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Synthesis of a heteroglycuronan derivative containing the β-D-galactopyranosyluronic acid (1 → 3)-L-rhamnose repeating unit *

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ABSTRACT

Helferich glycosylation of the cyanoethylidene L-rhamnose derivative **3** with the galactosyluronic bromide **2** gave the disaccharide **4** as a key intermediate in the synthesis of the monomer **13** for trityl-cyanoethylidene condensation (TCC). The following formation of the monomer **13**, including introduction of a trityl group at O-3′, proceeded in six steps. Because of the difficulty of some steps, an alternative route for **13** was tested. Model compounds **20**, **21**, and **22** were synthesized in order to confirm the stereoregularity of the products of the polycondensation. The polycondensation of the monomer gave D-Gal*p*A-(1 → 3)-L-Rha-oligomer derivatives consisting mainly of three repeating units. This result is in contrast with the degree of polymerisation (dp ≥ 22) of other synthetic rhamnans, but is very similar to dp 2–7 of homo- and hetero-glucuronan derivatives.

INTRODUCTION

As a part of our investigation on the synthesis of pectin fragments, we required various D-galacturonic acid derivatives and methods of polycondensation to obtain biopolymers, which involve D-galactosiduronates of specific stereochemistry. The synthesis of stereoregular polysaccharides has become possible with the development of the polycondensation methodology of trityl ethers of cyanoethylidene derivatives of mono- and oligo-saccharides[2]. The first approach to a heteroglycuronan applying this method gave only a limited average chain-length of five repeating units. The disaccharidic monomer (**1**) used for this polycondensation was built up

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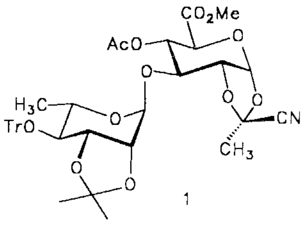
in such a way that the cyanoethylidene group was borne by the glucuronic acid moiety, whereas the trityl ether group was located at the L-rhamnose fragment[3].



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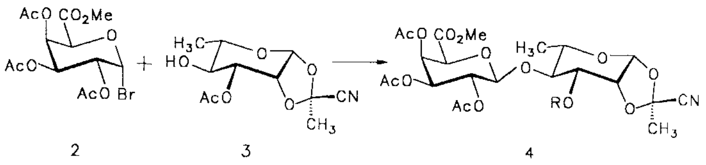
However, L-rhamnans with a degree of polymerisation (dp) of 22 and higher have been obtained by polycondensation of cyanoethylidene-trityl-rhamnopyranoses[4], whereas the cyanoethylidene monomers of D-glucuronic acid led[3] to a dp not higher than 7. Following these experiences, we elaborated an approach to a disaccharide monomer containing the cyanoethylidene group at the L-rhamnose moiety and the trityl ether at the D-galacturonic acid moiety. In order to test the magnitude of the glycosylating reaction by application of the trityl-cyanoethylidene condensation (TCC) and for NMR studies, some model reactions were performed, in which the D-galacturonic acid derivatives served as glycosyl acceptors and L-rhamnose derivatives as glycosyl donors.

RESULTS AND DISCUSSION

Helferich glycosylation of the cyanoethylidene rhamnose derivative **3**, which was obtained from **19** in 78% overall yield[4], with the D-galactosyluronic bromide **2** (ref. 5) gave the disaccharide **4** as a key intermediate in the synthesis of the monomer **13**. The best results were achieved when the reaction was promoted by $Hg(CN)_2$–$HgBr_2$ in $MeCN$–CH_2Cl_2 at room temperature, resulting in a 35% yield of the crystalline disaccharide **4** after chromatographic separation from several unidentified side products.

The ^1H NMR spectra, which showed a vicinal coupling constant $^3J_{1',2'}$ of 8.0 Hz for compound **4**, unequivocally confirmed that the anomeric carbon atom of the D-galacturonic acid moiety had the β-(D) configuration. Furthermore, the ^{13}C NMR signal for C-1′ was found to fall within the expected range of 101.0 ppm. Finally, the remaining NMR data were in full accord with the structure of the disaccharide **4** (Scheme 1).

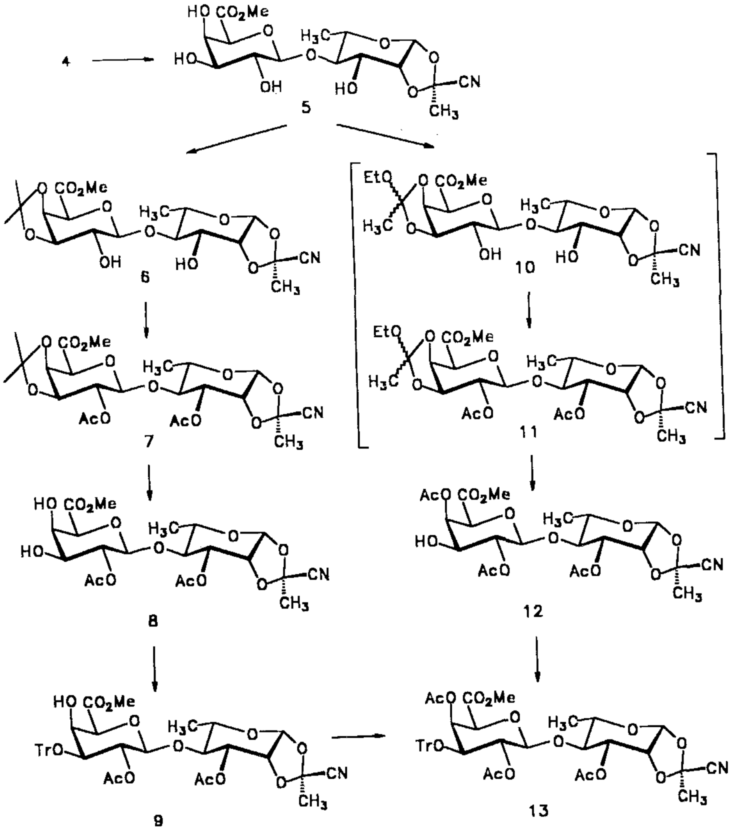
Cleavage of the acetyl groups of **4** was achieved with methanolic HCl in 78% yield. The product **5** was successively treated with acetone–2,2-dimethoxypropane–TsOH and with Ac_2O–pyridine to give **7**. The isopropylidene group of **7** was removed with 90% CF_3CO_2H in a mixture of $MeOH$–$CHCl_3$ at room temperature during 20 min. After purification by column chromatography, 80% of crystalline **8** was obtained. Tritylation of **8** with $TrClO_4$ in the presence of 2,4,6-collidine, followed by acetylation (Ac_2O–pyridine) with 4-dimethylamino-



Scheme 1.

pyridine as catalyst afforded the desired monomer **13** in an overall yield of 20% from **4** (Scheme 2).

