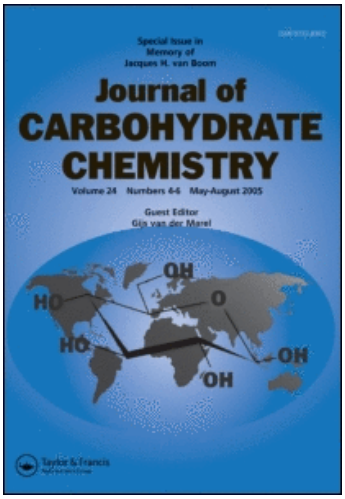

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SYNTHESIS OF RHAMNOGALACTURONAN I FRAGMENTS[1]

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Dedicated to Professor Helmut Kristen on the Occasion of his 70th Birthday

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ABSTRACT

The partially deprotected trisaccharide **17** has been synthesized as an analogue of the repeating unit of the backbone of rhamnogalacturonan I. The trisaccharide **17** was obtained after prior selective derivatization of HO-3 and HO-4 of a rhamnopyranose cyanoethylidene glycosyl donor, followed by coupling with a tritylated galactopyranosyluronic acceptor (**11**), selective removal of the acetyl group at the O-2' position of the formed disaccharide **12**, and glycosylation of the HO-2' position with methyl (ethyl 2,3-di-*O*-benzyl-4-*O*-*p*-methoxybenzyl-1-thio-β-D-galactopyranosid)uronate (**14**) providing methyl (methyl 2,3-di-*O*-benzyl-4-*O*-*p*-methoxybenzyl-α-D-galactopyranosyluronate)-(1→2)-(4-*O*-benzoyl-3-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-(allyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate (**15**). Finally, palladium chloride catalyzed deallylation (**16**) and hydrogenolysis over Pd-C resulted in methyl (methyl α-D-galactopyranosyluronate)-(1→2)-(4-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→4)-α/β D-galactopyranuronate (**17**).

INTRODUCTION

Dietary fibers are mainly composed of pectic polysaccharides and are a nondigestible food ingredient that beneficially affect human health. These effects include several

immunostimulating activities as well as selectively promoting the growth of a limited number of bacteria in the colon, which have the potential to improve host health.[2] Pectins are very complex plant cell wall polysaccharides which consist of α(1→4)-linked homogalacturonan chains,[3] so-called smooth regions, interspersed with hairy regions of rhamnogalacturonan I (RG-I). The backbone of the RG-I polymer is composed of repeating units of the disaccharide α(1→2)-L-Rha-α(1→4)-D-GalA. In these oligomers, neutral glycosyl side-chains composed of arabinofuranosyl-, galactopyranosyl-, and fucopyranosyl residues, can be 4-linked to a rhamnose residue.[4] For a better understanding of the correlation between the structure of dietary fiber constituents and their functionality in the colon, we embarked on a program directed at the synthesis of pectin fragments with a defined structure and in sufficient amounts. Furthermore, these fragments could be labeled with several stains or dyes in order to serve as biomarkers in nutritional studies. Thus, the trisaccharide fragment **17** related to the backbone structure of rhamnogalacturonan I has been synthesized using the trityl-cyanoethylidene condensation (TCC) and the thioglycoside methodology.

RESULTS AND DISCUSSION

A previous paper[5] described the syntheses of the potential galactopyranosyluronic acceptor **10** and the galacturonic glycosyl donor **14**. Herein we report two alternative routes for the synthesis of the potential rhamnopyranosyl donor **5**, starting from the acetylated cyanoethylidene derivative **1** (Scheme 1). Regioselective cleavage of the acetyl group at *O*-3 of **1**[6] was achieved with 0.28 N methanolic hydrochloric acid at room temperature in 57% yield. The optimum time for this reaction was determined by TLC. The benzylation of **2** with benzyl trichloroacetimidate and a catalytic amount of trifluoromethanesulfonic acid,[7] followed by deacetylation of **3** with sodium methoxide in dry pyridine, and benzoylation of **4** provided the desired donor **5** in an overall yield of 15% from **1**. In subsequent investigations, we will use the *p*-nitrobenzoyl group instead of the benzoyl group, since the former group can be functionalized by reduction of the nitro group to an amino group as a tether for stains or dyes.

The second approach to the donor **5** (Scheme 1) required complete deacetylation[8] of **1** and subsequently the regioselective acetylation of the *O*-3 of diol **6**. In the synthesis

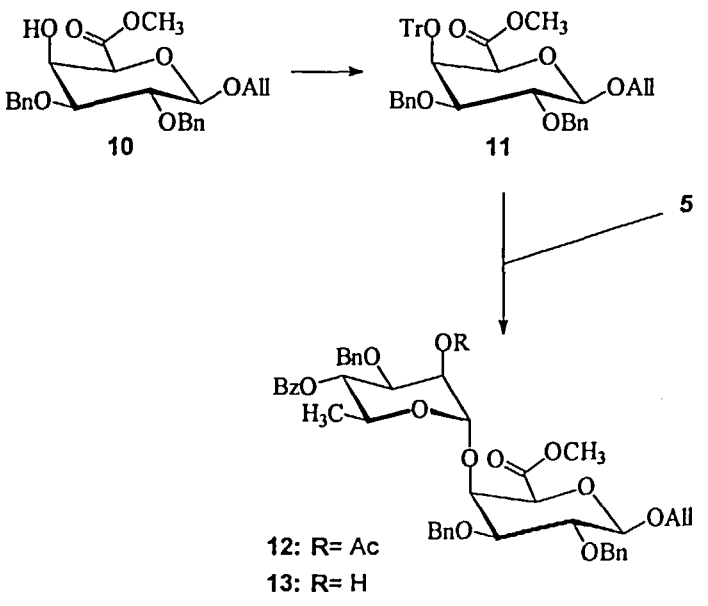
1: R_1= R_2= Ac **6:** R_1= R_2= H
2: R_1= H R_2= Ac **7:** R_1= Ac R_2= H
3: R_1= Bn R_2= Ac **8:** R_1= Ac R_2= Bz
4: R_1= Bn R_2= H **9:** R_1= H R_2= Bz

Scheme 1

of the monoacyl derivative 7 according to the literature,[9] the addition of a solution of acetyl chloride in benzene (better in toluene) to **6** should be carried out at -40 °C and not at 0 °C as previously described. The benzoylation of **7** led to the fully acylated derivative **8**, after which the selective removal of the *O*-acetyl group, in the presence of the *O*-benzoyl group by acid-catalyzed methanolysis,[10] gave **9**. Benzylation of **9** under conditions described for **3** provided **5** in an overall yield of 21% related to **1**.

