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Syntheses and reactions of 5-*O*-acetyl-1,2-anhydro-3-*O*-benzyl-α-D-ribofuranose and -β-D-lyxofuranose, 5-*O*-acetyl-1,2-anhydro-3,6-di-*O*-benzyl- and 1,2-anhydro-5,6-di-*O*-benzoyl-3-*O*-benzyl-β-D-mannofuranose, and 6-*O*-acetyl-1,2-anhydro-3,4-di-*O*-benzyl-α-D-glucopyranose and -β-D-talopyranose

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Abstract

The title compounds 5-*O*-acetyl-1,2-anhydro-3-*O*-benzyl-α-D-ribofuranose and 5-*O*-acetyl-1,2-anhydro-3-*O*-benzyl-β-D-lyxofuranose, and 6-*O*-acetyl-1,2-anhydro-3,4-di-*O*-benzyl-α-D-glucopyranose and 6-*O*-acetyl-1,2-anhydro-3,4-di-*O*-benzyl-β-D-talopyranose, and 5-*O*-acetyl-1,2-anhydro-3,6-di-*O*-benzyl-β-D-mannofuranose and 1,2-anhydro-5,6-di-*O*-benzoyl-3-*O*-benzyl-β-D-mannofuranose have each been synthesized from the corresponding 2-*O*-tosylate and 1-free hydroxyl intermediates by base-initiated intramolecular S_N2 ring closure in almost quantitative yields. Acetyl and benzoyl groups were not affected in the ring closure reactions. Condensation of 6-*O*-acetyl-1,2-anhydro-3,4-di-*O*-benzyl-α-D-glucopyranose and 5-*O*-acetyl-1,2-anhydro-3,6-di-*O*-benzyl-β-D-mannofuranose with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose in the presence of $ZnCl_2$ as the catalyst afforded the 1,2-*trans*-linked 6-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose and 5-*O*-acetyl-3,6-di-*O*-benzyl-α-D-mannofuranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose as the sole products in satisfactory yields, while condensation of 5-*O*-acetyl-1,2-anhydro-3-*O*-benzyl-β-D-lyxofuranose with 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose yielded the 1,2-*trans*-linked 5-*O*-acetyl-3-*O*-benzyl-α-D-lyxofuranosyl-(1→5)-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose as the sole product in a good yield. The 6-*O*-acetyl group in the glycosyl donor, 6-*O*-acetyl-1,2-anhydro-3,4-di-*O*-benzyl-α-D-glucopyranose, did not influence the stereoselectivity of the ring-opening–coupling reaction.

Keywords: Carbohydrate; 1,2-Anhydro sugars; Furanose; Pyranose

1. Introduction

As useful intermediates for the syntheses of oligosaccharides, 1,2-anhydro sugar derivatives have received considerable attention recently because of their excellent reactivity and stereoselectivity,[1] and many natural and unusual oligosaccharides have been synthesized by this method.[1] Preparation of 1,2-anhydro sugars was reported by Danishefsky's group using direct epoxidation of the glycals.[1a–j]

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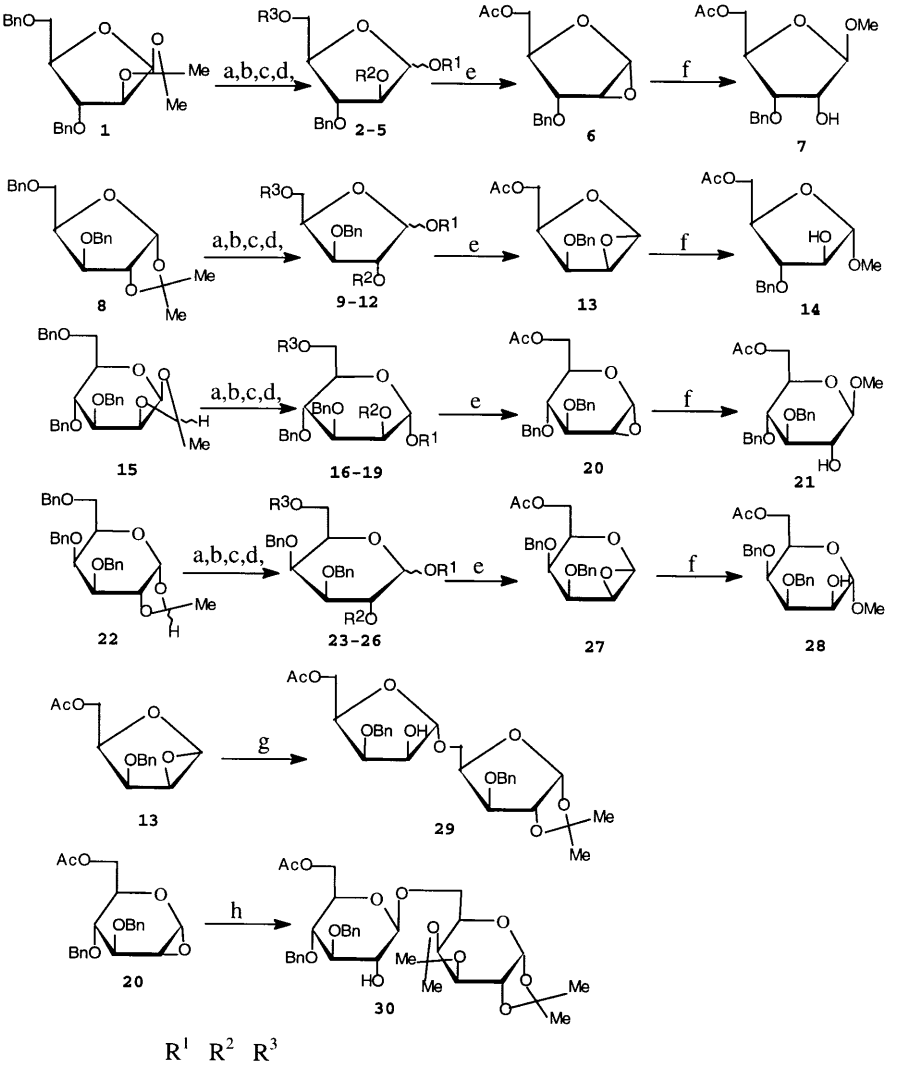
However, it would be difficult to prepare 1,2-anhydro sugars having a *cis* arrangement of the 3-hydroxy group and the epoxide ring by this method, and large-scale preparation would be inconvenient. Intramolecular S_N2 ring closure reaction initiated by Schuerch's group is an effective approach.[2] In a continuing effort to synthesize 1,2-anhydro sugars by this latter method, a variety of 1,2-anhydro sugar benzyl ethers have been prepared in our laboratory.[1k–u] However, in the stepwise syntheses of oligosaccharides, the preparation of sugar derivatives with both persistent and temporary groups is required.[3] Benzyl and allyl groups are usually used as persistent, while esters are considered as temporary blocking groups.[3,4] In our previous communication, we reported a facile method for syntheses of 6-*O*-acetyl-1,2-anhydro-3,4-di-*O*-benzyl-D-glycopyranoses and 5-*O*-acetyl-1,2-anhydro-3-*O*-benzyl-glycofuranoses.[5] We present here the full account of this synthesis, and also give two more examples, i.e., synthesis of 5-*O*-acetyl-1,2-anhydro-3,6-di-*O*-benzyl- and 1,2-anhydro-5,6-di-*O*-benzoyl-3-*O*-benzyl-β-D-mannofuranose starting from D-glucose by the intramolecular S_N2 ring-closure method.