Since chromatographic purification at the last step proved to be difficult in view of the presence of side-products formed under forcing conditions, we looked for an alternative route to **13**. This approach started from compound **5** using an orthoester function. The action of triethyl orthoacetate on derivative **5** gave the non-isolated orthoacetate **10**, which was readily acetylated to give **11**. The cyclic orthoester **11** was opened by treatment with aq acetic acid to form the triacetate **12**. However, tritylation of the remaining hydroxyl group at C-3 was surprisingly

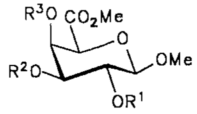


Scheme 2.

slow, compared with the results in the monosaccharide series[1]. The overall yield for this 5-step sequence of **13** was 6% related to **4** (Scheme 2).

The analytical data for compounds **5**–**13** are in full agreement with the structures proposed. Additionally, compounds **4**, **5**, **8**, and **12** constitute a series of derivatives with acetyl groups at different positions of the galacturonic acid moiety. The stepwise acetylation of **5** via **8** (at O-2′), and **12** (at O-2′ and O-4′) to the fully acetylated derivative **4** caused a significant downfield shift (δ 1.6 ± 0.4 ppm) for each ring proton signal geminal to an acetyl group, with respect to the corresponding signals for **5**. Applying these results, possible acetyl group migration during a reaction should be readily monitored.

Model reactions were carried out to investigate the possibility of creating an $\alpha(\rightarrow 3)$-linkage between L-rhamnose and D-galacturonic acid by TCC condensation and in order to compare the NMR data. The glycosyl acceptor **17** was prepared by the approach already illustrated for **13** via **9**.

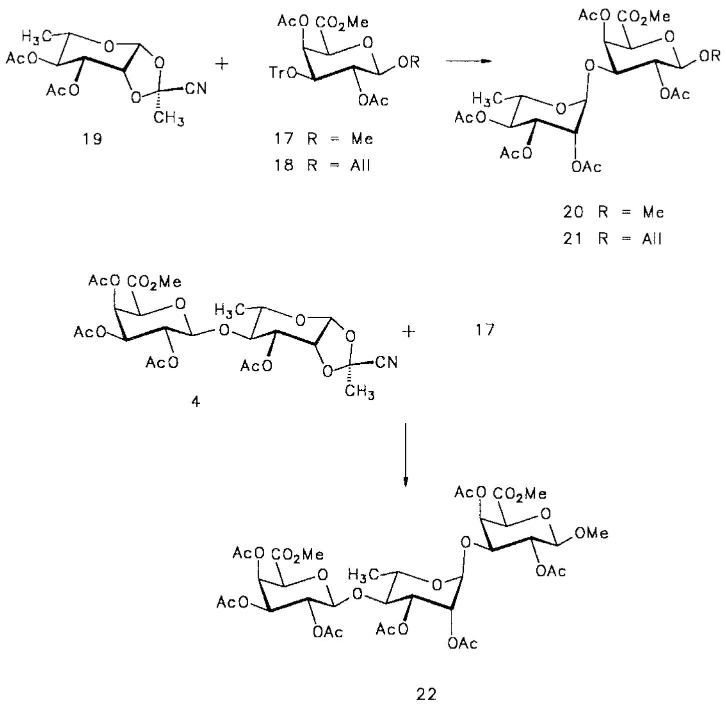


14 R^1 = Ac, R^2 and R^3 = C(Me)$_2$
15 R^1 = Ac, R^2 and R^3 = H
16 R^1 = Ac, R^2 = Tr, R^3 = H
17 R^1 = Ac, R^2 = Tr, R^3 = Ac

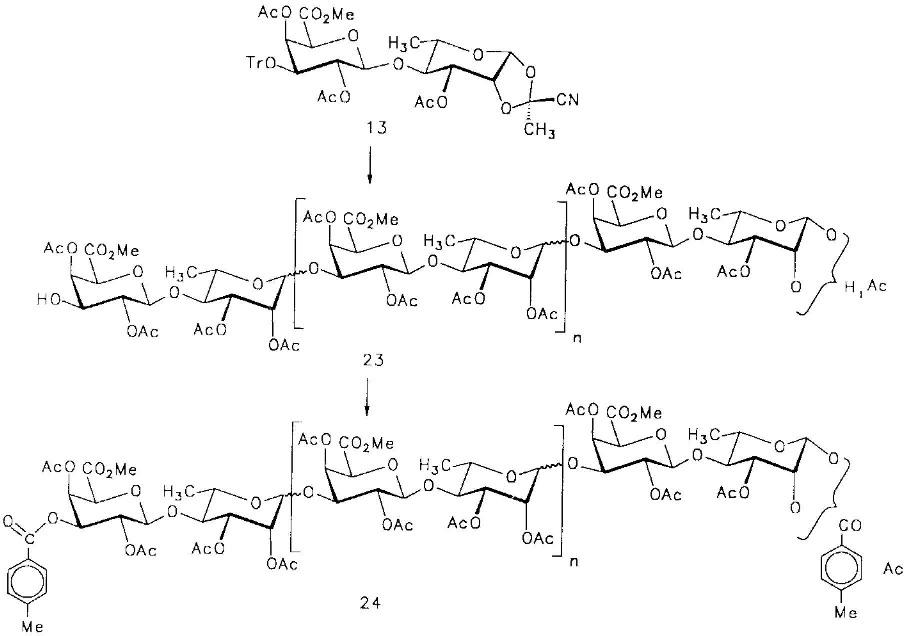
Under the standard conditions for TCC described previously by Kochetkov et al.[6], the coupling of **19** with **17** and **18** (ref. 1) gave the expected disaccharides **20** and **21** in 86 and 83% yield, respectively. Furthermore, the reaction of the disaccharide **4** with **17** gave similar results leading to the trisaccharide **22** in 70% yield. The stereoselectivity of TCC is quite remarkable, and 1,2-*cis*-glycosides were formed only in trace amounts (TLC) (Scheme 3).

Although compounds **20**, **21**, and **22** exhibited all of the expected spectral properties, neither the signals and coupling constants in the ^{1}H NMR spectra nor the signals in the ^{13}C NMR spectra established the stereochemical situation at the anomeric centre of the L-rhamnose residues unambiguously. In order to establish the 1,2-*trans*-glycosidic linkage of L-rhamnose to D-galacturonic acid, the geminal ^{13}C–^{1}H coupling constants ($J_{\text{C-1}',\text{H-1}'}$) were determined. Because the observed values for **20**, **21**, and **22** are 170 ± 0.5 Hz, a comparison with the data reported for other acetylated α-L-rhamnose examples verified the expected structure of 1,2-*trans*-glycosides. In the other case, $J_{\text{C-1}',\text{H-1}'}$ should be ~ 10 Hz smaller when H-1′ is axial than when it is equatorial[7].

Polycondensation of the monomer **13** was performed in dichloromethane in the presence of 0.1 equivalent of triphenylmethylium perchlorate, using a vacuum technique[2]. After 48 h at room temperature in the dark, no traces of the starting monomer were detectable in the reaction mixture (TLC) and the carbohydrate



Scheme 3.



