Synthesis of Tetrameric Arabinogalactans Based on 1,2-Anhydrosugars

Cornelis M. Timmers, Suzanne C.M. Wigchert, Michiel A. Leeuwenburgh, Gijsbert A. van der Marel, and Jacques H. van Boom*

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P.O. Box 9502, NL-2300 RA Leiden, The Netherlands
Fax: (internat.) +31(0)71-5274307
E-mail: marel_g@rulgca.leidenuniv.nl

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The spacer-containing tetrameric arabinogalactans **1**–**3**, suitable for CCRC-M7 epitope characterization, are readily accessible by $ZnCl_2$-assisted stepwise elongation of 11-methoxycarbonylundecanol **9** with the 1,2-anhydrogalactose building unit **6**. NIS/*cat.* TfOH-mediated glycosylation of the newly formed 2-OH, 2′-OH, or 2′′-OH function in the β-(1→6)-galactoside backbone with the 1-thioarabinofuranoside donor **8**, followed by deprotection, provided the target tetramers in high overall yield.

Introduction

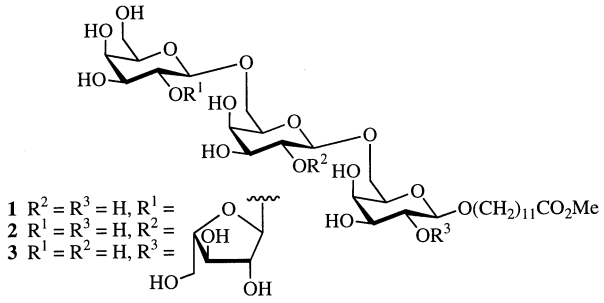
The study of complex carbohydrates present at plant cell-surfaces using monoclonal antibodies is an expanding field of phytobiology.[1] Antibodies generated against specific plant cell-wall carbohydrates may serve as probes in identifying cognate structural elements in outer membrane saccharides of other plant species. The usefulness of this concept relies upon characterization of the epitopes recognized by the antibodies.

Albersheim et al. recently reported[2] the elicitation of several monoclonal antibodies directed against pectic polysaccharide rhamnogalacturonan I (RG-I), isolated from suspension-cultured sycamore maple (*Acer pseudoplatanus*). A representative example of this class of antibodies is CCRC-M7, which recognizes an epitope widely distributed among plant complex carbohydrates, such as RG-I, several arabinogalactans and membrane glycoproteins. It was established[3] that this immunogenic region consists of a β-(1→6)-linked galactan containing at least three D-galactopyranosyl residues functionalized at one hydroxyl function with an α-linked L-arabinofuranosyl unit. In order to study the minimal epitope perceived by CCRC-M7 in more detail, the availability of tetrameric arabinogalactans in which a L-arabinosyl moiety is attached to a predefined position in a trimeric β-(1→6)-linked galactan backbone is highly desirable. We here report the assembly of the tetrameric arabinogalactosides **1**–**3** (see Scheme 1) suitable for further CCRC-M7 epitope characterization.

Results and Discussion

In the target tetramers **1**–**3** the L-arabinosyl residue is either α-anchored to position O-2 (i.e. **3**), O-2′ (i.e. **2**) or O-2′′ (i.e. **1**) of the β-(1→6)-linked galactosyl framework. Furthermore, the reducing end of the arabinogalactosides

Scheme 1



is functionalized with a dodecanoate spacer to enable conjugation to a solid support via a peptide linkage. It occurred to us that the arabinogalactosides **1**–**3** are accessible by oxidative coupling of galactals.[4][5] This methodology comprises stereoselective epoxidation of a suitably protected galactal with 3,3-dimethyldioxirane (DMD)[6] followed by $ZnCl_2$-catalyzed condensation of the resulting 1,2-anhydrosugar with a galactal acceptor to give a dimeric galactal. The oligosaccharide chain may then be iteratively elongated from the non-reducing end using an excess of glycal acceptor. A propitious feature of the glycal approach is the formation of an unprotected 2-hydroxyl function, which is amenable to direct arabinosylation. Earlier studies from our laboratory revealed[7] that ethyl 1-thiofuranosides are useful starting compounds for the introduction of furanoside residues in oligosaccharides. However, the presence of a glycal function in the growing β-(1→6)-linked galactoside backbone excludes iodonium ion-mediated arabinosylation of the 2-OH group with a thioethyl donor. Iodonation of the enol ether moiety could be circumvented by stepwise extension of the galactoside framework from the reducing end (i.e. the spacer moiety) via condensation of the acceptor

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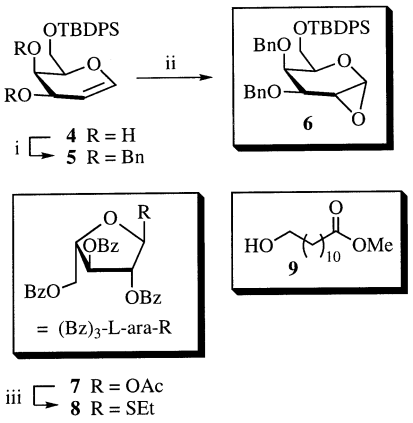
function in the growing chain with an excess of monomeric 1,2-anhydrogalactose donor.

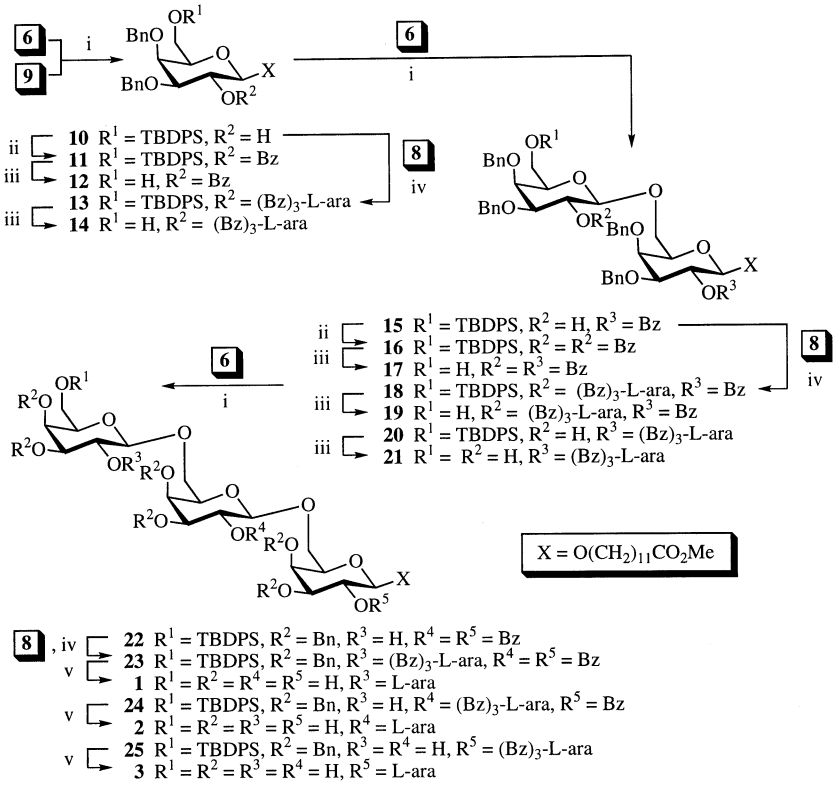
Scheme 2. Reagents and conditions: (i) NaH, BnBr, Ph_3PMeI, THF, 30 °C, 3 h, 82%; (ii) 3,3-dimethyldioxirane, CH_2Cl_2/acetone, 0 °C, 1 min, quant.; (iii) EtSH, $SnCl_4$, toluene, 0 °C, 1 h, 72%.



