, v/v) showed that all the starting compound had disappeared. Methanol was then added, and the mixture was diluted with dichloromethane (750 ml), filtered, washed with water, dried ($MgSO_4$) and concentrated. Purification of the residue by column chromatography (petroleum ether [b.p. 40/60]/ethyl acetate 85/15, v/v) yielded **23** as a syrup (10.55 g, 97%), $[\alpha]_D$ −132.8° (*c* 1, chloroform), R_f 0.63

(petroleum ether [b.p. 40/60]/ethyl acetate 5/1, v/v). Anal. calcd. for $C_{25}H_{32}O_4$ (428.58): C 70.1, H 7.5: found: C 70.1, H 7.6%. NMR data ($CDCl_3$): ^{13}C, δ 138.2, 137.9 and 128.1–127.4 ($C_6H_5CH_2O$), 135.0 ($H_2C=CH-CH_2O$), 116.3 ($H_2C=CH-CH_2O$), 81.8, 80.3, 79.9, 76.6, 68.2 (C-1–C-5), 73.9, 72.0, 71.9 ($H_2C=CH-CH_2O$ and 2 $C_6H_5CH_2O$), 25.1 (CH_3CH_2S), 17.6 (C-6), 14.8 (CH_3CH_2S); ^1H, δ 7.375–7.251 (m, 10H, 2 $C_6H_5CH_2O$), 5.932 (m, 1H, $H_2C=CH-CH_2O$), 5.257 and 5.140 (2 m, 2H, $H_2C=CH-CH_2O$), 5.238 (d, 1H, H-1), 4.703, 4.662, 4.585 and 4.536 (4 d, 4H, 2 $C_6H_5CH_2O$), 4.390 and 4.130 (2 m, 2H, $H_2C=CH-CH_2O$), 3.978 (m, 1H, H-5), 3.802 (dd, 1-H, H-2), 3.714 (dd, 1H, H-3), 3.494 (t, 1H, H-4), 2.619–2.493 (m, 2H, CH_3CH_2S), 1.316 (d, 3H, H-6), 1.228 (t, 3H, CH_3CH_2S), $J_{1,2}$ 1.6, $J_{2,3}$ 3.1, $J_{3,4} = J_{4,5}$ 9.4, $J_{5,6}$ 6.2 and $J_{CH_2CH_3}$ 7.4 Hz.

Ethyl 2,3-di-O-benzyl-1-thio-α-L-rhamnopyranoside (**24**)

A solution of **23** (1.63 g, 3.81 mmol) in dry dimethylformamide (38 ml) was heated at 90°C and potassium *tert*-butoxide was added until the mixture formed black. After 15 min, TLC showed complete conversion into a new spot (R_f 0.95; dichloromethane/ethyl acetate 85/15, v/v). The mixture was then cooled and diluted with water (38 ml). After extraction with dichloromethane (3 × 100 ml), the organic layer was dried ($MgSO_4$) and concentrated. The residue was suspended in acetone (34.0 ml) and 1 M hydrochloric acid (3.8 ml) and boiled under reflux until TLC showed only one spot (**24** R_f 0.52; dichloromethane/ethyl acetate 85/15, v/v). The mixture was neutralised with saturated aqueous sodium hydrogen carbonate (50 ml), concentrated and diluted with dichloromethane (100 ml) and water (100 ml). The water layer was extracted with dichloromethane (3 × 75 ml) and the combined organic layer was dried ($MgSO_4$), concentrated and the residue purified by column chromatography (dichloromethane/ethyl acetate 85/15, v/v) yielding **24** (1.29 g, 87%), $[\alpha]_D$ −67.5° (*c* 1, chloroform). Anal. calcd. for $C_{22}H_{28}O_4S$ (388.52): C 68.0, H 7.3; found: C 67.7, H 7.5%. NMR data ($CDCl_3$): ^{13}C, δ 137.6 and 128.4–127.6 ($C_6H_5CH_2O$), 81.8, 79.7, 75.5, 71.8 and 68.5 (C-1–C-5), 71.9 and 71.3 (2 $C_6H_5CH_2O$), 25.3 (CH_3CH_2S), 17.6 (C-6), 14.8 (CH_3CH_2S); 1H, δ 7.386–7.263 (m, 10H, 2 $C_6H_5CH_2O$), 5.334 (d, 1H, H-1), 4.709, 4.575, 4.523 and 4.380 (4 d, 4H, 2 $C_6H_5CH_2O$), 3.988 (m, 1H, H-5), 3.862 (dd, 1H, H-2), 3.748 (m, 1H, H-4), 3.591 (dd, 1H, H-3), 2.661–2.540 (m, 2H, CH_3CH_2S), 2.272 (d, 1H, HO-4), 1.326 (d, 3H, H-6), 1.263 (t, 3H, CH_3CH_2S), $J_{1,2}$ 1.4, $J_{2,3}$ 3.1, $J_{3,4}$ 9.5, $J_{4,5}$ 9.0, $J_{5,6}$ 6.2, $J_{CH_2CH_3}$ 7.4 and $J_{OH,4}$ 2.5 Hz.

Methyl 4-O-allyl-2,3-di-O-benzyl-α/β-L-rhamnopyranoside (**25**α/β)