Scheme 4.

products did not contain triphenylmethyl group (spraying with H_2SO_4 did not produce a yellow coloration of the spots in TLC followed by darkening upon heating). The reaction mixture was neutralized by the addition of pyridine containing 2% water. After standard work-up and chromatographic purification on silica gel, the oligosaccharide mixture (**23**) was treated with 4-methylbenzoyl chloride in pyridine to determine the degree of polymerisation[3]. To estimate the average chain-length of the proposed oligosaccharides, the ratio of the respective integral intensities of the following signals in the ^{1}H NMR spectrum were determined: δ 1.2 (9, m, *Me*-Rha):2.1 (36, m, O_2C*Me*):2.4 (6, s, *Me*-Bz):3.6–5.7 (39, m, *H-1)–H-5*, CO_2*Me*):7.3, 8.0 (8, 2 m, *Ph*), indicating an average chain length of three linked disaccharide units (**24**, dp 3, *n* = 1 in Scheme 4). The configuration of the glycosidic bonds linked in the process of polycondensation was not established because the coupling constants of $J_{\text{C-1,H-1}}$ of the rhamnosyl moieties could not be determined due to the complexity of the ^{1}H NMR spectrum. The low degree of polycondensation is in full agreement with results obtained earlier in the uronic acid series [3].

EXPERIMENTAL

General methods.—See ref. 8. All washing solutions were cooled to ~ 5°C. The $NaHCO_3$ solution was saturated. Triphenylmethylium perchlorate was obtained and purified as described in ref. 2. The following solvent systems (v/v) were used for chromatography: (A_1) 2:1, (A_2) 3:1, (A_3) 7:2, (A_4) 5:1, (A_5) 10:1, (A_6) 2:3 PhMe–EtOAc; (B_1) 1:1, (B_2) 5:1, (B_3) 10:1, (B_4) 20:1 $CHCl_3$–MeOH; (*C*) 10:5:1 $CHCl_3$–Et_2O–MeOH; (*D*) 2:1:0.1 EtOAc–PhMe–EtOH; (*E*) 5:1 hexane–EtOAc; (*F*) 2:1 heptane–$CHCl_3$; (*G*) 3:1 PhMe–Et_2O; (H_1) 5:1; (H_2) 10:1 PhMe–EtOH; (I) 5:1:1 PhMe–heptane–EtOH; (*J*) 20:1 $CHCl_3$–EtOH.

*Methyl (2,3,4-tri-*O*-acetyl-α-*D*-galactopyranosyl bromide)uronate* (**2**).—To a stirred solution of methyl (1,2,3,4-tetra-*O*-acetyl-α,β-D-galactopyranosid) uronate[9] (3.76 g, 10 mmol) in dry $CHCl_3$ (5 mL) was added acetic acid (40%), HBr (5%), Ac_2O (45 mL, prepared by adding at −10°C of H_2O (33 mL) to a mixture of AcBr (136 mL), of AcOH (100 mL), and Ac_2O (4 mL))[10] at 0°C. After 4 h at ambient temperature (TLC, solvent A_4) the solution was poured into ice–water (400 mL). The aqueous layer was extracted (solvent *F*, 3 × 200 mL). The combined organic layers were washed successively with ice–water (200 mL), aq $NaHCO_3$ (2 × 200 mL) and ice–water (2 × 200 mL), dried, and evaporated. The syrupy product **2** (3.77 g, 95% yield) was used without further purification for the next step. Crystallization from dry Et_2O gave an analytical sample of **2**; mp 128–130°C; $[\alpha]_D^{20}$ +240° (*c* 1.0, $CHCl_3$); lit.[5] mp 130°C; $[\alpha]_D$ +242° (*c* 1.0, $CHCl_3$). *Anal.* Calcd for $C_{13}H_{17}O_9Br$: C, 39.31; H, 4.31. Found: C, 39.00; H, 4.10.

*3-*O*-Acetyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-4-*O*-[methyl (2,3,4-tri-*O*-acetyl-β-*D*-galactopyranosyl)uronate]-β-*D*-rhamnopyranose* (**4**).—To a solution of 3-*O*-acetyl-1,2-*O*-[1-(exo-cyano)ethylidene]-β-L-rhamnopyranose **3**[4] (2.05 g, 8 mmol), $Hg(CN)_2$

(4.01 g, 16 mmol), and $HgBr_2$ (2.88 g, 8 mmol) in dry MeCN (50 mL), a solution of **2** (6.36 g, 16 mmol) in dry CH_2Cl_2 (30 mL) was added during 1 h with stirring. The reaction was performed under Ar in the dark. Stirring was continued for 24 h (TLC, solvent A_4) at room temperature with the exclusion of atmospheric moisture. Chloroform (400 mL) was added, the organic phase was washed successively with water (200 mL), aq 10% NaI (2 × 200 mL), aq $NaHCO_3$ (2 × 200 mL), and water (2 × 200 mL), dried, and evaporated. The crude material was purified by column chromatography (solvent A_4) to yield **4** (1,61 g, 35%) mp 208–211°C (from EtOH); $[\alpha]_D^{19}$ +3.2° (*c* 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.43 (d, 3 H, $J_{6,5}$ 6.2 Hz, H-6), 1.91 [s, 3 H, Me(CN)C], 2.00, 2.04, 2.12, 2.22 (4 s, 4 × 3 H, OAc), 3.51 (m, 1 H, H-5), 3.75 (s, 3 H, CO_2Me), 3.81 (t, 1 H, $J_{4,5}$ 9.1 Hz, H-4), 4.29 (d, 1 H, $J_{5',4'}$ 1.5 Hz, H-5′), 4.51 (dd, 1 H, $J_{2,3}$ 4.1 Hz, H-2), 4.66 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 5.00 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3′), 5.17 (dd, 1 H, $J_{2',3'}$ 10.7 Hz, H-2′), 5.20 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-3), 5.38 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1), and 5.71 (dd, 1 H, H-4′); ^{13}C NMR ($CDCl_3$): δ 17.8 (C-6), 20.5, 20.9 (3 C, $\mathit{C}H_3CO$), 26.5 [$\mathit{C}H_3(CN)C$], 52.6 (OCH_3), 68.1 (C-4′), 68.4 (C-2′), 70.5 (2 C, C-3′, C-5), 71.6 (C-3), 72.2 (C-5′), 75.6 (C-4), 78.5 (C-2), 96.7 (C-1), 101.0 (C-1′), 101.5 [$\mathit{C}(CN)CH_3$], 116.7 (CN), 166.0 (C-6′), 169.3, and 169.8 (3 C, $CH_3\mathit{C}O$). *Anal.* Calcd for $C_{24}H_{31}NO_{15}$: C, 50.26; H, 5.45; N, 2.44. Found: 50.20; H, 5.24; N, 2.51.

