Synthesis of α-D-Gal*p*-(1→3)-*β*-D-Gal*f*-(1→3)-D-Man, a Terminal Trisaccharide of *Leishmania* Type-2 Glycoinositolphospholipids

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The synthesis of α-D-Gal*p*-(1→3)-*β*-D-Gal*f*-(1→3)-D-Man, present in the type-2 glycoinositolphospholipids and in the core of the lipophosphoglycan of *Leishmania*, is described. The glycosyl aldonolactone approach, followed by reduction of the lactone with diisoamylborane, was utilized for the introduction of the internal galactofuranosyl unit and the trichloroacetimidate method for the O-glycosidation reaction. A high-yield synthesis of the *β*-D-Gal*f*-(1−3)-D-Man unit, also present in the lipopeptidophosphoglycan of *Trypanosoma cruzi*, is reported.

Introduction

Leishmania parasites are the agents of leishmaniasis, a disease which in the mammalian host experiences ailments ranging from cutaneous lesions to fatal visceral infections. The life cycle of *Leishmania* consists of two stages, the promastigote extracellular form, which is present in the midgut of the sand fly vector, and the intracellular amastigotes, which reside within the phagolisosome in the mammalian macrophage. The glycoinositolphospholipids (GIPLs) are a family of low molecular weight glycolipids[1,2] that are major surface constituents of promastigotes and amastigotes. On the basis of the structure of the oligosaccharide, GIPLs are classified into three types. Type 2 is characterized by the α-D-Gal*p*-(1−3)-*β*-D-Gal*f*-(1−3)-D-Man **(1)** unit, which is also internally present in the lipophosphoglycan (LPG). Moreover, patients with leishmaniasis are known to have elevated levels of antibodies directed against the GIPLs containing the terminal α-D-Gal*p*-(1−3)-D-Gal*f* structure.[1] The LPG is the predominant cell surface glycoconjugate of *Leishmania* promastigotes, whereas it is substantially down-regulated in amastigotes. The unusual feature of LPG and GIPL-2 is the internal galactofuranose. Compound **1** is the smallest moiety containing the sugar. The biosynthesis of D-Gal*f* containing glycoconjugates is a topic of great interest, as the sugar in this configuration is present in pathogenic microorganisms but not in mammals.[3] A UDP-Gal*p* mutase that catalyzes interconversions of UDP-Gal*p* and UDP-Gal*f* in bacteria was described.[4] A gene, LPG1, that encodes a putative galactofuranosyl transferase was described; in *Leishmania*,[5,6] however, a null mutant of *L. major* lacking LPG1 did not express LPG, whereas the GIPLs, with the same type of Gal*f*-Man linkage, were unaffected. This implied the existence of two different galactofuranosyl transferases.[7] In contrast, in *Mycobacterium tuberculosis* a bifunctional UDP-galactofuranosyltransferase was identified.[8]

Very recently, the synthesis of the *Leishmania* LPG core heptasaccharyl *myo*-inositol was reported.[9] They used the thioglycoside method for the glycosidation of the galactofuranose derivative, which was prepared in seven steps from galactose. In our case, we used a D-galactono-1,4-lactone derivative, easily prepared in two steps from the commercial lactone, as the precursor of the furanoic ring. The mild trichloroacetimidate method[10] was employed for the O-glycosidation reaction.

We report here for the first time the synthesis of α-D-Gal*p*(1−3)*β*-D-Gal*f*(1−3)-D-Man (**1**). The α-D-Gal*p*-(1−3)-*β*-D-Gal*f* derivative prepared by the glycosyl-aldonolactone approach[11,12] is a convenient intermediate for further glycosylation of the reducing end.

Results and Discussion

The synthesis of an oligosaccharide with internal galactofuranose represents a challenge because of the comparative instability of the glycofuranosidic linkage. Thus, protective groups must be carefully chosen in order

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(1) McConville, M. J.; Homans, S. W.; Thomas-Oates, J. E.; Dell, A.; Bacic, A. *J. Biol. Chem.* **1990**, *265*, 7385−7394.

(2) McConville, M. J.; Ferguson, M. A. J. *Biochem. J.* **1993**, *294*, 305−324.

(3) Lederkremer, R. M.; Colli, W. *Glycobiology* **1995**, *5*, 547−552.

(4) Sanders, D. A. R.; Staines, A. G.; McMahon, S. A.; McNeil, M. R.; Whitfield, C.; Naismith, J. H. *Nat. Struct. Biol.* **2001**, *8*, 858−863 and references therein.

(5) Ryan, K. A.; Garraway, L. A.; Descoteaux, A.; Turco, S. J.; Beverley, S. M. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 8609−8613.

(6) Turco, S. J.; Späth, G. F.; Beverly, S. M. *Trends Parasitol.* **2001**, *17*, 233−226.

(7) Späth, G. F.; Epstein, L.; Leader, B.; Singer, S. M.; Avila, H. A.; Turco, S. J.; Beverly, S. M. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 9258−9263.

(8) Kremer, L.; Dover, L. G.; Morehouse, C.; Hitchin, P.; Everett, M.; Morris, H. R.; Dell, A.; Brennan, P. J.; McNeil, M. R.; Flaherty, C.; Duncan, K.; Besra, G. S. *J. Biol. Chem.* **2001**, *276*, 26430−26440.

(9) Ruda, K.; Lindberg, J.; Garreg, P. J.; Oscarson, S.; Konradsson, P. *J. Am. Chem. Soc.* **2000**, *122*, 11067−11072.

(10) Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21−123. Schmidt, R. R. In *Modern Method in Carbohydrate Synthesis*; Khan, S. H., O'Neil, P. A., Eds.; Harwood Academic Publishers: Amsterdam, 1996; pp 20−54. Schmidt, R. R.; Jung, K.-H. In *Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Marcel Dekker: 1997; pp 283−312.

(11) Marino, C.; Chiocconi, A.; Varela, O.; Lederkremer, R. M. *Carbohydr. Res.* **1998**, *311*, 183−189.

(12) Lederkremer, R. M.; Marino, M.; Varela, O. *Carbohydr. Res.* **1990**, *200*, 227−230.