The glycosylation procedure using TCC requires a tritylated hydroxyl group in the acceptor molecule. Thus, the tritylation of **10**[5] with triphenylmethylium perchlorate in the presence of 2,4,6-collidine and *N,N*-dimethyl-4-aminopyridine resulted in the acceptor **11** in 72% yield. The coupling of **5** with **11** was carried out with triphenylmethylium perchlorate promotion in dichloromethane with rigorous exclusion of moisture. After medium pressure column chromatography (MPLC), the disaccharide **12** was obtained in 47% yield. The analytical data of **12** are in complete agreement with the structure proposed. The stereoselectivity of TCC is excellent, since no 1,2-*cis*-glycoside was detectable by either TLC or in the NMR spectra of the crude reaction mixture. In order to secure the *trans*-glycosidic linkage of L-rhamnose to the D-galactopyranosyluronic moiety, the geminal ^{13}C-^{1}H coupling constants ($J_{C\text{-}1',H\text{-}1'}$) were determined. The observed value of 172.5 Hz verified the expected structure. In the other case, $J_{C\text{-}1',H\text{-}1'}$ should be ca. 10 Hz smaller when H-1' is axial than when it is equatorial.[11]

For a stepwise buildup of rhamnogalacturonan I fragments, the acetyl group at *O*-2' of **12** was selectively removed by methanolic hydrogen chloride resulting quantitatively in the glycosyl acceptor **13**. In the ^{1}H NMR spectrum, the upfield shift of the H-2' signal

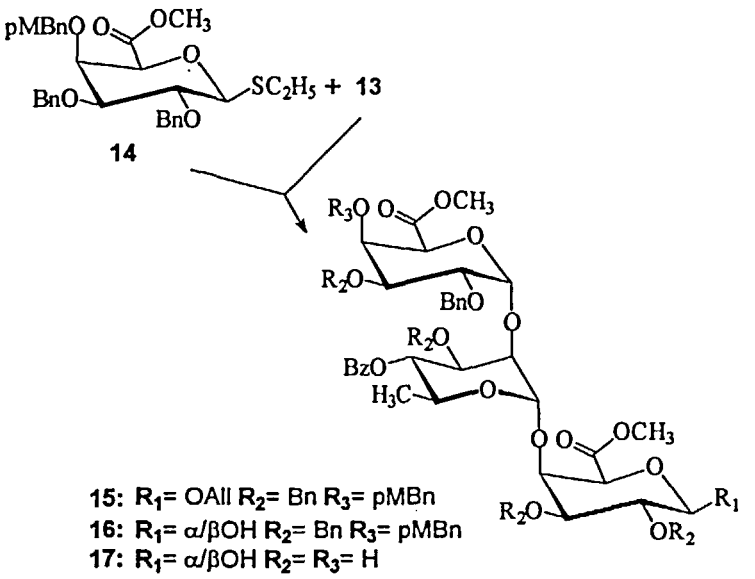


Scheme 2

at δ 4.19 (**13**) compared to that of the acetylated compound **12** (δ 5.60) confirmed the deacetylation at the *O*-2' position.

Next, the coupling of the D-galactopyranosyluronic thioglycoside **14** as glycosyl donor with acceptor **13** was performed in the presence of freshly prepared[12] iodonium di-*sym*-collidine perchlorate.[5] After standard workup and purification by MPLC, the trisaccharide **15** was isolated in 48% yield. Again, the glycosylation was strictly stereoselective and provided exclusively the α(1''→2')-linked oligomer. The value of $J_{1'',2''}$ in the ^1H NMR spectrum (3.4 Hz) and the signal for C-1'' in the ^{13}C NMR spectrum (δ 97.36) proved the 1,2-*cis*-glycosidic linkage. The remaining NMR data also agreed with the depicted structure of trisaccharide **15**.

Finally, the allyl and benzyl protective groups of **15** were removed by palladium chloride catalyzed deallylation (**16**) and hydrogenolysis over Pd-C to result in the partially deprotected trisaccharide **17**. The evaluation of the NMR spectra of **17** is complicated by the free reducing end of one of the galacturonic acid moieties, but the exactly related signals are in accord with the proposed structure of the trisaccharide **17**. Thus, in the ^1H



Scheme 3

NMR spectra, the small coupling constants $J_{1',2'}$= 1.8 Hz (δ 5.14) and $J_{1'',2''}$= 3.2 Hz (δ 4.95) which are nearly unchanged compared with the data of **15**, provide evidence for the α-glycosidic bonds between the D-galacturonosyl and L-rhamnosyl constituents. In the ^{13}C NMR spectra, this statement is supported by the signals of the anomeric carbon atoms at δ 97.44 (C-1'') and δ 100.56 (C-1'). Additionally, the FAB^+ mass spectrum provides the molar peak at *m/z* 740.7 $(M+glycerine)^+$, whereas the CI mass spectrum (isobutane) offers significant peaks at *m/z* 173.1 (Rha-4-CO-fragment), 191.1 ($GalAOCH_3$-fragment), and 250.3 (Rha-4-OBz-fragment).

EXPERIMENTAL

General methods. Melting points were determined on a micro-heating plate BHMK 05 by BOETIUS and are not corrected. For measurement of optical rotations a High Precision Digital Automatic Polarimeter ("GYROMAT" from the DR. KERNCHEN Co.) was used. NMR spectra were recorded with BRUKER AC-250 or ARX-300 spectrometers, at 250 MHz or 300 MHz for ^1H, and as well as at 62.9 MHz or 75.5 MHz for

^{13}C, respectively. Tetramethylsilane ($\delta = 0$ ppm) was utilized as an internal standard. Most samples were dissolved in $CDCl_3$, and the chemical shifts are given in ppm. The heteronuclear coupling constants were determined by means of GD-measurements. All reactions were monitored by thin-layer chromatography (TLC, Silica Gel 60, F_{254}, 0.25 mm plates E. MERCK Co). The following solvent systems (v/v) were used for chromatography: (A) 3:1, (B) 1:1 chloroform-diethyl ether,(C) 2:1, (D) 1.5:1, (E) 1:1 heptane-ethyl acetate, and (F) 5:3:1 ethyl acetate-methanol-water. Components were detected through UV absorption or after treatment with methanolic 10% H_2SO_4 solution and charring them for a few minutes with a heat gun. Column chromatographic purifications were conducted with Silica Gel 60 (40-63 μm) using an MPLC-unit (BUECHI Co.) as well as a preparative HPLC-unit (KNAUER Co). The HPLC column contained a packing material consisting of Nucleosil 100-7 with a particle diameter of 7 μm. Depending upon the amount separated, a column with 20 mm or 32 mm inner diameter and 250 mm length was utilized. Detection was performed with a differential-refractometer as well as with a UV absorption detector. All solvents and reagents were purified and dried according to standard procedures.[13] Molecular sieves were activated under high vacuum at 350 °C. After classical work up of the reaction mixtures, the organic layers as a rule, were dried over $MgSO_4$, and then concentrated under diminished pressure (rotary evaporator).