1,2-O-[1-(exo-Cyano)ethylidene]-4-O-[methyl (β-D-galactopyranosyl)uronate]-β-L-rhamnopyranose (**5**).—To methanolic HCl (1% prepared by adding 7.5 mL of AcCl to 370 mL of ice-cold dry MeOH) was added **4** (5.74 g, 10 mmol) with stirring, and the mixture kept for 24 h at ambient temperature (TLC, solvent B_1). The solution was made neutral by addition of $(PbCO_3)_2 \cdot Pb(OH)_2$ (30 g). After stirring for 2 h, the lead salts were centrifuged off, washed with MeOH, and the filtrate and washings were combined and concentrated. The residue was applied to a column of silica gel (solvent B_2) to give **5** as a solid. A solution of **5** in solvent B_1 was passed through a layer of Sephadex LH-20 to remove traces of silica gel, and evaporated, to give chromatographically homogeneous, crystalline **5** (3.16 g, 78%). An analytical sample of **5**, prepared by recrystallization from 2:1:1, (v/v/v) $CHCl_3$–EtOAc–hexane, had mp 121–122°C, $[\alpha]_D^{18}$ −38.6° (*c* 0.4, H_2O); ^{1}H NMR [3:1 $CDCl_3$–$(CD_3)_2CO$]: δ 1.13 (d, 3 H, $J_{6,5}$ 5.8 Hz, H-6), 1.60 [s, 3 H, Me(CN)C], 3.23 (m, 1 H, H-5), 3.32 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 3.39 (dd, 1 H, $J_{3',4'}$ 3.0 Hz, H-3′), 3.45 (m, 1 H, $J_{2',3'}$ 9.4 Hz, H-2′), 3.50 (s, 3 H, CO_2Me), 3.65 (d, 1 H, *J* 5.1 Hz, OH), 3.83 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 3.83 (dd, 1 H, OH), 3.97 (m, 2 H, H-4′,5′), 4.25 (dd, 1 H, $J_{2,3}$ 3.9 Hz, H-2), 4.31 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.59 (d, 1 H, *J* 2.6 Hz, OH), 5.00 (d, 1 H, *J* 3.7 Hz, OH), and 5.16 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1); ^{13}C NMR [3:1 $CDCl_3$–$(CD_3)_2CO$]: δ 17.2 (C-6), 26.0 [$\mathit{C}H_3(CN)C$], 51.5 (OCH_3), 69.4 (C-4′), 69.9 (C-5), 70.1 (C-3), 71.4 (C-2′), 72.9 (C-3′), 73.9 (C-5′), 80.3 (C-2), 82.4 (C-4), 96.5 (C-1), 104.3 (C-1′), 116.9 (CN), and 168.5 (C-6′). *Anal.* Calcd for $C_{16}H_{23}NO_{11}$: C, 47.41; H, 5.72; N, 3.46. Found: C, 47.70; H, 5.61; N, 3.21.

1,2-O-[1-(exo-Cyano)ethylidene]-4-O-[methyl (3,4-O-isopropylidene-β-D-galactopyranosyl)uronate]-β-L-rhamnopyranose (**6**).—To a suspension of **5** (1.62 g, 4 mmol) in dry Me_2CO (20 mL) and 2,2-dimethoxypropane (5 mL), was added TsOH (100 mg), and the mixture was stirred for 48 h at ambient temperature (TLC, solvent B_4). The mixture was then passed through a layer of alkaline alumina (2 × 2 cm), the eluate evaporated, and the residue was purified by column chromatography (solvent A_1) to give **6** (1.30 g, 73%); mp 207–208°C (from EtOAc–heptane); $[\alpha]_D^{20}$ -24.9° (*c* 1.0, $CHCl_3$); ^1H-NMR ($CDCl_3$): δ 1.37 (s, 3 H, Me_2C), 1.43 (d, 3 H, $J_{6,5}$ 5.9 Hz, H-6), 1.53 (s, 3 H, Me_2C), 1.90 [s, 3 H, Me(CN)C], 3.38 (d, 1 H, $J_{OH,2'}$ 2.9 Hz, OH-2'), 3.47 (m, 1 H, H-5), 3.55 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 3.69 (ddd, 1 H, $J_{2',3'}$ 7.2 Hz, H-2'), 3.85 (s, 3 H, CO_2Me), 4.04 (m, 1 H, $J_{3,4}$ 9.0, $J_{OH,3}$ 4.6 Hz, H-3), 4.15 (dd, 1 H, $J_{3',4'}$ 5.3 Hz, H-3'), 4.29 (d, 1 H, OH-3), 4.45 (d, 1 H, $J_{5',4'}$ 2.6 Hz, H-5'), 4.48 (dd, 1 H, H-4'), 4.55 (d, 1 H, $J_{1',2'}$ 8.7 Hz, H-1'), 4.55 (dd, 1 H, $J_{2,3}$ 4.0 Hz, H-2), and 5.40 (d, 1 H, $J_{1,2}$ 2.3 Hz, H-1); ^{13}C NMR ($CDCl_3$): δ 17.9 (C-6), 26.3 [$\mathit{C}H_3$(CN)C], 26.6, 28.1 [$C(\mathit{C}H_3)_2$], 52.7 (OCH_3), 70.5 (C-5), 71.0 (C-3), 72.4 (C-5'), 73.8 (C-4'), 73.9 (C-2'), 79.2 (C-3'), 80.4 (C-2), 83.1 (C-4), 97.0 (C-1), 104.0 (C-1'), 111.2 [$\mathit{C}(CH_3)_2$], 116.9 (CN), and 167.0 (C-6'). *Anal.* Calcd for $C_{19}H_{27}NO_{11}$: C, 51.32; H, 6.11; N, 3.14. Found: C, 51.30; H, 6.05; N, 3.33.

3-O-Acetyl-1,2-O-[1-(exo-cyano)ethylidene]-4-O-[methyl (2-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranosyl)uronate]-β-L-rhamnopyranose (**7**).—A solution of **6** (2.67 g, 6 mmol) in dry pyridine (30 mL) was treated with Ac_2O (10 mL) at 0°C and kept for 24 h at that temperature (TLC, solvent A_2). Ethanol (4 mL) was added dropwise at 0°C. After 30 min, the mixture was diluted with $CHCl_3$ (200 mL), and the organic layer was successively washed with ice–water (70 mL), aq 15% $NaHSO_4$ (3 × 70 mL), ice–water (70 mL), aq $NaHCO_3$ (2 × 70 mL), ice–water (70 mL), dried, and evaporated. The residue was coevaporated with added solvent *I* (3 × 100 mL) and processed by column chromatography (solvent A_4, 0.1% pyridine) to give **7** (3.02 g, 95%); mp 208–210°C (from EtOAc–heptane); $[\alpha]_D^{20}$ −1.8° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.34 (s, 3 H, Me_2C), 1.43 (d, 3 H, $J_{6,5}$ 6.2 Hz, H-6), 1.54 (s, 3 H, Me_2C), 1.90 [s, 3 H, Me(CN)C], 2.07, 2.21 (2 s, 2 × 3 H, OAc), 3.50 (m, 1 H, H-5), 3.72 (t, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 3.83 (s, 3 H, CO_2Me), 4.18 (dd, 1 H, $J_{3',4'}$ 5.6 Hz, H-3'), 4.42 (d, 1 H, $J_{5',4'}$ 2.4 Hz, H-5'), 4.50 (dd, 1 H, H-4'), 4.51 (dd, 1 H, $J_{2,3}$ 4.3 Hz, H-2), 4.57 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.97 (t, 1 H, $J_{2',3'}$ 7.2 Hz, H-2'), 5.17 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-3), and 5.37 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1); ^{13}C NMR ($CDCl_3$): δ 17.9 (C-6), 20.6, 20.8 ($\mathit{C}H_3CO$), 26.1 [$\mathit{C}H_3$(CN)C], 26.5, 27.3 [$C(\mathit{C}H_3)_2$], 52.5 (OCH_3), 70.9 (C-5), 71.7 (C-3), 71.8 (C-2'), 71.9 (C-5'), 73.7 (C-4'), 75.9 (C-4), 76.5 (C-3'), 78.5 (C-2), 96.7 (C-1), 100.8 (C-1'), 101.6 [$\mathit{C}(CN)CH_3$], 111.2 [$\mathit{C}(CH_3)_2$], 116.7 (CN), 167.0 (C-6'), and 169.7 (2 C, $CH_3\mathit{C}O$). *Anal.* Calcd for $C_{23}H_{31}NO_{13}$: C, 52.17; H, 5.90; N, 2.65. Found: C, 51.94; H, 5.81; N, 2.80.