Based on the above described considerations, the synthesis of target molecules **1**–**3**, starting from the 1,2-anhydrogalactose derivative **6** (see Scheme 2), thioethyl L-arabinofuranosyl donor **8** and spacer alcohol **9**,[8] was undertaken. Zinc chloride-assisted condensation of donor **6**, prepared by benzylation of known[9] 6-*O*-*tert*-butyldiphenylsilyl (TBDPS)-D-galactal **4** and subsequent DMD-mediated epoxidation of fully protected galactal **5**, with methoxycarbonylundecanol **9** gave exclusively the β-linked spacer-containing galactoside **10** (see Scheme 3) in 78% yield. Glycosylation of the 2-OH in **10** with ethyl 1-thio-arabinofuranoside donor **8**, obtained by $SnCl_4$-mediated thioethylation of previously described[10] arabinofuranosyl acetate **7**, under the agency of *N*-iodosuccinimide (NIS) and catalytic triflic acid (TfOH),[11] proceeded stereoselectively to afford the α-linked dimer **13** in a yield of 91%. Tetra-*n*-butylammonium fluoride (TBAF)-mediated desilylation of **13** and stereoselective condensation of the primary hydroxyl in **14** with the 1,2-anhydrogalactose **6** led to the isolation of trimer **20**. Repetition of the latter sequence of reactions, i.e. desilylation of **20**, followed by regioselective coupling of the primary hydroxyl in **21** with donor **6**, furnished the tetrameric fragment **25**. Removal of the silyl protective group in **25** with TBAF, Zemplén debenzoylation, and then hydrogenolysis gave the target tetrasaccharide **3** (64% overall yield), the spectral data of which were in full accord with the proposed structure.

Isomer **2**, bearing one arabinosyl residue at position O-2′ of the trimeric galactosyl backbone, was constructed in a similar fashion starting from galactoside **10**. In order to prevent undesired arabinosylation, the free 2-hydroxyl in **10** was benzoylated. Desilylation of the fully protected galactoside **11** gave the partially protected monomeric building unit **12**. $ZnCl_2$-catalyzed elongation of **12** with 1,2-anhydro-

Scheme 3. Reagents and conditions: (i) $ZnCl_2$, THF, 0 °C, 10 min, **10**: 78%, **15**: 71%, **20**: 68%, **22**: 67%, **24**: 63%, **25**: 60%; (ii) BzCl, pyr, 2–3 h, **11**: 91%, **16**: 90%; (iii) TBAF, THF, 3–5 h, **12**: 82%, **14**: 80%, **17**: 76%, **19**: 81%, **21**: 76%; (iv) NIS, *cat.* TfOH, $ClCH_2CH_2Cl$/THF (3:1, v/v), 0 °C, 1 h, **13**: 91%, **18**: 69%, **23**: 82%; (v) a. TBAF, THF, 3–5 h; b. KO*t*Bu, CH_2Cl_2/MeOH (1:2, v/v), 30 min; c. H_2 (3 atm.), Pd/C, *t*BuOH/H_2O (3:1, v/v), 12 h, **1**: 66%, **2**: 70%, **3**: 64%



galactose **6** led to the exclusive formation of the β-linked dimer **15**, the 2′-hydroxyl of which was arabinosylated with donor **8** under the agency of NIS/*cat.* TfOH, affording the fully protected trimer **18** in 49% overall yield from **12**. Desilylation of **18** and introduction of the terminal galactosyl residue by $ZnCl_2$-assisted condensation of trimer **19** with 1,2-oxirane **6** led to the tetrasaccharide **24**, deprotection of which gave homogeneous arabinogalactoside **2** (70% yield).

The assembly of target tetrasaccharide **1** commences with the benzoylation of dimer **15** to give the fully protected digalactoside **16**. Removal of the TBDPS-group in **16** followed by stereoselective $ZnCl_2$-assisted condensation of disaccharide **17** with 1,2-anhydrogalactose **6** furnished trimer **22** in 51% overall yield. Finally, arabinosylation of the 2′′-hydroxyl in **22** by coupling with thioethyl donor **8** provided the fully protected tetrameric fragment **23**, which was further processed to give the deprotected galactoside **1** (66% yield). The biological activity of tetramers **1**−**3** is presently under investigation.[12]

Conclusion

The stereoselective assembly of arabinogalactosides **1**−**3** illustrates that (1→2)-branched oligosaccharides are readily accessible via stepwise elongation of the sugar chain from the reducing end with 1,2-anhydroglycoside building blocks (e.g. **6**). Moreover, the absence of a glycal function in the growing chain permits iodonium ion-mediated glycosylation of the free 2-OH function with thioethyl donors (e.g. **8**). Extension of this so-called "reversed glycal approach" to a solid support is currently under investigation.

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Experimental Section

General: ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Jeol JNM-FX-200 (200/50.1 MHz), a Bruker WM-300 (300/75.1 MHz), or a Bruker DMX-600 spectrometer (600/150.3 MHz). Chemical shifts are given in ppm (δ) relative to tetramethylsilane as internal standard. − Mass spectra were recorded on a Finnigan MAT TSQ70 triple quadrupole mass spectrometer. − Optical rotations were determined using a Propol automatic polarimeter. − Dichloromethane, pyridine and toluene were boiled under reflux with CaH_2 for 3 h, distilled, and stored over molecular sieves (4 Å). Triethylamine was distilled from CaH_2. Acetone (Boom Chemicals, c.p.), 1,2-dichloroethane (Biosolve, HPLC-grade), *N,N*-dimethylformamide (DMF, Baker, p.a.), dimethyl sulfoxide (DMSO, Baker, p.a.), 1,4-dioxane (Baker, p.a.), and tetrahydrofuran (THF, Biosolve, HPLC-grade) were stored over molecular sieves (4 Å). Methanol (Biosolve, HPLC-grade) was stored over molecular sieves (3 Å). Zinc chloride ($ZnCl_2$, Merck, p.a.) was dissolved in THF (1.0 M solution) and stored over molecular sieves (3 Å). Benzoyl chloride (Merck), benzyl bromide (Merck), *tert*-butyldiphenylsilyl chloride (TBDPSCl, Acros), ethanethiol (Fluka), *N*-iodosuccinimide (NIS, Aldrich), methyltriphenylphosphonium iodide (Aldrich), oxone® (Aldrich), and trifluoromethanesulfonic acid (TfOH, Fluka) were used as received. − Column chromatography was performed on Merck Kieselgel 60 (230−400 mesh). − Gel permeation chromatography was accomplished on Sephadex LH-20 (Pharmacia). − TLC-analysis was carried out on DC-Fertigfolien (Schleicher & Schüll F1500, LS254) with detection by UV-absorption (254 nm) where applicable and charring with 20% H_2SO_4 in MeOH or ammonium molybdate (25 g/l) and ceric ammonium sulfate (10 g/l) in 10% aq. H_2SO_4. − Reactions were run at ambient temperature, unless otherwise stated. Traces of water in the glycosides were removed by coevaporation with acetonitrile, 1,2-dichloroethane, pyridine or toluene.

1,5-Anhydro-2-deoxy-3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-D-lyxo-hex-1-enitol (**5**): A solution of 6-*O*-*tert*-butyldiphenylsilyl-D-galactal[9] (**4**, 3.84 g, 10.0 mmol) in THF (30 ml) was heated to 30 °C. To this solution, NaH (60% dispersion in mineral oil, 2.4 g, 60 mmol) was added and the mixture was stirred for 10 min. Subsequently, methyltriphenylphosphonium iodide (8.1 g, 20 mmol) and benzyl bromide (7.2 ml, 60 mmol) were added and the reaction mixture was stirred at 30 °C for 3 h. Methanol (3 ml) was added and the heterogeneous mixture was concentrated in vacuo. The residue was dissolved in diethyl ether (200 ml), washed with sat. aq. NaCl (3 × 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue was effected by silica gel chromatography (0−10% EtOAc/light petroleum) to give fully protected galactal **5** (4.62 g, 8.2 mmol, 82%) as a colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 7.65−7.23 (m, 20 H, H_{arom}), 6.25 (dd, 1 H, H^1, $J_{1,2}$ = 6.2 Hz, $J_{1,3}$ = 1.0 Hz), 4.80 (dd, 1 H, H^2, $J_{2,3}$ = 0.9 Hz), 4.82 (AB, 2 H, CH_2 Bn), 4.60 (AB, 2 H, CH_2 Bn), 4.10 (ddd, 1 H, H^3, $J_{3,4}$ = 4.0 Hz), 3.91 (dd, 1 H, H^4, $J_{4,5}$ = 3.4 Hz), 3.89−3.78 (m, 3 H, H^5/H^6/$H^{6'}$), 1.03 (s, 9 H, CH_3 *t*Bu). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 144.3 (C^1), 138.8, 138.5 (C^q Bn), 135.8−127.5 (C_{arom}), 133.7, 133.3 (C^q TBDPS), 100.0 (C^2), 77.5, 71.7, 71.2 (C^3/C^4/C^5), 73.6, 71.0 (CH_2 Bn), 62.3 (C^6), 27.0 (CH_3 *t*Bu), 19.5 (C^q *t*Bu).