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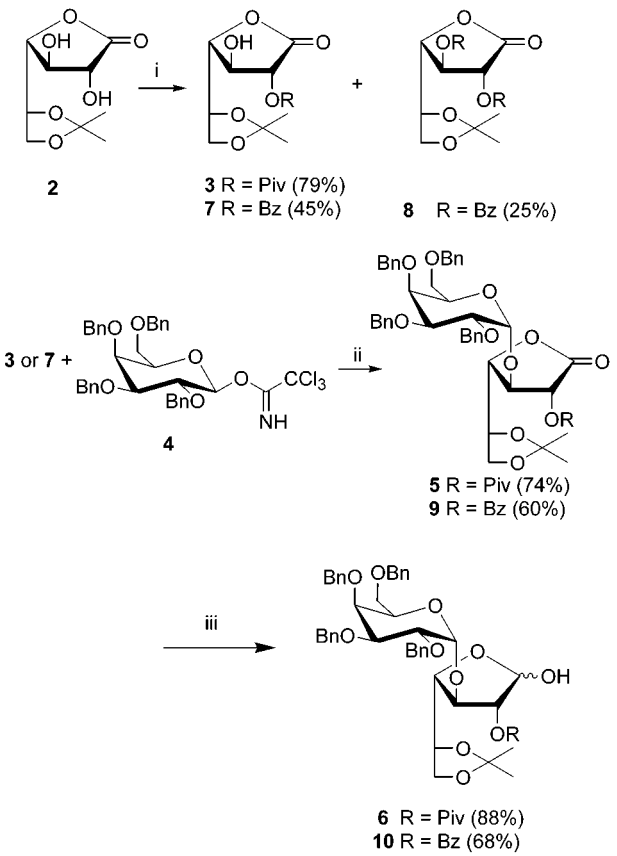
Scheme 1. Synthesis of the α-D-Gal*p*(1−3)-Gal*f* Unit[a]



[a] Reagents: (i) RCl, C_5H_5N; (ii) TMSOTf, 4 Å molecular sieves, ether, 0 °C; (iii) diisoamylborane.

to preserve the structure when the free oligosaccharide is the target.

In the present work, a derivative of D-galactono-1,4-lactone with free OH-3 was envisioned as a precursor of an internal galactofuranose. This choice has the advantage that once the former has been glycosylated with a convenient derivative of galactopyranose to construct the α linkage, reduction of the lactone would give the free anomeric OH group. Indeed, D-galactone-1,4-lactone could be considered as a virtually protected galactofuranose.

Taking into account that selective acylation of D-galactono-1,4-lactone gave the 2,5,6-tri-*O*-acyl derivative in low yield,[13] an alternative strategy was considered. Thus, 5,6-*O*-isopropylidene-D-galactono-1,4-lactone[14] (**2**) was selectively pivaloylated, foreseeing the higher reactivity of OH-2 due to stereoelectronic effects, which increase the nucleophilicity of the α-hydroxyl group. Treatment of **2** with 1 equiv of pivaloyl chloride in pyridine at 0 °C gave the 2-*O*-pivaloyl derivative **3** that crystallized from the reaction mixture in 79% yield (Scheme 1). With the aldonolactone acceptor **3** in hand, the next step was the construction of the α-Gal*p*-(1−3) linkage. We have previously described the use of aldonolactones as acceptors in glycosidations with peracylated sugars as donors and $SnCl_4$ as promoter.[11,12] In the present case, construction of the α-D-Gal*p* linkage was performed by the trichloroacetimidate method, using trimethylsilyl triflate as catalyst and donor **4**[15] to afford the glycosyl lactone **5** in 74% yield. The α-anomeric configuration was assigned on the basis of the NMR spectra. In the ^{1}H NMR spectrum, the H-1′ signal appeared as a doublet centered at 4.82 ppm with $J = 3.8$ Hz and the ^{13}C NMR spectrum showed the anomeric carbon at 99.1 ppm confirming the α assignment.

Reduction of the glycosyl lactone **5** using diisoamylborane (DSB) yielded the furanoic derivative **6** in 88% yield. Careful quenching of this reaction was important due to the removal of the isopropylidene funcionality that showed hydrolysis even by weak acidic aqueous conditions.

The straightforward formation of the trichloroacetimidate from the free sugar and the mild conditions for glycosidation were notorious advantages for this route. Thus, the trichloroacetimidate derivative of **6** was obtained as an α/*β* mixture of anomers as shown by the ^{1}H NMR spectrum. The characteristic resonances due to the anomeric protons were located at 6.46 ppm (bs, *β* anomer) and 6.65 ppm (d, $J = 4.38$ Hz, α anomer) in a 6:1 ratio. Unfortunately, this compound was very unstable and could not be used for the following step. However, compound **6** is a good precursor for the disaccharide α-D-galactopyranosyl-(1→3)-D-galactopyranose since after deprotection, the reducing sugar would isomerize into the more stable pyranose. The disaccharide is present in the mucins of infective trypomastigotes of *Trypanosoma cruzi* and represents the major target for trypanolytic anti αGal antibodies from chagasic patients.[16]

Taking into account that trichloroacetimidates with a benzoyl in OH-2 of galactofuranose have been successfully used for glycosidation,[17] the benzoyl derivative **10** was synthesized. Benzoylation of **2** (45% yield) was not as selective as pivaloylation, but it was a simple strategy for obtaining the precursor **7** with the OH-3 free for glycosidation.

Coupling of **7** with the galactopyranosyl donor **4** gave the α-lactonic disaccharide **9** in 60% yield. Reduction with DSB produced the furanoic synthon **10**. Treatment of **10** with trichloroacetonitrile and DBU gave the corresponding trichloroacetimidate **11**, which, in this case, could be purified by column chromatography without decomposition.

To study the regioselectivity of glycosidation of the mannose derivative **14** by the trichloroacetimidate method, we performed the reaction with the simple galactofuranose derivative **13** (Scheme 2). Compound **13** was easily prepared from the byproduct **8** (Scheme 1). Compound **8** could be obtained in high yield by benzoylation of **2** with an excess of benzoyl chloride.[18] The substituted disaccharide **15** was obtained in 70% yield by selective substitution at OH-3 (Scheme 2). Acetylation of OH-2 of compound **15** and comparison of the spectra (Table 1) confirmed the high selectivity of the reaction. Compound **15** was deprotected to yield methyl *β*-D-galactofuranosyl-(1−3)-α-D-mannopyranoside (**17**). The ^{13}C NMR spectrum of **17** previously described[19] was recorded at 70 °C; for