3-O-Acetyl-1,2-O-[1-(exo-cyano)ethylidene]-4-O-[methyl (2-O-acetyl-β-D-galactopyranosyl)uronate]-β-L-rhamnopyranose (**8**).—A solution of **7** (5.30 g, 10 mmol) in a mixture of $CHCl_3$ (50 mL), MeOH (50 mL), and 90% aq CF_3COOH (100 mL) was kept for 10 min at ambient temperature (TLC, solvent B_2), diluted with MePh (200 mL), and evaporated. Solvent H_1 (4 × 200 mL) was evaporated from the residue which was then purified by column chromatography (solvent B_4) to yield **8** (3.92 g, 80%); mp 213–215°C (from dry EtOH); $[\alpha]_D^{20}$ $-18.0°$ (c 1.0, $CHCl_3$): ^1H NMR ($CHCl_3$): δ 1.43 (d, 3 H, $J_{6,5}$ 6.2 Hz, H-6), 1.91 [s, 3 H, Me(CN)C], 2.08 , 2.25 (2 s, 2 × 3 H, OAc) 2.60, 2.96 (m, 2 H, OH), 3.50 (m, 1 H, H-5), 3.72 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3′), 3.76 (s, 3 H, CO_2Me), 3.82 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 4.11 (d, 1 H, $J_{4',5'}$ 1.3, H-5′), 4.21 (dd, 1 H, H-4′), 4.51 (dd, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 4.65 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 5.03 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′), 5.22 (dd, 1 H, $J_{3,4}$ 9.6 Hz, H-3), 5.38 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1); ^{13}C NMR ($CDCl_3$): δ 17.8 (C-6), 20.7, 20.9 (CH_3CO), 26.6 [CH_3(CN)C], 52.7 (OCH_3), 69.9 (C-4′), 70.5 (C-5), 71.6 (C-3), 72.2 (C-2′), 72.3 (C-3′), 73.9 (C-5′), 75.8 (C-4), 78.7 (C-2), 96.7 (C-1), 100.8 (C-1′), 101.4 [C(CN)CH_3], 116.7 (CN), 167.9 (C-6′), and 169.7 (2 C, CH_3CO). *Anal.* Calcd for $C_{20}H_{27}NO_{13}$: C, 49.08; H, 5.56; N, 2.86. Found: C, 48.99; H, 5.71; N, 2.91.

3-O-Acetyl-1,2-O-[1-(exo-cyano)ethylidene]-4-O-[methyl (2-O-acetyl-3-O-trityl-β-D-galactopyranosyl)uronate]-β-L-rhamnopyranose (**9**).—To a solution of **8** (2.45 g, 5 mmol) in dry CH_2Cl_2 (50 mL) were added in portions 2,4,6-collidine (2 mL, 15 mmol) and $TrClO_4$ (4.80 g, 14 mmol), and the mixture was stirred for 3 h (TLC, solvent C) at ambient temperature. Then $CHCl_3$ (250 mL) was added, and the solution was washed with water (3 × 100 mL), dried, and evaporated. The residue was applied to a column of silica gel (solvent A_5, 0.1% pyridine) to give **9** (2,49 g, 68%); mp 225–228°C (from EtOAc–heptane), $[\alpha]_D^{20}$ $+2.7°$ (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.39 (d, 3 H, $J_{6,5}$ 6.2 Hz, H-6), 1.84 (s, 3 H, OAc), 1.87 [s, 3 H, Me(CN)C], 2.06 (s, 3 H, OAc), 2.36 (d, 1 H, $J_{OH,4'}$ 4.4 Hz, OH-4′), 3.42 (m, 1 H, $J_{4',5'}$ 1.2 Hz, H-4′), 3.48 (dd, 1 H, H-5), 3.52 (dd, 1 H, $J_{3',4'}$ 3.0 Hz, H-3′), 3.66 (t, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 3.71 (bs, 1 H, H-5′), 3.72 (s, 3 H, CO_2Me), 4.28 (d, 1 H, $J_{1',2'}$ 8.3 Hz, H-1′), 4.46 (dd, 1 H, $J_{2,3}$ 4.2 Hz, H-2), 5.13 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 5.35 (d, 1 H, $J_{1,2}$ 2.3 Hz, H-1), 5.39 (dd, 1 H, $J_{2',3'}$ 10.2 Hz, H-2′), and 7.25–7.55 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 17.9 (C-6), 20.9 (2 C, CH_3CO), 26.6 [CH_3(CN)C], 52.5 (OCH_3), 69.2, 69.4 (C-2′, C-4′), 70.7 (C-5), 71.8 (C-3), 73.7 (C-3′), 74.0 (C-5′), 75.5 (C-4), 78.7 (C-2), 87.3 [$C(C_6H_5)_3$], 96.8 (C-1), 101.2 (C-1′), 101.4 [C(CN)CH_3], 116.8 (CN), 127.7, 128.1, 129.0, 144.3 (C_6H_5), 167.6 (C-6′), and 169.6 (2 C, CH_3CO). *Anal.* Calcd for $C_{39}H_{41}NO_{13}$: C, 64.01; H, 5.65; N, 1.91. Found: C, 63.74; H, 5.71; N, 1.69.