A mixture of cupric bromide (1.65 g, 7.39 mmol), tetrabutylammonium bromide (258 mg, 0.79 mmol), silver silicate (250 mg), molecular sieves (3 Å, 4.0 g) and dry methanol (385 µl, 9.53 mmol) in dry dichloromethane (25 ml) was stirred for 1 h under argon in the dark. A solution of **23** (1.02 g, 2.38 mmol) in dry dichloromethane (10 ml) was then added. After 2 h, the reaction was complete, as shown by two new spots on TLC (R_f 0.39 **25**β, R_f 0.47 **25**α; petroleum ether [b.p. 40/60]/ethyl acetate 5/1, v/v). The mixture was filtered over celite, diluted with dichloromethane (100 ml), washed with saturated aqueous sodium hydrogen carbonate, saturated aqueous sodium chloride and water, dried ($MgSO_4$) and concentrated. Separation by column chromatography (petroleum ether [b.p. 40/60]/ethyl acetate 5/1, v/v) gave crystalline **25**β (422 g, 45%), $[\alpha]_D$ +65.2° (*c* 1, chloroform), m.p. 55.3°C (from ethanol), and syrupy **25**α (249 mg, 26%), $[\alpha]_D$ −31.0° (*c* 1, chloroform). Anal. calcd. for **25**β $C_{24}H_{30}O_5$ (398.50): C 72.3, H 7.6; found: C 72.0, H 7.6%. NMR data **25**β ($CDCl_3$): ^{13}C, δ 138.7–138.2 and 128.1–127.1 ($C_6H_5CH_2O$), 134.9 ($H_2C=CH-CH_2O$), 116.6 ($H_2C=CH-CH_2O$), 102.4 (C-1), 81.8, 80.0, 74.0 and 71.8 (C-2–C-5), 74.1, 73.8 and 71.3 (2 $C_6H_5CH_2O$ and $H_2C=CH-CH_2O$), 56.8 (OCH_3), 17.8 (C-6); ^1H, δ 7.440–7.241 (m, 10H, 2 $C_6H_5CH_2O$), 5.935 (m, 1H, $H_2C=CH-CH_2O$), 5.252 and 5.150 (2 m, 2H, $H_2C=CH-CH_2O$), 4.937, 4.809, 4.484 and 4.442 (4 d, 4H, 2 $C_6H_5CH_2O$), 4.419 and 3.970 (2 m, 2H, $H_2C=CH-CH_2O$), 4.240 (s, 1H, H-1), 3.854 (d, 1H, H-2), 3.505 (s, 3H, OCH_3), 3.469 (t, 1H, H-4), 3.372 (dd, 1H, H-3), 3.271 (m, 1H, H-5), 1.379 (d, 3H, H-6), $J_{1,2} \sim 0$, $J_{2,3}$ 3.0, $J_{3,4} = J_{4,5}$ 9.4, $J_{5,6}$ 6.2 Hz. NMR data **25**α ($CDCl_3$): ^{13}C, δ 138.5–138.1 and 128.1–127.3 ($C_6H_5CH_2O$), 135.0 ($H_2C=CH-CH_2O$), 116.4 ($H_2C=CH-CH_2O$), 98.9 (C-1), 80.2, 79.8, 74.7 and 67.7 (C-2–C-5), 74.0, 72.6 and 72.0 ($H_2C=CH-CH_2O$ and 2 $C_6H_5CH_2O$), 54.4 (OCH_3), 17.8 (C-6); ^1H, δ 7.380–7.240 (m, 10H, 2 $C_6H_5CH_2O$), 5.932 (m, 1H, $H_2C=CH-CH_2O$), 5.252 and 5.141 (2 m, 2H, $H_2C=CH-CH_2O$), 4.744, 4.692, 4.617 and 4.576 (4 d, 4H, 2 $C_6H_5CH_2O$), 4.630 (d, 1H, H-1), 4.394 and 4.140 (2 m, 2H, $H_2C=CH-CH_2O$), 3.773–3.724 (m, 2H, H-2 and H-3), 3.615 (m, 1H, H-5), 3.472 (t, 1H, H-4), 3.290 (s, 3H, OCH_3), 1.336 (d, 3H, H-6), $J_{1,2}$ 1.8, $J_{3,4} = J_{4,5}$ 9.4 and $J_{5,6}$ 6.2 Hz.

Methyl 2,3-di-O-benzyl-β-L-rhamnopyranoside (**26**)

To a solution of **25**β (422 mg, 1.06 mmol) in dry dimethylformamide (10.6 ml) at 90°C was added potassium *tert*-butoxide until the mixture turned black. After 15 min, TLC showed the absence of starting compound (R_f 0.26; toluene/acetone 50/1, v/v) and the presence of a new spot (R_f 0.59). The mixture was worked up as described for **24** and the residue was taken up in acetone (9.6 ml) and 1 M hydrochloric acid (1.1 ml) and boiled under reflux. When only one new compound was present, as detected by TLC ($1\frac{1}{2}$ h), the mixture was worked up as described for **24**. Column chromatography (dichloromethane/ethyl acetate 85/15, v/v) of the residue afforded **26** (331 mg, 71%), $[\alpha]_D$ +190.8° (*c* 1, chloroform), R_f 0.50 (dichloromethane/ethyl acetate 85/15, v/v). NMR data ($CDCl_3$): ^{13}C, δ 138.5 and 128.2–127.1 ($C_6H_5CH_2O$), 102.5 (C-1), 81.2, 73.1, 72.0 and 71.3 (C-2–C-5), 73.8 and 70.5 (2 $C_6H_5CH_2O$), 56.8 (OCH_3), 17.5 (C-6); ^1H, δ 7.441–7.224 (m, 10H, 2 $C_6H_5CH_2O$), 4.966, 4.735, 4.449 and 4.231 (4 d, 4H, 2 $C_6H_5CH_2O$), 4.306 (s, 1H, H-1), 3.918 (d, 1H, H-2), 3.697 (t, 1H, H-4), 3.536 (s, 3H, OCH_3), 3.277 (m, 1H, H-5), 3.229 (dd, 1H, H-3), 1.388 (d, 3H, H-6), $J_{1,2} \sim 0$, $J_{2,3}$ 3.0, $J_{3,4} = J_{4,5}$ 9.3 and $J_{5,6}$ 6.2 Hz.

Methyl 2,4,6-tri-O-acetyl-3-O-benzyl-β-D-galactopyranoside (**27**)

Methyl 3-*O*-benzyl-β-D-galactopyranoside[5] (5.41 g, 19.06 mmol) in dry pyridine (50 ml) and acetic anhydride (50 ml) was stirred overnight at room temperature. The mixture was concentrated using toluene, ethanol and dichloromethane and the residue was crystallised from ethanol to give **27** (5.49 g, 70%) as white crystals, $[\alpha]_D$ +52.9° (*c* 1, chloroform), m.p. 122.2°C, R_f 0.31 (dichloromethane/acetone 97/3, v/v); lit.[12] $[\alpha]_D$ +48°, m.p. 121–123°C. NMR data ($CDCl_3$): ^1H, δ 7.336–7.235 (m, 5H, $C_6H_5CH_2O$), 5.495 (bd, 1H, H-4), 5.100 (dd, 1H, H-2), 4.684 and 4.388 (2d, 2H, $C_6H_5CH_2O$), 4.286 (d, 1H, H-1), 4.167 (d, 2H, H-6), 3.787 (bt, 1H, H-5), 3.528 (dd, 1H, H-3), 3.647 (s, 3H, OCH_3), 2.136, 2.064 and 2.017 (3 s, each 3H, 3 $COCH_3$), $J_{1,2}$ 8.0, $J_{2,3}$ 10.0, $J_{3,4}$ 3.5, $J_{4,5} < 1$ and $J_{5,6}$ 6.6 Hz.

2,4,6-Tri-O-acetyl-3-O-benzyl-α-D-galactopyranosyl trichloroacetimidate (**30**)

