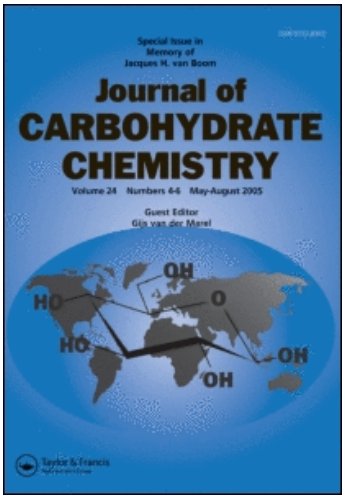

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TALOPYRANOSE DERIVATIVES SUITABLE FOR THE PLANNED SYNTHESIS OF TEICHOIC ACIDS CONTAINING DI-GLYCOSYLATED RIBITOL UNITS

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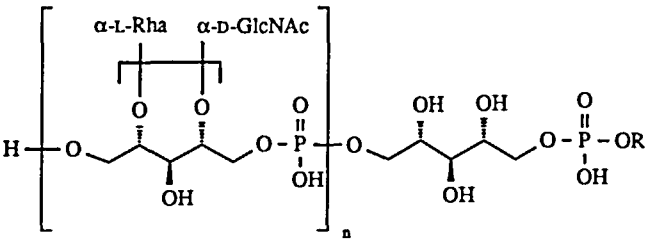
ABSTRACT

Easily accessible 1,6-anhydro-2,3-*O*-(S)-benzylidene-β-D-mannopyranose was converted in four steps to 1,6-anhydro-3,4-di-*O*-benzyl-β-D-talopyranose. Glycosylation of the latter with ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside gave, after further processing, 1-*O*-allyl-3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-L-ribitol.

INTRODUCTION

Teichoic acids[1] consist of repeating linear or branched saccharide units which are covalently linked together by phosphodiester bonds. The charged biopolymers are characteristic components of the cell wall of Gram-positive bacteria where they play a role in the bacterial economy by maintaining a high concentration of magnesium cations near the cell membrane.[2] Apart from this, it has also been established that teichoic acids are responsible for the binding of bacteria to host cells,[3] the formation of dental plaque[4] and, further, that some may act as receptor sites[5] during phage attack. In addition, many teichoic acids are responsible for the immunological properties of Gram-positive bacteria.[6] Despite the great variety and



R = Saccharide Linker To Peptidoglycan

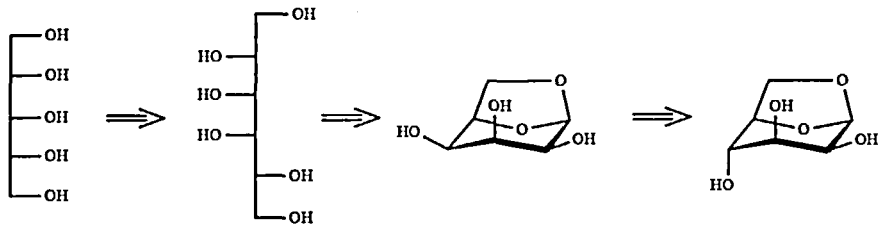
Figure 1

diversity in sugar composition of teichoic acids, an interesting class of these biopolymers is characterised by the fact that the repeating units comprise solely mono-glycosylated ribitols.[7-13] Recently, however, *Kamisango et al.*[14] showed that the repeating unit of the immunologically active teichoic acid from the cell wall of *Listeria monocytogenes* strain EGD consists of a di-glycosylated ribitol (see Figure 1). Thus in this particular case[14,15] the ribitol-1(5)-phosphate moiety, the absolute configuration of which was not determined, is α-linked to L-rhamnopyranosyl and 2-acetamido-2-deoxy-D-glucopyranosyl residues at C-4(2) and C-2(4), respectively.

As part of a programme directed towards the synthesis of teichoic acids,[7,8,16-19] we now report an alternative route to the preparation of the partially protected 2-*O*-(α-L-rhamnopyranosyl)-L-ribitol derivative **29** starting from 1,6-anhydro-2,3-*O*-(S)-benzylidene-β-D-talopyranose. The suitably protected L-rhamnosyl-ribitol derivative may be used as a building block for the synthesis of a teichoic acid which contains the major antigenic determinant[14] (*e.g.* the L-rhamnopyranosyl residue) of the immunologically active teichoic acid.

RESULTS AND DISCUSSION

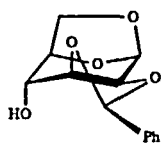
It is well established that teichoic acids containing mono-glycosylated ribitol units can be prepared most conveniently starting from suitably protected ribitol units[7-13] which, in turn, are easily accessible from the chiral precursors D- or



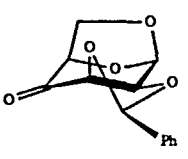
Scheme 1

L-ribonolactone[20] or ribose.[11,12] However, a similar approach resulting in the successful preparation of the di-glycosylated ribitol unit present in *Listeria monocytogenes* would require a rather complex and stringently controlled protecting group strategy.

An attractive and economical approach would be the development of a more versatile chiral precursor. Retrosynthetic analysis reveals (see Scheme 1) that 1,6-anhydro-β-D-talopyranose, which can be prepared from readily available 1,6-anhydro-β-D-mannopyranose,[21-23] may be a suitable chiral precursor for the synthesis of di-



1



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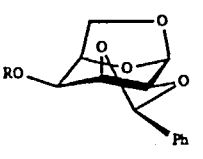
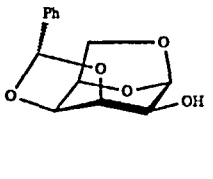


3 R = H
5 R = Bn
10 R = All



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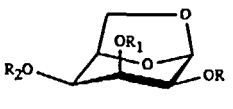
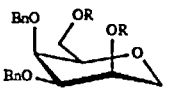


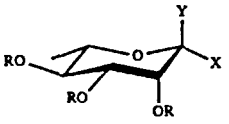
6 R = H, $R_1 = R_2$ = Bn
7 R = R_2 = Bn, R_1 = H
11 R = H, R_1 = Bn, R_2 = All
12 R = Bn, R_1 = H, R_2 = All



8 R = H
9 R = Ac

glycosylated ribitol derivatives. The spatial arrangement of the individual hydroxyl groups, due to the rigidity of the 1,6-anhydro-β-D-mannopyranose system, will enhance the feasibility of selective protection and transformation.

In order to examine the viability of the retrosynthetic approach, the 1,6-anhydro-β-D-talopyranose derivative **6** was prepared first by the following sequence of reactions. *Swern* oxidation of 1,6-anhydro-2,3-*O*-(S)-benzylidene-β-D-mannopyranose[22] (**1**) furnished ketone **2**. Reduction of **2** with sodium borohydride in methanol did not proceed satisfactory. The crude reaction mixture contained, the required 1,6-anhydro-2,3-*O*-(S)-benzylidene-β-D-talopyranose **3**, its positional isomer **4** and 1,6-anhydro-2,3-*O*-(S)-benzylidene-β-D-mannopyranose (**1**). It was also observed that the formation of **4** increased during the work-up protocol, which included *inter alia* addition of excess ammonium chloride to the reaction mixture, and purification on silica gel: indicating that **3** is very prone to acid catalyzed isomerisation. Apart from this, it was expected that the use of the solvent 1,2-dimethoxyethane (DME), instead of the more polar and not completely inert solvent methanol, would have a beneficial effect on the stereochemical outcome of the reduction: *i.e.* eliminate the formation of unwanted **1**. Indeed, reduction of **2** in DME, followed by a neutral work-up protocol, afforded crystalline **3** in an excellent yield. The equatorial orientation of the hydroxyl group at C-4 of compound **3** could be derived from the observed typical values of the coupling constants of the H-3 and H-5 protons with the H-4 proton (*i.e.* 6.0 and 5.3 Hz, respectively). Benzylation of alcohol **3** with benzyl bromide and sodium hydride gave **5**. The next step, which entails a reductive ring-opening of the (*endo*-phenyl)-benzylidene function in **5** with excess lithium aluminium hydride/aluminium chloride,[22,24] did not proceed satisfactory. Separation and careful analysis (^{1}H and ^{13}C NMR spectroscopy) of the individual products thus obtained revealed the presence of 1,6-anhydro-3,4-di-*O*-benzyl-β-D-talopyranose (**6**: 20% yield), the positional isomer of **6** (**7**: 5% yield) and 1,5-anhydro-3,4-di-*O*-benzyl-β-D-talopyranose (**8**: 49% yield). The structure of the latter unusual product was corroborated further by ^{1}H and ^{13}C NMR spectroscopy of its fully acetylated derivative **9**. Fortunately, it was established that the formation of **8** could be prevented by using an equimolar amount of the active reductive



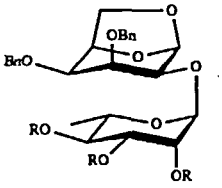
13 R = Bn, Y = OC(=NH)CCl$_3$, X = H

14 R = Bn, Y = SEt(α), X = H

15 R = Bn, Y = H, X = SEt(β)

16 R = Ac, Y/X = H/F

17 R = Ac, Y= H, X = SEt(β)



18 R = Bn

19 R = Ac

20 R = H

hydridoaluminium chloride [AlClH$_2$] species.[25] Thus in executing the reductive ring-opening of **5** under these established conditions the required alcohol **6** could be isolated, after purification by chromatography, in 70% yield. Despite this encouraging result, it was found that the reduction of **5** was accompanied by the *exo*-phenyl isomer of **5**, as evidenced by the characteristic chemical shift value (δ 6.42 ppm) of the benzylidene proton.[26,27]

Allylation of **3** with allyl bromide and sodium hydride, and subsequent reductive ring-opening of the *endo*-phenyl benzylidene acetal in **10** with an equimolar amount of LiAlH$_4$/AlCl$_3$ in DME, afforded homogeneous **11** in 64% yield, after separation from a small amount (16%) of its positional isomer **12**.