3-O-Acetyl-1,2-O-[1-(exo-cyano)ethylidene]-4-[methyl (2,4-di-O-acetyl)-β-D-galactopyranosyl)uronate]-β-L-rhamnopyranose (**12**).—Compound **5** (2.03 g, 5 mmol) and TsOH (9 mg, 0.05 mmol) were dried by a threefold distillation with PhMe. Then $(EtO)_3CMe$ (8 mL) was added and the suspension was stirred for 12 h at room temperature (TLC, solvent A_6). After adding Et_3N (2.5 mL), the mixture was diluted with $CHCl_3$ (150 mL), washed with water (3 × 50 mL), dried, and evaporated. The residue (**10**) was dissolved in a mixture of pyridine (16 mL) and Ac_2O (4 mL) and kept for 24 h at room temperature (TLC, solvent A_6). After dilution with $CHCl_3$ (50 mL), the reaction mixture was poured into ice–water and extracted with $CHCl_3$ (3 × 80 mL). The combined organic layers were washed with aq $NaHCO_3$ (2 × 100 mL) and water (100 mL), dried, and evaporated. After coevaporation with solvent *I* (4 × 100 mL) and drying in high vacuum, the residue (**11**) was immediately dissolved in 80% aq AcOH (50 mL) and kept for 20 min at room temperature. Repeat coevaporation with solvent *I* and column chromatographic purification (solvent A_1) afforded **12** (1.20 g, 45% with regard to **5**); mp 217–219°C (from EtOAc–heptane), $[\alpha]_D^{20}$ +4.5° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.42 (d, 3 H, $J_{6,5}$ 6.0 Hz, H-6), 1.90 [s, 3 H, Me(CN)C], 2.09, 2.14, 2.22 (3 s, 3 × 3 H, OAc), 2.56 (m, 1 H, OH-3′), 3.50 (m, 1 H, $J_{5,4}$ 9.1 Hz, H-5), 3.75 (s, 3 H, CO_2Me), 3.78 (m, 2 H, H-3′, H-4), 4.20 (d, 1 H, $J_{5',4'}$ 1.1 Hz, H-5′), 4.51 (dd, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 4.63 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.95 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′), 5.22 (dd, 1 H, $J_{3,4}$ 9.4 Hz, H-3), 5.38 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1), and 5.56 (dd, 1 H, $J_{4',3'}$ H-4′). *Anal.* Calcd for $C_{22}H_{29}NO_{14}$: C, 49.72; H, 5.50; N, 2.64. Found: C, 49.80; H, 5.71; N, 2.54.

2-O-Acetyl-1,2-O-[1-(exo-cyano)ethylidene]-4-O-[methyl (2,4-di-O-acetyl-3-O-trityl-β-D-galactopyranosyl)uronate]-β-L-rhamnopyranose (**13**).—*A. via* **9**. Compound **9** (2.20 g, 3 mmol) was dissolved in a mixture of dry pyridine (60 mL), Ac_2O (20 mL), and 4-dimethylaminopyridine (366 mg, 3 mmol) and kept for 6 h at 40°C (TLC, solvent A_4). Then EtOH (12 mL) was added at 0°C, and, after 20 min, the mixture was diluted with $CHCl_3$ (200 mL) and poured into ice–water. The phases were separated, and the aqueous phase was extracted with $CHCl_3$ (2 × 50 mL). The combined organic solutions were washed with aq $NaHCO_3$ (3 × 100 mL), ice–water (2 × 100 mL), dried, and evaporated. Traces of pyridine were removed by evaporation with repeated addition of PhMe. The residue was purified by column chromatography (solvent A_5, 0.1% pyridine) to yield **13** (1.51 g, 65%), syrup, $[\alpha]_D^{23}$ +12.2° (*c* 1.0, $CHCl_3$); ^1H NMR ($CHCl_3$): δ 1.35 (d, 3 H, $J_{6,5}$ 5.8 Hz, H-6), 1.77 (s, 3 H, OAc), 1.84 [s, 3 H, Me(NC)C], 2.04, 2.22 (2 s, 2 × 3 H, OAc), 3.21 (bs, 1 H, H-5′), 3.37 (dd, 1 H, $J_{3',4'}$ 3.0 Hz, H-3′), 3.47 (m, 2 H, H-4,5), 3.62 (s, 3 H, CO_2Me), 4.23 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.44 (dd, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 4.75 (d, 1 H, H-4′), 5.11 (dd, 1 H, $J_{3,4}$ 9.4 Hz, H-3), 5.33 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1), 5.42 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′), and 7.2–7.5 (m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 17.8 (C-6), 20.9, 21.0 (3 C, $\mathit{C}H_3CO$), 26.6 [$\mathit{C}H_3(CN)C$], 52.4 (OCH_3), 69.7 (C-2′), 70.1 (C-4′), 70.5 (C-5), 71.7 (C-3), 72.3 (C-3′), 72.4 (C-5′), 75.1 (C-4), 78.6 (C-2), 87.5 [$\mathit{C}(C_6H_5)_3$], 96.7 (C-1), 101.3 (C-1′), 101.5 [$\mathit{C}(CN)CH_3$], 116.8 (CN), 127.6, 128.0, 128.4, 144.1 (C_6H_5), 166.7 (C-6′), and 169.6, 170.0 (3 C, $CH_3\mathit{C}O$). *Anal.* Calcd for $C_{14}H_{43}NO_{14}$: C, 63.64; H, 5.60; N, 1.81. Found: C, 63.40; H, 5.73; N, 1.66.

B. via **12**. To a solution of **12** (531 mg, 1 mmol) in CH_2Cl_2 (15 mL) and 2,4,6-collidine (0.2 mL, 1.5 mmol) was added $TrClO_4$ (450 mg, 1.3 mmol) with stirring at ambient temperature. After 30 min, another portion of 2,4,6-collidine (0.2 mL, 1.5 mmol) and $TrClO_4$ (450 mg, 1.3 mmol) were added. When the reaction was complete (TLC, solvent A_4), the mixture was diluted with $CHCl_3$ (100 mL), washed with ice–water (3 × 30 mL), dried, and evaporated. Column chromatography (solvent *E*, containing 0.1% pyridine) gave **13** as a syrup (124 mg, 16%); $[\alpha]_D^{22}$ +11.8° (*c* 1.1, $CHCl_3$).

Methyl (methyl 2-O-acetyl-β-D-galactopyranosid)uronate (**15**).—A solution of **14** (ref. 11) (1.83 g, 6 mmol) in a mixture of $CHCl_3$ (30 mL), MeOH (30 mL), and 90% aq CF_3COOH (65 mL) was kept for 20 min at ambient temperature (TLC, solvent B_2), diluted with MePh (200 mL), and evaporated. Solvent H_1 (4 × 200 mL) was evaporated from the residue which was then purified by column chromatography (solvent D) to yield **15** (1.43 g, 90%); mp 167°C (from EtOAc–heptane); $[\alpha]_D^{20}$ $-28.6°$ (c 5.0, MeOH); ^1H NMR ($CDCl_3$, CD_3OD): δ 2.02 (s, 3 H, OAc), 3.44 (s, 3 H, OMe), 3.60 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 3.72 (s, 3 H, CO_2Me), 4.09 (d, 1 H, $J_{5,4}$ 1.4 Hz, H-5), 4.14 (dd, 1 H, H-4), 4.22 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), and 4.90 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2); ^{13}C NMR ($CDCl_3$, CD_3OD): δ 20.7 (CH_3CO), 52.4 (CO_2CH_3), 56.8 (OCH_3), 69.9 (C-4), 71.6 (C-3), 71.8 (C-2), 74.2 (C-5), 101.7 (C-1), 168.7 (C-6), and 171.2 (CH_3CO). *Anal.* Calcd for $C_{10}H_{16}O_8$: C, 45.46; H, 6.10. Found: C, 45.71; H, 6.01.