To a solution of **27** (2.04 g, 4.98 mmol) in acetic anhydride (16 ml), 4% sulfuric acid (v/v) in acetic anhydride (16 ml) was added over 40 min at 0°C. After 4 h stirring at room temperature, the mixture was poured into ice-water (1 l) containing sodium hydrogen carbonate (20 g) and stirred for a further 2 h. The mixture was extracted with dichloromethane (3 × 75 ml) and the organic layer was washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$) and concentrated to give **28** quantitatively. To a stirred solution of **28** in dry dimethylformamide (10 ml) was added hydrazine acetate (588 mg, 6.38 mmol) and the temperature was raised to 55°C. After $1\frac{1}{2}$ h, TLC showed a total conversion of **28** (R_f 0.76; dichloromethane/acetone 9/1, v/v) into a spot with R_f 0.59. The mixture was then cooled, diluted with ethyl acetate (150 ml), washed with aqueous 5% sodium chloride (3 × 25 ml) and water and the combined water layers were extracted once with ethyl acetate. The combined organic layer was dried ($MgSO_4$) and concentrated. To a solution of **29** and trichloroacetonitrile (6.6 ml, 65.9 mmol) in dry dichloromethane (20 ml) was added a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (0.79 ml, 5.27 mmol) in dry dichloromethane (10 ml) at −5°C. After stirring for 1 h at room temperature, the reaction was complete as shown by TLC **30** (R_f 0.78; dichloromethane/acetone 9/1, v/v). After concentration of the mixture, column chromatography (dichloromethane/acetone 95/5, v/v) of the residue yielded **30** as a yellow syrup (1.86 g, 71%), $[\alpha]_D$ +108.2° (*c* 1, chloroform). Anal. calcd. for $C_{21}H_{24}O_9NCl_3$ (540.78): C 46.6, H 4.5; found: C 46.7, H 4.7%. NMR data ($CDCl_3$): ^{13}C, δ 169.9, 169.8 and 169.6 (3 $COCH_3$), 160.2 ($OCNHCCl_3$), 137.0 and 128.0–127.6 ($C_6H_5CH_2O$), 93.5 (C-1), 90.5 ($OCNHCCl_3$), 72.0, 69.2, 68.4 and 66.2 (C-2–C-5), 71.2

$C_6H_5CH_2O$), 61.5 (C-6), 20.3 (3 ×) (3 $COCH_3$); ^1H, δ 8.593 (s, 1H, $OCNHCCl_3$), 7.312–7.306 (m, 5H, $C_6H_5CH_2O$), 6.578 (d, 1H, H-1), 5.659 (dd, 1H, H-4), 5.272 (dd, 1H, H-2), 4.743 and 4.498 (2d, 2H, $C_6H_5CH_2O$), 4.346 (m, 1H, H-5), 4.217 (dd, 1H, H-6a), 4.073 (dd, 1H, H-6b), 4.032 (dd, 1H, H-3), 2.164, 2.043 and 1.997 (3 s, each 3H, 3 $COCH_3$), $J_{1,2}$ 3.5, $J_{2,3}$ 10.4, $J_{3,4}$ 3.3, $J_{4,5}$ 1.2, $J_{5,6a}$ 6.0, $J_{5,6b}$ 6.9 and $J_{6a,6b}$ −11.4 Hz.

Ethyl 2,3-di-O-benzyl-4-O-(2,4,6-tri-O-acetyl-3-O-benzyl-β-D-galactopyranosyl)-1-thio-α-L-rhamnopyranoside (**31**)

A solution of **24** (113 mg, 0.29 mmol) and **30** (230 mg, 0.44 mmol) in dry dichloromethane (8 ml) was stirred in the presence of molecular sieves (4 Å, 2.0 g) for 1 h under argon. A solution of trimethylsilyl triflate (28 μl, 0.15 mmol) in dry dichloromethane (2 ml) was then added dropwise at −30°C. After 20 min, the reaction was complete as shown by TLC (**31** R_f 0.53; petroleum ether [b.p. 40/60]/ethyl acetate 2/1, v/v) and pyridine (2 ml) was added. The mixture was filtered over celite, concentrated and the residue was deacetylated conventionally (R_f 0.39; dichloromethane/methanol 95/5, v/v) and purified by column chromatography (dichloromethane/methanol 95/5, v/v). Reacetylation gave syrupy **31** (180 mg, 81%), $[\alpha]_D$ −12.7° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 170.3 ($COCH_3$), 137.7–137.3 and 128.2–127.6 ($C_6H_5CH_2O$), 100.7 (C-1'), 81.1, 80.2, 77.4, 76.7, 75.8, 70.6, 70.3, 67.5 and 65.8 (C-1–C-5, C-2'–C-5'), 72.0, 71.6 and 71.0 (3 $C_6H_5CH_2O$), 61.7 (C-6'), 25.1 (CH_3CH_2S), 20.7, 20.6 and 20.4 (3 $COCH_3$), 17.7 (C-6), 14.7 (CH_3CH_2S); ^1H, δ 7.359–7.237 (m, 15H, 3 $C_6H_5CH_2O$), 5.489 (bd, 1H, H-4'), 5.307 (bs, 1H, H-1), 5.117 (dd, 1H, H-2'), 4.835 (d, 1H, H-1'), 4.688, 4.635, 4.569, 4.478, 4.394 and 4.363 (6d, 6H, 3 $C_6H_5CH_2O$), 4.145 and 4.106 (2 dd, 2H, H-6a' and H-6b'), 3.981 (m, 1H, H-5), 3.798 t, 1H, H-4), 3.783 (t, 1H, H-5'), 3.747 dd, 1H, H-2), 3.669 (dd, 1H, H-3), 3.477 (dd, 1H, H-3'), 2.628–2.504 (m, 2H, CH_3CH_2S), 2.160, 2.032 and 1.945 (3 s, each 3H, 3 $COCH_3$), 1.310 (d, 3H, H-6), 1.238 (t, 3H, CH_3CH_2S), $J_{1,2}$ 1.5, $J_{2,3}$ 3.2, $J_{3,4} = J_{4,5}$ 9.4, $J_{5,6}$ 6.1, $J_{1',2'}$ 8.1, $J_{2',3'}$ 10.1, $J_{3',4'}$ 3.5, $J_{4,5} < 1$, $J_{5',6a'} = J_{5',6b'}$ 6.6 and $J_{6a',6b'}$ −11.2 Hz.

Methyl 2,3-di-O-benzyl-4-O-(2,4,6-tri-O-acetyl-3-O-benzyl-β-D-galactopyranosyl)-α/β-L-rhamnopyranoside (**32α/β**)