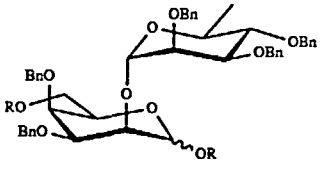
TABLE I

RELEVANT DATA ON THE GLYCOSYLATION OF ACCEPTOR **6** WITH L-RHAMNOPYRANOSYL DONORS **13-17**

Entry	Donor	Catalyst	Glycoside	Yield/%	α/β Ratio[a]
1	**13**	TfOH	**18**	95	1/1
2	**14**	TfOMe	**18**	80	1/1
3	**15**	TfOMe	**18**	75	3/2
4	**16**	$BF_3 \cdot OEt_2$	**19**	70	2/1
5	**17**	NIS/TfOH	**19**	95	8/1

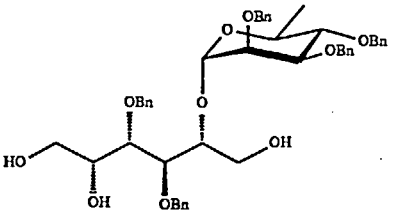
[a] The α/β ratio was determined by ^{1}H NMR spectroscopy.

At this stage of the synthetic route, the feasibility to realize a stereospecific 1,2-*trans* glycosylation of acceptor **6** with a suitably protected L-rhamnosyl donor was examined. The results of the different glycosylation experiments are summarized in Table I. It can be seen (entries 1-3) that glycosylation of **6** with the L-rhamnosyl donors **13-15**, having a non-participating benzyl group at C-2, did not proceed with a high degree of stereospecificity. Thus coupling of α-trichloroacetimidate **13** with



21 R = Ac

22 R = H



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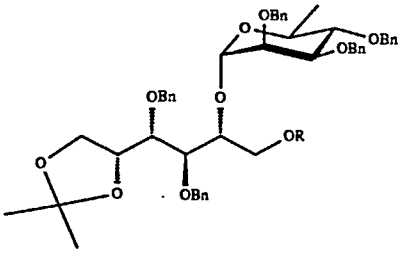
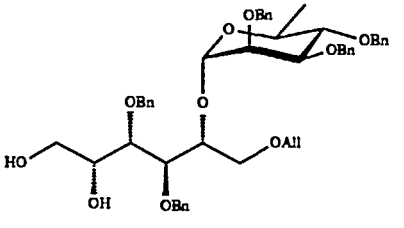


24 R = H

25 R = $C(CH_3)_2OCH_3$

26 R = All



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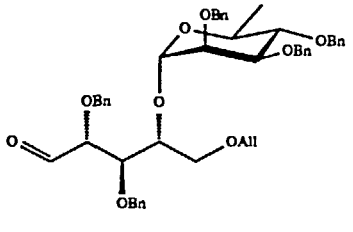
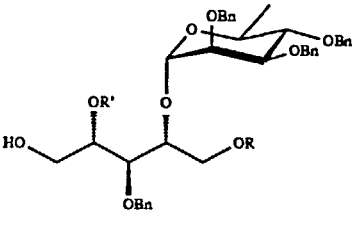


28



29 R = All, R' = Bn

30 R = Bn, R' = All

6, in the presence of the promoter trifluoromethanesulfonic acid (TfOH) resulted in a high yield of disaccharide **18** but with an unexpected[28,29] poor α/β ratio. On the other hand, methyl triflate (TfOMe) assisted condensation of **6** with the ethyl-β-thio donor **15** showed, in comparison with the corresponding α-thio donor **14** (entry 2), a more favourable α/β ratio but a slightly lower yield of disaccharide **18**. It is also evident (entry 5) that a high stereoselectivity and yield of disaccharide **19** could be attained by condensing **6**, in the presence of *N*-iodosuccinimide (NIS) and a catalytic amount of TfOH,[30] with ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside[31] (**17**) having at C-2 a participating acetyl group. The latter result is in sharp contrast (entry 4) with the boron trifluoride etherate mediated coupling of 2,3,4-tri-*O*-acetyl-α/β-L-rhamnopyranosyl fluoride[32] (**16**) with **6**. *Zemplén* deacetylation of disaccharide **19** (α/β mixture) in entry 5 followed by benzylation of **20** afforded, after chromatography on silica gel, the fully benzylated and α-linked disaccharide **18** in an excellent yield. Disaccharide **18**(α) was then converted by the following consecutive reactions to 1-*O*-allyl-3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-L-ribitol (**29**). Acetolysis of **18**(α) with acetic anhydride and catalytic sulfuric acid gave the di-*O*-acetate **21**. *Zemplén* deacetylation of **21**, and reduction of the intermediate talopyranose **22** with sodium borohydride, afforded the triol **23** in a high yield. Acetonation of D-talitol derivative **23** with 2,2-dimethoxypropane and a catalytic quantity of *p*-toluenesulfonic acid led, as gauged by TLC analysis, to a mixture of the desired 5,6-*O*-isopropylidene-D-talitol **24** and **25**. Addition of a small amount of water to the crude reaction mixture resulted in a quantitative transformation[33] of **25** to **24**. Allylation of **24** gave the fully protected talitol **26** in 95% yield (based on **23**). Deacetonation of **26** with catalytic *p*-toluenesulfonic acid in methanol, and subsequent oxidation of the vicinal diol in **27** with sodium periodate in dioxane/water, yielded the *aldehydo*-D-ribose **28**. The latter unstable product was reduced immediately with sodium borohydride to give **29** in overall 76% yield for the two steps. The structure of **29** was unambiguously ascertained by ^1H and ^{13}C NMR spectroscopy.

In conclusion, the results presented in this paper indicate that the now relatively easy accessible 1,6-anhydro-3,4-di-*O*-benzyl-β-D-talopyranose (**6**) is an interesting chiral synthon for the preparation of mono-glycosylated ribitol derivatives (*e.g.* compound **29**). Further, the corresponding 4-*O*-allyl derivative of **6** (*i.e.*

compound **11**) is a suitable starting compound for the synthesis of the mono-glycosylated compound **30** which, in turn, may be further amenable to the preparation of the di-glycosylated ribitol repeating unit of the teichoic acid isolated from the cell wall of *Listeria monocytogenes*.

EXPERIMENTAL

General Procedures. Triethylamine was dried by refluxing with CaH_2 for 16 h, then distilled and stored over molecular sieves (0.4 nm). Pyridine was dried by refluxing with CaH_2 for 16 h and then distilled, redistilled from *p*-toluenesulfonyl chloride (60 g/L), redistilled from KOH (40 g/L) and stored over molecular sieves (0.4 nm). Dioxane, diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane were dried by refluxing with CaH_2 for 16 h, then distilled and redistilled from $LiAlH_4$ directly before use. Toluene and dichloromethane were dried by refluxing with P_2O_5 (5 g/L) for 2 h and then distilled directly before use. *N,N*-Dimethylformamide was stirred with CaH_2 for 16 h and then distilled under reduced pressure and stored over molecular sieves (0.4 nm). Methanol and ethanol were dried by refluxing with magnesium, distilled and stored over molecular sieves (0.3 nm). All solvents were stored under a nitrogen atmosphere.

Melting points were uncorrected. TLC analysis was performed on silica gel (Schleicher & Schull, F 1500 LS 254). Compounds were visualized by UV light and by spraying with the appropriate reagents. Compounds containing alkene functions were visualized by spraying the TLC plates with $KMnO_4$ (1%) in aqueous Na_2CO_3 (2%); saccharides were visualized by treatment with conc. H_2SO_4 in methanol (2/8, v/v) followed by charring at 140 °C for a few minutes. Column chromatography was performed on Merck Kieselgel (230-400 mesh, ASTM). Evaporations were carried out below 40 °C under reduced pressure (20 mm or 1 mm Hg). ^1H NMR spectra were measured at 300 MHz using a Bruker WM-300 spectrometer, equipped with an ASPECT-2000 computer, operating in the Fourier transform mode. ^{13}C NMR spectra were measured at 50.1 MHz using a Jeol JNM-FX 200 spectrometer on line with a JEC 980 B computer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (TMS) as internal standard at 295 K.