Methyl (methyl 2-O-acetyl-3-O-trityl-β-D-galactopyranosid)uronate (**16**).—To a solution of **15** (529 mg, 2 mmol) in dry CH_2Cl_2 (15 mL) and 2,4,6-collidine (0.4 mL, 3 mmol) was added $TrClO_4$ (900 mg, 2.6 mmol) with stirring at ambient temperature. After 20 min another portion of 2,4,6-collidine (0.2 mL, 1.5 mmol) and $TrClO_4$ (450 mg, 1.3 mmol) were added. When the reaction was complete (TLC, solvent A_3), the mixture was diluted with $CHCl_3$ (100 mL), washed with ice–water (3 × 30 mL), dried, and evaporated. Column chromatography (EtOAc gradient 12–25% in heptane, containing 0.1% pyridine) was performed to give **16** (912 mg, mp 172°C (from EtOAc– heptane); $[\alpha]_D^{25}$ $+20.4°$ (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.94 (s, 3 H, OAc), 2.47 (dd, 1 H, $J_{OH,5}$ 0.8 Hz, OH-4), 3.19 (m, 1 H, $J_{4,5}$ 1.6, $J_{OH,4}$ 4.6 Hz, H-4), 3.48 (s, 3 H, OMe), 3.68 (dd, 1 H, $J_{3,4}$ 3.7 Hz, H-3), 3.72 (s, 3 H, CO_2Me), 3.72 (d, 1 H, H-5), 4.13 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 5.43 (dd, 1 H, $J_{2,3}$ 9.3 Hz, H-2), and 7.30, 7.57 (2 m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 21.2 (CH_3CO), 52.5 (CO_2CH_3), 56.8 (OCH_3), 68.9 (C-4), 70.1 (C-2), 73.7, 73.8 (C-3, C-5), 88.2 [$C(C_6H_5)_3$], 101.9 (C-1), 127.6, 128.1, 128.8, 144.3 (C_6H_5), 168.2 (C-6), and 169.7 (CH_3CO). *Anal.* Calcd for $C_{29}H_{30}O_8$: C, 68.76; H, 5.97. Found: C, 69.02; H, 6.10.

Methyl (methyl 2,4-di-O-acetyl-3-O-trityl-β-D-galactopyranosid)uronate (**17**).—Compound **16** (507 mg, 1 mmol) was dissolved in a mixture of dry pyridine (18 mL), Ac_2O (6 mL), and 4-dimethylaminopyridine (122 mg, 1 mmol) and kept for 24 h at ambient temperature (TLC, solvent G). EtOH (4 mL) was added at 0°C, and, after 20 min, the mixture was diluted with $CHCl_3$ (100 mL) and poured into ice–water. The phases were separated, and the aqueous phase was extracted with $CHCl_3$ (2 × 50 mL). The combined organic solutions were washed with aq $NaHCO_3$ (3 × 70 mL), ice–water (2 × 70 mL), dried, and evaporated. Traces of pyridine were removed by evaporation with repeated addition of PhMe. The residue was purified by column chromatography (solvent A_5, containing 0.1% pyridine) to yield **17** (521 mg, 95%); mp 177°C (from EtOAc–heptane), $[\alpha]_D^{25}$ $+67.5°$ (c 3.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.85, 2.22 (2 s, 2 × 3 H, OAc), 3.45 (s, 3 H, OMe), 3.52 (dd, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 3.62 (d, 1 H, $J_{5,4}$ 1.5 Hz, H-5), 3.62 (s, 3 H, CO_2Me), 4.04 (d, 1

H, $J_{1,2}$ 8.0 Hz, H-1), 4.62 (d, 1 H, H-4), 5.51 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2), and 7.26, 7.45 (2 m, 15 H, Ph); ^{13}C NMR ($CDCl_3$): δ 21.0, 21.2 (CH_3CO), 52.5 (CO_2CH_3), 57.0 (OCH_3), 70.0 (C-2), 70.6 (C-4), 72.5, 72.6 (C-3, C-5), 88.3 [$C(C_6H_5)_3$], 102.5 (C-1), 127.6, 128.0, 129.0, 144.2 (C_6H_5), 167.2 (C-6), and 169.7, 169.9 (CH_3CO). *Anal.* Calcd for $C_{31}H_{32}O_9$: C, 67.87; H, 5.88. Found: C, 68.01; H, 6.00.

Synthesis of oligosaccharides **20–22**, *and polycondensation of* **13**.—*General procedure.* Solutions of the reagents [1,2-*O*-cyanoethylidene derivative (CED) and 10 mol% excess of trityl ether] in CH_2Cl_2 (1 mL/mmol) and $TrClO_4$ (10 mol% of the amount of CED) in $MeNO_2$ (1 mL/0.1 mmol) were placed in separate limbs of a tuning-fork-shaped tube. The reaction components were dried by a twofold lyophilization (0.4 Pa) with dry PhH and kept for 2 h at 50°C under high vacuum. Then the components were dissolved in CH_2Cl_2 (~2 mL/mmol CED) under reduced pressure, mixed, and kept overnight at ambient temperature in the dark. When the reaction was complete (TLC, solvent A_1), pyridine (0.05 mL/mmol, 2% water) was added. The mixture was filtered, diluted with $CHCl_3$ (50 mL), and washed with water (3 × 20 mL). The organic phase was dried and evaporated. The crude material was purified by column chromatography (EtOAc gradient 9–50% in PhMe).

*Methyl [methyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-rhamnopyranosyl)-β-*D*-galactopyranosid]uronate* (**20**).—Reagents: **17** (604 mg, 1.1 mmol), CED **19** (ref. 12) (299 mg, 1 mmol); initiator: $TrClO_4$ (34 mg, 0.1 mmol); product: **20** (498 mg, 86%); mp 200°C (from $CHCl_3$–hexane), $[\alpha]_D^{25}$ −7.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.20 (d, 3 H, $J_{6',5'}$ 6.0 Hz, H-6′), 1.96, 2.04, 2.18 (3 s, 3 × 3 H, OAc), 2.11 (s, 2 × 3 H, OAc), 3.53 (s, 3 H, OMe), 3.75 (s, 3 H, CO_2Me), 3.91 (dd, 1 H, $J_{2,3}$ 3.7 Hz, H-3), 3.98 (m, 1 H, H-5′), 4.23 (d, 1 H, $J_{5,4}$ 1.3 Hz, H-5), 4.33 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.91 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.97 (dd, 1 H, $J_{2',3'}$ 3.0 Hz, H-2′), 5.04 (t, 1 H, $J_{4',5'}$ 9.0 Hz, H-4′), 5.12 (dd, 1 H, $J_{3',4'}$ 9.9 Hz, H-3′), 5.27 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), and 5.63 (dd, 1 H, H-4); ^{13}C NMR ($CDCl_3$): δ 17.5 (C-6′), 20.6, 20.7, 20.8 (5 C, CH_3CO), 52.6 (CO_2CH_3), 57.0 (OCH_3), 67.6 (C-5′), 68.3 (C-3′), 69.7 (C-4), 70.4 (C-2′), 70.5 (C-2), 70.9 (C-4′), 72.7 (C-5), 76.0 (C-3), 98.7 (C-1′), 102.1 (C-1), 166.7 (C-6), and 169.4, 170.0, 170.1 (5 C, CH_3CO). *Anal.* Calcd for $C_{24}H_{34}O_{16}$: C, 49.83; H, 5.92. Found: C, 50.01; H, 6.15.