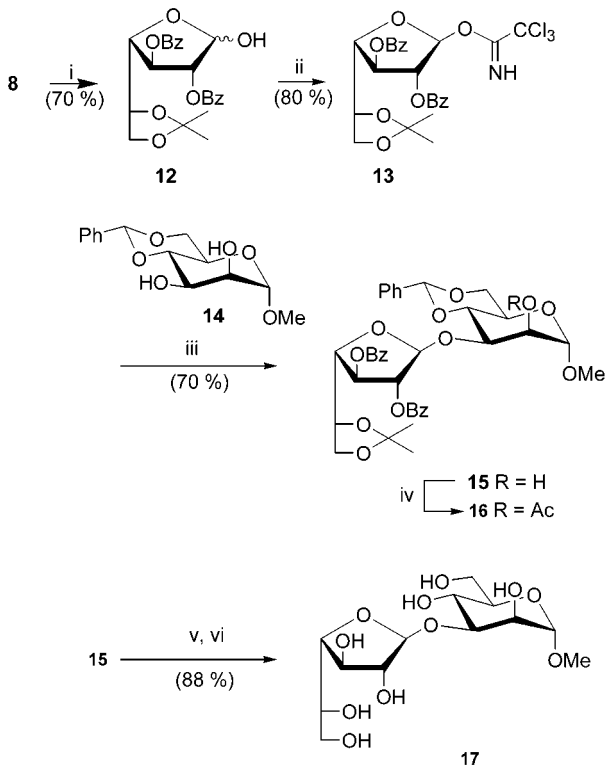
(13) Gallo, C.; Jeroncic, L.; Varela, O.; Lederkremer, R. M. *J. Carbohydr. Chem.* **1993**, *12*, 841−851.
(14) Fleet, G. W. J.; Son, J. C. *Tetrahedron* **1988**, *44*, 2637−2647.
(15) Wegmann, B.; Schmidt, R. R. *J. Carbohydr. Chem.* **1987**, *6*, 357−375.
(16) Almeida, I. C.; Ferguson, M. A.; Schenkman, S.; Travassos, L. R. *Biochem. J.* **1994**, *304*, 793−802.
(17) Gallo-Rodriguez, C.; Gandolfi, L.; Lederkremer, R. M. *Org. Lett.* **1999**, *1*, 245−247; Choudhury, A. K.; Roy, N. *Carbohydr. Res.* **1998**, *308*, 207−211.
(18) Limberg, G.; Thiem, J. *Carbohydr. Res.* **1995**, *275*, 107−115.

Table 1. ^{1}H NMR (500 MHz) Chemical Shifts for Compounds 9, 15, 16, and 19−21

		δ (ppm), J(Hz)[a]						
compd		H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{5,6b}$)	H-6b ($J_{6a,6b}$)
9	Gal-one		5.88	4.66	4.29	4.29	3.99−3.97	3.99−3.97
			(8.1)	(7.2)	nd[b]	nd	nd	nd
	Gal*p*	4.89	4.03	3.89	4.01	3.93	3.42	3.18
		(3.7)	(10.1)	(2.7)		(8.7)	(5.0)	(8.7)
15	Man	4.82	4.12	4.34	4.04	3.87	4.28	3.84
		(1.3)	(3.4)	(9.7)	(9.3)	(4.0)	(10.2)	(9.4)
	Gal*f*	5.37	4.42	5.46	4.37	4.29	3.78	3.76
			(1.4)	(5.2)	(4.6)	(6.9)	(6.5)	(8.4)
16	Man	4.7	5.36	4.46	3.96	3.9	4.28	3.83
		(1.6)	(3.8)	(9.9)	(9.6)	(4.5)	(10.0)	(10.0)
	Gal*f*	5.35	5.37	5.32	4.35	4.32	3.85	3.77
			(1.0)	(4.8)	(5.1)	(6.4)	(6.1)	(8.7)
19	Man	4.9	3.8	4.15	3.91	3.87	4.22	3.73
		(1.3)	(3.4)	(9.2)	(9.4)	(4.5)	(10.1)	(10.1)
	Gal*f*	5.11	5.67	4.07	4.32	4.07	3.67	3.57
		−	(1.7)	(4.9)	(4.9)	(6.7)	(6.9)	(8.4)
	Gal*p*	5.21	4.08	3.81	3.87	4.27	3.54	3.49
		(3.7)	(10.3)	(2.9)		(7.0)	(4.9)	(9.9)
20	Man	4.8	3.67	3.8	3.91	3.62−3.66	3.84	3.84
		(1.6)	(3.2)	(9.3)	(9.6)	nd	nd	nd
	Gal*f*	5.17	5.57	4.19	4.42	3.76	3.62−3.66	3.62−3.66
		−	(1.7)	(5.5)	(5.7)	(5.2)	(5.0)	nd
	Gal*p*	5.02	4.05	3.94	3.92	4.15	3.46	3.41
		(3.7)	(9.9)	(2.8)		(6.7)	(5.4)	(9.8)
21	Man	4.83	3.8	3.76	3.9	3.62−3.65	3.81	3.83
		(1.1)	(3.2)	(9.1)	(9.6)	nd	nd	nd
	Gal*f*	5.02	4.26	3.84	4.28	3.68	3.60−3.62	3.60−3.62
		(2.3)	(4.2)	(7.0)	(4.4)	(4.6)	(4.5)	nd
	Gal*p*	4.85	4.05	3.88	3.81	4.04−4.07	3.57	3.24
		(3.7)	(10.2)	(2.6)		(8.3)	(3.2)	(9.7)

[a] NMR assigments are derived from two-dimensional experiments. The signals for the protective groups are shown in the Experimental Section. [b] nd, not determined.

Scheme 2. Synthesis of Methyl β-D-Gal*f*(1-3)-α-D-Man[a]



[a] Reagents: (i) diisoamylborane; (ii) Cl_3CCN, DBU, CH_2Cl_2; (iii) TMSOTf, 4 Å molecular sieves, CH_2Cl_2, −10 °C; (iv) Ac_2O, C_5H_5N; (v) 65% aqueous AcOH, 80 °C; (vi) 0.5 M NaOMe in MeOH.

that reason, all our values are slightly shifted (0.8−1 ppm) to higher field. This synthesis is a good alternative for the preparation of the disaccharide β-D-Gal*f*(1→3)-D-Man*p*[11] present as external unit in the lipopeptidophosphoglycan of *T. cruzi*.[20] The good yield obtained in the coupling reaction proved that it was not necessary to protect the OH-2 group of compound **14** as previously described, using other glycosidation methods.[21] It was reported that glycosidation of methyl glycoside **14** by the orthoacetate method also took place selectively at OH-3.[19]