2. Results and discussion

The syntheses of anhydro sugars **6**, **13**, **20**, and **27** are depicted in Scheme 1. Methanolysis of **1**, **8**, **15**, and **22** gave **2**, **9**, **16**, and **23**, respectively, and subsequent tosylation afforded the corresponding methyl 2-sulfonate glycosides **3**, **10**, **17**, and **24**. Selective acetolysis of **3**, **10**, **17**, and **24** using 7:1:0.6 (v/v) HOAc–Ac_2O–H_2SO_4 gave the corresponding diacetates **4**, **11**, **18**, and **25**. Attempts for selective removal of the 1-*O*-acetyl group of the diacetates by known methods such as $SnCl_4$[6] or N_2H_4·HOAc[7] suffered from low yields and tedious separation. However, in these examples the 1-*O*-acetyl group of **4**, **11**, **18**, and **25** was removed almost quantitatively in anhydrous ether saturated with dry ammonia[8] to yield the key intermediates **5**, **12**, **19**, and **26**, respectively. Since all of the reactions described above gave very high yields, the intermediates involved in the procedure could be subjected to the next reaction without chromatographic separation. We were gratified to find that ring closure of **5**, **12**, **19**, and **26** with *t*-BuOK or NaH in THF gave the 5-*O*-acetyl-1,2-anhydro-3-*O*-benzyl-α-D-ribofuranose (**6**), 5-*O*-acetyl-1,2-anhydro-3-*O*-benzyl-β-D-lyxofuranose (**13**), 6-*O*-acetyl-1,2-anhydro-3,4-di-*O*-benzyl-α-D-glucopyranose (**20**), and 6-*O*-acetyl-1,2-anhydro-3,4-di-*O*-benzyl-α-D-talopyranose (**27**), respectively, in almost quantitative yields. Acetyl groups were not affected under the basic conditions. The anhydro sugars **6**, **13**, **20**, and **27** were identified from their ^1H NMR spectra showing upfield peaks from H-2 at δ 3.57, 3.60, 3.06, and 3.50 ppm, respectively, a salient feature of the epoxide ring. Methanolysis of **6**, **13**, **20**, and **27** quantitatively gave the corresponding 1,2-*trans* methyl glycosides **7**, **14**, **21**, and **28**, confirming the anhydro sugar structures. Condensation of **13** with 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose using $ZnCl_2$ as the catalyst in CH_2Cl_2 yielded an α-linked disaccharide **29** (1,2-*trans*) as the sole product in a high yield, while condensation of **20** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose afforded a β-link disaccharide **30** (1,2-*trans*) as the sole product in a satisfactory yield. It is noted that the 6-*O*-acetyl group in **20** did not influence the stereoselectivity of the ring-opening–coupling reaction, although it is known that replacement of 6-*O*-benzyl with 6-*O*-acetyl alters the stereoselectivity of the coupling reaction of benzylated galactopyranosyl phosphite from 1,2-*trans* to predominant 1,2-*cis*.[9] Compounds **29** or **30** having a free 2-OH group and a potential 5-OH or 6-OH group can be used for further selective functionalization or glycosylation at the C-2 and C-5, or C-6 positions.