1,2-Anhydro-3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-α-D-galactopyranose (**6**): To a stirred and cooled (0 °C) solution of galactal **5** (2.82 g, 5.0 mmol) in CH_2Cl_2 (10 ml) a freshly prepared solution of 3,3-dimethyldioxirane (DMD, 67 ml, 0.09 M, 6.0 mmol) in acetone was added dropwise. Immediately after the last addition, the reaction mixture was concentrated under reduced pressure to afford epoxide **6** as a white solid in quantitative yield (2.90 g, 5.0 mmol). − ^{1}H NMR ($CDCl_3$): δ = 7.71−7.25 (m, 20 H, H_{arom}), 4.90 (d, 1 H, H^1, $J_{1,2}$ = 3.8 Hz), 4.76 (AB, 2 H, CH_2 Bn), 4.58 (AB, 2 H, CH_2 Bn), 3.92 (dd, 1 H, H^3, $J_{2,3}$ = 1.4 Hz, $J_{3,4}$ = 3.0 Hz), 3.71 (dd, 1 H, H^4, $J_{4,5}$ = 4.3 Hz), 3.67 (m, 1 H, H^5), 3.64 (dd, 1 H, H^6, $J_{5,6}$ = 3.5 Hz, $J_{6,6'}$ = 10.8 Hz), 3.52 (dd, 1 H, $H^{6'}$, $J_{5,6'}$ = 1.9 Hz), 3.12 (dd, 1 H, H^2), 1.04 (s, 9 H, CH_3 *t*Bu). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 138.2, 137.4 (C^q Bn), 135.0−127.0 (C_{arom}), 132.7, 132.6 (C^q TBDPS), 76.6 (C^1), 76.2, 71.7, 69.1 (C^3/C^4/C^5), 74.3, 71.0 (CH_2 Bn), 61.7 (C^6), 51.2 (C^2), 26.4 (CH_3 *t*Bu), 18.7 (C^q *t*Bu).

Ethyl 2,3,5-Tri-O-benzoyl-1-thio-α-L-arabinofuranoside (**8**): To a cooled (0 °C) and stirred solution of arabinofuranosyl acetate **7**[11] (5.04 g, 10 mmol) and ethanethiol (0.81 ml, 11 mmol) in toluene (20 ml), tin tetrachloride ($SnCl_4$, 0.12 ml, 1.0 mmol) was added dropwise. The reaction mixture was stirred for 1 h after which triethylamine (1 ml) and diethyl ether (250 ml) were sequentially added. The resulting solution was washed with aq. KF (1.0 M, 2 × 50 ml) and aq. $NaHCO_3$ (1.0 M, 2 × 50 ml), dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue was effected by silica gel chromatography (10−30% EtOAc/light petroleum) to give **8** as an oil, which was crystallized from EtOH (50 ml), resulting in the isolation of **8** as colorless needles (3.64 g, 7.2 mmol, 72%). − mp. 70−72 °C. − $[\alpha]_D$ = −34.4 (*c* = 1, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 8.12−7.25 (m, 15 H, H_{arom}), 5.64 (dd, 1 H, H^3, $J_{2,3}$ = 3.6 Hz, $J_{3,4}$ = 1.9 Hz), 5.60 (d, 1 H, H^1, $J_{1,2}$ = 1.9 Hz), 5.56 (dd,

1 H, H^2), 4.86 (dd, 1 H, H^5, $J_{4,5}$ = 3.1 Hz, $J_{5,5'}$ = 10.2 Hz), 4.77−4.71 (m, 2 H, $H^4/H^{5'}$), 2.77 (q, 2 H, CH_2 Et), 1.36 (t, 3 H, CH_3 Et). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 165.6, 165.1, 164.9 (C=O Bz), 133.1−127.9 (C_{arom}), 128.5 (C^q Bz), 87.7 (C^1), 82.6, 80.3, 77.8 ($C^2/C^3/C^4$), 63.0 (C^5), 24.8 (CH_2 Et), 14.5 (CH_3 Et). − $C_{28}H_{26}O_7S$ (506.1): calcd. C 66.39; H 5.17; found: C 66.28; H 5.22.

General Procedure for the Introduction of β-(1→6)-Galactosidic Linkages: To a stirred and cooled (0 °C) solution of the appropriate glycosyl acceptor (1.0 mmol) and 1,2-anhydrogalactose **6** (0.87 g, 1.5 mmol) in THF (5 ml) was added dropwise, under a continuous stream of dry nitrogen, a solution of $ZnCl_2$ in THF (1.0 M, 2.5 ml, 2.5 mmol). The reaction mixture was stirred for 10 min, after which the solution was diluted with EtOAc (100 ml), washed with sat. aq. NaCl (3 × 25 ml) and aq. $NaHCO_3$ (1.0 M, 25 ml), dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue was accomplished by silica gel chromatography (0−50% EtOAc/light petroleum) and Sephadex LH-20 gel filtration (eluent: CH_2Cl_2/MeOH, 2:1, v/v) to give the respective oligomer as a white solid.

11-Methoxycarbonylundecanyl 3,4-Di-O-benzyl-6-O-tert-butyldiphenylsilyl-β-D-galactopyranoside (**10**): Yield: 1.90 g, 2.34 mmol, 78% based on 0.690 g, 3.00 mmol of **9**. − ^1H NMR ($CDCl_3$): δ = 7.64−7.19 (m, 20 H, H_{arom}), 4.77 (AB, 2 H, CH_2 Bn), 4.74 (bs, 2 H, CH_2 Bn), 4.15 (d, 1 H, H^1, $J_{1,2}$ = 7.3 Hz), 4.13 (dd, 1 H, H^2, $J_{2,3}$ = 9.0 Hz), 3.95 (m, 3 H, CH_2O spacer, H^5), 3.79 (dd, 1 H, H^3, $J_{3,4}$ = 2.6 Hz), 3.74 (t, 1 H, H^4, $J_{4,5}$ = 2.4 Hz), 3.66 (s, 3 H, OMe), 3.48 (dd, 1 H, H^6, $J_{5,6}$ = 2.9 Hz, $J_{6,6'}$ = 10.4 Hz), 3.39 (dd, 1 H, $H^{6'}$, $J_{5,6'}$ = 4.0 Hz), 2.40 (bs, 1 H, OH), 2.34 (t, 2 H, CH_2C=O spacer), 1.58−1.00 (m, 18 H, CH_2 spacer), 1.05 (s, 9 H, CH_3 *t*Bu). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.1 (C=O spacer), 138.5, 138.2 (C^q Bn), 135.3−127.1 (C_{arom}), 132.7 (C^q TBDPS), 103.1 (C^1, $J_{C,H}$ = 161.2 Hz), 81.8, 74.9, 73.2, 71.3 ($C^2/C^3/C^4/C^5$), 74.4, 72.4 (CH_2 Bn), 69.6 (CH_2O spacer), 62.3 (C^6), 51.1 (OMe), 33.8 (*C*H_2C=O spacer), 29.3, 29.3, 29.2, 29.2, 29.1, 29.0, 28.9, 25.7, 24.7 (CH_2 spacer), 26.7 (CH_3 *t*Bu), 19.0 (C^q *t*Bu). − MS (ESI): *m/z* = 811 $[M + H]^+$, 828 $[M + NH_4]^+$, 833 $[M + Na]^+$. − $C_{49}H_{66}O_8Si$ (810.5): C, 72.56; H 8.20; Si 3.46; found: C, 72.42; H 8.26; Si 3.50.

General Procedure for 2-O-Benzoylation: Benzoyl chloride (0.17 ml, 1.5 mmol) was added to a stirred solution of the appropriate oligomer (1.0 mmol) in pyridine (5 ml). The reaction mixture was stirred until TLC analysis (30% EtOAc/light petroleum) revealed complete consumption of the starting compound (2−3 h). Water (1.0 ml) was added and the reaction mixture was concentrated in vacuo. The residue was taken up in diethyl ether (100 ml), washed with aq. $NaHCO_3$ (1.0 M, 2 × 25 ml), dried ($MgSO_4$), and concentrated under reduced pressure. Traces of pyridine in the residue were removed by coevaporation with toluene (3 × 25 ml). Further purification was effected by silica gel chromatography (0−25% EtOAc/light petroleum) to give the respective oligomer as a white solid.