4-*O*-Acetyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose (2). A suspension of 3,4-di-*O*-acetyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose[6] (**1**, 4.0 g, 13.36 mmol) in methanolic hydrochloric acid (0.28 N, 112 mL, prepared by adding 2.2 mL of acetyl chloride to 110 mL dry methanol) was stirred for 1 h at room temperature (TLC, solvent B). Then, the reaction mixture was neutralized by filtration through a layer of alkaline alumina, and the eluate was concentrated. Column chromatography (eluent solvent A) was performed to give the initial reactant **1** (TLC solvent B R_f 0.70, 1.12 g, 28%) and **2** (1.96 g , 57%): TLC solvent B R_f 0.36; mp 114 °C (from ethyl acetate-heptane); $[\alpha]_D^{22}$ -26.3° (*c* 1.0, chloroform); ^1H NMR ($CDCl_3$) δ 1.21 (d, 3H, $J_{5,6} = 6.1$ Hz, H-6), 1.90 [s, 3H, $CH_3(CN)C$], 2.13 (s, 3H, $OCOCH_3$), 2.37 (d, 1H, J = 9.5 Hz, 3-OH), 3.49 (m, 1H, H-5), 3.92 (m, 1H, $J_{3,4} = 9.5$ Hz, H-3), 4.54 (dd, 1H, $J_{2,3} = 4.3$ Hz, H-2), 4.84 (t, 1H, $J_{4,5} = 9.5$ Hz, H-4), 5.38 (d, 1H, d, $J_{1,2} = 2.1$ Hz, H-1); ^{13}C NMR ($CDCl_3$) δ 17.42 (C-6), 20.90 ($OCOCH_3$), 26.90 [$CH_3(CN)C$], 69.73 (C-5), 70.04 (C-3), 73.54 (C-

4), 80.47 (C-2), 96.81 (C-1), 101.27 [$CH_3(CN)C$], 116.67 [$CH_3(CN)C$], 169.74 ($OCOCH_3$).

Anal. Calcd for $C_{11}H_{15}NO_6$ (257.24): C, 51.34; H, 5.88; N, 5.45. Found: C, 51.41; H, 6.00; N, 5.51.

4-*O*-Acetyl-3-*O*-benzyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose (3). To a solution of **2** (1.74 g, 6.77 mmol) and benzyl 2,2,2-trichloroacetimidate (2.4 mL, 13.6 mmol) in dry dichloromethane (10 mL) and dry heptane (15 mL) was added trifluoromethanesulfonic acid (100 μL) under argon at 0 °C. The mixture was stirred for 3 h at that temperature (TLC solvent C), passed through a layer of alkaline alumina, and concentrated. Purification of the residue by column chromatography (eluent solvent C) gave **3** (1.42 g, 60%) as colorless crystals: mp 89 °C (from ethyl acetate-heptane); $[\alpha]_D^{23}$ +11.1° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.18 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6), 1.91 [s, 3H, s, $CH_3(CN)C$], 2.04 (s, 3H, $OCOCH_3$), 3.41 (m, 1H, H-5), 3.76 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 4.46 (dd, 1H, $J_{2,3}$ = 4.0 Hz, H-2), 4.62, 4.73 (2d, 2H, J = 12.2 Hz, $CH_2C_6H_5$), 5.03 (t,1H, $J_{4,5}$ = 9.5 Hz, H-4), 5.29 (d, 1H, $J_{1,2}$ = 2.1 Hz, H-1), 7.17-7.41 (m, 5H, $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 17.41 (C-6), 20.88 ($OCOCH_3$), 26.38 [$CH_3(CN)C$], 69.91 (C-5), 71.57 (C-4), 72.02 ($CH_2C_6H_5$), 75.01 (C-3), 78.27 (C-2), 96.87 (C-1), 101.50 [$CH_3(CN)C$], 116.86 [$CH_3(CN)C$]; 127.81, 128.24, 128.65, 128.89, 129.14, 137.13 ($CH_2C_6H_5$), 169.82 ($OCOCH_3$).

Anal. Calcd for $C_{18}H_{21}NO_6$ (347.37): C, 62.24; H, 6.09; N, 4.03. Found: C, 62.20; H, 6.22; N, 4.14.

3-*O*-Benzyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose (4). To a solution of **3** (1.16 g, 3.34 mmol) in dry pyridine (30 mL) sodium methoxide solution (0.5 N, 1 mL) was added at ambient temperature. After 5 min (TLC solvent E), the mixture was neutralized with a solution of acetic acid in toluene (0.05 N, 10 mL), and concentrated. Traces of pyridine and acetic acid were removed by evaporation with repeated addition of toluene. The residue was dissolved in toluene and precipitating salts were filtered off. The filtrate was concentrated and purified by column chromatography (ethyl acetate gradient 0%→50% in heptane) to yield **4** (612 mg, 60%) as a colorless foam: $[\alpha]_D^{24}$ +38.7° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.30 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6), 1.89 [s, 3H, $CH_3(CN)C$], 2.27 (bs,1H, 4-OH), 3.34 (m, 1H, H-5), 3,57 (m, 1H, H-3), 3.59 (t, 1H,

$J_{4,5}$ = 10.4 Hz, H-4)), 4.45 (dd, 1H, dd, $J_{2,3}$ = 3.4 Hz, H-2), 4.65, 4.82 (2d, 2H, J = 11.9 Hz, $CH_2C_6H_5$), 5.31 (d, 1H, $J_{1,2}$ = 2.1 Hz, H-1), 7.14-7.42 (m, 5 H, $CH_2C_6H_5$); ^{13}C NMR δ 17.62 (C-6), 26.42 [CH_3(CN)C], 71.08 (C-3), 71.30 (C-5), 72.01 ($CH_2C_6H_5$), 77.71 (C-2), 77.91 (C-4), 97.06 (C-1), 101.41 [CH_3(CN)*C*], 116.94 [CH_3(*C*N)C]; 127.81, 128.12, 128.83, 128.93, 129.20, 137.00 ($CH_2C_6H_5$).