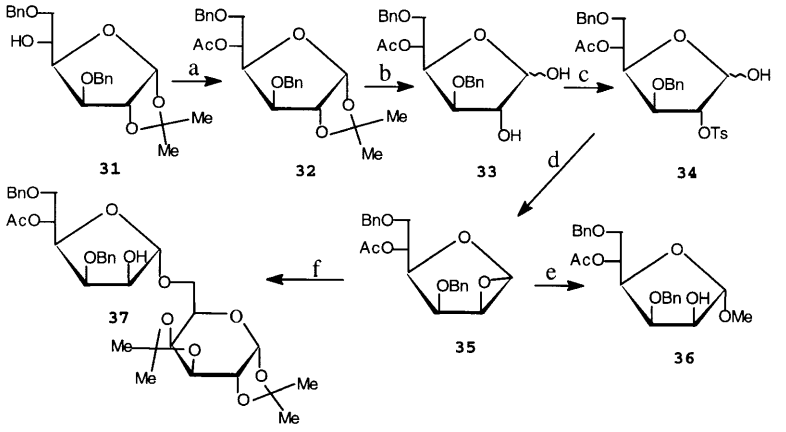
Acetylation of **31**[10] with acetic anhydride in pyridine afforded 5-*O*-acetyl-3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**32**) quantitatively (Scheme 2). Hydrolysis of **32** in 50% acetic acid under reflux gave 5-*O*-acetyl-3,6-di-*O*-benzyl-D-glucofuranose (**33**) in 92% yield as a mixture of α and β anomers. Compound **33** was treated with 5% aqueous

NaOH, 1.5 equiv of TsCl, and tetrabutylammonium hydrogensulfate (TBAHS) in dichloromethane at room temperature to give the key intermediate, 5-*O*-acetyl-3,6-di-*O*-benzyl-2-*O*-(*p*-toluenesulfonyl)-D-glucofuranose (**34**) as a mixture of α and β isomers, in 71% yield, from which the starting material could be recovered. Ring closure of **34** with *t*-BuOK or NaH in dry tetrahydrofuran gave the 5-*O*-acetyl-1,2-anhydro-3,6-di-*O*-benzyl-β-D-mannofuranose (**35**) quantitatively within 10 min, and the acetyl group in **34** was not affected under the alkaline conditions. Compound **35** was very sensitive to acidic and hydroxylic

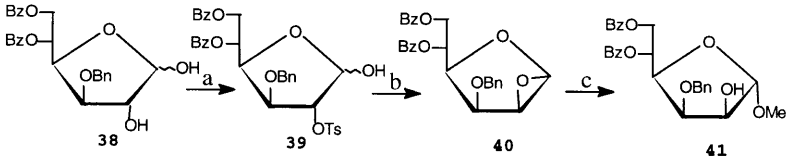


	R¹	R²	R³
2, 9, 16, 23	Me	H	Bn
3, 10, 17, 24	Me	Ts	Bn
4, 11, 18, 25	Ac	Ts	Ac
5, 12, 19, 26	H	Ts	Ac

Scheme 1. Reactions and conditions: (a) cat. H_2SO_4, MeOH, reflux, 3 h, 98% (**2**), 97% (**9**), 98% (**16**), 98% (**23**). (b) TsCl, pyridine, 50 °C, 20 h, 98% (**3**), 98% (**10**), 97% (**17**), 98% (**24**). (c) 7:1:0.6 HOAc–Ac_2O–H_2SO_4, rt, 16 h, 97% (**4**), 96% (**11**), 96% (**18**), 96% (**25**). (d) anhyd Et_2O satd with dry ammonia, rt, 24 h, 97% (**5**), 97% (**12**), 96% (**19**), 97% (**26**). (e) *t*-BuOK (1.1 equiv), THF, rt, 20 min, 95% (**6**), 94% (**13**), 92% (**20**), 94% (**27**). (f) anhyd MeOH, rt, 1 h, 100% (**7**, **14**, **21**, **28**). (g) 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose, CH_2Cl_2, $ZnCl_2$, rt, 4 h, 81% (**29**). (h) 1,2:3,4-di-*O*-Isopropylidene-α-D-galactopyranose, CH_2Cl_2, $ZnCl_2$, rt, 4 h, 83% (**30**).



Scheme 2. Reactions and conditions: (a) pyridine, Ac_2O, rt, 3 h, 100%. (b) 50% HOAc, reflux, 5 h, 92%. (c) TsCl, TBAHS, 5% aq NaOH, CH_2Cl_2, rt, 15 h, 71%. (d) *t*-BuOK (1.1 equiv), THF, rt, 20 min, 96%. (e) Anhyd MeOH, rt, 1 h, 100%. (f) 1,2:3,4-di-*O*-Isopropylidene-α-D-galactopyranose, CH_2Cl_2, $ZnCl_2$, rt, 4 h, 84%.



Scheme 3. Reactions and conditions: (a) TsCl, TBAHS, 5% aq NaOH, CH_2Cl_2, rt, 15 h, 69%. (b) *t*-BuOK (1.1 equiv), THF, rt, 20 min, 97%. (c) Anhyd MeOH, rt, 1 h, 100%.

solvent, and attempts to obtain an accurate elemental analysis of **35** were unsuccessful. The ^{1}H NMR spectrum of **35** showed an upfield signal for H-2 at δ 3.62 ppm, which is a characteristic feature of the 1,2-epoxide ring of carbohydrate compounds. The structure of **35** was further confirmed by methanolysis, giving the methyl 5-*O*-acetyl-3,6-di-*O*-benzyl-α-D-mannofuranoside (**36**) quantitatively, and also by its coupling reaction with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose in the presence of $ZnCl_2$ as the catalyst, giving the 1,2-*trans*-linked disaccharide **37** in 84% yield.

1,2-Anhydro-5,6-di-*O*-benzoyl-3-*O*-benzyl-β-D-mannofuranose (**40**) was prepared by a procedure similar to that used for the synthesis of compound **35** (see Scheme 3).