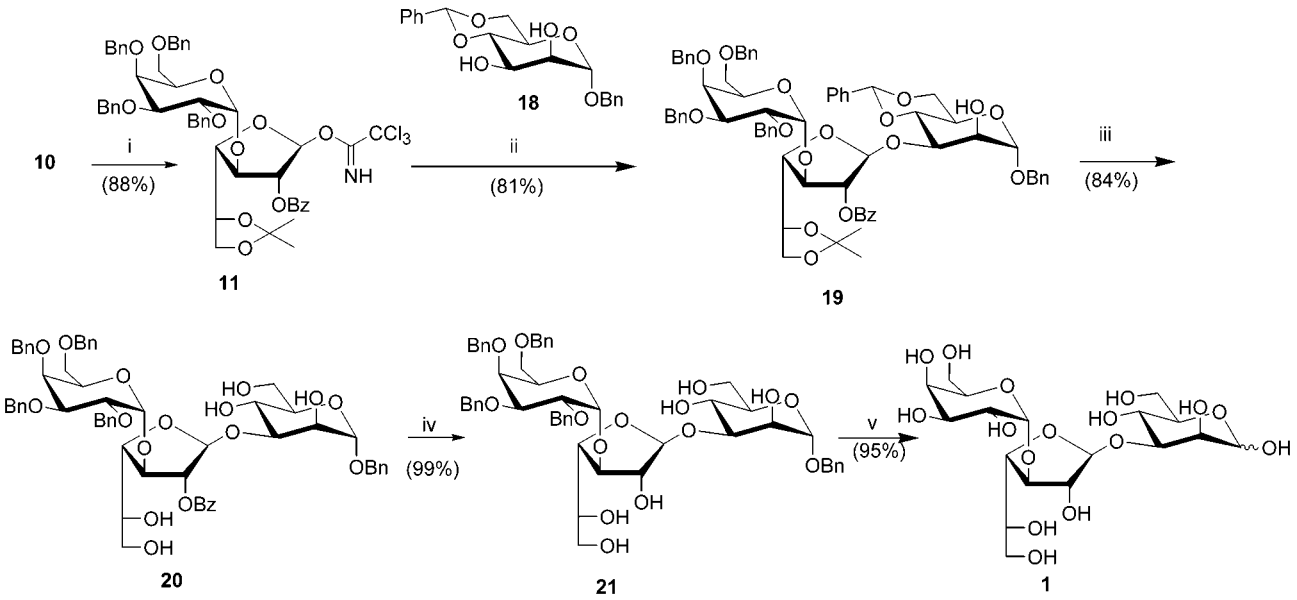
In agreement, glycosidation of benzyl mannopyranoside **18** with the disaccharide imidate **11** afforded **19** in 80% yield (Scheme 3). The aqueous acidic removal of both acetal groups to afford **20** proceeded without galactofuranosidic cleavage. Debenzoylation of **20** and subsequent catalytic hydrogenation produced the fully deprotected trisaccharide **1**, in good yield. The ^{1}H NMR spectrum of **1** was complex because signals correponding to both anomers at the reducing end were shown. The anomeric signals for the three monosaccharide units are in accordance with the structure. The ^{13}C NMR spectrum could be completely assigned showing signals for the anomeric carbon of the internal galactofuranose at δ 105.8 and 105.4 ppm. The anomeric region also showed the signals for the α-D-Gal*p* at 100.5 ppm and two signals at 94.7 and 94.5 ppm corresponding to the reducing end

(19) Gorin, P. A. J.; Barreto-Bergter, E. M.; Da Cruz, F. S. *Carbohydr. Res.* **1981**, *88*, 177−188.

(20) Lederkremer, R. M.; Lima, C.; Ramirez, M. I.; Ferguson, M. A. J.; Homans, S. W.; Thomas-Oates. *J. Biol. Chem.* **1991**, *266*, 23670−23675.

(21) Johnston, B. D.; Pinto, B. M. *Carbohydr. Res.* **1999**, *315*, 356−360.

Scheme 3[a]



[a] Reagents: (i) Cl_3CCN, DBU, CH_2Cl_2, 0 °C; (ii) TMSOTf, 4 Å molecular sieves, CH_2Cl_2, −10 °C; (iii) 65% aqueous AcOH, 80 °C; (iv) 0.5 M NaOMe in MeOH; (v) H_2 (3 atm), 10% Pd(C), MeOH.

of the Man*p*. The low field signals at 85.7 for C-4′ and 82.7 ppm for C-2′ are also characteristic of the galactofuranosyl unit and coincident with signals reported for the *Leishmania* heptasaccharide containing the galactofuranosyl unit.[9]

Conclusions

The synthesis of the trisaccharide containing the internal galactofuranose present in *Leishmania* GIPLs and in the core of the LPG is described for the first time. The strategy was based on the synthesis of the glycosyllactone as precursor for the galactofuranosyl ring. The choice of the protecting groups facilitated the preparation of the totally unprotected trisaccharide of special interest for studies on the glycosyl transferases of *Leishmania*.

Experimental Section

General Methods. TLC was performed on 0.2 mm silica gel 60 F254 (Merck) aluminum supported plates. Detection was effected by exposure to UV light or by spraying with 5% (v/v) sulfuric acid in EtOH and charring. Column chromatography was performed on silica gel 60 (230−400 mesh, Merck). Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 343 polarimeter. NMR spectra were recorded with a Bruker AC 200 spectrometer at 200 MHz (^{1}H) and 50.3 MHz (^{13}C) or with a Bruker AM 500 spectrometer at 500 MHz (^{1}H) and 125 MHz (^{13}C).