1,6-Anhydro-2,3-*O*-(S)-benzylidene-β-D-*lyxo*-hexopyranos-4-ulose (2). To a cooled (-78 °C) solution of oxalyl chloride (40 mmol; 3.4 mL) in dichloromethane (60 mL) was added a solution of dimethyl sulfoxide (80 mmol; 7.2 mL) in dichloromethane (20 mL). The mixture was stirred for 5 min. at -78 °C under a nitrogen atmosphere, after which a suspension of 1,6-anhydro-2,3-*O*-(S)-benzylidene-β-D-mannopyranose[22] (**1**) (20 mmol) in dry dimethyl sulfoxide/dichloromethane (1/3, v/v, 40 mL) was injected slowly. The temperature was kept at -78 °C for 30 min. and triethylamine (10 mL) was added. TLC analysis (methanol/dichloromethane,

2/98, v/v), after stirring the mixture for an additional 1 h period, showed the absence of starting material. The mixture was diluted with dichloromethane (150 mL) and extracted twice with brine (2 × 15 mL). The organic layer was dried with magnesium sulfate, concentrated under reduced pressure and the residue was diluted with dichloromethane (20 mL). Compound **2** (16.4 mmol; 82%) crystallized after addition of hexane (45 mL): mp 233 °C (decomposes); R_f 0.48 (methanol/dichloromethane, 2/98, v/v); ^{1}H NMR (CD_3SOCD_3) {A mixture of compound **2**, and its mono hydrate} δ 3.40 (m, 0.5 H), 3.78 (m, 1 H), 3.87 (dd, 0.5 H, J = 3.0 Hz, J = 5.5 Hz), 4.42 (d, 0.5 H, J = 7.4 Hz), 4.66 (d, 0.5 H, J = 5.5 Hz), 4.82 (d, 0.5 H, J = 6.5 Hz), 4.90 (t, 0.5 H, J = 0.6 Hz), 5.03 (d, 0.5 H, J = 3.5 Hz), 5.39 (d, 0.5 H, J = 2.8 Hz), 5.80 (s, 0.5 H), 6.00 (d, 0.5 H, J = 3.9 Hz), 6.22 (s, 0.5 H), 6.55 (s, 0.5 H), 7.42-7.73 (m, 5 H); ^{13}C{^{1}H} NMR (CD_3SOCD_3) δ 62.9, 67.8, 72.4, 73.7, 75.4, 75.6, 77.3, 78.7, 98.2, 98.8, 103.3, 105.4, 127.4-129.7, 136.8, 205.8 (C-4).

Anal. Calcd for $C_{13}H_{12}O_5$ (248.23): C 62.90, H 4.87; found: C 62.54, H 4.82%.

1,6-Anhydro-2,3-*O*-(S)-benzylidene-β-D-talopyranose (3). Method A: To a solution of compound **2** (2 mmol) in methanol (10 mL) was added sodium borohydride (10 mmol). The mixture was stirred for 1 h at 20 °C until TLC analysis (methanol/dichloromethane, 2/98, v/v) indicated complete disappearance of the starting material. Excess sodium borohydride was destroyed with ammonium chloride and the mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (25 mL) and washed with two portions of brine (10 mL). The organic phase was dried (sodium sulfate), filtered, concentrated *in vacuo* and the residue was applied to a column of Kieselgel (15 g) suspended in dichloromethane/triethylamine (99.9/0.1, v/v). Elution was effected with dichloromethane/methanol/triethylamine (98/2/0.1, v/v/v). Concentration of the appropriate fractions, gave **3** (1.6 mmol, 81%). Analytical and spectral data of compound **3** thus obtained are in complete agreement with the data reported for compound **3** prepared by method B.

Further elution gave 1,6-anhydro-2,3-*O*-(S)-benzylidene-β-D-mannopyranose (**1**) (0.2 mmol, 10%) as a colourless solid.[22]

Mixtures of **3** and 1,6-anhydro-3,4-*O*-benzylidene-β-D-talopyranose (**4**) usualy resulted when no precautions were taken to avoid acidic condition during work-up, purification or prolonged storage. Analysis of the mistreated batch, using ^{1}H NMR spectroscopy, revealed the presence of more than one benzylidene proton signal: ^{1}H NMR ($CDCl_3$) δ 5.77 and 5.84 (*endo*-benzylidene), 6.33 and 6.49 (*exo*-benzylidene).

Method B: Compound **2** (13 mmol) dissolved in dry 1,2-dimethoxyethane (50 mL), was reduced with sodium borohydride (25 mmol) which was added to the cooled 10 °C solution in small portions over a period of 30 minutes. TLC analysis revealed complete conversion of the starting material into **3**. The mixture was quenched with acetone (10 mL) and concentrated *in vacuo*. The residue was dissolved in ethyl acetate (100 mL) and extracted twice with brine

(2 × 20 mL). The organic layer was dried with sodium sulfate, concentrated under reduced pressure and the residue was dissolved in dichloromethane (90 mL) and compound **3** (16.4 mmol; 98%) crystallized after addition of hexane (45 mL): mp 131.5-132 °C; $[\alpha]_D^{20}$ -70° (c 3.5, chloroform); R_f 0.34 (methanol/dichloromethane, 2/98, v/v); ^{1}H NMR ($CDCl_3$) δ 2.78 (d, 1 H, O-H, $J_{4,OH}$ = 9,2 Hz), 3.72 (dd, 1 H, H-6', $J_{6',6}$ = 7.9 Hz), 4.18-4.21 (m, 3 H, H-2, H-6, H-4), 4.43 (t, 1 H, H-5, $J_{5,4}$ = $J_{5,6'}$ = 5.3 Hz), 4.48 (t, 1 H, H-3, $J_{3,2}$ = $J_{3,4}$ = 6.0 Hz), 5.40 (d, 1 H, H-1, $J_{1,2}$ = 3.1 Hz), 5.81 (s, 1 H, O_2CHPh), 7.40-7.71 (m, 5 H, $H_{arom.}$ Phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 63.0 (C-6), 66.0, 72.9, 74.6 and 75.6 (C-2, C-3, C-4 and C-5), 98.3 (C-1), 105.0 (CHPh), 127.4, 127.9 and 129.4 ($CH_{arom.}$), 135.8 ($C_{arom.}$).

Anal. Calcd for $C_{13}H_{14}O_5$ (250.25): C 62.39, H 5.64; found: C 62.31, H 5.60%.

1,6-Anhydro-4-*O*-benzyl-2,3-*O*-(S)-benzylidene-β-D-talopyranose (5). To a cooled (-10 °C) solution of compound **3** (20 mmol) in dry *N,N*-dimethylformamide (100 mL) was added sodium hydride (40 mmol). The suspension was stirred for 15 min. under a nitrogen atmosphere. Benzyl bromide (24 mmol) was injected into the mixture and the temperature of the mixture was allowed to rise to room temperature. Progress of the reaction was monitored by TLC analysis (methanol/dichloromethane, 4/96, v/v). After 1 h, excess sodium hydride and benzyl bromide were destroyed with 20 mL dry methanol. The mixture was stirred for an additional 30 min. at 20 °C and was subsequently neutralised with 1 M acetic acid, diluted with diethyl ether (150 mL) and washed twice with a saturated aqueous solution of sodium chloride (2 × 50 mL). The combined organic layers were dried (sodium sulfate), concentrated and applied to a column of Kieselgel (150 g) suspended in hexane. Elution was effected with hexane/diethyl ether (1/0 to 1/1, v/v) and concentration of the appropriate fractions, gave **5** (19 mmol, 95%): $[\alpha]_D^{20}$ -113.3° (c 1.1, chloroform); R_f 0.78 (methanol/dichloromethane, 4/96, v/v), 0.41 (hexane/diethyl ether, 1/2, v/v); ^{1}H NMR ($CDCl_3$) δ 3.73 (t, 1 H, H-6'), 3.96 (t, 1 H, H-4, $J_{4,5}$ = $J_{4,3}$ = 5.0 Hz), 4.13 (dd, 1 H, H-2, $J_{2,3}$ = 6.1 Hz), 4.42 (t, 1 H, H-5, $J_{5,4}$ = $J_{5,6'}$ = 5.1 Hz), 4.46 (d, 1 H, H-6, $J_{6,6'}$ = 7.3 Hz), 4.51 (t, 1 H, H-3, $J_{3,4}$ = $J_{3,2}$ = 5.7 Hz), 4.63 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 12.1 Hz), 4.81 (d, 1 H, CH_2 benzyl), 5.38 (d, 1 H, H-1, $J_{1,2}$ = 2.9 Hz), 5.81 (s, 1 H, O_2CHPh), 7.27-7.73 (m, 10 H, $H_{arom.}$ 2 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 63.7 (C-6), 70.5 (CH_2Ph), 71.2, 72.3, 74.1 and 74.6 (C-2, C-3, C-4 and C-5), 98.7 (C-1), 105.2 (CHPh), 127.1-129.2 ($CH_{arom.}$ phenyl), 136.2 and 137.3 (2 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{20}H_{20}O_5$ (340.38): C 70.58, H 5.92; found C 70.28, H 5.90%.