To a solution of **31** (155 mg, 0.20 mmol) in dry dichloromethane (10 ml) was added bromine (34 μl, 0.66 mmol) in dichloromethane (2 ml). After 10 min, **31** had been completely converted into the corresponding bromide and the mixture was concentrated using dry toluene. The bromide derivative in dry toluene (5 ml) was added to a stirred mixture of methanol (350 μl, 8.65 mmol), molecular sieves (3 Å, 0.3 g) and silver silicate (510 mg) in dry dichloromethane (9.5 ml). After 1 h, the mixture was filtered over celite, diluted with dichloromethane (100 ml), washed with water, aqueous saturated sodium hydrogen carbonate and water, dried ($MgSO_4$) and concentrated. Column chromatography (petroleum ether [b.p. 40/60]/ethyl acetate 2/1, v/v) of the residue gave **32α** (13 mg, 8%), $[\alpha]_D$ +22.9° (*c* 1, chloroform), R_f 0.21 (petroleum ether [b.p. 40/60]/ethyl acetate 2/1, v/v) and **32β** (106 mg, 71%), $[\alpha]_D$ +83.5° (*c* 1, chloroform), R_f 0.16 (petroleum ether [b.p. 40/60]/ethyl acetate 2/1, v/v). Anal. calcd. for **32β** $C_{40}H_{48}O_{13}$ (736.81): C 65.2, H 6.6; found: C 65.3, H 6.7%. NMR data **32α** ($CDCl_3$): ^{13}C, δ 170.4 ($COCH_3$), 138.2 and 128.3–127.6 ($C_6H_5CH_2O$), 100.8 (C-1'), 98.5 (C-1), 80.1, 77.3, 76.7, 73.9, 70.8, 70.4, 67.0 and 65.9 (C-2–C-5, C-2'–C-5'), 72.4, 72.0 and 71.1 (3 $C_6H_5CH_2O$), 61.8 (C-6'), 54.6 (OCH_3), 20.9, 20.7 and 20.6 (3 $COCH_3$), 17.9 (C-6); ^1H, δ 7.336–7.230 (m, 15H, 3 $C_6H_5CH_2O$), 5.479 (dd, 1H, H-4'), 5.107 (dd, 1H, H-2), 4.842 (d, 1H, H-1'), 4.647 (d, 1H, H-1), 4.682, 4.623 (2 ×), 4.492, 4.424 and 4.390 (6 d, 6H, 3 $C_6H_5CH_2O$), 4.147 and 4.105 (2 dd, 2H, H-6a' and H-6b'), 3.612 (m, 1H, H-5), 3.465 (dd, 1H, H-3'), 3.304 (s, 3H, OCH_3), 2.152, 2.029 and 1.931 (3 s, each 3H, 3 $COCH_3$), 1.320 (d, 3H, H-6), $J_{1,2}$ 1.5, $J_{4,5}$ 9.0, $J_{5,6}$ 6.2, $J_{1',2'}$ 8.1, $J_{2',3'}$ 10.1, $J_{3',4'}$ 3.5, $J_{4',5'}$ 0.9, $J_{5',6a'} = J_{5',6b'}$ 6.6 and $J_{6a',6b'}$ −11.2 Hz. NMR data **32β** ($CDCl_3$): ^{13}C, δ 137.0 and 128.1–127.3 ($C_6H_5CH_2O$), 102.4 (C-1), 100.7 (C-1'), 73.6, 71.3 and 71.0 (3 $C_6H_5CH_2O$), 61.8 (C-6'), 56.9 (OCH_3), 20.6 (2 ×) and 20.5 ($COCH_3$), 17.8 (C-6); ^1H, δ 7.378–7.209 (m, 15H, 3 $C_6H_5CH_2O$), 5.478 (bd, 1H, H-4'), 5.094 (dd, 1H, H-2'), 4.839 (d, 1H, H-1'), 4.893, 4.747, 4.676, 4.384, 4.353 and 4.317 (6d, 6H, 3 $C_6H_5CH_2O$), 4.252 (s, 1H, H-1), 4.150 (dd, 1H, H-6a'), 4.084 (dd, 1H, H-6b'), 3.846 (d, 1H, H-2), 3.787 (bt, 1H, H-5'), 3.761 (t, 1H, H-4), 3.509 (s, 3H, OCH_3), 3.468 (dd, 1H, H-3'), 3.358 (dd, 1H, H-3), 3.304 (m, 1H, H-5), 2.151, 2.021 and 1.889 (3 s, each 3H, 3 $COCH_3$), 1.383 (d, 3H, H-6), $J_{1,2} \sim 0$, $J_{2,3}$ 3.2, $J_{3,4} = J_{4,5}$ 9.3, $J_{5,6}$ 6.2, $J_{1',2'}$ 8.1, $J_{2',3'}$ 10.0, $J_{3',4'}$ 3.5, $J_{4',5'} < 1$, $J_{5',6a'}$ 6.0, $J_{5',6b'}$ 6.9 and $J_{6a',6b'}$ −11.3 Hz.

Methyl 2,3-di-O-benzyl-4-O-(2,4,6-tri-O-acetyl-3-O-benzyl-β-D-galactopyranosyl)-β-L-rhamnopyranoside (**32β**)

A mixture of **26** (125 mg, 0.35 mmol) and **30** (308 mg, 0.58 mmol) in dry dichloromethane (9 ml) was stirred in the presence of molecular sieves (4 Å, 2.0 g) for 1 h at room temperature. Trimethylsilyl triflate (34 μl, 0.18 mmol) in dry dichloromethane (2 ml) was then added at −30°C. After 10 min at this temperature, pyridine (2 ml) was added and the mixture was filtered over celite and concentrated. The crude product (R_f 0.16; petroleum ether [b.p. 40/60]/ethyl acetate 2/1, v/v) was purified by column chromatography after conventional deacetylation (dichloromethane/methanol 95/5, v/v). Subsequent reacetylation afforded **32β** (186 mg, 88%) with analytical data as described above.

Methyl 2,3-di-O-benzyl-4-O-(3-O-benzyl-β-D-galactopyranosyl)-β-L-rhamnopyranoside (**33**)

Compound **32β** (614 mg, 0.84 mmol) in dry methanol (5 ml) was deacetylated using sodium methoxide (pH 10). The mixture was stirred overnight, neutralised with Dowex-50 (H^+) resin, filtered and concentrated, yielding **33** quantitatively as a white amorphous solid, $[\alpha]_D$ +42.4° (*c* 1, chloroform). NMR data ($CDCl_3$): ^1H, δ 7.434–7.248 (m, 15H, 3 $C_6H_5CH_2O$), 4.943, 4.776, 4.726, 4.701, 4.478 and 4.306 (6 d, 6H, 3 $C_6H_5CH_2O$), 4.461 (d, 1H, H-1'), 4.246 (s, 1H, H-1), 3.511 (s, 3H, OCH_3), 3.318 (m, 1H, H-5), 1.438 (d, 3H, H-6), $J_{1,2} \sim 0$, $J_{5,6}$ 6.2 and $J_{1',2'}$ 7.7 Hz.

Methyl 2,3-di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-β-L-rhamnopyranoside (**34**)