5,6-*O*-Isopropylidene-2-*O*-pivaloyl-D-galactono-1,4-lactone (3). To a stirred solution of 5,6-*O*-isopropylidene-D-galactono-1,4-lactone[14] (**2**; 1.1 g, 5.0 mmol) in dry pyridine (20 mL), cooled to 0 °C, was added pivaloyl chloride (0.68 mL, 5.5 mmol) during 1 h. After 1 h of stirring at room temperature, the mixture was poured into ice−water (300 g) and the stirring continued for 1 h. The mixture was extracted with CH_2Cl_2 (2 × 50 mL), and the organic layer was sequentially washed with HCl 5% (100 mL), water (100 mL), saturated aqueous $NaHCO_3$ (100 mL), and water, dried ($MgSO_4$), and concentrated. The residue crystallized upon addition of hexanes−EtOAc to give **3** (1.2 g, 79%): mp 127−128 °C (hexanes−EtOAc); R_f 0.5 (toluene-EtOAc 1:1); $[\alpha]_D$ −73.3° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.22 (d, J = 7.4 Hz, 1 H), 4.42 (ddd, J = 7.4, 7.3, 2.1 Hz, 1 H), 4.38 (ddd, J = 3.3, 6.7, 6.6 Hz, 1 H), 4.24 (dd, J = 3.3, 7.3 Hz, 1 H), 4.14 (dd, J = 6.7, 8.5 Hz, 1 H), 4.02 (dd, J = 6.6, 8.5 Hz, 1 H), 3.51 (d, 1 H, J = 2.1 Hz, OH), 1.44 (s, 3 H), 1.39 (s, 3 H), 1.29 (s, 9 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 179.4, 172.4, 110, 79.8, 76.8, 74.1, 73.4, 65.0, 38.9, 27.0, 26.0, 25.5. Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.33. Found: C, 55.76; H, 7.53.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-5,6-*O*-isopropylidene-2-*O*-pivaloyl-D-galactono-1,4-lactone (5). A mixture of *O*-(2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl)-trichloroacetimidate[15] (**4**, 300 mg, 0.44 mmol), **3** (141 mg, 0.47 mmol), and powdered 4 Å molecular sieves (500 mg) in dry ether was vigorously stirred at 0 °C under an argon atmosphere. After 20 min, TMSOTf (25 μL, 0.14 mmol) was slowly added, and the stirring was continued for 2 h. The suspension was neutralized by addition of *N*,*N*-diisopropyl-*N*-ethylamine, filtered through Celite, and concentrated under reduce pressure. Column chromatography (20:1 toluene−EtOAc) of the residue gave **5** (269 mg, 74%) as a colorless syrup: R_f 0.71 (5:1 toluene−EtOAc), $[\alpha]_D$ +31.5° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42−7.23 (m, 20 H), 5.55 (d, J = 7.7 Hz, 1 H), 4.92 (d, J = 11.2 Hz, 1H), 4.87 (d, J = 11.6 Hz, 1H), 4.82 (d, J = 3.8 Hz, 1H), 4.78, 4.75 (2d, J = 11.6 Hz, 2H), 4.60 (d, J = 11.6 Hz, 1H), 4.59 (d, J = 11.2 Hz, 1H), 4.48 (d, J = 11.6 Hz, 1H), 4.43 (dd, J = 7.1, 7.7 Hz, 1H), 4.41 (d, J = 11.6 Hz, 1H), 4.26 (dt, J = 3.2, 6.6 Hz, 1H), 4.20 (dd, J = 7.1, 3.2 Hz, 1H), 4.06 (bs, 1 H), 4.04 (dd, J = 10.3, 3.8 Hz, 1H), 3.93−4.00 (m, 3H), 3.88 (dd, J = 10.3, 2.6 Hz, 1H), 3.60 (t, J = 8.7 Hz, 1H), 3.44 (dd, J = 8.7, 5.0 Hz, 1H), 1.41, 1.34 (2s, 6 H, $(CH_3)_2C$), 1.20 (s, 9 H, $((CH_3)_3C)$; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 176.7, 169.1, 138.5−127.3, 110.2 ($(CH_3)_2C$), 99.3, 78.8, 78.4, 76.2, 75.0, 74.4, 74.0, 73.9, 73.5, 73.1, 72.6, 70.1, 67.7, 64.9, 38.6, 26.9, 25.9, 25.4. Anal. Calcd for $C_{48}H_{56}O_{12}$: C 69.88, H 6.84. Found: C 69.92, H 7.09.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-5,6-*O*-isopropylidene-2-*O*-pivaloyl-D-galactofuranose (6). To a solution of bis(2-butyl-3-methyl)borane (1.6 mmol) in anhydrous THF (0.8 mL) cooled to 0 °C and under an argon atmosphere was added a solution of **5** (132 mg; 0.16 mmol) in anhydrous THF (1.5 mL), and the solution was stirred for 20 h at room temperature and then processed as already described.[22] The organic layer was washed with water, dried (Na_2SO_4), and concentrated. Boric acid was eliminated by coevap-

(22) Lerner, L. M. *Methods Carbohydr. Chem.* **1972**, *6*, 131−134.

oration with MeOH (5 × 3 mL), and the product was purified by column chromatography (7:1 toluene−EtOAc) to give **6** (117 mg; 88%) as an amorphous solid: R_f 0.33 toluene−EtOAc; $[\alpha]_D$ +43.3° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36−7.29 (m, 20 H), 5.45 (d, 0.4 H, J = 4.5 Hz, H-1α), 5.21 (s, 0.6 H, H-1*β*), 5.16 (d, J = 1 Hz, 1H), 4.98 (d, J = 3.8 Hz, 1H), 4.92−3.80 (m), 3.60−3.40 (m), 1.45, 1.37 (2s, 6 H), 1.21,1.20 (2s, 9 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 177.2, 138.6−127.4, 109.8 ($(CH_3)_2C$), 101.0 (C-1*β*), 98.1, 97.2 (C-1′of α and *β* anomers), 95.2 (C-1α), 83.4, 81.7, 81.4, 80.2, 79.3, 78.8, 78.6, 78.4, 76.6, 76.2, 75.5, 74.9, 74.7, 73.9, 73.8, 73.5, 72.9, 70.0, 69.0, 68.2, 65.6, 38.6, 38.5, 27.1, 27.0, 26.4, 26.1, 25.5, 25.2. Anal. Calcd for $C_{48}H_{58}O_{12}$: C 69.71, H 7.07. Found: C 69.57, H, 7.15.

2-*O*-Benzoyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (7) and 2,3-Di-*O*-benzoyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (8). To a suspension of d-galactono-1,4-lactone (3 g, 16.8 mmol) in a mixture of acetone-2,2-dimethoxypropane 3:1 (40 mL) cooled at 0 °C was added concentrated H_2SO_4 (0.03 mL). After 30 min, NH_4OH was added to pH 7, and the suspension was filtered and concentrated. The syrup was dissolved in dry pyridine (15 mL) and cooled to −10 °C, benzoyl chloride (2.4 mL, 20.7 mmol) was slowly added during 30 min, and stirring was continued for additional 30 min. The reaction mixture was processed as described for **3**, and the resulting syrup was purified by column chromatography (7:1 toluene−EtOAc and then 6:1 toluene−EtOAc). The fastest migrating component (R_f 0.71, 6:1 toluene−EtOAc) was identified as 2,3-di-*O*-benzoyl-5,6-*O*-isopropylidene-D-galactono-1,4-lactone (**8**, 1.81 g, 25%), which after crystallization from hexanes−ethyl acetate gave the following data: mp 112−113 °C; $[\alpha]_D$ +87.2° (*c* 1, $CHCl_3$) (lit.[18] $[\alpha]_D$ +59.0° (*c* 1, $CHCl_3$)); ^{1}H NMR was identical as decribed;[18] ^{13}C NMR (50.35 MHz, $CDCl_3$) δ 169.0 (C-1), 165.5, 165.0, 133.8−128.4, 110.5 ($(CH_3)_2C$), 79.8, 74.4, 72.4, 65.0, 25.8, 25.3.