Reduction of 1,6-Anhydro-4-*O*-benzyl-2,3-*O*-(S)-benzylidene-β-D-talopyranose (5). Method A: employing excess AlH_2Cl. To a cooled (0 °C) and stirred suspension of compound **5** (7.9 mmol) and lithium aluminium hydride (19.8 mmol) in dichloromethane (80 mL) was injected a solution of aluminium chloride (19.8 mmol) in diethyl ether (40 mL) over a period of 30 minutes. The mixture was refluxed and the progress of the reaction was monitored by TLC analysis (ether/hexane, 2/1, v/v). After 1 h, ethyl acetate (10 mL) was added, the

suspension was stirred for 15 min. at 0 °C, and subsequently water (10 mL) and an aqueous solution of sodium hydroxide (15%, 50 mL) were added. The mixture was stirred vigorously for 1 h and the organic layer was separated and washed twice with water (40 mL). The inorganic layer was diluted with water (150 mL) and extracted twice with diethyl ether (60 mL). The combined organic layers were dried (sodium sulfate) and concentrated *in vacuo*. The residue was applied to a column of Kieselgel (100 g) suspended in hexane. Elution was effected with hexane/ether (1/0 to 1/1, v/v). Concentration of the appropriate fractions gave 1,6-anhydro-3,4-di-*O*-benzyl-β-D-talopyranose (6) (1.7 mmol; 22 %): R_f 0.24 (diethyl ether/hexane, 2/1, v/v); ^{1}H NMR ($CDCl_3$) δ 3.14 (d, 1 H, OH, $J_{OH,2}$ = 11.8 Hz), 3.56 (ddd, 1 H, H-2, $J_{2,3}$ = 5.3 Hz), 3.66 (t, 1 H, H-6'), 3.78 (t, 1 H, H-4, $J_{4,5}$ = 4.0 Hz), 4.10 (t, 1 H, H-3, $J_{3,4}$ = 4.7 Hz), 4.44 (t, 1 H, H-5, $J_{5,6'}$ = 4.7 Hz), 4.56 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 10.8 Hz), 4.58 (d, 1 H, H-6, $J_{6,6'}$ = 6.2 Hz), 4.69 (s, 2 H, CH_2 benzyl), 5.01 (d, 1 H, CH_2 benzyl), 5.23 (d, 1 H, H-1, $J_{1,2}$ = 2.0 Hz), 7.29-7.38 (m, 10 H, $H_{arom.}$ 2 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 64.8 (C-6), 68.6, 71.6, 75.5 and 76.4 (C-2, C-3, C-4 and C-5), 71.4 and 75.9 (CH_2Ph), 101.1 (C-1), 127.0-128.3 ($CH_{arom.}$ phenyl), 137.6 and 138.0 (2 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{20}H_{22}O_5$ (342.39): C 70.16 H 6.48; found: C 69.98, H 6.59%.

Further elution gave 1,6-anhydro-2,4-di-*O*-benzyl-β-D-talopyranose (7) (0.4 mmol, 5 %) as a colourless oil: R_f 0.18 (diethyl ether/hexane, 2/1, v/v); ^{1}H NMR ($CDCl_3$) δ 2.97 (d, 1 H, OH, $J_{OH,3}$ = 2.8 Hz), 3.42 (dd, 1 H, H-2, $J_{2,1}$ = 1.9 Hz, $J_{2,3}$ = 4.6 Hz), 3.61 (t, 1 H, H-4, $J_{4,5}$ = 4.1 Hz), 3.66 (dd, 1 H, H-6', $J_{6',5}$ = 5.0 Hz), 4.38 (t, 1 H, H-5, $J_{5,4}$ = $J_{5,6'}$ = 4.6 Hz), 4.39 (m, 1 H, H-3), 4.55 (d, 1 H, H-6, $J_{6,6'}$ = 7.2 Hz), 4.58 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 12.9 Hz), 4.61 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 12.0 Hz), 4.74 (d, 1 H, CH_2 benzyl), 4.76 (d, 1 H, CH_2 benzyl), 5.35 (t, 1 H, H-1, $J_{1,2}$ = $J_{1,3}$ = 1.5 Hz), 7.31-7.38 (m, 10 H, $H_{arom.}$ 2 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 65.4 (C-6), 70.6 (2 × CH_2Ph), 65.6, 73.0, 73.6 and 75.1 (C-2, C-3, C-4 and C-5), 99.8 (C-1), 127.6-128.4 ($CH_{arom.}$ phenyl), 137.0 and 137.6 (2 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{20}H_{22}O_5$ (342.39): C 70.16 H 6.48; found: C 69.59, H 6.54%.

Continued elution gave 1,5-anhydro-3,4-di-*O*-benzyl-β-D-talitol (8) (3.6 mmol; 49 %) as colourless oil: R_f 0.07 (diethyl ether/hexane, 2/1, v/v); ^{1}H NMR ($CDCl_3$/CD_3OD =95/5 v/v) δ 3.38-3.54 (m, 4 H), 3.80 (dd, 1 H, H-6, $J_{6,6'}$ = 11.5 Hz, $J_{6,5}$ = 7.0 Hz), 3.94 and 4.03 (2 × m, 2 H, 4.09 (dd, 1 H, H-1, $J_{1,2}$ = 1.5 Hz, $J_{1,1'}$ = 12.0 Hz), 4.61 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 11.5 Hz), 4.65 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 10.6 Hz), 4.84 (d, 1 H, CH_2 benzyl), 4.99 (d, 1 H, CH_2 benzyl), 7.30-7.43 (m, 10 H, $H_{arom.}$ 2 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 61.5 (C-1), 66.7, 75.2, 76.1 and 79.0 (C-2, C-3, C-4 and C-5), 69.6 (C-6), 71.3 and 74.7 (2 × CH_2Ph), 126.9-128.0 ($CH_{arom.}$ phenyl), 137.2 and 137.4 (2 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{20}H_{24}O_5$ (344.41): C 69.75, H 7.02; found C 68.67, H 7.01%.

Method B: employing an equimolar amount of AlH_2Cl. To a cooled (0 °C) and stirred suspension of compound **5** (10 mmol, *endo*-phenyl) and lithium aluminium hydride (5

mmol) in dichloromethane (100 mL) was injected a solution of aluminium chloride (5 mmol) in diethyl ether (50 mL) over a period of 10 minutes. The mixture was stirred at 20 °C and the reduction was monitored by TLC analysis (ether/hexane, 2/1, v/v). After 1.5 h, ethyl acetate (10 mL) was added to the suspension, which was stirred for 15 min. at 0 °C, subsequently water (10 mL) and an aqueous solution of sodium hydroxide (15%, 50 mL) were added. The mixture thus obtained was stirred vigorously for 1 h. The layers were separated and the organic layer was washed twice with water (40 mL). The inorganic layer was diluted with water (150 mL) and extracted twice with diethyl ether (60 mL). The combined organic layers were dried (sodium sulfate) and concentrated *in vacuo*. The residue was applied to a column of Kieselgel (120 g) suspended in hexane. Elution was effected with hexane/ether (1/0 to 1/1, v/v). Concentration of the appropriate fractions gave 1,6-anhydro-4-*O*-benzyl-2,3-*O*-(R)-benzylidene-β-D-talopyranose (**5**, *exo*-phenyl, 1.1 mmol, 11%) as a colourless oil: R_f 0.63 (diethyl ether/hexane, 2/1, v/v); ^{1}H NMR ($CDCl_3$) δ 3.74 (t, 1 H, H-6', $J_{6',6}$ = 6.3 Hz), 3.88 (t, 1 H, H-4, $J_{4,5}$ = 5.0 Hz), 4.28 (dd, 1 H, H-2, $J_{2,3}$ = 5.4 Hz), 4.43 (t, 1 H, H-5, $J_{5,6'}$ = 5.0 Hz), 4.50 (t, 1 H, H-3, $J_{3,4}$ = 5.1 Hz), 4.52 (d, 1 H, H-6, $J_{6,6'}$ = 7.2 Hz), 4.62 (d, 1 H, CH benzyl, $J_{A,B}$ = 12.0 Hz), 4.80 (d, 1 H, CH benzyl), 5.45 (d, 1 H, H-1, $J_{1,2}$ = 2.7 Hz), 6.42 (s, 1 H, CH *exo*-phenyl), 7.30-7.44 (m, 10 H, $H_{arom.}$ 2 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 64.4 and 70.4 (C-6 and CH_2 benzyl), 71.3, 71.5, 72.6 and 76.2 (C-2, C-3, C-4 and C-5), 99.2 and 105.4 (C-1 and CH benzylidene), 125.5-128.3 ($CH_{arom.}$ benzyl), 137.3 and 139.5 (2 × $C_{arom.}$ benzyl).

Further elution gave 1,6-anhydro-3,4-di-*O*-benzyl-β-D-talopyranose (**6**) (6.9 mmol; 69 %) as a colourless oil. Continued elution gave 1,6-anhydro-2,4-di-*O*-benzyl-β-D-talopyranose (**7**) (0.9 mmol, 9 %) as a colourless oil. Analytical and spectral data of compounds **6** and **7** thus isolated are in complete agreement with the data reported for compound **6** and **7**, respectively, prepared by method A.