*Methyl [allyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-rhamnopyranosyl)-β-*D*-galactopyranosid]uronate* (**21**).—Reagents: **18** (ref. 1) (632 mg, 1.1 mmol), CED **19** (299 mg, 1 mmol); initiator: $TrClO_4$ (34 mg, 0.1 mmol); product: **21** (500 mg, 83%); mp 175–176°C (from EtOAc–heptane); $[\alpha]_D^{26}$ −6.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.17 (d, 3 H, $J_{6',5'}$ 6.2 Hz, H-6′), 1.94, 2.02, 2.09, 2.10, 2.16 (5 s, 5 × 3 H, OAc), 3.73 (s, 3 H, CO_2Me), 3.90 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 3.96 (m, 1 H, H-5′), 4.07 (m, 1 H, $OCH_2CH{=}CH_2$), 4.21 (d, 1 H, $J_{5,4}$ 1.2 Hz, H-5), 4.37 (m, 1 H, $OCH_2CH{=}CH_2$), 4.43 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.88 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1′), 4.93 (dd, 1 H, $J_{2',3'}$ 3.1 Hz, H-2′), 5.02 (dd, 1 H, $J_{4',5'}$ 10.0 Hz, H-4′), 5.09 (dd, 1 H, $J_{3',4'}$ 10.0 Hz, H-3′), 5.16 (m, 1 H, $OCH_2CH{=}CH_2$), 5.22 (m, 1 H, $OCH_2CH{=}CH_2$), 5.27 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2), 5.60 (dd, 1 H, H-4), and 5.79 (m, 1 H,

$OCH_2C\mathit{H}{=}CH_2$); ^{13}C NMR data ($CDCl_3$): δ 17.4 (C-6′), 20.5, 20.6, 20.8 (5 C, $\mathit{C}H_3CO$), 52.6 (OCH_3), 67.4 (C-5′), 68.0 (C-3′), 69.5 (C-4), 69.8 ($O\mathit{C}H_2CH{=}CH_2$), 70.2, 70.3, 70.6 (C-2, C-2′, C-4′), 72.5 (C-5), 75.5 (C-3), 98.3 (C-1′), 99.6 (C-1), 117.5 ($OCH_2CH{=}\mathit{C}H_2$), 133.2 ($OCH_2\mathit{C}H{=}CH_2$), 166.6 (C-6), and 169.3, 169.5, 169.9, 170.0 (5 C, $CH_3\mathit{C}O$). *Anal.* Calcd for $C_{26}H_{36}O_{16}$: C, 51.65; H, 6.00. Found: C, 51.81; H, 5.90.

Methyl {methyl O-*[methyl (2,3,4-tri-*O*-acetyl-β-*D*-galactopyranosyl)uronate]-(1 → 4)-*O*-(2,3-di-*O*-acetyl-α-*L*-rhamnopyranosyl)-(1 → 3)-2,4-di-*O*-acetyl-β-*D*-galactopyranosid}uronate* (**22**).—Reagents: **17** (211 mg, 0.38 mmol), CED **4** (201 mg, 0.35 mmol); initiator: $TrClO_4$ (12 mg, 0.035 mmol); product: **22** as syrup (209 mg, 70%); $[\alpha]_D^{29}$ −2.8° (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.41 (d, 3 H, $J_{6',5'}$ 6.6 Hz, H-6′), 1.96, 2.00, 2.05, 2.07, 2.08, 2.09, 2.14 (7 s, 7 × 3 H, OAc), 3.51 (s, 3 H, OMe), 3.71 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4′), 3.72, 3.75 (2 s, 2 × 3 H, CO_2Me), 3.91 (m, 1 H, H-5′), 3.91 (dd, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 4.22 (d, 1 H, $J_{5,4}$ 1.3 Hz, H-5), 4.31 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.32 (d, 1 H, $J_{5'',4''}$ 1.5 Hz, H-5″), 4.67 (d, 1 H, $J_{1'',2''}$ 8.3 Hz, H-1″), 4.87 (dd, 1 H, $J_{2',3'}$ 6.2 Hz, H-2′), 4.89 (d, 1 H, $J_{1',2'}$ 2.0 Hz, H-1′), 4.98 (dd, 1 H, $J_{3'',4''}$ 3.4 Hz, H-3″), 5.12 (dd, 1 H, $J_{3',4'}$ 10.0 Hz, H-3′), 5.23 (dd, 1 H, $J_{2'',3''}$ 10.9 Hz, H-2″), 5.24 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-2), 5.63 (dd, 1 H, H-4), and 5.66 (dd, 1 H, H-4″); ^{13}C NMR ($CDCl_3$): δ 17.6 (C-6), 20.3, 20.4, 20.5, 20.6, 20.8, 20.9 (7 C, $\mathit{C}H_3CO$), 52.5, 52.6 (2 C, $CO_3\mathit{C}H_3$), 57.0 (OCH_3), 67.9 (C-5′), 68.1 (C-2″), 68.2 (C-4″), 69.4 (C-4), 70.0 (C-3′), 70.5 (2 C, C-2, C-2′), 70.6 (C-3″), 72.1 (C-5″), 72.5 (C-5), 76.0 (C-3), 76.3 (C-4′), 97.9 (C-1′), 100.3 (C-1″), 101.8 (C-1), 166.3, 166.7 (2 C, C-6, C-6″), and 169.3, 169.5, 169.7, 170.0, 170.1 (7 C, $CH_3\mathit{C}O$). *Anal.* Calcd for $C_{35}H_{48}O_{24}$: C, 49.29; H, 5.67. Found: C, 49.50; H, 5.93.

Polycondensation of monomer **13**.—Reagents: monomer **13** (387 mg, 0.5 mmol); initiator: $TrClO_4$ (17 mg, 0.05 mmol), TLC, solvent B_3. The crude material was submitted to column chromatography (PhMe, then solvent H_2) which afforded **23** (175 mg) as an amorphous white solid.

Reaction that determined the degree of polymerization of **23**.—A solution of **23** (110 mg) and 4-methylbenzoyl chloride (0.3 mL) in dry pyridine (3 mL) was kept for 12 h at ambient temperature (TLC, solvent B_4). Then EtOH (3 mL) was added at 0°C, and, after 1 h, the mixture evaporated. The residue was dissolved in $CHCl_3$ (50 mL), the organic layer was washed with H_2O (2 × 30 mL), dried, and evaporated. Column chromatography (PhMe, $CHCl_3$, and then solvent J) was performed to give **24** (100 mg); $[\alpha]_D^{22}$ +3.3° (c 1.0, $CHCl_3$). The ratio of the respective integral intensities of the following signals in the ^{1}H NMR ($CDCl_3$) spectrum were determined: δ 1.2 (9, m, *Me*-Rha) : 2.1 (36, m, $O_2C\mathit{Me}$) : 2.4 (6, s, *Me*-Bz) : 3.6–5.7 (39, m, *H-1-H-5*, $CO_2\mathit{Me}$) : 7.3, 8.0 (8, 2 m, *Ph*).

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