To a solution of **33** (1.26 g, 2.07 mmol) in α,α-dimethoxytoluene (7.5 ml) and acetonitrile (7.5 ml) was added *p*-toluenesulfonic acid monohydrate (400 mg). After 30 min at room temperature, TLC showed a new spot at R_f 0.50 (dichloromethane/ethyl acetate 9/1, v/v) and the mixture was neutralised with solid sodium hydrogen carbonate and diluted with dichloromethane (250 ml). The organic layer was washed with water, dried ($MgSO_4$) and concentrated. Crystallization from ethanol gave **34** (1.14 g, 79%), $[\alpha]_D$ +75.5° (*c* 1, chloroform), m.p. 78.3°C. Anal. calcd. for $C_{41}H_{46}O_{10}$ (698.81): C 70.5, H 6.6; found: C 70.1, H 6.3%. NMR data ($CDCl_3$): ^{13}C, δ 138.5–136.9 and 128.7–126.3 ($C_6H_5CH_2O$ and C_6H_5CH), 104.8 (C-1'), 102.4 C-1), 100.9 (C_6H_5CH), 80.0 (2x), 78.8, 73.2 (2 ×), 71.6, 71.1 and 66.5 (C-2–C-5, C-2'–C-5'), 73.8, 71.4, 70.7 and 69.1 (3 $C_6H_5CH_2O$ and C-6'), 56.9 (OCH_3), 17.6 (C-6); ^1H, δ 7.528–7.252 (m, 20H, 3 $C_6H_5CH_2O$ and C_6H_5CH), 5.420 (s, 1H, C_6H_5CH), 4.937, 4.788, 4.736 (2 ×), 4.486 and 4.365 (6 d, 6H, 3 $C_6H_5CH_2O$), 4.533 (d, 1H, H-1'), 4.235 (dd, 1H, H-6a'), 4.066 (bd, 1H, H-4'), 3.974 (dd, 1H, H-6b'), 3.974 (m, 1H, H-2'), 3.864 (d, 1H, H-2) 3.823 (t, 1H, H-4), 3.503 (s, 3H, OCH_3), 3.477 (dd, 1H, H-3), 3.464 (dd, 1H, H-3'), 3.339 (m, 1H, H-5), 3.325 (m, 1H, H-5'), 1.456 (d, 3H, H-6), $J_{1,2} \sim 0$, $J_{2,3}$ 3.0, $J_{3,4} = J_{4,5}$ 9.4, $J_{5,6}$ 6.2, $J_{1',2'}$ 7.7, $J_{2',3'}$ 9.7, $J_{3',4'}$ 3.6, $J_{4',5'} < 1$, $J_{5',6a'}$ 1.3, $J_{5',6b'}$ 1.8 and $J_{6a',6b'}$ −12.3 Hz.

Methyl 2,3-di-O-benzyl-4-O-[3-O-benzyl-4,6-O-benzylidene-2-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranosyl]-β-L-rhamnopyranoside (**35**)

A mixture of **34** (460 mg, 0.66 mmol), mercuric bromide (402 mg, 1.12 mmol), mercuric cyanide (289 mg, 1.15 mmol) and powdered molecular sieves (4 Å, 3.2 g) in dry dichloromethane (10 ml) was stirred for 1 h under argon. A solution of **6**[6] (233 mg, 0.66 mmol) in dry dichloromethane (3 ml) was than added. After 16 h, a further portion of **6**[6] (233 mg, 0.66 mmol) was added. After 5 days, TLC (dichloromethane/ethyl acetate 9/1, v/v) showed that the composition of the mixture was not changing. Dichloromethane (150 ml) was then added. After filtration over celite, the organic layer was washed with aqueous 10% potassium iodide (3 × 25 ml), aqueous sodium hydrogen carbonate, water, dried ($MgSO_4$) and concentrated. Column chromatography (dichloromethane/ethyl

acetate 95/5, v/v) of the residue afforded, in addition to the starting compound **34** (69 mg, 15%), **35** (504 mg, 79%), $[\alpha]_D$ +9.6° (*c* 1, chloroform), R_f 0.69 (dichloromethane/ethyl acetate 9/1, v/v). Anal. Calcd. for $C_{53}H_{62}O_{17}$ (971.06): C 65.6, H 6.4; found: C 65.7, H 6.7%. NMR data ($CDCl_3$): ^{13}C, δ 102.7 (C-1), 100.8 (C_6H_5CH), 99.7 (C-1'), 98.0 (C-1''), 56.9 (OCH_3); ^1H, δ 7.436–7.256 (m, 20H, 3 $C_6H_5CH_2O$ and C_6H_5CH), 5.392 (s, 1H, C_6H_5CH), 5.380 (dd, 1H, H-2''), 5.322 (dd, 1H, H-3''), 5.245 (d, 1H, H-1''), 5.052 (t, 1H, H-4''), 4.948 (d, 1H, H-1'); 4.457 (m, 1H, H-5''), 4.932, 4.776, 4.645, 4.607, 4.578 and 4.416 (6 d, 6H, 3 $C_6H_5CH_2O$), 4.266 (s, 1H, H-1), 4.210 (dd, 1H, H-6a'), 4.021 (bd, 1H, H-4'), 3.950 (dd, 1H, H-2'), 3.937 (d, 1H, H-2), 3.933 (t, 1H, H-4), 3.924 (dd, 1H, H-6b'), 3.525 (s, 3H, OCH_3), 3.509 (dd, 1H, H-3), 3.434 (dd, 1H, H-3'), 3.267 (m, 1H, H-5), 3.215 (m, 1H, H-5'), 2.086, 1.998 and 1.925 (3 s, each 3H, 3 $COCH_3$), 1.455 (d, 3H, H-6), 1.199 (d, 3H, H-6''), $J_{1,2} \sim 0$, $J_{2,3}$ 3.1, $J_{3,4} = J_{4,5}$ 9.2, $J_{5,6}$ 6.2, $J_{1',2'}$ 7.8, $J_{2',3'}$ 9.7, $J_{3',4'}$ 3.6, $J_{4',5'} < 1$, $J_{5',6a'}$ 0.9, $J_{5',6b'}$ 1.8, $J_{6a',6b'}$ −12.3, $J_{1'',2''}$ 1.7, $J_{2'',3''}$ 3.6, $J_{3'',4''} = J_{4'',5''}$ 10.0 and $J_{5'',6''}$ 6.2 Hz.

Methyl 2,3-di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-O-α-L--rhamnopyranosyl-β-D-galactopyranosyl)-β-L-rhamnopyranoside (**36**)

To a solution of **35** (1.03 g, 1.07 mmol) in dry dichloromethane (5 ml) and dry methanol (20 ml) was added sodium methoxide (pH 10). After stirring overnight, the solvent was evaporated and the residue was dissolved in dichloromethane (250 ml), washed with water, dried ($MgSO_4$) and concentrated, yielding **36** (899 mg, 99%), $[\alpha]_D$ +22.8° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 138.5–137.6 and 128.8–126.2 $C_6H_5CH_2O$ and C_6H_5CH), 102.5 (C-1), 100.9 (C_6H_5CH), 100.5 (2×) (C-1', C-1''), 82.6, 79.9, 75.2, 74.4, 73.1, 72.6 (2×), 71.6 (2×), 70.4, 67.5, 65.5 (C-2–C-5, C-2'–C-5', C-2''–C-5''), 73.6 and 70.8 (2×) (3 $C_6H_5CH_2O$), 69.0 (C-6'), 56.7 (OCH_3), 18.0 and 17.7 (C-6 and C-6'').