2,6-Di-*O*-acetyl-1,5-anhydro-3,4-di-*O*-benzyl-β-D-talitol (9). Compound **8** (3.5 mmol) was dissolved in dry pyridine (35 mL) and acetic acid anhydride (17 mL). The mixture was stirred for 16 h at ambient temperature. The mixture was diluted with toluene (50 mL), concentrated under reduced pressure, and concentrated several times with toluene (3 × 50 mL). The residue was applied to a column of Kieselgel (30 g) suspended in hexane. Elution was effected with hexane/ether (1/0 to 1/2, v/v) and compound **9** (3.2 mmol, 91 %) was isolated as a colourless oil; R_f 0.27 (hexane/diethyl ether, 1/2, v/v), 0.59 (ethanol/toluene, 5/95, v/v); ^{1}H NMR ($CDCl_3$) δ 2.02 (s, 3 H, CH_3 acetyl), 2.09 (s, 3 H, CH_3 acetyl), 3.59 (dd, 1 H, H-1'), 3.66 (ddd, 1 H, H-5, $J_{5,6}$ = 7.7 Hz, $J_{5,6'}$ = 3.9 Hz), 3.71 (t, 1 H, H-4, $J_{4,3}$ = $J_{4,5}$ = 3.1 Hz), 3.77 (t, 1 H, H-3, $J_{3,4}$ = 2.7 Hz), 4.10 (dd, 1 H, H-6'), 4.26 (dd, 1 H, H-1, $J_{1,2}$ = 4.1 Hz, $J_{1,1'}$ = 12.0 Hz), 4.42 (dd, 1 H, H-6, $J_{6,6'}$ = 11.9 Hz), 4.42 (dd, 1 H, H-6'), 4.60 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 12.0 Hz), 4.68 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 11.6 Hz), 4.75 (d, 1 H, CH_2 benzyl), 4.88 (d, 1 H, CH_2 benzyl), 5.24 (q, 1 H, H-2, $J_{2,3}$ = 2.8 Hz), 7.28-7.36 (m, 10 H, $H_{arom.}$ 2 × phenyl);

$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 20.2 (CH_3 acetyl), 20.6 (CH_3 acetyl), 62.7 (C-1), 66.3, 73.0, 75.9 and 75.95 (C-2, C-3, C-4 and C-5), 71.0 (C-6), 72.8 (2 × CH_2Ph), 126.8-127.9 ($CH_{arom.}$ phenyl), 137.4 and 137.8 (2 × $C_{arom.}$ phenyl), 170.1 (2 × C=O acetyl).

Anal. Calcd for $C_{24}H_{28}O_7$ (428.48): C 67.28, H 6.59; found C 67.19, H 6.57%.

4-*O*-Allyl-1,6-anhydro-2,3-*O*-(S)-benzylidene-β-D-talopyranose (10). To a cooled (-10 °C) solution of compound **3** (3.2 mmol) in dry *N,N*-dimethylformamide (20 mL) was added sodium hydride (6 mmol). The suspension was stirred for 15 min. under a nitrogen atmosphere. Allyl bromide (3.8 mmol) was injected into the mixture and the temperature of the mixture was allowed to rise to room temperature. TLC analysis (methanol/dichloromethane, 4/96, v/v), after 1 h showed the reaction to be complete. Excess sodium hydride and benzyl bromide were destroyed with dry methanol (2 mL), and the mixture was stirred for an additional 30 min. at 20 °C. The mixture was subsequently neutralised with 1 M acetic acid, diluted with diethyl ether (50 mL) and washed twice with a saturated aqueous solution of sodium chloride (2 × 25 mL). The combined organic layers were dried (sodium sulfate), concentrated and applied to a column of Kieselgel (50 g) suspended in hexane. Elution was effected with hexane/diethyl ether (1/0 to 1/1, v/v). Concentration of the appropriate fractions gave **10** (3.0 mmol, 95%): $[\alpha]_D^{20}$ -126.3° (c 1.0, chloroform); R_f 0.73 (methanol/dichloromethane, 2/98, v/v), 0.41 (hexane/diethyl ether, 1/2, v/v); ^1H NMR ($CDCl_3$) δ 3.75 (t, 1 H, H-6', $J_{6',5} = J_{6',6} = 6.3$ Hz), 3.96 (t, 1 H, H-4, $J_{4,5} = J_{4,3} = 4.9$ Hz), 4.09-4.26 (m, 2 H, CH_2=CH-CH_2), 4.15 (dd, 1 H, H-2, $J_{2,3} = 6.1$ Hz), 4.42 (d, 1 H, H-6, $J_{6,6'} = 7.4$ Hz), 4.49 (t, 1 H, H-5, $J_{5,4} = J_{5,6'} = 5.0$ Hz), 4.51 (t, 1 H, H-3, $J_{3,2} = J_{3,3} = 5.6$ Hz), 5.21-5.35 (m, 2 H, CH_2 allyl), 5.39 (d, 1 H, H-1, $J_{1,2} = 3.0$ Hz), 5.79 (s, 1 H, O_2CHPh), 5.86-5.99 (m, 1 H, CH_2=C*H*-CH_2), 7.31-7.72 (m, 5 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 63.5 (C-6), 69.7 (CH_2=CH-*C*H_2), 71.1, 72.3, 74.0 and 74.5 (C-2, C-3, C-4 and C-5), 98.6 (C-1), 105.0 (O_2CHPh), 117.2, (CH_2=CH-*C*H_2), 127.4, 127.6 and 129.0 ($CH_{arom.}$ benzyl), 133.9, (CH_2=*C*H-CH_2), 136.0 (2 × $C_{arom.}$ benzyl).

Anal. Calcd for $C_{16}H_{18}O_5$ (290.32): C 66.20, H 6.25; found C 66.63, H 6.24%.

Reduction of 1,6-anhydro-4-*O*-allyl-2,3-*O*-(S)-benzylidene-β-D-talopyranose (10). Compound **10** (5 mmol) was treated with lithium aluminum hydride and aluminium chloride as described under method **B** for the reduction of compound **5**. After work-up and Kieselgel chromatography 4-*O*-allyl-1,6-anhydro-3-*O*-benzyl-β-D-talopyranose (**11**) was obtained (3.2 mmol, 64 %) as a colourless oil, which cystallized upon standing: R_f 0.59 (methanol/dichloromethane, 2/98, v/v); ^1H NMR ($CDCl_3$) δ 3.18 (br d, 1 H, OH, $J_{OH,2} = 9.9$ Hz), 3.59 (br m, 1 H, H-2), 3.69 (m, 2 H, H-4 and H-6'), 4.08 (t, 1 H, H-3, $J_{3,4} = 4.6$ Hz), 4.14 (m, 2 H, CH_2=CH-CH_2), 4.44 (t, 1 H, H-5, $J_{5,6'} = 4.6$ Hz), 4.52 (d, 1 H, CH_2 benzyl, $J_{A,B} = 11.2$ Hz), 4.54 (d, 1 H, H-6, $J_{6,6'} = 6.7$ Hz), 5.29 (m, 2 H, CH_2=CH-CH_2), 5.00 (d, 1 H, CH_2 benzyl), 5.25 (d, 1 H, H-1, $J_{1,2} = 1.3$ Hz), 5.94 (m, 1 H, CH_2=C*H*-CH_2), 7.27-7.33 (m, 10 H, $H_{arom.}$ 2 × phenyl); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 65.1 (C-6), 65.3, 72.7, 73.6 and 75.0 (C-2, C-3, C-4 and C-5), 69.6 and 70.3

(CH_2Ph and CH_2=CH-CH_2), 99.6 (C-1 $^2J_{C,H}$ = 172.9 Hz), 117.3 (CH_2=CH-CH_2), 127.5-128.1 ($CH_{arom.}$ phenyl), 134.1 (CH_2=CH-CH_2) 136.9 ($C_{arom.}$ phenyl).

Anal. Calcd for $C_{16}H_{20}O_5$ (292.33): C 65.74, H 6.90; found: C 65.59, H 6.87%.

Further elution gave 4-*O*-allyl-1,6-anhydro-2-*O*-benzyl-β-D-talopyranose (**12**), (0.8 mmol, 16 %) which was isolated as a colourless oil: R_f 0.49 (methanol/dichloromethane, 2/98, v/v); ^{1}H NMR ($CDCl_3$) δ 2.94 (d, 1 H, OH, $J_{OH,3}$ = 2.8 Hz), 3.45 (ddd, 1 H, H-2, $J_{2,3}$ = 4.6 Hz), 3.59 (t, 1 H, H-4, $J_{4,5}$ = 4.1 Hz), 3.68 (dd, 1 H, H-6', $J_{6',5}$ = 4.5 Hz), 4.06 (m, 2 H, CH_2=CH-CH_2), 4.39 (m, 1 H, H-5), 4.42 (t, 1 H, H-3, $J_{3,4}$ = 4.3 Hz), 4.54 (d, 1 H, H-6, $J_{6,6'}$ = 7.2 Hz), 4.58 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 11.8 Hz), 4.75 (d, 1 H, CH_2 benzyl), 5.28 (m, 2 H, CH_2=CH-CH_2), 5.36 (t, 1 H, H-1, $J_{1,2}$ = $J_{1,3}$ = 1.5 Hz), 5.94 (m, 1 H, CH_2=CH-CH_2), 7.27-7.39 (m, 10 H, $H_{arom.}$ 2 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 64.9 (C-6), 65.2, 72.6, 73.4 and 74.9 (C-2, C-3, C-4 and C-5), 69.7 and 70.3 (CH_2Ph and CH_2=CH-CH_2), 99.5 (C-1), 117.4 (CH_2=CH-CH_2), 127.4-128.1 ($CH_{arom.}$ phenyl), 133.8 (CH_2=CH-CH_2), 137.7 ($C_{arom.}$ phenyl).

Anal. Calcd for $C_{16}H_{20}O_5$ (292.33): C 65.74, H 6.90; found C 65.58, H 6.86%.