Anal. Calcd for $C_{16}H_{19}NO_5$ (305.33): C, 62.94; H, 6.27; N, 4.59. Found: C, 62.86; H, 6.41; N, 4.73.

3-*O*-Acetyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose (7). To a solution of 1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose[8] (**6**, 1.18g, 5.48 mmol) in dry pyridine (20 mL) was added a solution of acetyl chloride (0.45 mL) in toluene (10 mL) during 30 min with stirring and cooling at -40 °C (at this point there is a crucial misprint in the original literature[9]). Then, the reaction mixture was further treated as described by Malysheva and Kochetkov.[9]

3-*O*-Acetyl-4-*O*-benzoyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose (8). To a solution of 7 (515 mg, 2.0 mmol) in dry pyridine (40 mL) benzoyl chloride (2.3 mL, 6.0 mmol) was added, and the reaction mixture was kept for 18 h at room temperature under argon (TLC solvent C). The mixture was concentrated and repeatedly co-distilled with toluene. The residue was dissolved in toluene and the precipitating salts filtered off. The filtrate was concentrated and the residue purified by column chromatography (ethyl acetate gradient 0%→30% in heptane) to yield crystalline **8** (510 mg, 72 %): mp 239 °C (from ethyl acetate-heptane); $[\alpha]_D^{24}$ +10.8° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6), 1.92 [s,3H, CH_3(CN)C], 1.98 (s, 3H, $OCOCH_3$), 3.72 (m, 1H, H-5), 4.52 (dd, 1H, $J_{2,3}$ = 4.27 Hz, H-2), 5.30 (t, 1H, H-4, $J_{4,5}$ = 9.5 Hz, H-4), 5.45 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 5.46 (d,1H, $J_{1,2}$ = 2.1 Hz, H-1), 7.31-7.93 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 17.36 (C-6), 20.36 ($OCOCH_3$), 26.35 [CH_3(CN)C], 69.06 (C-5), 70.00 (C-4), 70.50 (C-3), 78.47 (C-2), 96.74 (C-1), 101.52 [CH_3(CN)*C*], 116.55 [CH_3(*C*N)C], 128.43, 128.90, 129.18, 129.56, 129.76, 133.52 (C_6H_5), 165.27 ($OCOC_6H_5$), 169.88 ($OCOCH_3$).

Anal. Calcd for $C_{18}H_{19}NO_7$ (361.35): C, 59.83; H, 5.30; N, 3.88. Found: C, 59.90; H, 5.24; N, 4.02.

4-*O*-Benzoyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose (9). Compound **8** (480 mg, 1.4 mmol) was suspended in methanolic hydrochloric acid (0.28 N, 10 mL, prepared by adding 0.1 mL of acetyl chloride to 10 mL dry methanol). After stirring for a few minutes, the reaction mixture became homogeneous and was kept for 6 h at room temperature (TLC solvent C). Then, the solution was made neutral by filtration over alkaline alumina, the filtrate was concentrated, and the residue was applied to a column of silica gel (eluent solvent C) to give crystalline **9** (362 mg, 81 %): mp 156-157 °C (from ethyl acetate-heptane; $[\alpha]_D^{25}$ -15.5° (*c* 1.0, chloroform); lit.[10] mp 155-157 °C, $[\alpha]_D^{20}$ -13° (*c* 1.0-2.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6), 1.92 [s, 3H, s, $CH_3(CN)C$], 2.76 (d,1H, J = 8.9 Hz, 3-OH), 3.64 (m, 1H, H-5), 4.09 (m,1H, H-3), 4.57 (dd, 1H, $J_{2,3}$ = 4.3 Hz, H-2), 5.08 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 5.42 (d,1H, $J_{1,2}$ = 2.1 Hz, H-1), 7.42-8.05 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 17.50 (C-6), 26.41 [$CH_3(CN)C$], 69.84 (C-5), 69.96 (C-3), 74.11 (C-4), 80.54 (C-2), 96.80 (C-1), 101.27 [$CH_3(CN)C$], 116.66 [$CH_3(CN)C$], 128.50, 129.13, 129.56, 129.77, 129.80, 133.59 ($OCOC_6H_5$), 166.61 ($OCOC_6H_5$)

Anal. Calcd for $C_{16}H_{17}NO_6$ (319.31): C, 60.18; H, 5.37; N, 4.39. Found: C, 60.20; H, 5.12; N, 4.44.

4-*O*-Benzoyl-3-*O*-benzyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-L-rhamnopyranose (5). *Via* **4**: Compound **4** (243 mg, 0.8 mmol) was dissolved in a mixture of dry pyridine (20 mL) and benzoyl chloride (1 mL, 2.7 mmol) and kept for 2 h in an inert atmosphere at room temperature. When the reaction was complete (TLC solvent E), the reaction mixture was concentrated with repeated addition of toluene. Then, the residue was dissolved in a minimum of toluene. Precipitated crystals containing no carbohydrate were separated by filtration. After concentration of the filtrate, the residue was purified by column chromatography (ethyl acetate gradient 0%→30% in heptane) to yield crystalline **5** (234 mg, 72 %).

Via **9**: To a solution of **9** (320 mg, 1.0 mmol) and benzyl 2,2,2-trichloracetimidate (0.4 mL, 2.0 mmol) in dry dichloromethane (9 mL) and dry heptane (9 mL) trifluoromethanesulfonic acid (17 μL) was added under an inert atmosphere at 0 °C. After stirring for 2 h at that temperature, the reaction mixture was allowed to warm up to room temperature and stirring was continued for 24 h (TLC solvent C). The workup involved first

neutralizing the reaction mixture by filtration through a layer of alkaline alumina. The filtrate was then concentrated, and the residue processed by column chromatography (ethyl acetate gradient 0%→30% in heptane) to give pure **5** (172 mg, 42%) as colorless crystals: mp 132 °C (from ethyl acetate-heptane); $[\alpha]_D^{24}$ +36.2° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6), 1.98 [s, 3H, CH_3(CN)C], 3.59 (m, 1H, H-5), 3.95 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 4.55 (dd, 1H, $J_{2,3}$ = 4.3 Hz, H-2), 4.65, 4.74 (2d, 2H, J = 12.5 Hz, C*H*$_2$C$_6$H$_5$), 5.35 (t,1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 5.37 (d, 1H, $J_{1,2}$ = 2.1 Hz, H-1), 7.14-8.21 (m, 10H, CH$_2$C$_6$*H*$_5$, OCOC$_6$H$_5$); ^{13}C NMR ($CDCl_3$) δ 17.43 (C-6), 26.36 [*C*H$_3$(CN)C], 69.99 (C-5), 71.72 (*C*H$_2$C$_6$H$_5$), 72.07 (C-4), 74.57 (C-3), 78.27 (C-2), 96.88 (C-1), 101.47 [CH$_3$(CN)*C*], 116.85 [CH$_3$(*C*N)C], 126.85, 127.08, 127.46, 127.51, 127.93, 128.25, 128.52, 128.75, 129.11, 129.52, 132.36, 135.91 (CH$_2$*C*$_6$H$_5$, OCO*C*$_6$H$_5$), 165.35 (O*C*OC$_6$H$_5$).