Methyl 2,3-di-O-benzyl-4-O-[3-O-benzyl-4,6-O-benzylidene-2-O--(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D-galactopyranosyl]-β--L-rhamnopyranoside (**37**)

To a stirred solution of sodium hydride (0.51 g, 20.8 mmol) in dry dimethylformamide (10 ml) at 0°C was added a solution of **36** (899 mg, 1.06 mmol) and benzyl bromide (7.7 ml, 63.9 mmol) in dry dimethylformamide (15 ml). After 2 h, methanol was added and the mixture was poured into ice-water (300 ml). The crude product (R_f 0.73; dichloromethane/ethyl acetate 9/1, v/v) was then extracted with diethyl ether (3× 75 ml) and the organic layer was dried ($MgSO_4$) and concentrated. Column chromatography (petroleum ether [b.p. 40/60]/ethyl acetate 7/3, v/v) of the residue yielded **37** (1.15 g, 97%), $[\alpha]_D$ +42.3° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 139.1–137.7 and 128.7–126.2 ($C_6H_5CH_2O$ and C_6H_5CH), 102.6 (C-1), 100.8 (C_6H_5CH), 100.5 (C-1'), 98.2 (C-1''), 98.2 (C-1'''), 82.3, 80.1 (2×), 80.0, 75.3, 74.1 (2×), 72.3, 72.2, 71.7, 67.2 and 65.5 (C-2–C-5, C-2'–C-5', C-2''–C-5''), 74.5, 73.3, 71.6, 70.8, 70.2 (2×) (6 $C_6H_5CH_2O$), 69.0 (C-6'), 56.8 (OCH_3), 17.9 and 17.5 (C-6 and C-6''); ^1H, δ 7.542–7.049 (m, 35H, 6 $C_6H_5CH_2O$ and C_6H_5CH), 5.431 (s, 1H, C_6H_5CH), 5.285 (d, 1H, H-1''), 4.915 (d, 1H, H-1'), 4.306 (m, 1H, H-5''), 4.166 (s, 1H, H-1), 4.126 (bd, 1H, H-4'), 3.758 (d, 1H, H-2), 3.514 (s, 3H, OCH_3), 3.294 (m, 1H, H-5'), 3.277 (m, 1H, H-5), 1.472 (d, 3H, H-6), 1.302 (d, 3H, H-6''), $J_{1,2} \sim 0$, $J_{2,3}$ 3.1, $J_{4,5}$ 9.3, $J_{5,6}$ 6.1, $J_{1',2'}$ 7.8, $J_{3',4'}$ 3.4, $J_{4',5'} < 1$, $J_{1'',2''}$ 2.0, $J_{4'',5''}$ 9.6 and $J_{5'',6''}$ 6.3 Hz.

Methyl 4-O-(2-O-α-L-rhamnopyranosyl-β-D-galactopyranosyl)-β-L--rhamnopyranoside (**2**)

A suspension of **37** (390 mg, 0.35 mmol) in ethanol (20 ml) was hydrogenolysed using 10% Pd/C (20 mg) at 4 kg cm^{-2} at room temperature. After 16 h, TLC showed one new compound (R_f 0.68; methanol). The mixture was then filtered over celite and concentrated to give **2** (148 mg, 89%), $[\alpha]_D$ −13.0° (*c* 1, water. NMR data ($CDCl_3$): ^{13}C, δ 102.4, 102.2 (2×) (C-1, C-1' and C-1''), 78.6, 78.3, 76.1, 74.8, 74.7, 73.1, 72.3, 72.1, 71.4 (2×), 70.4, 70.0 (C-2–C-5, C-2'–C-5', C-2''–C-5''), 62.2 (C-6'), 58.1 (OCH_3), 18.4 and 17.8 (C-6 and C-6''); ^1H, see Table I.

Methyl 2,3-di-O-benzyl-4-O-[3,6-di-O-benzyl-2-O-(2,3,4-tri-O--benzyl-α-L-rhamnopyranosyl)-β-D-galactopyranosyl]-β-L--rhamnopyranoside (**38**)

Compound **37** (703 mg, 0.63 mmol) in freshly distilled tetrahydrofuran (12.6 ml) was stirred in the presence of molecular sieves (4 Å, 4.4 g) for 1 h. The suspension was then cooled to 0°C and aluminium(III) chloride was added. The mixture was stirred at room temperature (1 h) until TLC indicated the disappearance of **37** (R_f 0.73; dichloromethane/ethyl acetate 9/1, v/v) and a new spot with R_f 0.56. The mixture was then diluted with dichloromethane (300 ml). After filtration over celite, the organic phase was washed with cold 1 M sulfuric acid (3× 50 ml), water, aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$) and concentrated. Purification by column chromatography (dichloromethane/ethyl acetate 9/1, v/v) of the residue gave **38** (602 mg, 86%), $[\alpha]_D$ +16.0° (*c* 1, chloroform). Anal. Calcd. for $C_{68}H_{74}O_{14}$ (1115.32): C 73.2, H 6.7; found: C 73.0, H 6.8%. NMR data ($CDCl_3$): ^{13}C, δ 139.5–137.2 and 128.3–126.7 ($C_6H_5CH_2O$), 102.6 (C-1), 100.8 (C-1'), 98.2 (C-1''), 82.4, 81.7, 80.2 (2×), 75.5, 74.2, 73.7, .72.4, 72.1, 71.5, 67.2, 65.6 (C-2–C-5, C-2'–C-5', C-2''–C-5''), 74.5, 73.5, 73.2, 71.9, 70.8, 70.5, 70.0 (7 $C_6H_5CH_2O$), 68.7 (C-6'), 56.8 (OCH_3), 17.9 and 17.5 (C-6 and C-6''); ^1H, δ 7.377–7.074 (m, 35H, 7 $C_6H_5CH_2O$), 5.297 (d, 1H, H-1''), 4.895 (d, 1H, H-1'), 4.298 (m, 1H, H-5''), 4.110 (s, 1H, H-1), 3.494 (s, 3H, OCH_3), 3.236 (m, 1H, H-5), 1.399 (d, 3H, H-6), 1.272 d, 3H, H-6''), $J_{1,2} \sim 0$, $J_{4,5}$ 9.2, $J_{5,6}$ 6.1, $J_{1',2'}$ 7.9, $J_{1'',2''}$ 1.3, $J_{4'',5''}$ 9.4 and $J_{5'',6''}$ 6.2 Hz.

Methyl 2,3-di-O-benzyl-4-O-[3,6-di-O-benzyl-4-O-(2,4,6-tri-O-acetyl--3-O-allyl-β-D-glucopyranosyl)-2-O-(2,3,4-tri-O-benzyl-α-L-rhamno-pyranosyl)-β-D-galactopyranosyl]-β-L-rhamnopyranoside (**39**)