1,6-Anhydro-3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-β-D-talopyranose (18α) and its β-anomer. Method A: using glycosyl donors 13, 14 and 15 having a non-participating group at C-2: To a solution of alcohol **6** (2 mmol) in dry dichloromethane (20 mL) was added activated molecular sieves (8 g, 0.4 nm). The mixture was stirred for 0.5 h at ambient temperature under a argon atmosphere and was then cooled to -20 °C. A solution of imidate **13** (4 mmol) in dichloromethane (20 mL) was injected, shortly followed by a solution of trifluoromethanesulfonic acid (0.15 M, 2 mL) in dichloromethane. Stirring was continued for 0.5 h. TLC analysis (ether/hexane, 2/1, v/v) revealed complete disappearance of compound **6**. The mixture was treated with triethylamine (2 mL) and filtered. The filtrate was washed with a saturated aqueous solution of sodium bicarbonate (10 mL), and water (10 mL). The combined organic layers were dried with magnesium sulfate, concentrated to a small volume and applied to a column of Sephadex LH-20 suspended in dichloromethane/ methanol (2/1, v/v). Elution was effected with the same solvent, and compound **18** (α/β mixture) was isolated in 95 % yield, after concentration of the appropriate fractions. The residue was applied to a column of Kieselgel (30 g) suspended in toluene. Elution was effected with toluene/acetone (1/0 to 97/3, v/v) and compound **18α** (1.0 mmol, 45%) was isolated as a colourless oil: R_f 0.45 (toluene/acetone, 95/5, v/v); $[\alpha]_D^{20}$ -62.5° (c 1.6, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.30 (d, 3 H, Rha: H-6, $J_{6,5}$ = 5.6 Hz), 3.58-3.73 (m, 5 H, Rha: H-4 and H-5, Tal: H-2, H-4 and H-6'), 3.83 (dd, 1 H, Rha: H-3, $J_{3,4}$ = 8.9 Hz), 3.97 (t, 1 H, Rha: H-2, $J_{2,3}$ = 2.5 Hz), 4.10 (t, 1 H, Tal: H-3, $J_{3,4}$ = 4.4 Hz), 4.40 (t, 1 H, Tal: H-5, $J_{5,4}$ = $J_{5,6'}$ = 4.3 Hz), 4.45-5.31 (5 × AB, 10 H, 5 × CH_2 benzyl), 4.71 (d, 1 H, Tal: H-6, $J_{6,6'}$ = 7.1 Hz), 4.97 (br s, 1 H, Rha: H-1), 5.34 (s, 1 H, Tal: H-1), 7.17-7.39 (m, 25 H, $H_{arom.}$ 5 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 18.0 (Rha, C-6), 65.8, 71.1, 71.7, 73.06, 75.02 and 75.7 (CH_2Ph), 68.7, 72.8, 73.1,

74.6, 75.0, 76.1, 79.8 and 80.0 (2 × C-2, 2 × C-3, 2 × C-4 and 2 × C-5), 96.4 and 98.1 (2 × C-1 $^2J_{C,H}$ = 168.5 Hz and $^2J_{C,H}$ = 175.8 Hz), 127.0-128.3 ($CH_{arom.}$ phenyl), 137.5, 138.0, 138.3, 138.5 and 138.6 (5 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{47}H_{50}O_9$ (758.91): C 74.39, H 6.64; found C 74.03, H 6.60%.

Further elution gave **18β** (0.4 mmol, 43%) as a colourless oil: R_f 0.29 (toluene/acetone, 95/5, v/v); $[\alpha]_D^{20}$ 17.0° (c 1.3, chloroform); ^1H NMR ($CDCl_3$) δ 1.31 (d, 3 H, Rha: H-6, $J_{6,5}$ = 6.2 Hz), 3.11 (dq, 1 H, Rha: H-5 $J_{5,6}$ = 6.2 Hz), 3.20 (dd, 1 H, Rha: H-3, $J_{3,4}$ = 9.3 Hz), 3.54 (t, 1 H, Rha: H-4 $J_{4,5}$ = 9.3 Hz), 3.70-3.77 (m, 3 H, Rha: H-2, Tal: H-4 and H-6'), 3.81 (dd, 1 H, Tal: H-2, $J_{2,1}$ = 1.8 Hz, $J_{2,3}$ = 4.5 Hz), 4.11 (s, Tal: H-6), 4.17 (t, 1 H, Tal: H-3, $J_{3,4}$ = 4.3 Hz), 4.36 (AB, 2 H, CH_2 benzyl, $J_{A,B}$ = 12.0 Hz), 4.45 (t, 1 H, Tal: H-5, $J_{5,4}$ = $J_{5,6'}$ = 4.9 Hz), 4.58-5.01 (3 × AB and s, 8 H, 5 × CH_2 benzyl), 4.76 (d, 1 H, Rha: H-1, $J_{1,2}$ = 7.0 Hz), 5.46 (s, 1 H, Tal: H-1), 7.13-7.44 (m, 25 H, $H_{arom.}$ 5 × phenyl).

To a dry solution of **6** (1 mmol), **14** (1.5 mmol) and molecular sieves (1g, 0.4 nm) in diethyl ether (10 mL) was added methyl triflate (2.5 mmol) at 0 °C under an argon atmosphere. After 10 min., the mixture was quenched with triethylamine (1 mL). Work-up and purification as described above gave **18** (0.8 mmol, α/β ratio: 1/1) in 80 % yield.

To a dry, cooled (0 °C) solution of alcohol **6** (0.5 mmol), **15** (0.75 mmol) and molecular sieves (0.5 g, 0.4 nm) in diethyl ether (10 mL) was added methyl triflate (1.25 mmol) under an argon atmosphere. After 10 min., the mixture was quenched with triethylamine (1 mL). Work-up and purification as described above gave **18** (0.38 mmol, α/β ratio: 3/2) in 75 % yield.

Method B: using glycosyl donors 17 and 16 having a participating group at C-2: Synthesis of 1,6-anhydro-3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-talopyranose (19α) and its β-anomer. To a solution of **6** (8 mmol) and **17** (10.5 mmol) in dry 1,2-dichloroethane (70 mL) was added activated molecular sieves (14 g, 0.4 nm). The mixture was stirred for 30 min. at ambient temperature under a argon atmosphere and was then cooled to 0 °C. A solution of freshly prepared *N*-iodo-succinimide (10.7 mmol) and trifluoromethanesulfonic acid (2.2 mmol) in dichloroethane (104 mL) was injected, and stirring was continued for 0.5 h. TLC analysis (ether/hexane, 2/1, v/v) revealed complete disappearance of compound **6**. The mixture was treated with triethylamine (10 mL) and filtered. The filtrate was washed with a saturated aqueous solution of sodium bicarbonate (10 mL), and water (10 mL). The organic layers were dried with magnesium sulfate, concentrated to a small volume and applied to a column of Sephadex LH-20 suspended in dichloromethane/methanol (2/1, v/v). Elution was effected with the same solvent, and compound **19** (7.6 mmol; α/β mixture) was obtained in 95 % yield: R_f 0.20 (toluene/acetone, 95/5, v/v); ^1H NMR of the mixture thus obtained revealed an α/β ratio of 8 to 1: ^1H NMR of the α-isomer in ($CDCl_3$) δ 1.16 (d, 3 H, Rha: H-6), 1.98, 2.03 and 2.10 (3 × s, 9 H, 3 × CH_3 acetyl), 3.70 (dd, 1 H, Tal: H-2, $J_{2,3}$ =

4.4 Hz), 3.71-3.74 (m, 2 H, Tal: H-4 and H-6), 3.79 (dq, 1 H, Rha: H-5, $J_{5,6}$ = 6.3 Hz), 4.17 (tt, 1 H, Tal: H-3, $J_{3,2} \approx J_{3,4}$ = 4.4 Hz, $J_{3,5} \approx J_{3,1}$ = 1.3 Hz), 4.44 (dt, 1 H, Tal: H-5, $J_{5,4} \approx J_{5,6}$ = 4.5 Hz), 4.57 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 11.9 Hz), 4.66 (d, 1 H, CH_2 benzyl), 4.73 (d, 1 H, Tal: H-6', $J_{6',6}$ = 7.0 Hz), 4.84 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 11.7 Hz), 4.90 (d, 1 H, CH_2 benzyl), 5.03 (t, 1 H, Rha: H-4, $J_{4,5}$ = 9.9 Hz), 5.13 (d, 1 H, Rha: H-1, $J_{1,2}$ = 1.8 Hz), 5.32 (dd, 1 H, Rha: H-2, $J_{2,3}$ = 3.5 Hz), 5.38 (dd, 1 H, Rha: H-3, $J_{3,4}$ = 10.0 Hz), 5.48 (t, 1 H, Tal: H-1, $^3J_{1,2} \approx {}^4J_{1,3}$ = 1.4 Hz), 7.22-7.47 (m, 10 H, $H_{arom.}$ 2 × phenyl); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.2 (C-6, Rha), 20.3 and 20.4 (3 × CH_3, acetyl), 65.7, 71.2 and 75.2 (2 × CH_2Ph and C-6 Tal), 66.6, 68.4, 69.5, 70.7, 71.2, 72.6, 74.5, 75.3 and 76.2 (2 × {C-2, C-3, C-4 and C-5} Tal and Rha), 95.6 and 96.0 (2 × C-1 $^1J_{C,H}$ = 172.9 Hz and $^1J_{C,H}$ = 172.9 Hz), 126.8-128.2 ($CH_{arom.}$), 137.5 and 138.4 (2 × $C_{arom.}$ phenyl), 169.2, 169.4 and 169.5 (3 × C=O, acetyl).