Anal. Calcd for $C_{23}H_{23}NO_6$ (409.44): C, 67.47; H, 5.66; N, 3.42. Found: C, 67.40; H, 5,72; N 3,56.

Methyl (allyl 2,3-di-*O*-benzyl-4-*O*-trityl-β-D-galactopyranosid)uronate (11). To a solution of methyl (allyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate[5] (**10**, 627 mg, 1.65 mmol) in dry dichloromethane (15 mL) were added triphenylmethylium perchlorate (1.13 g, 3.3 mmol), *N,N*-dimethyl-4-aminopyridine (101 mg, 0.825 mmol) and *sym*-collidine (0.55 mL, 4.1 mmol), and the mixture was stirred under an inert atmosphere overnight at room temperature (TLC solvent E). The mixture was then diluted with chloroform (50 mL), and the organic solution washed with cold aq 15% $NaHSO_4$ (2 x 20 mL), ice-water (3 x 20 mL), dried, and concentrated. The residue was diluted with a minimum of toluene, and the precipitate of carbohydrate-free crystals was filtered off. After concentration of the filtrate, the residue was purified by column chromatography (ethyl acetate gradient 0%→25% in heptane) to yield **11** (795 mg, 72%) as colorless crystals: mp 152 °C (from ethyl acetate-heptane); $[\alpha]_D^{23}$ -39.3° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 3.23 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.31 (s, 3H, OCH_3), 3.86 (d, 1H, H-5), 4.10, 4.33 (2d, 2H, J = 12.1 Hz, C*H*$_2$C$_6$H$_5$), 4.21 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 4.26 (m,1H, C*H*$_2$CH=CH$_2$), 4.30 (dd, 1H, $J_{4,5}$ = 1.2 Hz, H-4), 4.44 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1), 4.61 (m,1H, C*H*$_2$CH=CH$_2$), 4.78, 4.94 (2d, 2H, J = 11.0 Hz, C*H*$_2$C$_6$H$_5$), 5.25, 5.41 (2m,2H, CH$_2$CH=C*H*$_2$), 6.05 (m, 1H, CH$_2$C*H*=CH$_2$), 6.78-7.50 [m, 25H, 2 x CH$_2$C$_6$*H*$_5$, C(C$_6$H$_5$)$_3$];

^{13}C-NMR ($CDCl_3$) δ 51.89 (OCH_3), 70.65, 70.69 (2 x $CH_2C_6H_5$), 72.91 (C-5), 74.71 ($CH_2CH=CH_2$), 75.18 (C-4), 79.37 (C-2), 81.43 (C-3), 89.19 [$C(C_6H_5)_3$], 103.20 (C-1), 117.44 ($CH_2CH=CH_2$), 126.31, 126.72, 126.84, 127.28, 127.60, 127.96, 128.27, 128.36, 129.83, 138.42, 139.37, 144.81 [$C(C_6H_5)_3$, 2 x $CH_2C_6H_5$], 134.18 ($CH_2CH=CH_2$), 168.48 (C-6).

Anal. Calcd for $C_{43}H_{42}O_7$ (670.80): C, 76.99; H, 6.31: Found: C, 77.00; H, 6.42.

Methyl (2-*O*-acetyl-4-*O*-benzoyl-3-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-(allyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate (12). To a suspension of **5** (205 mg, 0.5 mmol), **11** (369 mg, 0.55 mmol) and molecular sieves (4Å, 300 mg) in dry dichloromethane (15 mL) was added triphenylmethylium perchlorate (18 mg, 0.05 mmol), and the reaction mixture was stirred in the dark under an inert atmosphere at room temperature. After 4 h (TLC solvent E), the mixture was filtered, diluted with chloroform (50 mL), and washed with water (3 x 20 mL). The organic phase was dried, concentrated, and the resulting residue was purified by column chromatography under medium pressure (ethyl acetate gradient 0%→25% in heptane) to yield starting material **11** (44 mg, 0.07 mmol), crystalline **10** (65 mg) as a by-product, and desired **12** (191 mg, 47%) as a colorless foam: TLC solvent E R_f 0.53; $[\alpha]_D^{23}$ +46.5° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.24 (d, 3H, $J_{5',6'}$ = 6.1 Hz, H-6'), 2.09 (s, 3H, $OCOCH_3$), 3.57 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.75 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 3.77 (s, 3H, OCH_3), 3.84 (m, 1H, H-5'), 4.0 (dd, 1H, $J_{3',4'}$ = 9.8 Hz, H-3'), 4.11 (d, 1H, $J_{4,5}$ = 1.2 Hz, H-5), 4.17 (m, 1H, $CH_2CH=CH_2$), 4.34, 4.57 (2d, 2H, J = 12.2 Hz, $CH_2C_6H_5$), 4.38 (dd, 1H, $J_{4,5}$ = 1.2 Hz, H-4), 4.42 (d, 1H, $J_{1,2}$ = 7.6 Hz, $J_{C\text{-}1,\,H\text{-}1}$ = 159.5 Hz, H-1), 4.53 (m, 1H, $CH_2CH=CH_2$), 4.75, 4.81 (2d, 2H, $CH_2C_6H_5$), 4.81, 4.96 (2d, 2H, J = 11.0 Hz, $CH_2C_6H_5$), 5.17 (d, 1H, $J_{1',2'}$ = 1.8 Hz, $J_{C\text{-}1',\,H\text{-}1'}$ = 172.5 Hz, H-1'), 5.24 (t,1H, $J_{4',5'} = J_{3',4'}$ = 9.8 Hz, H-4'), 5.23, 5.36 (2m, 2H, $CH_2CH=CH_2$), 5.60 (dd, 1H, $J_{2',3'}$ = 3.4 Hz, H-2'), 6.00 (m, 1H, $CH_2CH=CH_2$), 7.04-8.01 (m, 20H, 3 x $CH_2C_6H_5$, $OCOC_6H_5$); ^{13}C NMR ($CDCl_3$) δ 17.55 (C-6'), 21.01 ($OCOCH_3$), 52.38 (OCH_3), 67.27 (C-5'), 68.46 (C-2'), 70.73, 71.23 (2 x $CH_2C_6H_5$), 72.80 (C-4'), 73.34 ($CH_2CH=CH_2$), 73.58 (C-5), 74.22 (C-3'), 75.15 ($CH_2C_6H_5$), 75.59 (C-4), 78.34 (C-2), 80.42 (C-3), 99.99 (C-1'), 102.70 (C-1), 117.65 ($CH_2CH=CH_2$), 133.79 ($CH_2CH=CH_2$), 127.38, 127.70, 127.81, 127.82, 127.84, 127.92, 128.05, 128.10, 128.12,