A solution of 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl bromide[8] **11** (60 mg, 0.15 mol) in dry dichloromethane (2 ml) was added to a stirred mixture of **38** (110 mg, 0.10 mmol), mercuric bromide (123 mg, 0.34 mmol) and powdered molecular sieves (4 Å, 1.2 g) in dry dichloromethane (3 ml). After 24 h, a further portion of **11** (20 mg, 0.05 mmol) was added. When TLC showed a complete disappearance of starting **38** (48 h) and the formation of a new compound (R_f 0.56; dichloromethane/ethyl acetate 85/15, v/v), the mixture was diluted with dichloromethane (50 ml), filtered over celite, washed with aqueous 10% potassium iodide (3× 15 ml) and water, dried ($MgSO_4$) and concentrated. Column chromatography (dichloromethane/ethyl acetate 85/15, v/v) of the residue afforded **39** (107 mg, 75%), $[\alpha]_D$ +12.5° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 170.3, 169.0, 168.9 (3 $COCH_3$), 139.0–137.5 and 128.4–126.8 ($C_6H_5CH_2O$), 134.2 ($H_2C{=}CH{-}CH_2O$), 116.6 ($H_2C{=}CH{-}CH_2O$), 102.6 (C-1), 100.4 (C-1'), 99.5 (C-1'''), 98.2 (C-1''), 56.8 (OCH_3), 20.6 ($COCH_3$), 17.8 and 17.6 (C-6 and C-6''); ^1H, δ 7.357–7.044 (m, 35H, 7 $C_6H_5CH_2O$), 5.786 (m, 1H, $H_2C{=}CH{-}CH_2O$), 5.263 (bs, 1H, H-1''), 5.220 and 5.146 (2 m, 2H, $H_2C{=}CH{-}CH_2O$), 4.104 (s, 1H, H-1), 3.495 (s, 3H, OCH_3), 3.204 (m, 1H, H-5), 2.163, 2.051 and 1.960 (3 s, each 3H, $COCH_3$), 1.389 (d, 3H, H-6), 1.267 (d, 3H, H-6''), $J_{1,2} \sim 0$, $J_{4,5}$ 9.4, $J_{5,6}$ 6.2 and $J_{1'',2''} < 1$ Hz.

Methyl 2,3-di-O-benzyl-4-O-[3,6-di-O-benzyl-4-O-(3-O-allyl-β-D-glu-copyranosyl)-2-O-(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D--galactopyranosyl]-β-L-rhamnopyranoside (**40**)

Compound **39** (88 mg, 0.06 mmol) was deacetylated with sodium methoxide in dry methanol (pH 10). After 16 h, the deacetylation was complete (TLC, R_f 0.10; dichloromethane/ethyl acetate 9/1, v/v) and Dowex-50 (H^+) resin was added (pH 7). The mixture was then filtered and concentrated to yield **40**, $[\alpha]_D$ +1.4° (*c* 0.5, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 138.0–136.8 and 128.4–126.7 ($C_6H_5CH_2O$), 135.0 ($H_2C{=}CH{-}CH_2O$), 117.0 ($H_2C{=}CH{-}CH_2O$), 105.1 (C-1'''), 102.6 (C-1), 100.9 (C-1'), 98.5 (C-1''), 56.7 (OCH_3), 17.9 and 17.6 (C-6 and C-6''); ^1H, δ 7.356–7.066 (m, 35H, 7 $C_6H_5CH_2O$), 5.990 (m, 1H, $H_2C{=}CH{-}CH_2O$), 5.324 and 5.211 (2 m, 2H, $H_2C{=}CH{-}CH_2O$), 5.196 (bs, 1H, H-1''), 4.114 (s, 1H, H-1), 3.496 (s, 3H, OCH_3), 1.356 (d, 3H, H-6), 1.272 (d, 3H, H-6''), $J_{1,2} \sim 0$, $J_{5,6}$ 6.1, $J_{1'',2''} < 1$ and $J_{5'',6''}$ 6.3 Hz.

Methyl 2,3-di-O-benzyl-4-O-[3,6-di-O-benzyl-4-O-(3-O-allyl-2,4,6--tri-O-benzyl-β-D-glucopyranosyl)-2-O-(2,3,4-tri-O-benzyl-α-L--rhamnopyranosyl)-β-D-galactopyranosyl]-β-L-rhamnopyranoside (**41**)

A solution of **40** (440 mg, 0.34 mmol) and benzyl bromide (2.5 ml, 20.4 mmol) in dry dimethylformamide (10 ml) was added to a stirred suspension of sodium hydride (300 mg, 12.5 mmol) in dry dimethylformamide (5 ml) at 0°C. After 16 h, the reaction was shown to be complete (TLC, R_f 0.57; petroleum ether [b.p.

40/60]/ethyl acetate 9/1, v/v) and methanol was added to destroy the excess sodium hydride. The mixture was poured into ice-water (250 ml), extracted with diethylether (3 × 25 ml) and the organic layer was dried ($MgSO_4$) and concentrated. Column chromatography (petroleum ether [b.p. 40/60]/ethyl acetate 9/1, v/v) of the residue yielded **41** (465 mg, 88%), $[\alpha]_D$ +23.4° (*c* 1, chloroform). Anal. calcd. for $C_{97}H_{108}O_{19}$ (1577.91): C 73.8, H 6.9; found: C 73.8, H 6.8%. NMR data ($CDCl_3$): ^{13}C, δ 139.3–137.6 and 128.7–126.8 ($C_6H_5CH_2O$), 135.2 ($H_2C=CH-CH_2O$), 116.3 ($H_2C=CH-CH_2O$), 102.7 (C-1), 101.9 (C-1‴), 100.9 (C-1′), 98.1 (C-1″), 56.9 (OCH_3), 17.8 (C-6 and C-6″); ^1H, δ 7.480–7.032 (m, 50H, 10 $C_6H_5CH_2O$), 5.950 (m, 1H, $H_2C=CH-CH_2O$), 5.300 (bs, 1H, H-1″), 5.276 and 5.154 (2 m, each 1H, $H_2C=CH-CH_2O$), 4.108 (s, 1H, H-1), 3.479 (s, 3H, OCH_3), 3.203 (m, 1H, H-5), 1.329 (d, 3H, H-6), 1.266 (d, 3H, H-6″), $J_{1,2} \sim 0$, $J_{4,5}$ 9.2, $J_{5,6}$ 6.1, $J_{1'',2''} < 1$ and $J_{5'',6''}$ 6.4 Hz.

Methyl 2,3-di-O-benzyl-4-O-[3,6-di-O-benzyl-4-O-(2,4,6-tri-O--benzyl-β-D-glucopyranosyl)-2-O-(2,3,4-tri-O-benzyl-α-L--rhamnopyranosyl)-β-D-galactopyranosyl]-β-L-rhamnopyranoside (**42**)

To a solution of **41** (102 mg, 0.06 mmol) in dry dimethylformamide (4 ml) at 85 °C was added potassium *tert*-butoxide until the mixture turned black. After 1 h at 85 °C, TLC indicated the disappearance of **41**. The mixture was then cooled, diluted with water (25 ml) and the product extracted with dichloromethane (3 × 15 ml). The combined organic layer was dried ($MgSO_4$), concentrated and the residue was boiled under reflux in acetone (2.7 ml) and 1 M hydrochloric acid (0.3 ml). When TLC indicated the reaction to be complete (1½ h) (**42** R_f 0.71; dichloromethane/ethyl acetate 95/5, v/v), aqueous saturated sodium hydrogen carbonate was added and, after evaporation of acetone, the water layer was extracted with dichloromethane (3 × 15 ml). The organic phase was dried ($MgSO_4$), concentrated and the residue purified by column chromatography (toluene/acetone 25/2, v/v) affording **42** (59 mg, 59%), $[\alpha]_D$ +24.3° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 139.3–137.6 and 128.6–126.8 ($C_6H_5CH_2O$), 102.7 (C-1), 101.6 (C-1‴), 100.8 (C-1′), 98.2 (C-1″), 56.9 (OCH_3), 17.8 and 17.7 (C-6 and C-6″); ^1H, δ 7.440–7.039 (m, 50H, 10 $C_6H_5CH_2O$), 5.321 (bs, 1H, H-1″), 4.092 (s, 1H, H-1), 3.473 (s, 3H, OCH_3), 1.327 (d, 3H, H-6), 1.228 (d, 3H, H-6″), $J_{1,2} \sim 0$, $J_{5,6}$ 6.1, $J_{1'',2''} < 1$ and $J_{5'',6''}$ 6.3 Hz.