Anal. Calcd for $C_{32}H_{38}O_{12}$ (614.65): C 62.53, H 6.23; found C 62.93, H 6.20%.

To a solution of compound **19** (6.7 mmol) in dry methanol (65 mL) sodium methoxide (0.6 mmol) was added. The mixture was stirred for two hours at 20 °C under a argon atmosphere until TLC analysis (methanol/dichloromethane, 4/96, v/v) indicated complete conversion of **19** into **20**. The mixture was treated with Dowex 50 XW [H^+] (25 mL), filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in toluene (25 mL) and concentrated under reduced pressure. The residue was dissolved in dry *N,N*-dimethylformamide (25 mL) under a argon atmosphere. The solution was cooled (0 °C) and sodium hydride (30 mmol) was added. Benzyl bromide (22 mmol) was injected and the temperature of the mixture was allowed to rise to room temperature. After 1 h, TLC analysis (methanol/dichloromethane, 4/96, v/v) indicated complete conversion of the starting material into **18**, and the excess sodium hydride and benzyl bromide were destroyed with dry methanol (20 mL). The mixture stirred for 30 min. and was then diluted with diethyl ether (150 mL) and washed twice with brine (2 × 50 mL). The combined organic layers were dried (calcium chloride) concentrated and applied to a column of Kieselgel (150 g) suspended in hexane. Elution was effected with toluene/acetone (1/0 to 97/3, v/v) and compound **18α** (4.3 mmol, 64%) was isolated as a colourless oil: analytical and spectral data of compound **18α** thus obtained were in excellent agreement with those reported for the same compound prepared under **A**.

To a dry solution of **6** (1 mmol) and fluoride **16** (1.2 mmol) in diethyl ether (10 mL) and 1,2-dichloroethane (1 mL) was added boron trifluoride etherate (final amount: 1.5 mmol) in small portions until TLC analysis indicated complete conversion of compound **6** into **19**. The mixture quenched with triethylamine (1 mL). Standard work-up and purification as described above gave **19** (0.7 mmol, α/β ratio: 2/1) in 70 % yield.

3,4-Di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-D-talitol (23). A solution of **18α** (1 mmol) in acetic acid anhydride (9 mL) and trifluoroacetic acid (1 mL) was cooled and stirred at -20 °C under a nitrogen atmosphere. Stirring was continued for 1 h until the

reaction mixture attained a temperature of 5 °C. The mixture was diluted with dry toluene (50 mL) and sodium acetate (5 g) was added. The mixture was filtered and the filtrate was concentrated *in vacuo* to a small volume. The residue was diluted with dichloromethane (30 mL) and washed with a saturated aqueous solution of sodium bicarbonate (10 mL), and water (10 mL). The organic layers were dried with magnesium sulfate, filtered and concentrated under reduced pressure to afford 1,6-di-*O*-acetyl-3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-α/β-D-talopyranose (**21**) in nearly quantitative yield: R_f 0.20 (toluene/acetone, 95/5, v/v). Crude **21** (1 mmol) was dissolved in methanol (10 mL) and sodium methoxide (2 mmol) was added. The reaction was monitored by TLC analysis (methanol/dichloromethane, 4/96, v/v) until complete conversion of the starting compound to 3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-α/β-D-talopyranose (**22**) was observed. After 1 h, **22** was reduced with sodium borohydride (5 mmol) and the mixture was stirred for 1 h at 20 °C. Acetone (1 mL) was added to destroy excess sodium borohydride and the mixture was diluted with dichloromethane (25 mL). The mixture was washed twice with water (10 mL) and the organic layer was dried with magnesium sulfate and concentrated *in vacuo*. The residue was applied to a column of Kieselgel (20 g) suspended in toluene. Elution was effected with toluene/ethanol (1/0 to 95/5, v/v) and after concentration of the appropriate fractions compound **23** (0.85 mmol, 85 %) was isolated as a colourless syrup: R_f 0.35 (methanol/dichloromethane, 4/96, v/v); $[\alpha]_D^{20}$ -25.2° (c 0.1, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 3 H, Rha: H-6, $J_{5,6}$ = 6.0 Hz), 2.0-2.4 (br s, 3 H, 3 × OH), 3.5-3.92 (m, 12 H), 4.48-4.93 (m, 10 H, 5 × CH_2 benzyl), 4.97 (d, 1 H, RHa: H-1, $J_{1,2}$ = 2.3 Hz), 7.15-7.40 (m, 25 H, $H_{arom.}$ 5 × phenyl); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.8 (Rha: C-6), 60.4 and 63.5 (Tal: C-1 and C-6), 68.6, 71.2, 75.0, 75.9, 77.6, 78.9, 79.9 and 80.2 (Rha and Tal: 2 × C-2, 2 × C-3, 2 × C-4 and 2 × C-5), 71.8, 72.5, 73.7, 73.8 and 75.1 (5 × CH_2Ph), 96.5 (Rha: C-1), 127.5-128.2 ($CH_{arom.}$ phenyl), 137.2, 137.6, 137.8, 138.05 and 138.1 (5 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{47}H_{54}O_{10}$ (778.94): C 72.47, H 6.99; found C 72.38, H 6.98%.

3,4-Di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-5,6-*O*-isopropylidene-D-talitol (24). A solution of compound **23** (0.85 mmol), 2,2-dimethoxypropane (1.1 mL) and a catalytic amount of *p*-toluenesulfonic acid in dry *N,N*-dimethylformamide (4 mL) was stirred for 1 h at ambient temperature under a nitrogen atmosphere. TLC analysis (ethanol/toluene, 5/95, v/v) revealed complete conversion of the starting material into **24** and **25**. Conversion of the acetal **25** into the alcohol **24** was effected smoothly by addition of water (1 mL) to the reaction mixture and TLC analysis, after 5 min. revealed complete conversion of compound **25** into **24**. The mixture was diluted with diethyl ether (50 mL) and washed with a saturated aqueous solution of sodium bicarbonate (20 mL) and brine (20 mL). The organic layers was dried (sodium sulfate) concentrated and applied to a column of Kieselgel (20 g) suspended in dichloromethane. Elution was effected with dichloromethane/methanol (1/0 to 99/1, v/v) and

concentration of the appropriate fractions, gave **24** (0.69 mmol, 81%) as a colourless oil: R_f 0.61 (ethanol/toluene, 5/95, v/v); ^{1}H NMR ($CDCl_3$) δ 1.24 (d, 3 H, Rha: H-6, $J_{6,5}$ = 6.0 Hz), 1.35 and 1.41 (2 × s, 6 H, $C(CH_3)_2$), 2.16 (br s, 1 H, Tal: OH), 3.53-3.82 (m, 9 H, Rha: H-2, H-3, H-5, Tal: H-1, H-1', H-2, H-3, H-6, H-6'), 3.91-3.96 (m, 2 H, Rha: H-4, Tal: H-4), 4.23 (dt, 1 H, Tal: H-5, J = 6.5 Hz, J = 7.5 Hz), 4.43-4.95 (m, 10 H, 5 × CH_2 benzyl), 4.98 (d, 1 H, Rha: H-1, $J_{1,2}$ = 2.1 Hz), 7.19-7.40 (m, 25 H, $H_{arom.}$ 5 × phenyl); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.8 (Rha: C-6), 25.5 and 26.3 ($C(CH_3)_2$), 60.7 (Tal: C-1), 66.3 (Tal: C-6), 68.4, 75.0, 76.1, 76.9, 77.4, 79.0, 80.2 and 81.0 (Rha and Tal: 2 × C-2, 2 × C-3, 2 × C-4 and 2 × C-5), 71.7, 72.4, 73.5, 73.8 and 74.9 (5 × CH_2Ph), 96.7 (Rha: C-1), 108.4 ($C(CH_3)_2$), 127.4-128.1 ($CH_{arom.}$ phenyl), 137.4, 137.7, 137.9, 138.1 and 138.3 (5 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{50}H_{58}O_{10}$ (819.00): C 73.33, H 7.14; found C 73.19, H 7.12%.