11-Methoxycarbonylundecanyl 2-O-benzoyl-3,4-di-O-benzyl-6-O-tert-butyl-diphenylsilyl-β-D-galactopyranoside (**11**): Yield: 1.30 g, 1.42 mmol, 91% based on 1.26 g, 1.56 mmol of **10**. − ^1H NMR ($CDCl_3$): δ = 8.62−7.19 (m, 25 H, H_{arom}), 5.61 (dd, 1 H, H^2, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 8.9 Hz), 4.90 (AB, 2 H, CH_2 Bn), 4.76 (AB, 2 H, CH_2 Bn), 4.41 (d, 1 H, H^1), 4.03 (d, 1 H, H^4, $J_{3,4}$ = 2.6 Hz), 3.92−3.87 (m, 3 H, $H^3/H^5/H^6$), 3.71 (m, 2 H, CH_2O spacer), 3.66 (s, 3 H, OMe), 3.48 (dd, 1 H, $H^{6'}$, $J_{5,6'}$ = 4.0 Hz, $J_{6,6'}$ = 10.7 Hz), 2.29 (t, 2 H, CH_2C=O spacer), 1.78−0.84 (m, 18 H, CH_2 spacer), 1.06 (s, 9 H, CH_3 *t*Bu). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.0 (C=O spacer), 164.8 (C=O Bz), 138.2, 137.4 (C^q Bn), 135.5−127.0 (C_{arom}), 132.9 (C^q TBDPS), 130.1 (C^q Bz), 101.1 (C^1), 79.7, 74.8, 72.5, 71.8 ($C^2/C^3/C^4/C^5$), 74.1, 71.6 (CH_2 Bn), 69.0 (CH_2O spacer), 62.2 (C^6), 50.9 (OMe), 33.7 (*C*H_2C=O spacer), 29.0, 29.0, 28.9, 28.8, 28.7, 28.6, 28.5, 25.4, 24.6 (CH_2 spacer), 26.5 (CH_3 *t*Bu), 18.8 (C^q *t*Bu).

General Procedure for 6-O-Desilylation: Tetra-*n*-butylammonium fluoride (1.0 M solution in THF, 1.5 ml, 1.5 mmol) was added to a stirred solution of the appropriate 6-*O*-TBDPS ether (1.0 mmol) in THF (5 ml). When TLC-analysis (50% EtOAc/light petroleum) showed complete disappearance of the starting compound (3−5 h) the reaction mixture was diluted with EtOAc (100 ml) and washed with sat. aq. NaCl (3 × 25 ml). The organic phase was dried ($MgSO_4$), and concentrated in vacuo, after which the residue was purified by silica gel chromatography (20−50% EtOAc/light petroleum) to furnish the corresponding primary alcohol as a white solid.

11-Methoxycarbonylundecanyl 2-O-Benzoyl-3,4-di-O-benzyl-β-D-galactopyranoside (**12**): Yield: 0.787 g, 1.16 mmol, 82% based on 1.30 g, 1.42 mmol of **11**. − ^1H NMR ($CDCl_3$): δ = 8.05−7.19 (m, 15 H, H_{arom}), 5.65 (dd, 1 H, H^2, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 8.7 Hz), 4.87 (AB, 2 H, CH_2 Bn), 4.77 (AB, 2 H, CH_2 Bn), 4.32 (d, 1 H, H^1), 3.90 (d, 1 H, H^4, $J_{3,4}$ = 2.6 Hz), 3.82 (dd, 1 H, H^3), 3.72−3.68 (m, 2 H, H^5/H^6), 3.78 (m, 2 H, CH_2O spacer), 3.66 (s, 3 H, OMe), 3.49 (dd, 1 H, $H^{6'}$, $J_{5,6'}$ = 4.2 Hz, $J_{6,6'}$ = 11.0 Hz), 2.29 (t, 2 H, CH_2C=O spacer), 1.72−0.96 (m, 18 H, CH_2 spacer). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.6 (C=O spacer), 164.7 (C=O Bz), 138.0, 137.3 (C^q Bn), 132.3−127.0 (C_{arom}), 129.8 (C^q Bz), 101.1 (C^1), 79.4, 74.7, 72.2, 71.6 ($C^2/C^3/C^4/C^5$), 73.8, 71.1 (CH_2 Bn), 69.0 (CH_2O spacer), 60.9 (C^6), 50.7 (OMe), 33.4 (*C*H_2C=O spacer), 28.9, 28.8, 28.6, 28.5, 28.4, 28.3, 28.3, 25.3, 24.4 (CH_2 spacer).

General Procedure for 2-O-Arabinosylation: A mixture of the appropriate glycosyl acceptor (1.0 mmol), thioethyl L-arabinofuranosyl donor **8** (0.61 g, 1.2 mmol), powdered molecular sieves (4 Å, 0.1 g) in 1,2-dichloroethane (3 ml) was stirred at 0 °C under a continuous stream of dry nitrogen for 30 min. Subsequently, a freshly prepared solution of NIS (0.27 g, 1.2 mmol) and TfOH (5 µl) in THF (1.0 ml) was added dropwise to the cooled solution and the reaction mixture was stirred for 1 h. Next, the reaction mixture was quenched with triethylamine (0.5 ml), diluted with EtOAc (50 ml), filtered and the filtrate was washed with aq. $Na_2S_2O_3$ (1.0 M, 2 × 25 ml) and aq. $NaHCO_3$ (1.0 M, 2 × 25 ml). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The resulting yellow oil was purified by silica gel chromatography (10−40% EtOAc/light petroleum) and Sephadex LH-20 gel filtration (eluent: CH_2Cl_2/MeOH, 2:1, v/v) to give the corresponding oligosaccharide as a white foam.

11-Methoxycarbonylundecanyl 2-O-(2,3,5-Tri-O-benzoyl-α-L-arabinofuranosyl)-3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-β-D-galactopyranoside (**13**): Yield: 0.891 g, 0.71 mmol, 91% based on 0.632 g, 0.78 mmol of **10**. − ^1H NMR ($CDCl_3$): δ = 8.17−7.12 (m, 35 H, H_{arom}), 5.58 (dd, 1 H, H^3-ara, $J_{2,3}$ = 0.7 Hz, $J_{3,4}$ = 1.2 Hz), 5.53 (d, 1 H, H^1-ara, $J_{1,2}$ = 5.0 Hz), 4.89 (m, 1 H, H^4-ara), 4.78 (dd, 1 H, H^{5A}-ara, $J_{4,5A}$ = 3.1 Hz, $J_{5A,5B}$ = 12.1 Hz), 4.76 (AB, 2 H, CH_2 Bn), 4.74 (bs, 2 H, CH_2 Bn), 4.72 (dd, 1 H, H^2-ara), 4.69 (dd, 1 H, H^{5B}-ara, $J_{4,5B}$ = 4.7 Hz), 4.28 (d, 1 H, H^1, $J_{1,2}$ = 7.7 Hz), 4.21 (dd, 1 H, H^2, $J_{2,3}$ = 9.4 Hz), 3.96 (d, 1 H, H^4, $J_{4,5}$ = 2.3 Hz), 3.78 (d, 1 H, H^3), 3.75 (dd, 1 H, H^{6A}, $J_{5,6A}$ = 2.0 Hz, $J_{6A,6B}$ = 10.9 Hz), 3.65 (s, 3 H, OMe), 3.62 (dd, 1 H, H^{6B}, $J_{5,6B}$ = 3.6 Hz), 3.47 (m, 2 H, CH_2O spacer), 3.23 (dt, 1 H, H^5), 2.25 (t, 2 H, CH_2C=O spacer), 1.70−0.89 (m, 18 H, CH_2 spacer), 1.05 (s, 9 H, CH_3 *t*Bu). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.6 (C=O spacer), 165.7, 165.3, 164.9 (C=O Bz), 138.2, 137.5 (C^q Bn), 135.1−127.0 (C_{arom}), 132.9 (C^q TBDPS), 129.0, 128.9, 128.8 (C^q Bz), 105.2 (C^1-ara, $J_{C,H}$ = 180.2 Hz), 101.8 (C^1, $J_{C,H}$ = 161.2 Hz), 83.3, 81.8, 80.6,

78.1, 74.6, 72.7, 72.6 (C^2/C^3/C^4/C^5/C^2-ara/C^3-ara/C^4-ara), 74.5, 72.2 (CH_2 Bn), 69.5 (CH_2O spacer), 63.5 (C^5-ara), 62.4 (C^6), 50.9 (OMe), 33.6 (*C*H_2C=O spacer), 29.3, 29.1, 29.0, 28.9, 28.9, 28.8, 28.7, 25.5, 24.6 (CH_2 spacer), 26.5 (CH_3 *t*Bu), 18.8 (C^q *t*Bu). – MS (ESI): *m/z* = 1256 $[M + H]^+$, 1273 $[M + NH_4]^+$, 1278 $[M + Na]^+$. – $C_{75}H_{86}O_{15}Si$ (1254.6): C, 71.75; H 6.90; Si 2.24; found: C, 71.70; H 6.96; Si 2.29.