128.14, 128.19, 128.23, 128.32, 128.41, 128.69, 128.91, 129.81, 129.91, 133.02, 137.73, 137.75, 138.26, 138.28 ($OCOC_6H_5$, 3 x $CH_2C_6H_5$), 165.75 ($OCOC_6H_5$), 167.96 (C-6), 169.85 ($OCOCH_3$).

Anal. Calcd for $C_{46}H_{50}O_{13}$ (810.90): C, 68.14; H, 6.21. Found: C, 68.05; H, 6.26.

Methyl (4-*O*-benzoyl-3-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-(allyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate (13). Compound **12** (175 mg, 0.22 mmol) was dissolved in methanolic hydrochloric acid (0.28 N, 10 mL, prepared by adding 0.2 mL of acetyl chloride to 10 mL dry methanol), and the mixture was stirred for 36 h in an inert atmosphere at room temperature. When the deacetylation was complete (TLC solvent E), the reaction mixture was passed through a layer of alkaline alumina, and the filtrate was concentrated. The residue was, if necessary, purified by HPLC (eluent solvent C) to give **13** (162 mg, 98%) as a colorless foam: $[\alpha]_D^{22}$ +21.7° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.22 (d, 3H, $J_{5',6'}$ = 6.1 Hz, H-6'), 2.90 (d, 1H, J = 16.5 Hz, OH-2'), 3.56 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.70 (dd, 1H, dd, $J_{2,3}$ = 9.8 Hz, H-2), 3.79 (s, 3H, OCH_3), 3.81 (m, 1H, H-5'), 3.91 (dd, 1H, $J_{3',4'}$ = 9.8 Hz, H-3'), 4.06 (d, 1H, $J_{4,5}$ = 1.2 Hz, H-5), 4.17 (m, 1H, $CH_2CH{=}CH_2$), 4.19 (dd, 1H, $J_{2',3'}$ = 3.4 Hz, H-2'), 4.4 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.42 (dd, 1H, $J_{4,5}$ = 1.2 Hz, H-4), 4.46, 4.56 (2d, 2H, J = 11.9 Hz, $CH_2C_6H_5$), 4.53 (m,1H, $CH_2CH{=}CH_2$), 4.75, 4.76, 4.77, 4.95 (4d, 4H, 2 x $CH_2C_6H_5$), 5.24 (m, 1H, $CH_2CH{=}CH_2$), 5.30 (d,1H, $J_{1',2'}$ = 1.8 Hz, H-1'), 5.30 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.8 Hz, H-4'), 5.37 (m, 1H, $CH_2CH{=}CH_2$), 5.98 (m, 1H, $CH_2CH{=}CH_2$), 7.12-8.02 (m, 20H, $OCOC_6H_5$, 3 x $CH_2C_6H_5$); ^{13}C NMR ($CDCl_3$) δ 17.50 (C-6'), 52.36 (OCH_3), 66.91 (C-5'), 68.53 (C-4'), 70.76, 71.95 (2 x $CH_2C_6H_5$), 73.04 ($CH_2CH{=}CH_2$), 73.44 (C-5), 73.67 (C-3'), 75.16 ($CH_2C_6H_5$), 75.19 (C-4), 76.49 (C-2'), 78.41 (C-2), 80.75 (C-3), 101.18 (C-1'), 102.71 (C-1), 117.66 ($CH_2CH{=}CH_2$), 133.81 ($CH_2CH{=}CH_2$), 127.70, 127.72, 127.85, 127.90, 128.16, 128.19, 128.39, 128.50, 128.82, 128.88, 129.75, 129.96, 130.85, 132.35, 133.06, 137.60, 137.68, 138.34, ($CH_2C_6H_5$, $OCOC_6H_5$), 165.79 ($OCOC_6H_5$), 167.96 (C-6).

Anal. Calcd for $C_{44}H_{48}O_{12}$ (768.86): C, 68.74; H, 6.29. Found: C, 68.61; H 6.33.

Methyl (methyl 2,3-di-*O*-benzyl-4-*O*-*p*-methoxybenzyl-α-D-galactopyranosyluronate)-(1→2)-(4-*O*-benzoyl-3-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-(allyl 2,3-di-*O*-benzyl-β-D-galactopyranosid)uronate (15). To a solution of **13** (162 mg, 0.21 mmol) and methyl (ethyl 2,3-di-*O*-benzyl-4-*O*-*p*-methoxybenzyl-1-thio-β-D-galacto-