The next fraction from the column (R_f 0.29, 6:1 toluene−EtOAc) afforded crystalline **7** (2.44 g, 45%): mp 94−95 °C (benzene); $[\alpha]_D$ −95.9° (*c* 1, CH Cl_3); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.08 (d, J = 7.7 Hz, 2 H), 7.7.64−7.41 (m, 3 H), 5.55 (d, J = 7.7 Hz, 1 H), 4.61 (J = 7.7 Hz, 1 H), 4.38 (dt, J = 3.3, 6.6 Hz, 1 H), 4.28 (dd, J = 3.3, 7.7 Hz, 1 H), 4.13 (dd, J = 6.6, 8.4 Hz, 1 H), 4.03 (dd, J = 6.6, 8.4 Hz, 1 H), 3.7 (bs, 1 H,), 1.43 (s, 3 H), 1.37 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 168.9 (C-1), 166.7, 134.1, 130.1, 128.5, 128.0, 110.3 ($(CH_3)_2C$), 79.9, 77.0, 73.9, 73.2, 64.9, 25.9, 25.3, 25.5. Anal. Calcd for $C_{16}H_{18}O_7$: C 59.62, H 5.63. Found: C 59.96, H 5.73.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-5,6-*O*-isopropylidene-2-*O*-benzoyl-D-galactono-1,4-lactone (9). To a stirred mixture of *O*-(2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl)trichloroacetimidate (**4**, 3.4 g, 5.0 mmol) and 5,6-*O*-isopropylidene-2-*O*-benzoyl-D-galactono-1,4-lactone (**7**; 2.36 g, 7.3 mmol) in anhydrous ether (80 mL), cooled to 0 °C under argon, was slowly added TMSOTf (0.355 mL, 2.0 mmol). After 2 h, saturated aqueous $NaHCO_3$ was added (100 mL) and the stirring continued for 20 min. The product was extracted with CH_2Cl_2 (200 mL), and the extract was washed with water (4 × 100 mL), dried (Na_2SO_4), and concentrated. Column chromatography (20:1 toluene−EtOAc and then 15:1 toluene−EtOAc) of the residue gave **9** (2.52 g, 60%) that crystallized upon addition of EtOH: R_f 0.56 (6:1 toluene−EtOAc); mp 133−134 °C (ethanol); $[\alpha]_D$ +53.3° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) only the values for protecting groups are listed δ 8.04 (d, J = 7.3 Hz, 2H), 7.65−7.00 (m, 23 H), 4.86, 4.60 (2d, J = 11.7 Hz, 2H), 4.86, 4.48 (2d, J = 11.4 Hz, 2H), 4.77, 4.73 (2d, J = 11.7 Hz, 2H), 4.18, 4.10 (2d, J = 11.7 Hz, 2H), 1.43, 1.37 (2s, 6 H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 168.4 (C-1), 165.0, 138.5−125.4, 110.3 ($(CH_3)_2C$), 99.6 (C-1′), 78.7, 78.6, 78.4, 76.1, 74.9, 74.4, 74.1, 73.6, 73.4, 73.2, 72.6, 70.1, 67.7, 65.0, 26.0, 25.5. Anal. Calcd for $C_{50}H_{52}O_{12}$: C 71.07; H 6.30. Found: C 71.00; H 6.16.

Unreacted **7** (1.2 g) was recovered from the column by further elution with 1:1 toluene−EtOAc.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-5,6-*O*-isopropylidene-2-*O*-benzoyl-D-galactofuranose (10). Compound **9** (1.42 g) was reduced as described for **6** to give **10** (0.97 g; 68%) as an amorphous solid that slowly crystallized from EtOH: mp 136−138 °C (EtOH); R_f 0.30 (5:1 toluene−EtOAc); $[\alpha]_D$ +65.5° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) anomeric region δ 5.58 (d, J = 4.0 Hz, α anomer, 0.3 H, H-1), 5.45 (d, J = 1.1 Hz, *β* anomer, 0.7 H, H-1), 5.38 (s, *β* anomer, 0.7 H, H-2), 5.22 (dd, J = 6.6, 4.6 Hz, α anomer, 0.3 H, H-2), 5.07 (d, J = 3.6 Hz, 0.7 H, H-1′), 1.44, 1.42, 1.36, 1.33 (4s, 6 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 165.4, 138.6−127.4, 109.8 ($(CH_3)_2C$), 100.9 (C-1*β*), 98.7, 97.6 (C-1′ of α and *β* anomers), 95.1 (C-1α), 83.0, 82.0, 80.5, 79.3, 78.9, 78.8, 78.7, 76.2, 75.4, 74.9, 74.7, 73.9, 73.7, 73.4, 73.3, 72.9, 70.1, 69.0, 68.3, 65.5, 26.4, 26.1, 25.5, 25.2. Anal. Calcd for $C_{50}H_{54}O_{12}$: C 70.91, H 6.43. Found: C 70.85, H 6.29.

2,3-Di-*O*-benzoyl-5,6-*O*-isopropylidene-D-galactofuranose (12). Compound **8** (0.72 g) was reduced with bis(2-butyl-3-methyl)borane (18.7 mmol) as described for compound **6** and purified by column chromatography (7:1 toluene−EtOAc) to give **12** (0.51 g; 70%) as a hygroscopic syrup: R_f 0.33 (4:1 toluene−EtOAc); $[\alpha]_D$ +59.0° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) anomeric region δ 5.84 (dd, J = 5.8, 4.4 Hz, α anomer, 0.4 H, H-2), 5.72 (d, J = 4.4 Hz, α anomer, 0.4 H, H-1), 5.66 (bs, *β* anomer, 0.6 H, H-1), 1.50, 1.46, 1.44, 1.39 (4s, 6 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 166.1−165.4, 137.8−125.2, 110.2, 109.9 ($(CH_3)_2C$), 100.9 (C-1*β*), 95.4 (C-1α), 83.2, 82.6, 80.2, 78.3, 77.8, 77.2, 75.7, 75.6, 65.6, 26.2, 26.0, 25.4, 25.3. Anal. Calcd for $C_{23}H_{24}O_8 \cdot {}^1/_2H_2O$: C 63.15, H 5.76. Found: C 62.68, 5.83.