11-Methoxycarbonylundecanyl 2-O-(2,3,5-Tri-O-benzoyl-α-L-arabinofuranosyl)-3,4-di-O-benzyl-β-D-galactopyranoside (**14**): Yield: 0.577 g, 0.57 mmol, 80% based on 0.891 g, 0.71 mmol of **13**. – ^{1}H NMR ($CDCl_3$): δ = 8.11–7.20 (m, 25 H, H_{arom}), 5.56 (dd, 1 H, H^3-ara, $J_{2,3}$ = 0.9 Hz, $J_{3,4}$ = 1.3 Hz), 5.54 (d, 1 H, H^1-ara, $J_{1,2}$ = 5.0 Hz), 4.92 (m, 1 H, H^4-ara), 4.80 (dd, 1 H, H^{5A}-ara, $J_{4,5A}$ = 3.1 Hz, $J_{5A,5B}$ = 12.0 Hz), 4.77 (AB, 2 H, CH_2 Bn), 4.74 (bs, 2 H, CH_2 Bn), 4.72 (dd, 1 H, H^2-ara), 4.68 (dd, 1 H, H^{5B}-ara, $J_{4,5B}$ = 1.8 Hz), 4.34 (d, 1 H, H^1, $J_{1,2}$ = 7.2 Hz), 4.26 (dd, 1 H, H^2, $J_{2,3}$ = 8.0 Hz), 3.83 (d, 1 H, H^4, $J_{3,4}$ = 2.6 Hz), 3.80–3.75 (m, 2 H, H^3/H^{6A}), 3.70 (dd, 1 H, H^{6B}, $J_{5,6B}$ = 3.0 Hz, $J_{6A,6B}$ = 11.0 Hz), 3.66 (s, 3 H, OMe), 3.50 (m, 2 H, CH_2O spacer), 3.32 (dd, 1 H, H^5, $J_{5,6A}$ = 4.2 Hz), 2.28 (t, 2 H, CH_2C=O spacer), 1.72 (bs, 1 H, OH), 1.68–0.94 (m, 18 H, CH_2 spacer). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 172.0 (C=O spacer), 165.8, 165.7, 165.5 (C=O Bz), 138.1, 137.5 (C^q Bn), 133.3–127.6 (C_{arom}), 129.4, 129.3, 129.3 (C^q Bz), 105.4 (C^1-ara), 102.1 (C^1), 83.6, 81.9, 80.8, 78.2, 74.5, 72.7, 71.9 (C^2/C^3/C^4/C^5/C^2-ara/C^3-ara/C^4-ara), 74.0, 72.6 (CH_2 Bn), 70.0 (CH_2O spacer), 63.7 (C^5-ara), 61.8 (C^6), 51.2 (OMe), 33.9 (*C*H_2C=O spacer), 29.6, 29.3, 29.2, 29.2, 29.1, 29.1, 29.0, 25.7, 24.8 (CH^2 spacer).

11-Methoxycarbonylundecanyl 2-O-Benzoyl-3,4-di-O-benzyl-6-O-(3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-β-D-galactopyranosyl)-β-D-galactopyranoside (**15**): Yield: 1.04 g, 0.82 mmol, 71% based on 0.787 g, 1.16 mmol of **12**. – ^{1}H NMR ($CDCl_3$): δ = 8.11–7.10 (m, 35 H, H_{arom}), 5.59 (dd, 1 H, H^2, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 10.1 Hz), 4.91 (AB, 2 H, CH_2 Bn), 4.74 (AB, 2 H, CH_2 Bn), 4.62 (AB, 2 H, CH_2 Bn), 4.59 (AB, 2 H, CH_2 Bn), 4.43 (d, 1 H, H^1), 4.25 (d, 1 H, $H^{1'}$, $J_{1',2'}$ = 7.7 Hz), 4.00 (m, 1 H, $H^{5'}$), 3.87 (d, 1 H, H^4, $J_{3,4}$ = 2.4 Hz), 3.82 (t, 1 H, $H^{2'}$, $J_{2',3'}$ = 7.8 Hz), 3.78–3.72 (m, 4 H, $H^{3'}$/$H^{4'}$/$H^{5'}$/CHO spacer), 3.69 (m, 2 H, H^5/H^{6A}), 3.66 (s, 3 H, OMe), 3.61 (dd, 1 H, H^3), 3.57 (dd, 1 H, H^{6B}, $J_{5,6B}$ = 2.9 Hz, $J_{6A,6B}$ = 10.7 Hz), 3.40 (m, 3 H, $H^{6'A}$/$H^{6'B}$/CHO spacer), 2.32 (t, 2 H, CH_2C=O spacer), 1.74–0.92 (m, 18 H, CH_2 spacer), 1.01 (s, 9 H, CH_3 *t*Bu). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 172.9 (C=O spacer), 165.0 (C=O Bz), 138.6, 138.0, 137.9, 137.4 (C^q Bn), 135.3–127.1 (C_{arom}), 132.9 (C^q TBDPS), 130.1 (C^q Bz), 103.3 (C^1/$C^{1'}$, $J_{C,H}$ = 162.7 Hz), 101.3 (C^1/$C^{1'}$, $J_{C,H}$ = 158.5 Hz), 81.8, 79.6, 74.6, 73.8, 73.0, 72.1, 71.7, 71.2 (C^2/C^3/C^4/C^5/$C^{2'}$/$C^{3'}$/$C^{4'}$/$C^{5'}$), 74.5, 74.0, 72.3, 72.2 (CH_2 Bn), 69.4 (CH_2O spacer), 68.2 (C^6), 61.6 ($C^{6'}$), 51.2 (OMe), 33.8 (*C*H_2C=O spacer), 29.2, 29.1, 29.0, 28.9, 28.7, 28.6, 28.4, 25.6, 24.7 (CH_2 spacer), 26.7 (CH_3 *t*Bu), 19.0 (C_q *t*Bu). – MS (ESI): *m/z* = 1258 $[M + H]^+$, 1280 $[M + Na]^+$. – $C_{76}H_{92}O_{14}Si$ (1256.6): C, 72.58; H 7.37; Si 2.23; found: C, 72.54; H 7.50; Si 2.21.

11-Methoxycarbonylundecanyl 2-O-Benzoyl-6-O-(2-O-benzoyl-3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-β-D-galactopyranosyl)-3,4-di-O-benzyl-β-D-galactopyranoside (**16**): Yield: 0.503 g, 0.37 mmol, 90% based on 0.521 g, 0.41 mmol of **15**. – ^{1}H NMR ($CDCl_3$): δ = 7.91–7.14 (m, 40 H, H_{arom}), 5.59 (dd, 1 H, H^2, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 10.0 Hz), 5.47 (dd, 1 H, $H^{2'}$, $J_{1',2'}$ = 8.0 Hz, $J_{2',3'}$ = 10.0 Hz), 4.93 (AB, 2 H, CH_2 Bn), 4.67 (AB, 2 H, CH_2 Bn), 4.52 (AB, 2 H, CH_2 Bn), 4.48 (d, 1 H, H^1), 4.43 (AB, 2 H, CH^2 Bn), 4.21 (d, 1 H, $H^{1'}$), 4.09 (d, 1 H, H^4, $J_{3,4}$ = 2.3 Hz), 3.90 (t, 1 H, H^5, $J_{5,6A}$ = $J_{5,6B}$ = 5.9 Hz), 3.80 (m, 2 H, H^{6A}/$H^{6'A}$), 3.73 (d, 1 H, $H^{4'}$, $J_{3',4'}$ = 2.6 Hz), 3.67 (s, 3 H, OMe), 3.64 (dd, 1 H, H^3), 3.61 (dd, 1 H, $H^{5'}$, $J_{5',6'A}$ = 4.0 Hz, $J_{5',6'B}$ = 6.2 Hz), 3.48 (m, 2 H, H^{6B}/CHO spacer), 3.42 (dd, 1 H, $H^{6'B}$, $J_{6'A,6'B}$ = 11.0 Hz), 3.39 (dd, 1 H, $H^{3'}$), 3.05 (m, 1 H, CHO spacer), 2.34 (t, 2 H, CH_2C=O spacer), 1.68–0.92 (m, 18 H, CH_2 spacer), 1.07 (s, 9 H, CH_3 *t*Bu). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.9 (C=O spacer), 164.9, 164.8 (C=O Bz), 138.3, 138.0, 137.4, 137.3 (C^q Bn), 135.2–127.1 (C_{arom}), 132.9 (C^q TBDPS), 130.1, 129.9 (C^q Bz), 101.2, 101.0 (C^1/$C^{1'}$), 79.5, 79.5, 74.5, 73.5, 72.5, 72.2, 72.0, 71.6 (C^2/C^3/C^4/C^5/$C^{2'}$/$C^{3'}$/$C^{4'}$/$C^{5'}$), 74.5, 74.1, 71.7, 71.3 (CH_2 Bn), 68.9 (CH_2O spacer), 67.9 (C^6), 61.6 ($C^{6'}$), 51.1 (OMe), 33.8 (*C*H_2C=O spacer), 29.1, 29.0, 28.9, 28.9, 28.8, 28.7, 28.6, 25.5, 24.6 (CH_2 spacer), 26.7 (CH_3 *t*Bu), 18.9 (C^q *t*Bu).