1-*O*-Allyl-3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-5,6-*O*-isopropylidene-D-talitol (26). To a cooled (-10 °C) solution of compound **24** (0.7 mmol) in dry *N,N*-dimethylformamide (5 mL) was added sodium hydride (1.4 mmol). The suspension was stirred for 15 min. under a nitrogen atmosphere. Allyl bromide (2 mmol) was injected into the mixture and the temperature of the mixture was allowed to rise to room temperature. Stirring was continued for 1 h and progress of the reaction was monitored by TLC analysis (ether/hexane, 1/1, v/v). Excess sodium hydride and allyl bromide were destroyed with 0.5 mL dry methanol. After 30 min., the mixture was neutralised with 1 M acetic acid and concentrated *in vacuo*. The residue was diluted with diethyl ether (50 mL) and washed twice with brine (2 × 10 mL). The organic layers was dried (sodium sulfate) concentrated and applied to a column of Kieselgel (30 g) suspended in hexane. Elution was effected with hexane/diethyl ether (1/0 to 8/2, v/v) and concentration of the appropriate fractions, gave **26** (0.67 mmol, 97 %): R_f 0.51 (hexane/diethyl ether, 1/1, v/v); $[\alpha]_D^{20}$ -13.5° (c 0.6, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.20 (d, 3 H, Rha: H-6, $J_{6,5}$ = 6.0 Hz), 1.34 and 1.40 (2 × s, 6 H, $C(CH_3)_2$), 3.46-3.94 (m, 12 H, Rha: H-2, H-3, H-4, H-5, Tal: H-1, H-1', H-3, H-4, H-6, H-6' and CH_2=CH-CH_2), 4.19-4.26 (m, 2 H, Tal: H-5 and H-2), 4.40-4.97 (m, 10 H, 5 × CH_2 benzyl), 5.01-5.23 (m, 3 H, Rha: H-1 and CH_2=CH-CH_2), 5.79 (m, 1 H, CH_2=CH-CH_2), 7.19-7.41 (m, 25 H, $H_{arom.}$ 5 × phenyl); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.9 (Rha: C-6), 25.6 and 26.5 ($C(CH_3)_2$), 66.9, 70.5, 71.8, 71.9, 72.3, 73.4, 74.0 and 75.2 (Tal: C-1 and C-6, CH_2=CH-CH_2 and 5 × CH_2Ph), 68.5, 75.0, 75.4, 77.9, 79.2, 79.4, 80.6 and 80.8 (Rha and Tal: 2 × C-2, 2 × C-3, 2 × C-4 and 2 × C-5), 97.6 (Rha: C-1, $^2J_{C,H}$ = 169.9 Hz), 108.4 ($C(CH_3)_2$), 116.6 (CH_2=CH-CH_2), 127.4-128.2 ($CH_{arom.}$ phenyl), 134.6 (CH_2=CH-CH_2), 137.8, 138.1, 138.3, 138.4 and 138.6 (5 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{53}H_{62}O_{10}$ (859.07): C 74.10, H 7.27; found C 74.29, H 7.28%.

1-*O*-Allyl-3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-D-talitol (27). Compound **26** (0.6 mmol) was dissolved in dichloromethane (5.5 mL) and methanol (0.5 mL) after which a catalytic amount of *p*-toluenesulfonic acid (pH ≈ 4.5) was added. The mixture

was stirred for 3 h at room temperature and was monitored by TLC analysis (ethanol/toluene, 5/95, v/v). The mixture was diluted with dichloromethane (30 mL), washed successively with a saturated aqueous solution of sodium bicarbonate (10 mL) and water (10 mL). The organic layer was dried with magnesium sulfate, filtered, concentrated *in vacuo*, and applied to a column of Kieselgel (30 g) suspended in hexane. Elution was effected with hexane/diethyl ether (2/1 to 0/1, v/v) and after concentration of the appropriate fractions compound **27** (0.48 mmol, 80 %) was isolated as a colourless syrup: R_f 0.35 (diethyl ether); $[\alpha]_D^{20}$ 2.8° (c 0.1, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.22 (d, 3 H, Rha: H-6, $J_{6,5}$ = 6.0 Hz), 1.9 (br s, 2 H, 2 × OH), 3.48-3.87 (m, 12 H, Rha: H-2, H-3, H-4, H-5, Tal: H-1, H-1', H-3, H-4, H-6, H-6' and CH_2=CH-C*H*$_2$), 3.91 and 4.16 (2 × dt, 2 H, Tal: H-5 and H-2), 4.42-4.96 (m, 10 H, 5 × CH_2 benzyl), 5.12 (d, 1 H, Rha: H-1, $J_{1,2}$ = 1.7 Hz), 5.14-5.27 (m, 2 H, C*H*$_2$=CH-CH$_2$), 5.81 (m, 1 H, CH$_2$=C*H*-CH$_2$), 7.20-7.41 (m, 25 H, $H_{arom.}$ 5 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.9 (Rha: C-6), 63.8, 69.6, 71.9, 72.0, 72.4, 73.4, and 73.7 (Tal: C-1 and C-6, CH$_2$=CH-*C*H$_2$ and 5 × CH$_2$Ph), 68.6, 71.3, 75.0, 75.04, 77.4, 79.2, 79.6 and 80.4 (Rha and Tal: 2 × C-2, 2 × C-3, 2 × C-4 and 2 × C-5), 97.1 (Rha: C-1), 116.9 (*C*H$_2$=CH-CH$_2$), 127.4-128.4 (CH$_{arom.}$ phenyl), 134.4 (CH$_2$=*C*H-CH$_2$), 137.4, 137.5, 138.2, 138.3 and 138.4 (5 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{50}H_{58}O_{10}$ (819.00): C 73.33 H 7.14; found: C 73.48, H 7.39%.

5-*O*-Allyl-2,3-di-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-*aldehydo*-D-ribose (28). To a solution of compound **27** (0.45 mmol) in dioxane (12 mL) and water (4 mL) was added over a period of 15 min. sodium periodate (0.9 mmol) in small portions. The mixture was stirred for 1 h at 20 °C, diluted with dichloromethane (50 mL) and washed twice with a saturated aqueous solution of sodium chloride (2 × 15 mL). The organic layers were combined, dried with magnesium sulfate and concentrated *in vacuo* to afford compound **28** in quantitative yield. Compound **28** thus obtained was used without further purification for the synthesis of **29**: R_f 0.30 (diethyl ether); ^{1}H NMR at 200 MHz ($CDCl_3$) δ 1.18 (d, 3 H, Rha: H-6, $J_{5,6}$ = 6.2 Hz), 3.3-4.1 (m, 11 H), 4.5-5.3 (m, 13 H), 5.81 (m, 1 H, CH$_2$=C*H*-CH$_2$), 7.22-7.32 (m, 25 H, $H_{arom.}$ 5 × phenyl), 9.54 (d, 1 H, Rib: H-1, $J_{1,2}$ = 1.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.8 (Rha, C-6), 71.9, 71.95, 72.6, 72.8 and 73.1 (Rib C-5, 6 × CH_2, CH$_2$=CH-*C*H$_2$ and benzyl), 68.6, 72.6, 79.4, 80.2 and 82.4 (Rib C-2, C-3, C-4 and Rha, C-2, C-3, C-4, C-5), 95.8 (Rha, C-1), 117.1 (*C*H$_2$=CH-CH$_2$), 127.4-128.3 (CH$_{arom.}$ phenyl), 134.4 (CH$_2$=*C*H-CH$_2$), 137.0, 137.4, 138.3, 138.4 and 138.7 (5 × $C_{arom.}$ phenyl), 201.1 (Rib, C-1).

1-*O*-Allyl-3,4-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-L-ribitol (29). Compound **28** (0.45 mmol) was concentrated several times with toluene (3 × 10 mL) and dissolved in dry diethyl ether (15 mL). The solution was cooled (0 °C) and stirred under a nitrogen atmosphere. Reduction of **28** was effected with sodium borohydride (1 mmol) and the reaction was monitored by TLC analysis (diethyl ether). After 1 h, conversion of the *aldehydo*-ribose **28** into **29** was complete, and ammonium chloride was added to destroy excess sodium

borohydride. The mixture was diluted with ether (15 mL), washed twice with a saturated aqueous solution of sodium chloride, dried with sodium sulfate, filtered and concentrated under reduced pressure. The residue was applied to a column of Kieselgel (20 g) suspended in hexane. Elution was effected with hexane/diethyl ether (1/0 to 2/1 v/v) and, after concentration of the appropriate fractions, compound **29** (0.43 mmol, 95 %) was isolated as a colourless oil: R_f 0.52 (diethyl ether); $[\alpha]_D^{20}$ -26.9° (c 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.22 (d, 3 H, Rha: H-6, $J_{6,5}$ = 6.1 Hz), 2.15 (s, 1 H, Rib: OH), 3.50-3.81 (complex, 10 H, Rha: H-2, H-3, H-4 and H-5, Rib: H-1, H-1', H-2, H-3, H-5 and H-5'), 3.85 (dt, 2 H, CH_2=CH-C*H*$_2$), 4.19 (m, 1 H, H-4), 4.46-4.69 (6 H, 3 × benzyl), 4.74 (s, 2 H, CH_2 benzyl), 4.94 (d, 1 H, CH_2 benzyl, $J_{A,B}$ = 10.9 Hz), 5.12-5.28 (ddq, 2 H, C*H*$_2$=CH-CH$_2$), 5.15 (d, 1 H, Rha: H-1, $J_{1,2}$ = 1.5 Hz), 5.75-5.88 (m, 1 H, CH_2=C*H*-CH$_2$), 7.18-7.43 (m, 25 H, $H_{arom.}$ 5 × phenyl); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 17.9 (Rha, C-6), 61.0 (Rib, C-5), 70.1, 71.9, 71.95, 72.4, 73.6 and 75.2 (Rib C-1, 6 × CH_2, CH_2=CH-*C*H$_2$ and benzyl), 68.6, 75.0, 75.3, 78.4, 79.5 and 80.5 (Rib C-2, C-3, C-4 and Rha, C-2, C-3, C-4, C-5), 97.5 (Rha, C-1), 116.8 (*C*H$_2$=CH-CH$_2$), 127.4-128.3 ($CH_{arom.}$ phenyl), 134.5 (CH_2=*C*H-CH$_2$), 137.8, 137.9, 138.3, 138.4 and 138.5 (5 × $C_{arom.}$ phenyl).

Anal. Calcd for $C_{49}H_{56}O_9$ (788.98): C 74.60, H 7.15; found C 74.58, H 7.10%.

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