Methyl *β*-D-Galactofuranosyl-(1→3)-α-D-mannopyranoside (17). To a stirred solution of **12** (0.22 g, 0.56 mmol) and trichloroacetonitrile (3.4 mL, 3.4 mmol) in CH_2Cl_2 (20 mL) cooled to 0 °C was slowly added DBU (0.033 mL, 0.22 mmol). After 40 min, the solution was concentrated under reduced pressure, and the residue was purified by column chromatography (25:1:0.25 toluene−EtOAc−TEA) to give 0.26 g (80%) of *O*-(2,3-di-*O*-benzoyl-5,6-*O*-isopropylidene-D-galactofuranosyl)trichloroacetimidate **13** as a syrup: R_f 0.75 (4:1 toluene−EtOAc); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.70 (N*H*, 1H), 8.13−7.42 (m, 10 H), 6.64 (bs, 1 H), 5.71 (bs, 1 H), 5.61 (d, J = 3.3 Hz, 1H), 4.60 (ddd, J = 5.1, 6.2, 6.6 Hz, 1H), 4.54 (dd, J = 5.1, 3.3, 1 H), 4.15 (dd, J = 6.6, 8.4 Hz, 1H), 4.06 (dd, J = 6.2, 8.4 Hz, 1H), 1.45, 1.40 (2s, 6H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ, 165.6, 133.7−128.5, 110.1 ($(CH_3)_2C$), 103.2 (C-1*β*), 86.0, 80.5, 80.2, 75.1, 65.5, 26.3, 26.0.

A vigorously stirred suspension of dried **13** (0.26 g, 0.45 mmol), methyl 4,6-*O*-benzylidene-D-mannopyranoside[23] (**14**, 0.24 g, 0.85 mmol), and 4 Å powdered molecular sieves (0.4 g) in anhydrous CH_2Cl_2 (15 mL) was cooled to −10 °C, and TMSOTf (15 *μ*L, 0.083 mmol) was slowly added. After 40 min, the mixture was quenched by addition of saturated aqueous $NaHCO_3$ (10 mL). After dilution with CH_2Cl_2 (150 mL) and additional saturated aqueous $NaHCO_3$, the organic phase was separated, washed with water, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (7:1 toluene−EtOAc) to give 243 mg of amorphous methyl 2,3-di-*O*-benzoyl-5,6-*O*-isopropylidene-*β*-D-galactofuranosyl-(1→3)-4,6-*O*-benzylidene-α-D-mannopyranoside (**15**, 70% yield): R_f 0.25 (4:1 toluene−EtOAc), $[\alpha]_D$ 9.3° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) only the values for the protecting groups are listed δ 8.06−7.97 (m, 4H), 5.44 (C*H*Ph, 1H), 3.38 (s, 3H), 1.37, 1.36 (2s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.9, 165.5, 137.4−126.0, 109.8 ($(CH_3)_2C$), 102.5, 102.0, 101.2 (C-1, C-1′, Ph*C*H), 82.5, 82.3, 77.3, 76.9, 74.9, 71.7, 67.0, 68.7, 65.5, 65.6, 55.0, 26.2, 24.4.

Usual acetylation of **15** in dry pyridine with acetic anhydride gave methyl 2,3-di-*O*-benzoyl-5,6-*O*-isopropylidene-*β*-D-galactofuranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**16**): ^{1}H NMR spectrum is described in Table 1; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.1, 165.4, 165.1, 137.3−125.9, 109.8 ($(CH_3)_2C$), 102.3 (C-1′), 101.9 (*C*HPh), 99.9 (C-1), 82.7, 81.6, 77.9, 77.2, 75.2, 69.0, 68.9, 68.8, 65.6, 63.7, 55.1, 26.3, 25.4, 20.9.

Compound **15** was further treated with AcOH/H_2O at 80 °C and then debenzoylated with 0.5 M NaOMe in methanol to

(23) Buchanan, J. G.; Schwarz, J. C. P. *J. Chem. Soc.* **1962**, 4770−4777.

give methyl β-D-galactofuranosyl-(1−3)-α-D-mannopyranose (**17**, 88% yield): R_f 0.25 (7:3:1:0.5 EtOAc−EtOH−H_2O−NH_3); $[\alpha]_D$ −49° (*c* 1,water) (lit.[19] $[\alpha]_D$ −37° (*c* 0.6, water)); ^{1}H NMR (D_2O, 200 MHz) anomeric region δ 5.03 (d, *J* = 1.5 Hz, 1H, H-1′), 4.7 (d, *J* = 1.8 Hz, 1H, H-1), 3.32 (bs, OCH_3, 3 H); ^{13}C NMR (D_2O, 25 °C, 50.3 MHz), δ 105.4 (C-1′), 101.5 (C-1), 83.9, 82.2, 77.9, 76.4, 73.4, 71.7, 67.5, 66.0, 63.7, 61.9, 55.7. The ^{13}C NMR spectrum of the literature was recorded at 70 °C; for that reason, all our values are shifted 0.8−1 ppm to higher field.

Benzyl 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl-(1→3)-4,6-*O*-benzylidene-α-D-mannopyranoside (19). To a stirred solution of **10** (0.55 g, 0.65 mmol) and trichloroacetonitrile (0.39 mL, 3.9 mmol) in CH_2Cl_2 (20 mL), cooled to 0 °C, was slowly added DBU (0.038 mL, 0.256 mmol), and the stirring was continued for 30 min. The solution was concentrated under reduced pressure, and the residue was purified by column chromatography (15:1:0.5 toluene−EtOAc−TEA) to give 0.57 g (88%) of syrupy **11**. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.60 (N*H*, 1H), 6.47 (s, H-1, 1H), 5.66 (s, H-2, 1H), 5.09 (d, *J* = 3.3 Hz, H-1′, 1H), 4.95−3.52 (m, 21H), 1.35, 1.24 (2s, 6H).