11-Methoxycarbonylundecanyl 2-O-Benzoyl-6-O-(2-O-benzoyl-3,4-di-O-benzyl-β-D-galactopyranosyl)-3,4-di-O-benzyl-β-D-galactopyranoside (**17**): Yield: 0.316 g, 0.28 mmol, 76% based on 0.503 g, 0.37 mmol of **16**. – ^{1}H NMR ($CDCl_3$): δ = 7.98–7.10 (m, 30 H, H_{arom}), 5.64 (dd, 1 H, H^2, $J_{1,2}$ = 8.9 Hz, $J_{2,3}$ = 10.0 Hz), 5.51 (dd, 1 H, $H^{2'}$, $J_{1',2'}$ = 8.0 Hz, $J_{2',3'}$ = 10.0 Hz), 4.87 (AB, 2 H, CH_2 Bn), 4.67 (AB, 2 H, CH_2 Bn), 4.62 (AB, 2 H, CH_2 Bn), 4.59 (AB, 2 H, CH_2 Bn), 4.53 (d, 1 H, H^1), 4.26 (d, 1 H, $H^{1'}$), 3.91 (d, 1 H, H^4, $J_{3,4}$ = 2.2 Hz), 3.89 (dd, 1 H, H_{6A}, $J_{5,6A}$ = 5.5 Hz, $J_{6A,6B}$ = 10.4 Hz), 3.83 (d, 1 H, $H^{4'}$, $J_{3',4'}$ = 2.2 Hz), 3.76 (dd, 1 H, $H_{6'A}$, $J_{5',6'A}$ = 5.6 Hz, $J_{6'A,6'B}$ = 11.2 Hz), 3.68 (m, 2 H, H^3/H^5), 3.66 (s, 3 H, OMe), 3.54 (m, 1 H, $H^{6'B}$), 3.50–3.46 (m, 3 H, H^{6B}/$H^{5'}$/CHO spacer), 3.42 (dd, 1 H, $H^{3'}$), 3.09 (m, 1 H, CHO spacer), 2.30 (t, 2 H, CH_2C=O spacer), 1.68–0.90 (m, 18 H, CH_2 spacer), 1.40 (bs, 1 H, OH). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.7 (C=O spacer), 164.7, 164.6 (C=O Bz), 138.0, 137.9, 137.3, 137.2 (C^q Bn), 135.0–127.1 (C_{arom}), 129.8, 129.7 (C^q Bz), 101.0, 100.9 (C^1/$C^{1'}$), 79.4, 79.2, 74.7, 73.1, 72.3, 72.2, 71.7, 71.4 (C^2/C^3/C^4/C^5/$C^{2'}$/$C^{3'}$/$C^{4'}$/$C^{5'}$), 74.1, 74.0, 71.7, 71.0 (CH_2 Bn), 68.8 (CH_2O spacer), 67.3 (C^6), 60.9 ($C^{6'}$), 50.9 (OMe), 33.6 (*C*H_2C=O spacer), 28.9, 28.9, 28.8, 28.8, 28.6, 28.6, 28.4, 25.3, 24.5 (CH_2 spacer).

11-Methoxycarbonylundecanyl 2-O-Benzoyl-3,4-di-O-benzyl-6-O-(3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-2-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-β-D-galactopyranosyl)-β-D-galactopyranoside (**18**): Yield: 0.481 g, 0.28 mmol, 69% based on 0.521 g, 0.41 mmol of **15**. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 172.6 (C=O spacer), 166.1, 165.7, 165.2, 165.1 (C=O Bz), 138.7, 138.3, 137.8, 137.7 (C^q Bn), 135.5–127.3 (C_{arom}), 133.1 (C^q TBDPS), 130.4, 129.1 (C^q Bz), 105.8 (C^1-ara, $J_{C,H}$ = 180.0 Hz), 102.8 (C^1/$C^{1'}$, $J_{C,H}$ = 159.9 Hz), 102.1 (C^1/$C^{1'}$, $J_{C,H}$ = 159.7 Hz), 82.1, 80.1, 79.8, 79.2, 78.3, 78.0, 77.6, 74.5, 73.9, 72.2, 71.7 (C^2-C^5/$C^{2'}$-$C^{5'}$/C^2-C^4-ara), 74.8, 74.3, 72.6, 71.7 (CH_2 Bn), 69.0 (CH_2O spacer), 67.7 (C^6), 63.9 (C^5-ara), 60.3 ($C^{6'}$), 51.4 (OMe), 34.0 (*C*H_2C=O spacer), 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.7, 25.8, 24.9 (CH_2 spacer), 26.9 (CH_3 *t*Bu), 19.2 (C^q *t*Bu). – MS (ESI): *m/z* = 1702 $[M + H]^+$, 1724 $[M + Na]^+$, 1740 $[M + K]^+$. – $C_{102}H_{112}O_{21}Si$ (1700.7): C, 71.98; H 6.63; Si 1.65 Found: C, 71.89; H 6.69; Si 1.68.

11-Methoxycarbonylundecanyl 2-O-Benzoyl-3,4-di-O-benzyl-6-O-(3,4-di-O-benzyl-2-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-β-D-galactopyranosyl)-β-D-galactopyranoside (**19**): Yield: 0.332 g, 0.23 mmol, 81% based on 0.481 g, 0.28 mmol of **18**. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.0 (C=O spacer), 165.8, 165.4, 164.8, 164.7 (C=O Bz), 138.0, 137.4, 137.3, 137.2 (C^q Bn), 132.6–127.0 (C_{arom}), 129.9, 129.8, 128.8, 128.7 (C^q Bz), 105.3 (C^1-ara), 101.7, 101.0 (C^1/$C^{1'}$), 81.6, 78.3, 76.9, 76.8, 76.1, 74.6, 73.3, 72.7, 72.3, 71.7, 70.9 (C^2-C^5/$C^{2'}$-$C^{5'}$/C^2-C^4-ara), 74.1, 73.9, 72.1, 71.4 (CH_2 Bn), 70.0 (CH_2O spacer), 68.8 (C^6), 63.4 (C^5-ara), 61.2 ($C^{6'}$), 51.0 (OMe), 33.6 (*C*H_2C=O spacer), 29.0, 28.9, 28.8, 28.8, 28.7, 28.6, 28.4, 25.4, 24.5 (CH_2 spacer).

11-Methoxycarbonylundecanyl 3,4-Di-O-benzyl-6-O-(3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-β-D-galactopyranosyl)-2-O-

(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-β-D-galactopyranoside (**20**): Yield: 0.623 g, 0.39 mmol, 68% based on 0.577 g, 0.57 mmol of **14**. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.9 (C=O spacer), 165.8, 165.4, 165.0 (C=O Bz), 138.5, 137.9, 137.4, 137.3 (C^q Bn), 135.2−127.1 (C_{arom}), 132.8 (C^q TBDPS), 129.0, 128.8, 128.7 (C^q Bz), 105.2 (C^1-ara, $J_{C,H}$ = 178.8 Hz), 103.3 ($C^1/C^{1'}$, $J_{C,H}$ = 158.6 Hz), 101.8 ($C^1/C^{1'}$, $J_{C,H}$ = 161.0 Hz), 83.2, 81.9, 81.8, 81.7, 80.7, 80.6, 78.1, 74.5, 73.0, 71.2, 71.1 (C^2-$C^5/C^{2'}$-$C^{5'}/C^2$-C^4-ara), 73.9, 73.8, 73.2, 72.3 (CH_2 Bn), 69.7 (CH_2O spacer), 66.7 (C^6), 62.9 (C^5-ara), 61.5 ($C^{6'}$), 51.0 (OMe), 33.7 (*C*H_2C=O spacer), 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 25.6, 24.6 (CH_2 spacer), 26.6 (CH_3 *t*Bu), 18.8 (C^q *t*Bu). − MS (ESI): *m/z* = 1598 $[M + H]^+$, 1620 $[M + Na]^+$. − $C_{95}H_{108}O_{20}Si$ (1596.7): C, 71.41; H 6.81; Si 1.76; found: C, 71.32; H 6.86; Si 1.79.