In conclusion, new procedures for the syntheses of 1,2-anhydro sugar derivatives with both benzoyl and acetyl groups were successfully developed. The synthetic pathway presented here may open a way to the further synthesis of other similar 1,2-anhydro sugars, and it is expected that these sugar derivatives will be valuable intermediates for the construction of some specific complex carbohydrates.

3. Experimental

General methods.—Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined at 20 °C with a Perkin–Elmer model 241-MC automatic polarimeter. ^{1}H NMR spectra were recorded with an Varian XL-200 spectrometer for solutions in $CDCl_3$. Chemical shifts are given in ppm downfield from internal Me_4Si. TLC was performed on silica gels G and HF, with detection either by charring with 30% (v/v) H_2SO_4 and MeOH or by UV light. Column chromatography was conducted on columns (16 × 240 mm, 18 × 300 mm) of silica gel (100–200 mesh). Solutions were concentrated at 60 °C under diminished pressure.

Methyl 3,5-di-O-*benzyl*-D-*arabinofuranoside* (**2**), *methyl 3,5-di*-O-*benzyl*-D-*xylofuranoside* (**9**), *methyl 3,4,6-tri*-O-*benzyl*-α-D-*mannopyranoside* (**16**), *and methyl 3,4,6-tri*-O-*benzyl*-D-*galactopyranoside* (**23**).—A solution of **1**[1k] (or

8,[10] **15**,[11] **22**[12]) (20 mmol) in anhydrous MeOH (100 mL) containing two drops of H_2SO_4 was stirred under reflux for 3 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. After rendering the solution basic with $NaHCO_3$, the mixture was concentrated to syrup, which was subjected to column chromatography with 2:1 petroleum ether–EtOAc as the eluent to afford the known compounds **2**,[13] **9**,[14] **16**,[15] and **23**[16] in 98, 97, 98, and 98% yields, respectively.

Methyl 3,5-di-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-D-*arabinofuranoside* (**3**), *methyl 3,5-di*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-D-*xylofuranoside* (**10**), *methyl 3,4,6-tri*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-α-D-*mannopyranoside* (**17**), *and methyl 3,4,6-tri*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-D-*galactopyranoside* (**24**).—To a solution of **2** (or **9**, **16**, **23**) (15.0 mmol) in pyridine (50 mL) was added TsCl (20.0 mmol). The mixture was stirred at 50 °C for about 24 h. Then the reaction mixture was poured onto ice-cold water and extracted with CH_2Cl_2 (3 × 25 mL). The organic layer was washed with N HCl (3 × 50 mL), dried over Na_2SO_4, and concentrated to syrup. The product was subjected to column chromatography with 3:1 petroleum ether–EtOAc as the eluent. Compounds **3** (98%), **10** (98%), **17** (97%), and **24** (98%) were obtained as syrups.

Data for **3**: mainly α, $[\alpha]_D$ +9.8° (*c* 1.9, $CHCl_3$); ^{1}H NMR: δ 7.82 (d, 2 H, Ph–*H* of Ts), 7.36–7.12 (m, 12 H, Ph–*H*), 4.83 (s, 1 H, H-1), 4.82 (d, 1 H, $J_{3,2}$ 2.0 Hz, H-2), 4.54, 4.50 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.45, 4.32 (2 d, 2 H, *J* 11.9 Hz, PhCH_2), 4.13 (m, 1 H, H-4), 3.97 (dd, 1 H, $J_{2,3}$ 2.0, $J_{4,3}$ 7.1 Hz, H-3), 3.57 (dd, 1 H, $J_{4,5}$ 3.7, $J_{5,5'}$ 10.8 Hz, H-5), 3.53 (dd, 1 H, $J_{4,5'}$ 5.5, $J_{5,5'}$ 10.8 Hz, H-5′), 3.28 (s, 3 H, OCH_3), 2.45 (s, 3 H, PhCH_3). Anal. Calcd for $C_{27}H_{30}O_7S$: C, 65.06; H, 6.02. Found: C, 65.20; H, 6.04.

Data for **10**: mainly β, $[\alpha]_D$ −16.1° (*c* 2.1, $CHCl_3$); ^{1}H NMR: δ 7.81 (d, 2 H, Ph–*H* of Ts), 7.37–7.10 (m, 12 H, Ph–*H*), 4.78 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1), 4.84 (dd, 1 H, $J_{1,2}$ 2.4, $J_{2,3}$ 4.0 Hz, H-2), 4.55, 4.50 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.43, 4.38 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.37–4.28 (m, 2 H, H-3, 4), 3.65 (dd, 1 H, $J_{4,5}$ 2.6, $J_{5,5'}$ 12.0 Hz, H-5), 3.55 (dd, 1 H, $J_{4,5'}$ 4.0, $J_{5,5'}$ 12.0 Hz, H-5′), 3.29 (s, 3 H, OCH_3), 2.41 (s, 3 H, PhCH_3).

Data for **17**: $[\alpha]_D$ −10.2° (*c* 0.5, $CHCl_3$); ^{1}H NMR: δ 7.81 (d, 2 H, Ph–*H* of Ts), 7.35–7.05 (m, 15 H, 3 Ph–*H*), 4.88 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 4.84 (t, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 2.0 Hz, H-2), 4.78, 4.44 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.62, 4.53 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.41, 4.38 (2 d, 2 H, *J* 10.4 Hz, PhCH_2), 3.93–3.68 (m, 5 H, H-3, 4, 5, 6, 6′), 3.33 (s, 3 H, OCH_3), 2.35 (s, 3 H, PhCH_3). Anal. Calcd for $C_{35}H_{38}O_8S$: C, 67.96; H, 6.15. Found: C, 67.81; H, 6.13.