pyranosid)uronate[5] (**14**, 143 mg, 0.26 mmol) in dry dichloromethane (2 mL) and dry diethyl ether (8 mL) were added molecular sieves (4Å, 200 mg), and the suspension was stirred in an inert atmosphere at room temperature. After 30 min, iodonium di-*sym*-collidine perchlorate (242 mg, 0.52 mmol) was added, and stirring was continued for 18 h in the dark at ambient temperature. As soon as the glycosyl donor **14** was consumed in the reaction mixture (TLC solvent E), the suspension was filtered, and the red-brown filtrate was diluted with heptane (40 mL) and chloroform (20 mL). The organic layer was washed with cold aq 15% sodium thiosulfate (5 x 20 mL, until the organic layer is colorless), cold aq sat $NaHCO_3$ (2 x 20 mL), ice-water (20 mL), cold aq 1% hydrochloric acid (2 x 20 mL), ice-water (30 mL), cold aq sat $NaHCO_3$ (3 x 20 mL), ice-water (3 x 20 mL), dried, and concentrated. The residue was purified by column chromatography under medium pressure (eluent solvent D) to give **15** (127 mg, 48%) as a colorless foam: $[\alpha]_D^{24}$ +57.6° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 3H, $J_{5',6'}$ = 6.1 Hz, H-6'), 3.32 (s, 3H, OCH_3), 3.51 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 3.76 (dd, 1H, $J_{2',3'}$ = 4.0 Hz, H-2'), 3.76 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 3.77 (s, 3H, OCH_3''), 3.80 (m, 1H, m, H-5'), 3.81 (s, 3H, $H_3COC_6H_4CH_2$), 3.98 (dd, 1H, $J_{3'',4''}$ = 3.1 Hz, H-3''), 4.03 (d, 1H, $J_{4,5}$ = 1.2 Hz, H-5), 4.03 (dd, 1H, $J_{3',4'}$ = 10.1 Hz, H-3'), 4.16 (dd, 1H, $J_{2'',3''}$ = 9.8 Hz, H-2''), 4.16 (m, 1H, CH_2-CH=CH_2), 4.28 (dd, 1H, $J_{4'',5''}$ = 1.2 Hz, H-4''), 4.32 (dd, 1H, $J_{4,5}$ = 1.2 Hz, H-4), 4.39 (d, 1H, $J_{1,2}$ = 7.6 Hz, $J_{C\text{-}1,H\text{-}1}$ = 158.5 Hz, H-1), 4.54 (m, 1H, CH_2CH=CH_2), 4.35-5.02 (12d, 12H, 5 x $CH_2C_6H_5$, $H_3COC_6H_4CH_2$), 4.89 (d, 1H, $J_{4'',5''}$ = 1.2 Hz, H-5''), 5.03 (d,1H, $J_{1'',2''}$ = 3.4 Hz, $J_{C\text{-}1'',H\text{-}1''}$ = 179.0 Hz, H-1''), 5.24 (m,1H, $CH_2CH=CH_2$), 5.34 (d, 1H, $J_{1',2'}$ = 1.8 Hz, $J_{C\text{-}1',H\text{-}1'}$ = 171.5 Hz, H-1'), 5.38 (m, 1H, $CH_2CH=CH_2$), 5.41 (t, 1H, t, $J_{3',4'}$ = $J_{4',5'}$ = 10.1 Hz, H-4'), 5.98 (m, 1H, $CH_2CH=CH_2$), 6.78-8.02 (m, 34 H,$OCOC_6H_5$, 5 x $CH_2C_6H_5$, $H_3COC_6H_4CH_2$); ^{13}C NMR ($CDCl_3$) δ 17.63 (C-6'), 51.65 (OCH_3''), 52.36 (OCH_3), 55.23 ($H_3COC_6H_4CH_2$), 67.45 (C-5'), 70.74, 71.54, 71.92, 72.91 (4 x CH_2-C_6H_5), 71.10 (C-4'), 73.18 ($CH_2CH=CH_2$), 73.27 (C-5''), 73.63 (C-5), 74.01 (H_3CO-$C_6H_4CH_2$), 74.18 (C-3'), 74.39 (C-4''), 75.10 ($CH_2C_6H_5$), 75.16 (C-4), 75.94 (C-2'), 77.96 (C-2''), 78.41 (C-2), 79.36 (C-3''), 80.09 (C-3), 97.36 (C-1''), 99.21 (C-1'), 102.81 (C-1), 117.6361 ($CH_2CH=CH_2$), 113.48, 127.02, 127.08, 127.28, 127.40, 127.66, 127.70, 127,86, 128.02, 128.05, 128.22, 128.28, 128.37, 128.51, 129.39, 129.69, 130.82, 132.98, 137.45, 137.92, 138.32, 138.51, 139.08, 159.0 ($OCOC_6H_5$, 5 x $C_6H_5CH_2$, H_3CO-

$C_6H_4CH_2$), 133.81 ($CH_2CH{=}CH_2$), 165.79 ($OCOC_6H_5$), 168.13 (C-6''), 169.25 (C-6).

Anal. Calcd for $C_{73}H_{78}O_{19}$ (1259.41): C, 69.62; H, 6.24. Found: C, 69.50; H, 6.21.

Methyl (methyl 2,3-di-*O*-benzyl-4-*O*-*p*-methoxybenzyl-α-D-galactopyranosyl-uronate)-(1→2)-(4-*O*-benzoyl-3-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-(2,3-di-*O*-benzyl-α/β-D-galactopyranuronate (16). To a solution of **16** (101 mg, 0.08 mmol) in a 20:1 mixture of acetic acid and water (5 mL), sodium acetate (67 mg, 0.8 mmol) and palladium chloride (57 mg, 0.32 mmol) were added. The mixture was stirred for 8 h at a temperature of 40-45 °C. As soon as no starting material (**16**) was evident (TLC solvent E), the reaction was terminated by filtration through a layer of silica gel (eluent chloroform). The combined filtrates were extracted with cold aq sat $NaHCO_3$ (3 x 15 mL), ice-water (2 x 15 mL), dried, and concentrated. The residue was purified by HPLC (eluent E) to provide **16** (72 mg, 74 %) as a colorless foam: ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 3H, $J_{5',6'}$ = 6.1 Hz, H-6'), 3.28 (s, $OCH_3\beta$), 3.53 (dd, $J_{3,4}$ = 3.1 Hz, H-3β), 3.63 (s, $OCH_3\alpha$), 3.64 (dd, $J_{3,4}$ = 3.1 Hz, H-3α), 3.75 (dd, $J_{2,3}$ = 9.8 Hz, H-2β), 3.77 (dd, 1H, $J_{2',3'}$ = 4.0 Hz, H-2'), 3.77 (s, 3 H, OCH_3''), 3.78 (m, 1H, H-5'), 3.82 (s, 3H, $H_3COC_6H_4CH_2$), 3.85 (dd, $J_{2,3}$ = 9.8 Hz, $J_{1,2}$ = 3.2 Hz, H-2α), 3.90 (d, 1H, $J_{4,5}$ = 0.9 Hz, H-5β), 3.96 (dd, 1H, $J_{3'',4''}$ = 3.3 Hz, H-3''), 4.07 (dd, 1H, $J_{3',4'}$ = 10.0 Hz, H-3'), 4.17 (dd, 1H, $J_{2'',3''}$ = 9.8 Hz, H-2''), 4.29 (dd, 1H, $J_{4'',5''}$ = 1.2 Hz, H-4''), 4.33 (dd, $J_{4,5}$ = 0.9 Hz, H-4β), 4.46 (dd, $J_{4,5}$ = 1.2 Hz, H-4α), 4.49 (d, H-5α), 4.57-5.00 (m, 12H, $CH_2C_6H_5$, $H_3COC_6H_4CH_2$), 4.83 (d, $J_{1,2}$ = 7.2 Hz, H-1β), 4.88 (d, 1H, $J_{4'',5''}$ = 1.2 Hz, H-5''), 5.04 (d, 1H, $J_{1'',2''}$ = 3.5 Hz, H-1''), 5.32 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1'), 5.36 (d, $J_{1,2}$ = 3.2 Hz, H-1α), 5.40 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 10.0 Hz, H-4'), 6.79-8.03 (m, 34 H, $OCOC_6H_5$, 5 x $CH_2C_6H_5$, $H_3COC_6H_4CH_2$); ^{13}C NMR ($CDCl_3$) δ 17.65 (C-6'), 51.66, 52.28, 52.36 ($OCH_3\alpha/\beta$, OCH_3''), 55.24 ($H_3COC_6H_4CH_2$), 67.43 (C-5'), 70.28 and 70.80 ($CH_2C_6H_5$), 71.02 (C-4'), 71.38, 71.92, 72.91, 73.40 (4 x $CH_2C_6H_5$), 73.28 (C-5''), 73.67 (C-5), 73.80 $H_3COC_6H_4CH_2$), 74.58 (C-3'), 74.66 (C-4''), 75.06 ($CH_2C_6H_5$), 75.66, 75.78 (C-4α/β), 75.99 (C-2'), 76.21, 76.76 (C-2α/β), 77.20 (C-2''), 77.89, 78.20 (C-3α/β), 78.44 (C-3''), 92.05 (C-1α), 97.31 (C-1''), 97.63 (C-1β), 98.97 (C-1'), 126.82, 126.93, 127.02, 127.15, 127.33, 127.49, 127.59, 127.64, 127.69, 127.75, 127.8, 127.89, 128.06, 128.09, 128.14, 128.17, 128.29, 128.41, 128.44, 128.58, 128.60, 128.98, 129.64, 129.96, 133.03, 137.44, 137.64, 137.84, 137.94, 138.14 ($OCOC_6H_5$, 3 x $CH_2C_6H_5$, 2 x CH_2-$C_6H_5\alpha/\beta$, $H_3COC_6H_4CH_2$), 165.71