11-Methoxycarbonylundecanyl 3,4-Di-O-benzyl-6-O-(3,4-di-O-benzyl-β-D-galactopyranosyl)-2-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-β-D-galactopyranoside (**21**): Yield: 0.403 g, 0.30 mmol, 76% based on 0.623 g, 0.39 mmol of **20**. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.2 (C=O spacer), 166.0, 165.3, 165.1 (C=O Bz), 138.1, 137.5, 137.2, 137.1 (C^q Bn), 133.2−127.4 (C_{arom}), 129.9, 129.7, 129.2 (C^q Bz), 105.3 (C^1-ara), 103.4, 101.9 ($C^1/C^{1'}$), 83.3, 81.9, 81.8, 81.7, 80.7, 78.1, 74.8, 73.5, 72.6, 72.2, 71.3 (C^2-$C^5/C^{2'}$-$C^{5'}/C^2$-C^4-ara), 74.1, 74.0, 72.5, 72.4 (CH_2 Bn), 69.9 (CH_2O spacer), 67.2 (C^6), 63.6 (C^5-ara), 61.5 ($C^{6'}$), 51.2 (OMe), 33.9 (*C*H_2C=O spacer), 29.3, 29.3, 29.1, 29.0, 29.0, 28.9, 28.6, 25.7, 24.7 (CH_2 spacer).

11-Methoxycarbonylundecanyl 2-O-Benzoyl-3,4-di-O-benzyl-6-O-(2-O-benzoyl-6-O-(3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-β-D-galactopyranosyl)-3,4-di-O-benzyl-β-D-galactopyranosyl)-β-D-galactopyranoside (**22**): Yield: 0.319 g, 0.19 mmol, 67% based on 0.316 g, 0.28 mmol of **17**. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.8 (C=O spacer), 164.8, 164.7 (C=O Bz), 138.4, 138.1, 138.1, 138.0, 137.8, 137.4 (C^q Bn), 135.1−127.0 (C_{arom}), 132.9, 132.7 (C^q TBDPS), 130.0, 129.9 (C^q Bz), 103.1 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 161.2 Hz), 101.1 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 156.8 Hz), 101.0 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 156.7 Hz), 81.8, 79.0, 78.8, 78.7, 73.3, 72.9, 72.8, 72.7, 71.7, 71.5, 70.9, 70.4 (C^2-$C^5/C^{2'}$-$C^{5'}/C^{2''}$-$C^{5''}$), 74.4, 73.6, 72.3, 72.2, 71.2, 71.0 (CH_2 Bn), 70.0 (CH_2O spacer), 69.2, 68.9 ($C^6/C^{6'}$), 61.8 ($C^{6''}$), 51.0 (OMe), 33.7 (*C*H_2C=O spacer), 29.0, 28.9, 28.8, 28.8, 28.7, 28.7, 28.5, 25.4, 24.6 (CH_2 spacer), 26.6 (CH_3 *t*Bu), 18.8 (C^q *t*Bu). − MS (ESI): *m/z* = 1704 $[M + H]^+$, 1726 $[M + Na]^+$, 1742 $[M + K]^+$. − $C_{103}H_{118}O_{20}Si$ (1702.8): C, 72.60; H 6.98; Si 1.65; found: C, 72.54; H 7.02; Si 1.67.

11-Methoxycarbonylundecanyl 2-O-Benzoyl-3,4-di-O-benzyl-6-O-(2-O-benzoyl-6-O-(3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-2-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-3,4-di-O-benzyl-β-D-galactopyranosyl)-3,4-di-O-benzyl-β-D-galactopyranosyl)-β-D-galactopyranoside (**23**): Yield: 0.334 g, 0.16 mmol, 82% based on 0.319 g, 0.19 mmol of **22**. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 173.9 (C=O spacer), 165.9, 165.5, 164.9, 164.8, 164.5 (C=O Bz), 138.1, 138.0, 137.9, 137.9, 137.4, 137.3 (C^q Bn), 135.2−127.0 (C_{arom}), 132.9, 132.8 (C^q TBDPS), 130.0, 129.9, 129.7 (C^q Bz), 105.3 (C^1-ara, $J_{C,H}$ = 177.9 Hz), 101.7 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 161.4 Hz), 101.1 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 158.2 Hz), 101.0 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 158.3 Hz), 83.1, 81.6, 80.7, 79.6, 79.3, 78.4, 78.2, 78.1, 74.6, 74.5, 73.1, 72.6, 71.5, 71.4, 70.6 (C^2-$C^5/C^{2'}$-$C^{5'}/C^{2''}$-$C^{5''}/C^2$-ara/C^3-ara/C^4-ara), 74.5, 74.3, 73.8, 72.6, 72.5, 72.0 (CH_2 Bn), 71.0 (CH_2O spacer), 69.0, 66.7 ($C^6/C^{6'}$), 63.6 (C^5-ara), 61.3 ($C^{6''}$), 51.1 (OMe), 33.8 (*C*H_2C=O spacer), 29.2, 29.1, 29.0, 28.9, 28.8, 28.6, 28.4, 25.5, 24.6 (CH_2 spacer), 26.7 (CH_3 *t*Bu), 19.0 (C^q *t*Bu). − MS (ESI): *m/z* = 2148 $[M + H]^+$; *m/2z* = 1075 $[M + 2\ H]^{2+}$. − $C_{129}H_{138}O_{27}Si$ (2146.9): C, 72.11; H 6.47; Si 1.31 Found: C, 72.08; H 6.55; Si 1.31.

General Procedure for Deprotection of the Tetrasaccharides: Tetra-*n*-butylammonium fluoride (1.0 M solution in THF, 0.15 ml, 0.15 mmol) was added to a stirred solution of the appropriate tetramer (0.10 mmol) in THF (1 ml). When TLC-analysis (50% EtOAc/light petroleum) showed complete disappearance of the starting material (3−5 h) the reaction mixture was diluted with EtOAc (25 ml) and washed with sat. aq. NaCl (3 × 10 ml). The organic phase was dried ($MgSO_4$), filtered through a bed of silica (5 g), and concentrated in vacuo. To a stirred solution of the residue in MeOH/CH_2Cl_2 (5 ml, 2:1, v/v) was added KO*t*Bu (11 mg, 0.10 mmol). After 30 min, the reaction was terminated by addition of Dowex 50WX4-H^+ (100 mg). The ion-exchange resin was filtered off and the filtrate was concentrated in vacuo. The resulting colorless oil was dissolved in *t*BuOH/H_2O (3:1, v/v, 4 ml) after which palladium on carbon (10%, 100 mg) was added. The heterogeneous mixture was hydrogenated at elevated pressure (3 atm.) in a Parr apparatus for 12 h and subsequently filtered. The filtrate was concentrated under reduced pressure and subjected to Pharmacia HW-40 gel filtration (eluent: MeOH/H_2O, 1:1, v/v). Lyophilization of the appropriate fractions afforded the corresponding spacer-containing tetrasaccharide as a white fluffy solid.

11-Methoxycarbonylundecanyl 6-O-(6-O-(2-O-(α-L-Arabinofuranosyl)-β-D-galactopyranosyl)-β-D-galactopyranosyl)-β-D-galactopyranoside (**1**): Yield: 89.5 mg, 0.11 mmol, 66% based on 0.334 g, 0.16 mmol of **23**. − $[\alpha]_D$ = +4.7 (*c* = 0.2, H_2O). − $^{13}C\{^1H\}$ NMR (D_2O/MeOD, 4:1, v/v): δ = 175.1 (C=O spacer), 109.3 (C^1-ara), 104.2, 104.0, 103.3 ($C^1/C^{1'}/C^{1''}$), 85.9, 81.8, 78.1, 76.6, 74.8, 74.5, 74.2, 74.1, 74.0, 73.9, 73.8, 71.9, 71.8, 69.9, 69.7 (C^2-$C^5/C^{2'}$-$C^{5'}/C^{2''}$-$C^{5''}/C^2$-ara/C^3-ara/C^4-ara), 71.3 (CH_2O spacer), 69.5, 69.4 ($C^6/C^{6'}$), 62.6 (C^5-ara), 61.9 ($C^{6''}$), 52.6 (OMe), 34.7 (*C*H_2C=O spacer), 30.1, 30.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.4, 25.6 (CH_2 spacer). − MS (ESI): *m/z* = 849 $[M + H]^+$; *m/2z* = 425 $[M + 2\ H]^{2+}$. − $C_{36}H_{64}O_{22}$ (848.4): C, 50.94; H 7.60; found: C, 50.91; H 7.62.