Data for **24**: mainly α, $[\alpha]_D$ +27.2° (*c* 1.9, $CHCl_3$); ^{1}H NMR: δ 7.85 (d, 2 H, Ph–*H* of Ts), 7.35–7.05 (m, 17 H, Ph–*H*), 4.90 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.84 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 8.0 Hz, H-2), 4.74, 4.44 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.51 (s, 2 H, PhCH_2), 4.46, 4.40 (2 d, 2 H, *J* 11.6 Hz, PhCH_2), 3.94–3.84 (m, 3 H, H-3, 4, 5), 3.52 (d, 2 H, $J_{5,6}$ 8.0 Hz, H-6, 6′), 3.35 (s, 3 H, OCH_3), 2.35 (s, 3 H, PhCH_3). Anal. Calcd for $C_{35}H_{38}O_8S$: C, 67.96; H, 6.15. Found: C, 68.02; H, 6.12.

1,5-Di-O-*acetyl-3*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-α-D-*arabinofuranose* (**4**), *1,5-di*-O-*acetyl-3*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-D-*xylofuranose* (**11**), *1,6-di*-O-*acetyl-3,4-di*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-α-D-*mannopyranose* (**18**), *and 1,6-di*-O-*acetyl-3,4-di*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-D-*galactopyranose* (**25**).—A solution of compound **3** (or **10**, **17**, **24**) (6.0 mmol) in AcOH (34 mL) and Ac_2O (5 mL) was cooled to 0 °C in an ice bath, and H_2SO_4 (3 mL) was added dropwise over 20 min. After the addition was complete, the ice bath was removed, and the reaction was allowed to continue for 16 h at ambient temperature. The reaction solution was poured into a solution of ice water (120 mL). Stirring was continued for an additional 30 min, and the aq solution was extracted with CH_2Cl_2 (3 × 25 mL). The combined CH_2Cl_2 extracts were carefully washed with 10% aq $NaHCO_3$ (3 × 70 mL), and the solvent was removed in vacuo to a constant weight affording **4** (97%), (or **11**, 96%; **18**, 96%; **25**, 96%).

Data for **4**: mp 102–104 °C; $[\alpha]_D$ +18.3° (*c* 1.3, $CHCl_3$); ^{1}H NMR: δ 7.82 (d, 2 H, Ph–*H* of Ts), 7.42–7.25 (m, 7 H, Ph–*H*), 6.02 (s, 1 H, H-1), 4.99 (d, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 4.62, 4.48 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.34–4.04 (m, 4 H, H-3, 4, 5, 5′), 2.48 (s, 3 H, PhCH_3),

2.05, 2.01 (2 s, 6 H, 2 COCH_3). Anal. Calcd for $C_{23}H_{26}O_9S$: C, 57.74; H, 5.44. Found: C, 57.82; H, 5.40.

Data for **11**: 2:1 α, β mixture; $[\alpha]_D$ −14.2° (*c* 3.2, $CHCl_3$); ^{1}H NMR: δ 7.80 (d, 2 H, Ph–*H* of Ts), 7.40–7.18 (m, 7 H, Ph–*H*), 6.22 (d, 0.67 H, $J_{1,2}$ 4.4 Hz, H-1 of α anomer), 5.99 (s, 0.33 H, H-1 of β anomer), 5.01 (s, 0.33 H, H-2 of β anomer), 4.95 (t, 0.67 H, $J_{1,2}$ 4.4, $J_{2,3}$ 4.4 Hz, H-2 of α anomer), 4.70–4.10 (m, 6 H, H-3, 4, 5, 5′, PhCH_2), 2.45 (s, 3 × 0.33 H, PhCH_3 of β anomer), 2.42 (s, 3 × 0.67 H, PhCH_3 of α anomer), 2.03–2.00 (m, 6 H, 2 COCH_3). Anal. Calcd for $C_{23}H_{26}O_9S$: C, 57.74; H, 5.44. Found: C, 57.74; H, 5.42.

Data for **18**: only α isomer: mp 114–116 °C; $[\alpha]_D$ −6.4° (*c* 3.0, $CHCl_3$); ^{1}H NMR: δ 7.85 (d, 2 H, Ph–*H* of Ts), 7.35–7.20 (m, 10 H, 2 Ph–*H*), 6.04 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1), 4.84 (t, 1 H, $J_{2,1}$ 2.2, $J_{3,2}$ 2.2 Hz, H-2), 4.86, 4.54 (2 d, 2 H, *J* 10.5 Hz, PhCH_2), 4.61, 4.48 (2 d, 2 H, *J* 11.3 Hz, PhCH_2), 4.30 (dd, 1 H, $J_{5,6}$ 2.0, $J_{6,6'}$ 12.0 Hz, H-6), 4.21 (dd, 1 H, $J_{5,6'}$ 3.9, $J_{6',6}$ 12.0 Hz, H-6′), 3.96–3.72 (m, 3 H, H-3, 4, 5), 2.40 (s, 3 H, PhCH_3), 2.05, 2.02 (2 s, 6 H, 2 COCH_3). Anal. Calcd for $C_{31}H_{34}O_9S$: C, 63.92; H, 5.84. Found: C, 63.90; H, 5.86.