To a vigorously stirred suspension of dried **11** (0.57 g, 0.58 mmol), benzyl 4,6-*O*-benzylidene-α-D-mannopyranoside[24] (**18**, 0.33 g, 1.17 mmol), and 4 Å powdered molecular sieves in Cl_2CH_2 (13 mL) cooled to −10 °C was added TMSOTf (10 μL, 0.055 mmol). After 30 min, TLC showed the absence of trichloroacetimidate **11**. The mixture was quenched by addition of saturated solution of $NaHCO_3$ (10 mL). After dilution with CH_2Cl_2 (150 mL) and additional saturated $NaHCO_3$ solution, the organic phase was separated and washed with water, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (13:1 toluene−EtOAc) to give 553 mg of amorphous solid **19** (81% yield): R_f 0.40 (4:1 toluene−EtOAc); $[\alpha]_D$ +38.3° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) only the values for the protecting groups are listed δ 5.34 (C*H*Ph), 4.94, 4.54 (2d, *J* = 11.6 Hz, 2H), 4.78, 4.63 (2d, *J* = 11.6 Hz, 2H), 4.70, 4.49 (2d, *J* = 11.9 Hz, 2H), 4.65, 4.56 (2d, *J* = 11.9 Hz, 2H), 4.40, 4.33 (2d, *J* = 11.4 Hz, 2H), 1.26, 1.22 (2s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.8 (Ph*C*O), 138.8−126.0, 109.3 ($(CH_3)_2C$), 102.7 (C-1′, βGal*f*), 101.6 (*C*HPh), 99.6 (C-1, Man), 98.8 (C-1″, αGal*p*), 84.0 (C-3′), 82.1 (C-4′), 80.9 (C-2′), 78.8 (C-3″), 77.0 (C-4), 76.5 (C-2″), 75.5 (C-4″), 75.0 (C-5′), 74.5, 73.8, 73.2, 72.8 (CH_2Ph), 72.3 (C-3), 70.4 (C-6″), 70.3 (C-5″), 69.2 (CH_2Ph), 68.7 (C-6, C-2), 65.2 (C-6′), 63.8 (C-5), 26.1, 25.4 ($(CH_3)_2$C). Anal. Calcd for $C_{70}H_{74}O_{17}$: C, 70.81; H, 6.28. Found: C, 71.04; H, 6.48.

Benzyl 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside (20). To a stirred solution of **19** (297 mg, 0.25 mmol) in HOAc (2 mL) at 80 °C was slowly added H_2O (0.65 mL) until turbidity, and heating was continued for 30 min. The mixture was cooled and concentrated, and the residue was subjected to successive dissolution and evaporation with toluene (3 × 5 mL). Column chromatography (1:4 toluene−EtOAc) of the residue afforded **20** (222 mg, 84%) as a hygroscopic syrup: R_f 0.33 (1:5 toluene−EtOAc); $[\alpha]_D$ +26.6° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) only the values for the protecting groups are listed δ 4.88, 4.49 (2d, *J* = 11.5 Hz, 2H), 4.82, 4.65 (2d, *J* = 11.7 Hz, 2H), 4.77, 4.75 (2d, *J* = 11.7 Hz, 2H), 4.43, 4.65 (2d, *J* = 12.0 Hz, 2H), 4.37, 4.27 (2d, *J* = 11.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.7 (Ph*C*O), 137.9−127.5, 104.7 (C-1′), 99.3, 98.9 (C-1, C-1″), 83.8, 83.4, 81.8, 79.5, 79.1, 75.9, 74.7, 74.6, 74.1, 73.8, 72.8 (*C*H_2-Ph), 72.2, 71.7, 70.5, 69.9, 69.0 (*C*H_2Ph), 68.6, 66.5, 63.5, 62.7. Anal. Calcd for $C_{60}H_{66}O_{17}\cdot{}^1/_2H_2O$: C, 66.35; H, 6.40. Found: C, 66.10; H, 6.17.

Benzyl 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside (21). To a solution of **20** (134 mg, 0.127 mmol) in anhydrous MeOH (0.7 mL), cooled at 0 °C, was added 0.5 M NaOMe in MeOH (0.6 mL). After the mixture was stirred at room temperature for 1 h, H_2O (0.1 mL) was added. The solution was passed through a column (1.5 × 4 cm) containing Amberlite IR-120 plus (H^+) resin and the latter washed with MeOH. The solvent was evaporated and the methyl benzoate eliminated by five successive coevaporations with H_2O. Column chromatography of the residue (1:5 toluene−EtOAc) afforded **21** (0.120 mg, 99%) as a hygroscopic syrup: R_f 0.19 (1:5 toluene-EtOAc); $[\alpha]_D$ +10.8° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, Table 1) only the values for the protecting groups are listed δ 4.89, 4.50 (2d, *J* = 11.7 Hz, 2H), 4.80, 4.64 (2d, *J* = 11.7 Hz, 2H), 4.78, 4.72 (2d, *J* = 11.7 Hz, 2H), 4.67, 4.46 (2d, *J* = 11.7 Hz, 2H), 4.46, 4.36 (2d, *J* = 11.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.4−127.6, 107.5 (C-1′), 99.6, 98.9 (C-1, C-1″), 86.8, 82.2, 80.1, 80.0, 79.0, 75.7, 74.9, 74.6, 74.1, 73.8, 73.2, 72.1, 72.0, 70.7, 70.2, 69.5, 69.2, 66.2, 63.5, 62.4. Anal. Calcd for $C_{53}H_{62}O_{16}\cdot 1/2H_2O$: C, 66.03; H, 6.59. Found: C, 65.96; H, 6.57.

α-D-Galactopyranosyl-(1→3)-β-D-galactofuranosyl-(1→3)-D-mannopyranose (1). A suspension of compound **21** (76 mg, 0.080 mmol) in MeOH (5.5 mL) and 10% Pd/C (30 mg) was hydrogenated at 45 psi (3 atm) for 4 h at room temperature. After filtration of the catalyst, the filtrate was evaporated under vacuum to give an amorphous solid that was dissolved in water (1 mL), passed through a C8-Maxi-Clean, and lyophilized. Trisaccharide **1** (39.3 mg, 98%) was obtained as a high hygroscopic syrup: R_f 0.17 (7:1:1 *n*-propanol−MeOH−H_2O); $[\alpha]_D$ +28.3° (*c* 1, H_2O); ^{1}H NMR (D_2O, 500 MHz) anomeric region for the α anomer δ 5.13 (d, *J* = 1.9 Hz, H-1, Man), 5.10 (bs, Gal*f*), 5.00 (d, *J* = 3.5 Hz, H-1, Gal*p*); ^{13}C NMR (D_2O, 50.34 MHz) δ 105.8, 105.4 (C-1′); 100.5 (C-1″, Gal*p*); 94.7 (C-1α), 94.5 (C-1 β), 85.7, 82.7, 80.4, 76.1, 73.4, 72.3, 71.7, 70.1, 69.1, 68.4, 66.1, 63.7, 62.1, 61.9. Anal. Calcd for $C_{18}H_{32}O_{16}\cdot H_2O$: C, 41.38; H, 6.56. Found: C, 41.09; H, 6.40.

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(24) Shaban, M. A.; Ary, I. E.; Jeanloz, D. A.; Jeanloz, R. W. *Carbohydr. Res.* **1975**, 45, 105−114.