11-Methoxycarbonylundecanyl 2-O-Benzoyl-3,4-di-O-benzyl-6-O-(2-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-6-O-(3,4-di-O-benzyl-6-O-tert-butyldiphenyl-silyl-β-D-galactopyranosyl)-3,4-di-O-benzyl-β-D-galactopyranosyl)-β-D-galactopyranoside (**24**): Yield: 0.296 g, 0.14 mmol, 63% based on 0.332 g, 0.23 mmol of **19**. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 172.8 (C=O spacer), 166.0, 165.6, 165.0, 164.8, (C=O Bz), 138.6, 138.3, 138.0, 137.9, 137.6, 137.5 (C^q Bn), 135.3−127.3 (C_{arom}), 133.4 (C^q TBDPS), 130.2, 129.0, 128.9, 128.8 (C^q Bz), 105.5 (C^1-ara, $J_{C,H}$ = 178.8 Hz), 103.1 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 159.7 Hz), 101.8 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 161.9 Hz), 101.2 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 161.1 Hz), 82.0, 80.0, 79.9, 77.8, 77.6, 76.8, 73.6, 73.4, 72.9, 72.7, 71.8, 71.6, 71.1, 70.8, 70.6 (C^2-$C^5/C^{2'}$-$C^{5'}/C^{2''}$-$C^{5''}/C^2$-ara/C^3-ara/C^4-ara), 74.7, 74.3, 73.8, 72.4, 72.2, 71.6 (CH_2 Bn), 69.1 (CH_2O spacer), 68.4, 67.2 ($C^6/C^{6'}$), 63.7 (C^5-ara), 61.6 ($C^{6''}$), 51.2 (OMe), 33.9 (*C*H_2C=O spacer), 29.3, 29.2, 29.1, 29.0, 28.9, 28.9, 28.8, 25.7, 24.8 (CH_2 spacer), 26.8 (CH_3 *t*Bu), 19.0 (C^q *t*Bu). − MS (ESI): *m/z* = 2044 $[M + H]^+$; *m/2z* = 1022 $[M + 2\ H]^{2+}$. − $C_{122}H_{134}O_{26}Si$ (2042.9): C, 71.67; H 6.61; Si 1.37; found: C, 71.54; H 6.64; Si 1.40.

11-Methoxycarbonylundecanyl 6-O-(2-O-(α-L-Arabinofuranosyl)-6-O-(β-D-galactopyranosyl)-β-D-galactopyranosyl)-β-D-galactopyranoside (**2**): Yield: 88.1 mg, 0.10 mmol, 70% based on 0.296 g, 0.14 mmol of **24**. − $[\alpha]_D$ = +5.9 (*c* = 0.2, H_2O). $^{13}C\{^1H\}$ NMR (D_2O/MeOD, 4:1, v/v): δ = 175.8 (C=O spacer), 109.6 (C^1-ara), 105.3, 104.7, 104.0 ($C^1/C^{1'}/C^{1''}$), 87.2, 82.0, 79.0, 76.7, 76.0, 75.2, 75.1, 75.0, 74.8, 74.7, 72.5, 72.4, 70.3, 70.2, 70.0 (C^2-$C^5/C^{2'}$-$C^{5'}/C^{2''}$-$C^{5''}/C^2$-ara/C^3-ara/C^4-ara), 71.0 (CH_2O spacer), 69.6, 69.4 ($C^6/C^{6'}$), 63.2 (C^5-ara), 62.6 ($C^{6''}$), 52.4 (OMe), 34.8 (*C*H_2C=O

spacer), 30.9, 30.7, 30.6, 30.6, 30.5, 30.3, 30.2, 27.1, 26.0 (CH_2 spacer). − MS (ESI): *m/z* = 849 [M + H]$^+$; *m/2z* = 425 [M + 2 H]$^{2+}$. − $C_{36}H_{64}O_{22}$ (848.4): C, 50.94; H 7.60; found: C, 50.90; H 7.65.

11-Methoxycarbonylundecanyl 3,4-Di-O-benzyl-6-O-(6-O-(3,4-di-O-benzyl-6-O-tert-butyldiphenylsilyl-β-D-galactopyranosyl)-3,4-di-O-benzyl-β-D-galactopyranosyl)-2-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-β-D-galactopyranoside (**25**): Yield: 0.351 g, 0.18 mmol, 60% based on 0.403 g, 0.30 mmol of **21**. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 172.9 (C=O spacer), 166.0, 165.5, 165.1 (C=O Bz), 138.6, 138.2. 138.2, 138.0, 137.9, 137.5 (C^q Bn), 135.3−127.2 (C_{arom}), 133.2 (C^q TBDPS), 129.4, 129.3, 129.2 (C^q Bz), 105.3 (C^1-ara, $J_{C,H}$ = 178.8 Hz), 103.3 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 156.9 Hz), 103.2 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 157.0 Hz), 101.9 ($C^1/C^{1'}/C^{1''}$, $J_{C,H}$ = 161.2 Hz), 83.3, 81.9, 81.8, 81.7, 81.6, 80.7, 78.1, 74.6, 73.5, 73.4, 73.0, 72.5, 72.2, 71.1, 71.0 (C^2-$C^5/C^{2'}$-$C^{5'}/C^{2''}$-$C^{5''}/C^2$-ara/C^3-ara/C^4-ara), 74.5, 74.2, 74.0, 72.4, 72.2, 72.1 (CH_2 Bn), 69.9 (CH_2O spacer), 68.0, 67.4 ($C^6/C^{6'}$), 63.7 (C^5-ara), 61.5 ($C^{6''}$), 51.1 (OMe), 33.8 (CH_2C=O spacer), 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 25.7, 24.7 (CH_2 spacer), 26.7 (CH_3 *t*Bu), 18.9 (C^q *t*Bu). − MS (ESI): *m/z* = 1940 [M + H]$^+$; *m/2z* = 970 [M + 2 H]$^{2+}$. − $C_{115}H_{130}O_{25}Si$ (1938.9): C, 71.19; H 6.75; Si 1.45; found: C, 71.12; H 6.82; Si 1.46.

11-Methoxycarbonylundecanyl 2-O-(α-L-Arabinofuranosyl)-6-O-(6-O-(β-D-galactopyranosyl)-β-D-galactopyranosyl)-β-D-galactopyranoside (**3**): Yield: 97.7 mg, 0.12 mmol, 64% based on 0.351 g, 0.18 mmol of **25**. − $[\alpha]_D$ = +13.6 (*c* = 0.2, H_2O). − $^{13}C\{^1H\}$ NMR (D_2O/MeOD, 4:1, v/v): δ = 178.6 (C=O spacer), 110.5 (C^1-ara), 105.8, 105.4, 104.2 ($C^1/C^{1'}/C^{1''}$), 86.7, 83.4, 78.9, 77.9, 77.5, 77.4, 76.0, 75.7, 75.4, 75.3, 75.2, 75.1, 75.0, 73.1, 71.0 (C^2-$C^5/C^{2'}$-$C^{5'}/C^{2''}$-$C^{5''}/C^2$-ara/C^3-ara/C^4-ara), 71.7 (CH_2O spacer), 69.8, 69.7 ($C^6/C^{6'}$), 63.3 (C^5-ara), 61.7 ($C^{6''}$), 54.1 (OMe), 36.1 (CH_2C=O spacer), 31.4, 31.3, 31.2, 31.1, 31.0, 30.9, 27.9, 27.4, 26.9 (CH_2 spacer). − MS (ESI): *m/z* = 849 [M + H]$^+$; *m/2z* = 425 [M + 2 H]$^{2+}$. − $C_{36}H_{64}O_{22}$ (848.4): C, 50.94; H 7.60; found: C, 50.87; H 7.69.

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[12] Prof. Dr. P. Albersheim, Complex Carbohydrate Research Center, University of Georgia, Athens, U.S.A.

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