Data for **25**: mainly α isomer: $[\alpha]_D$ +32.1° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 7.72 (d, 2 H, Ph–*H* of Ts), 7.40–7.10 (m, 12 H, Ph–*H*), 6.26 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.98 (dd, 1 H, $J_{1,2}$ 3.9, $J_{2,3}$ 9.3 Hz, H-2), 4.82, 4.52 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.62 (s, 2 H, PhCH_2), 4.18–3.86 (m, 5 H, H-3, 4, 5, 6, 6′), 2.38 (s, 3 H, PhCH_3), 2.10, 1.95 (2 s, 6 H, 2 COCH_3). Anal. Calcd for $C_{31}H_{34}O_9S$: C, 63.92; H, 5.84. Found: C, 63.88; H, 5.82.

5-O-*Acetyl-3*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-D-*arabinofuranose* (**5**), *5*-O-*acetyl-3*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-D-*xylofuranose* (**12**), *6*-O-*acetyl-3,4-di*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-α-D-*mannopyranose* (**19**), *and 6*-O-*acetyl-3,4-di*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-α-D-*galactopyranose* (**26**).—A solution of compound **4** (or **11**, **18**, **25**) (7.0 mmol) in anhyd Et_2O (100 mL) saturated with dry ammonia was stirred for 24 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **5** (97%), (or **12**, 97%; **19**, 96%; **26**, 97%).

Data for **5**: $[\alpha]_D$ +29.1° (*c* 1.4, $CHCl_3$); ^{1}H NMR: δ 7.82 (d, 2 × 0.2 H, Ph–*H* of β anomer), 7.80 (d, 2 × 0.8 H, Ph–*H* of α anomer), 7.41–7.18 (m, 7 H, Ph–*H*), 5.36 (d, 0.2 H, $J_{1,2}$ 3.8 Hz, H-1 of β anomer), 5.34 (s, 0.8 H, H-1 of α anomer), 4.81 (d, $J_{2,3}$ 2.8 Hz, H-2 of α anomer), 4.75 (dd, $J_{1,2}$ 3.8, $J_{2,3}$ 5.0 Hz, H-2 of β anomer), 4.55–4.32 (m, 2 H, PhCH_2), 4.23–3.93 (m, 4 H, H-3, 4, 5, 5′), 3.66 (bs, 1 H, OH), 2.46 (s, 3 × 0.8 H, PhCH_3 of α anomer), 2.43 (s, 3 × 0.2 H, PhCH_3 of β anomer), 2.03 (s, 3 × 0.2 H, COCH_3 of β anomer), 2.00 (s, 3 × 0.8 H, COCH_3 of α anomer). Anal. Calcd for $C_{21}H_{24}O_8S$: C, 57.80; H, 5.50. Found: C, 57.84; H, 5.48.

Data for **12**: 1:3 α, β mixture: $[\alpha]_D$ −24.1° (*c* 0.9, $CHCl_3$); ^{1}H NMR: δ 7.82 (d, 2 × 0.25 H, Ph–*H* of Ts of α anomer), 7.80 (d, 2 × 0.75 H, Ph–*H* of Ts of *β* anomer), 7.50–7.16 (m, 7 H, Ph*H*), 5.46 (d, 0.25 H, $J_{1,2}$ 4.1 Hz, H-1 of α anomer), 5.15 (s, 0.75 H, H-1 of β anomer), 4.80 (s, 0.75 H, H-2 of β anomer), 4.71 (t, 0.25 H, $J_{2,1}$ 4.1, $J_{3,2}$ 4.1 Hz, H-2 of α anomer), 4.63–4.12 (m, 6 H, H-3, 4, 5, 5′, PhCH_2), 2.46 (s, 3 × 0.75 H, PhCH_3 of β anomer), 2.42 (s, 3 × 0.25 H, PhCH_3 of α anomer), 2.03(s, 3 × 0.75 H, COCH_3 of β anomer), 2.00 (s, 3 × 0.25 H, COCH_3 of α anomer). Anal. Calcd for $C_{21}H_{24}O_8S$: C, 57.80; H, 5.50. Found: C, 57.77; H, 5.53.

Data for **19**: Only α isomer: $[\alpha]_D$ −16.5° (*c* 1.7, $CHCl_3$); ^{1}H NMR: δ 7.83 (d, 2 H, Ph–*H* of Ts), 7.39–7.17 (m, 10 H, 2 PhCH_2), 5.34 (d, 1 H, $J_{2,1}$ 2.0 Hz, H-1), 4.81 (t, 1 H, $J_{1,2} = J_{3,2}$ 2.0 Hz, H-2), 4.82, 4.53 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.39 (s, 2 H, PhCH_2), 4.37 (dd, 1 H, $J_{2,3}$ 2.0, $J_{4,3}$ 10.0 Hz, H-3), 4.14 (dd, 1 H, $J_{5,6}$ 6.0, $J_{6',6}$ 12.0 Hz, H-6), 3.98 (dd, 1 H, $J_{5,6'}$ 2.4, $J_{6,6'}$ 12.0 Hz, H-6′), 3.97 (m, 1 H, H-5), 3.72 (t, 1 H, $J_{3,4} = J_{5,4}$ 10.0 Hz, H-4), 2.90 (ds, 1 H, O*H*), 2.38 (s, 3 H, PhCH_3), 2.04 (s, 3 H, COCH_3). Anal. Calcd for $C_{29}H_{32}O_8S$: C, 64.44; H, 5.92. Found: C, 64.50; H, 5.91.