Methyl 2,3-di-O-benzyl-4-O-[3,6-di-O-benzyl-2-O-(2,3,4-tri-O--benzyl-α-L-rhamnopyranosyl)-4-O-[2,4,6-tri-O-benzyl-3-O-(diphenyl phosphoryl)-β-D-glucopyranosyl]-β-D-galactopyranosyl]-β--L-rhamnopyranoside (**43**)

To a solution of **42** (53 mg, 0.04 mmol) in anhydrous dichloromethane (3 ml) were added pyridine (19 µl, 0.23 mmol), 4-(dimethylamino)pyridine (19 mg, 0.15 mmol) and diphenylphosphochloridate (30 µl, 0.15 mmol). After 16 h stirring at room temperature, TLC showed a single new spot (R_f 0.55; dichloromethane/ethyl acetate 98/2, v/v). The mixture was then diluted with dichloromethane (50 ml), washed with 1 M hydrochloric acid (3 × 10 ml), water, queous saturated sodium hydrogen carbonate, and water, dried ($MgSO_4$) and concentrated. Column chromatography (dichloromethane/ethyl acetate 98/2, v/v) of the residue gave **43** (53 mg, 86%), $[\alpha]_D$ +25.6° (*c* 1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 150.6, 129.4 (2 ×), 124.8, 120.2 and 120.1 ($[C_6H_5O]_2P$), 139.3–137.4 and 128.7–127.1 ($C_6H_5CH_2O$), 102.7 (C-1), 101.9 (C-1‴), 101.0 (C-1′), 98.1 (C-1″), 56.9 (OCH_3), 17.9 and 17.7 (C-6 and C-6″); ^1H, δ 7.467–7.052 (m, 60H, 10 $C_6H_5CH_2O$ and $[C_6H_5O]_2P$), 5.108 (d, 1H, H-1″), 4.289 (m, 1H, H-5″), 3.477 (s, 3H, OCH_3), 3.190 (m, 1H, H-5), 1.324 (d, 3H, H-6), 1.231 (d, 3H, H-6″), $J_{4,5}$ 9.2, $J_{5,6}$ 6.1, $J_{1'',2''}$ 1.7, $J_{4'',5''}$ 9.4 and $J_{5'',6''}$ 6.3 Hz.

Methyl 4-O-[4-O-(3-O-disodium phosphoryl)-β-D-glucopyranosyl-2-O--α-L-rhamnopyranosyl-β-D-galactopyranosyl]-β-L-rhamnopyranoside (**3**)

A solution of **43** (47 mg, 26.6 µmol) in ethanol (15 ml) was hydrogenolysed using 10% Pd/C (15 mg) at 4 kg cm^{-2} for 16 h at room temperature. The catalyst was substituted by platinum oxide (15 mg) and the hydrogenolysis was continued for a further 16 h. Filtration and evaporation of the solvent afforded **3** (18 mg, 95%), $[\alpha]_D$ −12.5° (*c* 0.8, wxater). NMR data ($CDCl_3$): ^{13}C, δ 105.1, 102.4, 102.2 and 102.0 (C-1, C-1′, C-1″, C-1‴), 61.8 and 61.9 (C-6′ and C-6‴), 58.0 (OCH_3), 18.3 and 17.7 (C-6 and C-6″); ^1H, see Table I.

Acknowledgements

We wish to thank Dr. *J. Kerékgyártó* for valuable discussions and Drs. *G. J. Gerwig*, *P. de Waard*, *J. Breg* and *B. R. Leeflang* for recording the 360 MHz 1D- and 500 MHz 2D-^1H NMR spectra.

References

1 *J. B. Robbins, R. Austrian, C. J. Lee, S. C. Rastogi, G. Schiffman, J. Henrichsen, P. H. Mäkelä, C. V. Broome, R. R. Facklam, R. H. Tiesjema* and *J. C. Parke*, J. Infect. Dis. **148**, 1136 (1983).
2 *J. E. G. van Dam*, Thesis, Utrecht University, The Netherlands, 1988.
3 *C. Jones*, Carbohydr. Res. **139**, 75 (1985).
4 *J. C. Richards* and *M. B. Perry*, Biochem. Cell Biol. **66**, 758 (1988).
5 *P. Kovac* and *C. P. J. Glaudemans*, Carbohydr. Res. **142**, 158 (1985).
6 *E. Fisher*, *M. Bergmann* and *A. Rabe*, Chem. Ber. **53**, 2362 (1920).
7 *M. Ek*, *P. J. Garegg*, *H. Hultberg* and *S. Oscarson*, J. Carbohydr. Chem. **2**, 305 (1983).
8 *K. Takeo*, *T. Nakaji* and *K. Shinmitsu*, Carbohydr. Res. **133**, 275 (1984).
9 *H. Lönn*, Carbohydr. Res. **139**, 105 (1985).
10 *H. Lönn*, Carbohydr. Res. **139**, 115 (1985).
11 *P. A. Gent* and *R. Gigg*, J. Chem. Soc., Chem. Comm. 277 (1974).
12 *P. Szabo*, *S. R. Sarfati*, *C. Diolez* and *L. Szabo*, Carbohydr. Res. **111**, C9 (1983).
13 *H. Paulsen* and *W. Kutschker*, Carbohydr. Res. **120**, 25 (1983).
14 *T. Ogawa* and *M. Matsui*, Carbohydr. Res. **54**, C17 (1977).
15 *C. Laffite*, *A. M. Nguyen Phuoc Du*, *F. Winternitz*, *R. Wylde* and *F. Pratviel–Sosa*, Carbohydr. Res. **67**, 91 (1978).
16 *S. Sato*, *M. Mori*, *Y. Ito* and *T. Ogawa*, Carbohydr. Res. **155**, C6 (1986).
17 *F. Weygand* and *H. Ziemann*, Liebigs Ann. Chem. **657**, 179 (1962).
18 *G. Excoffier*, *D. Gagnaire* and *J. P. Utille*, Carbohydr. Res. **39**, 368 (1975).
19 *R. R. Schmidt* and *J. Michel*, Angew. Chem. **92**, 763 (1980).
20 *H. M. Flowers*, Carbohydr. Res. **100**, 418 (1982).
21 *D. Marion* and *K. Wütrich*, Biochem. Biophys. Res. Commun. **113**, 967 (1984).
22 *A. Bax* and *D. G. Davis*, J. Magn. Res. **65**, 355 (1985).