($OCOC_6H_5$), 168.87, 169.19, 169.26 (C-6α/β, C-6″).

Anal. Calcd for $C_{70}H_{74}O_{19}$ (1219.35): C, 68.95; H, 6.12. Found: C, 68.86; H, 6.28.

Methyl (methyl α-D-galactopyranosyluronate)-(1→2)-(4-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→4)-α/β-D-galactopyranuronate (17). To a solution of **16** (60 mg, 0.049 mmol) in ethyl acetate (5 mL) palladium-on-charcoal (20 mg) was added. The solution was stirred in an atmosphere of hydrogen for 16 h at ambient temperature. When the reaction was complete (TLC solvent F), the mixture was filtered over Celite, eluted successively with methanol, and the combined filtrates were concentrated in vacuum to dryness. Then, the residue was dissolved in water and lyophilized to provide **17** (31 mg, 98%) as a white powder: ^{1}H NMR (for NMR spectra, a sample was repeatedly dissolved and concentrated under dimished pressure with CH_3OD-d_1, and finally, dissolved and the spectrum measured in DMSO-d_6) δ 1.22 (d, 1 H, $J_{5',6'}$ = 6.1 Hz, H-6'), 3.36-4.21 (H-2α/β, H-3α/β, H-5β, H-2′, H-3′, H-5′, H-2″, H-3″), 3.31, 3.74, 3.80 (3 x s, OCH_3α/β, OCH_3″), 4.23 - 4.68 (H-4α/β, H-5α, H-4″, H-5″), 4.70 (d, $J_{1,2}$ = 7.5 Hz, H-1β), 4.95 (d, 1H, $J_{1'',2''}$ = 3.2 Hz, H-1″), 5.14 (d, 1H, $J_{1',2'}$ = 1.8 Hz, H-1′), 5.14 (d, $J_{1,2}$ = 3.0 Hz, H-1α), 5.17 (t, 1H, $J_{3',4'}$ = 9.9 Hz, H-4′), 7.69, 7.82, 8.11 (3 x m, 5 H, $OCOC_6H_5$); ^{13}C NMR (DMSO) δ 17.54 (C-6′), 51.34, 52.61, 51.83 (OCH_3α/β, OCH_3″), 61.74, 66.20, 66.69, 67.17, 67.95, 68.31, 69.23, 70.54, 70.94, 72.37, 73.89, 74.39, 75.33, 75.92, 77.54, 79.12 (C-2α/β, C-3α/β, C-4α/β, C-5α/β, C-2′, C-3′, C-4′, C-5′, C-2″, C-3″, C-4″, C-5″), 92.69 (C-1α), 97.44 (C-1″), 98.43 (C-1β), 100.56 (C-1′), 128.72, 129,28, 129.84, 133.28 ($OCOC_6H_5$), 165.43 ($OCOC_6H_5$), 168.81, 169.68, 169.78 (C-6α/β, C-6″); FAB^+ mass spectrum, matrix glycerine/LiCl ($C_{27}H_{36}O_{18}$ + $C_3H_8O_3$): *m/z* 740.7 [M+glycerine]; FAB^+ mass spectrum, matrix glycerine/LiCl ($C_{27}H_{36}O_{18}$ + Li): *m/z* 655.5 $[M + Li]^+$; FAB^+ mass spectrum, matrix nitrobenzylalcohol /NaCl/oxalic acid ($C_{27}H_{36}O_{18}$ + Na): *m/z* 671.6 $[M + Na]^+$; CI mass spectrum (isobutane): *m/z* 105.1 (C_7H_5O, Bz, 23 %), 130.1 ($C_5H_6O_4$, Rha-4-O without CH_3, 12 %), 145.1 ($C_6H_9O_4$, Rha-4-O, 6 %), 173.1 ($C_7H_9O_5$, Rha-4-OCO, 39 %), 191.1 ($C_7H_{11}O_6$, GalAOCH_3, 100 %), 233.3 ($C_{13}H_{13}O_3$, Rha-4-OBz without 3-OH, 10 %), 250.3 ($C_{13}H_{14}O_4$, Rha-4-OBz, 29 %), 364.3 ($C_{14}H_{20}O_{11}$, GalA-Rha-4-OCO, 3 %), 441.4 ($C_{20}H_{25}O_{11}$, GalA-Rha-4-OBz, 4 %).

Anal. Calcd for $C_{27}H_{36}O_{18}$ (648.57): C, 50.00; H, 5.59. Found: C, 50.13; H, 5.68.

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