Data for **26**: Only α isomer: $[\alpha]_D$ +43.1° (*c* 2.1, $CHCl_3$); ^{1}H NMR: δ 7.75 (d, 2 H, Ph–*H* of Ts), 7.35–7.08 (m, 12 H, Ph*H*), 5.49 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.84 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 9.6 Hz, H-2), 4.79, 4.49 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.54 (s, 2 H, PhCH_2), 4.20–4.04 (m, 3 H, H-5, 6, 6′), 3.98 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 2.6 Hz, H-3), 3.84 (d, 1 H, $J_{3,4}$ 2.6 Hz, H-4), 2.37

(s, 3 H, PhCH_3), 1.99 (s, 3 H, COCH_3). Anal. Calcd for $C_{29}H_{32}O_8S$: C, 64.44; H, 5.92. Found: C, 64.39; H, 5.94.

5-O-Acetyl-1,2-anhydro-3-O-benzyl-α-D-ribofuranose (**6**), *5-O-acetyl-1,2-anhydro-3-O-benzyl-β-D-lyxofuranose* (**13**), *6-O-acetyl-1,2-anhydro-3,4-di-O-benzyl-α-D-glucopyranose* (**20**), *and 6-O-acetyl-1,2-anhydro-3,4-di-O-benzyl-β-D-talopyranose* (**27**).—To a solution of **5** (or **12**, **19**, **26**) (2.0 mmol) in dry THF (6 mL) was added *t*-BuOK (2.2 mmol), and the mixture was stirred at rt for 10 min, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the starting material had disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether–EtOAc. Concentration of the combined extracts yielded **6** (95%) (or **13**, 94%; **20**, 92%; **27**, 94%).

Data for **6**: $[\alpha]_D$ +36.1° (*c* 1.1, $CHCl_3$); ^{1}H NMR: δ 7.38 (s, 5 H, Ph*H*), 5.20 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.76, 4.66 (ABdd, 2 H, *J* 12.0 Hz, Ph*H*), 4.30–3.90 (m, 4 H, H-3, 4, 5, 5′), 3.57 (t, 1 H, $J_{1,2} = J_{2,3}$ 1.7 Hz, H-2), 2.03 (s, 3 H, COCH_3).

Data for **13**: $[\alpha]_D$ −8.6° (*c* 2.4, $CHCl_3$); ^{1}H NMR: δ 7.38–7.24 (5 H, Ph*H*), 5.16 (d, 1 H, $J_{2,1}$ 1.9 Hz, H-1), 4.72, 4.64 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.58, 4.35 (m, 3 H, H-3, 5, 5′), 4.10 (m, 1 H, H-4), 3.60 (t, 1 H, $J_{1,2} = J_{3,2}$ 1.9 Hz, H-2), 2.08 (s, 3 H, COCH_3).

Data for **20**: mp 93–94 °C; $[\alpha]_D$ −10.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 7.42–7.23 (m, 10 H, 2 PhCH_2), 4.95 (d, 1 H, $J_{2,1}$ 1.7 Hz, H-1), 4.80, 4.60 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.79, 4.69 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.33 (dd, 1 H, $J_{5,6}$ 2.2, $J_{6',6}$ 11.9 Hz, H-6), 4.24 (dd, 1 H, $J_{5,6'}$ 3.9, $J_{6,6'}$ 11.9 Hz, H-6′), 4.01 (dd, 1 H, $J_{2,3}$ 1.0, $J_{4,3}$ 7.8 Hz, H-3), 3.81 (ddd, 1 H, $J_{4,5}$ 10.2, $J_{6,5}$ 2.2, $J_{6',5}$ 3.9 Hz, H-5), 3.51 (dd, 1 H, $J_{3,4}$ 7.8, $J_{5,4}$ 10.2 Hz, H-4), 3.06 (dd, 1 H, $J_{1,2}$ 1.7, $J_{3,2}$ 1.0 Hz, H-2), 2.03 (s, 3 H, COCH_3).

Data for **27**: mp 90–91 °C; $[\alpha]_D$ +11.4° (*c* 1.9, $CHCl_3$); ^{1}H NMR: δ 7.48–7.29 (m, 10 H, Ph*H*), 5.00 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.90, 4.67(2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.86, 4.77 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.24–4.00 (m, 3 H, H-5, 6, 6′), 3.95 (dd, 1 H, $J_{2,3}$ 4.0, $J_{3,4}$ 5.1 Hz, H-3), 3.77 (d, 1 H, $J_{3,4}$ 5.1 Hz, H-4), 3.50 (t, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 4.0 Hz, H-2), 1.96 (s, 3 H, COCH_3).

Methyl 5-O-acetyl-3-O-benzyl-β-D-ribofuranoside (**7**), *methyl 5-O-acetyl-3-O-benzyl-α-D-lyxofuranoside* (**14**), *methyl 6-O-acetyl-3,4-di-O-benzyl-β-D-glucopyranoside* (**21**), *and methyl 6-O-acetyl-3,4-di-O-benzyl-α-D-talopyranoside* (**28**).—Compound **6** (or **13**, **20**, **27**) (0.5 mmol) was dissolved in anhyd MeOH (5 mL) and kept for 1 h at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated to quantitatively afford **7** (or **14**, **21**, **28**).

Data for **7**: $[\alpha]_D$ +13.9° (*c* 0.9, $CHCl_3$); ^{1}H NMR: δ 7.35 (s, 5 H, Ph*H*), 4.88 (s, 1 H, H-1), 4.61, 4.57 (ABdd, 2 H, *J* 11.4 Hz, PhCH_2), 4.30–4.00 (m, 5 H, H-2, 3, 4, 5, 5′), 3.35 (s, 3 H, OCH_3), 2.05 (s, 3 H, COCH_3). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.81; H, 6.76. Found: C, 60.77; H, 6.72.

Data for **14**: $[\alpha]_D$ +35.6° (*c* 0.6, $CHCl_3$); ^{1}H NMR: δ 7.40–7.30 (5 H, Ph*H*), 4.90 (s, 1 H, H-1), 4.65, 4.57 (2 d, 2 H, *J* 12.6 Hz, PhCH_2), 4.48–4.30 (m, 3 H, H-3, 5, 5′), 4.19 (m, 1 H, H-4), 4.07 (d, 1 H, $J_{3,2}$ 4.6 Hz, H-2), 3.36 (s, 3 H, OCH_3), 2.04 (s, 3 H, COCH_3). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.81; H, 6.76. Found: C, 60.84; H, 6.75.

Data for **21**: $[\alpha]_D$ −31° (*c* 1.5, $CHCl_3$); ^{1}H NMR: δ 7.40–7.25 (m, 10 H, 2 Ph*H*), 4.95, 4.85 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.86, 4.57 (2 d, 2 H, *J* 10.2 Hz, PhCH_2), 4.33 (dd, 1 H, $J_{5,6}$ 1.0, $J_{6',6}$ 12.8 Hz, H-6), 4.24 (dd, 1 H, $J_{5,6'}$ 2.1, $J_{6,6'}$ 12.8 Hz, H-6′), 4.17 (d, 1 H, $J_{2,1}$ 8.0 Hz, H-1), 3.66–3.48 (m, 4 H, H-2, 3, 4, 5), 3.55 (s, 3 H, OCH_3), 2.50 (bs, 1 H, O*H*), 2.03 (s, 3 H, COCH_3). Anal. Calcd for $C_{23}H_{28}O_7$: C, 66.35; H, 6.73. Found: C, 66.40; H, 6.75.

Data for **28**: $[\alpha]_D$ +14.3° (*c* 2.5, $CHCl_3$); ^{1}H NMR: δ 7.44–7.30 (m, 10 H, Ph*H*), 4.99, 4.63 (2 d, 2 H, *J* 11.8 Hz, PhCH_2), 4.83, 4.55 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.82 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.22 (dd, 1 H, $J_{5,6}$ 7.4, $J_{6,6'}$ 12.0 Hz, H-6), 4.14 (dd, 1 H, $J_{5,6'}$ 6.0, $J_{6,6'}$ 12.0 Hz, H-6′), 4.0 (m, 1 H, H-5), 3.92–3.82 (m, 2 H, H-3, 4), 3.73 (t, 1 H, $J_{1,2} = J_{2,3} = 3.5$ Hz, H-2), 3.35 (s, 3 H, OCH_3), 2.00 (s, 3 H, COCH_3). Anal. Calcd for $C_{23}H_{28}O_7$: C, 66.35; H, 6.73. Found: C, 66.33; H, 6.71.

5-O-Acetyl-3-O-benzyl-α-D-lyxofuranosyl-(1→5)-3-O-benzyl-1,2-O-isopropylidene-α-D-xylofuranose (**29**).—To a solution of 1,2-

O-isopropylidene-3-*O*-benzyl-α-D-xylofuranose (196 mg, 0.70 mmol) in anhyd CH_2Cl_2 (5 mL) was added 4-Å molecular sieves (1 g) and $ZnCl_2$ (0.6 g). The mixture was stirred for 10 min at rt, and a solution of **13** (145.2 mg, 0.55 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at rt for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that **13** had disappeared. The suspension was filtered to remove solid material, and the filtrate was washed with water (3 × 50 mL), dried over Na_2SO_4, and concentrated to a syrup. The crude product was purified by column chromatography using 1:2 petroleum ether–EtOAc as the eluent. Compound **29** was obtained as a syrup (253 mg, 81%): $[\alpha]_D + 1.2°$ (*c* 1.4, $CHCl_3$); ^{1}H NMR: δ 7.40–7.30 (m, 10 H, Ph*H*), 5.91 (d, 1 H, $J_{2,1}$ 3.8 Hz, H-1), 4.98 (s, 1 H, H-1′), 4.68–4.45 (m, 5 H, H-2, 2 PhCH_2), 4.38–4.26 (m, 4 H, H-3′, 4, 5a, 5b), 4.17 (m, 1 H, H-4′), 4.06 (d, 1 H, $J_{3',2'}$ 4.3 Hz, H-2′), 3.94–3.68 (m, 3 H, H-3, 5′a, 5′b), 2.64 (bs, 1 H, O*H*), 2.05 (s, 3 H, COCH_3), 1.52, 1.31 (2 s, 6 H, 2 CCH_3). Anal. Calcd for $C_{31}H_{36}O_{10}$: C, 65.49; H, 6.34. Found: C, 65.63; H, 6.32.

6-O-*Acetyl-3,4-di*-O-*benzyl-β*-D-*glucopyranosyl - (1→6) - 1,2:3,4 - di* - O - *isopropylidene*-α-D-*galactopyranose* (**30**).—To a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (182 mg, 0.70 mmol) in anhyd CH_2Cl_2 (7 mL) was added 4-Å molecular sieves (1 g) and $ZnCl_2$ (0.5 g). The mixture was stirred for 10 min at rt, and a solution of **20** (234 mg, 0.61 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at rt for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that **20** had disappeared. The suspension was filtered, and the filtrate was washed with water (3 × 50 mL), dried over Na_2SO_4, and concentrated to a syrup. The crude product was purified by column chromatography with 1:2 petroleum ether–EtOAc as the eluent. Compound **30** was obtained as a syrup (326 mg, 83%): $[\alpha]_D + 1.6°$ (*c* 2.5, $CHCl_3$); ^{1}H NMR: δ 7.40–7.20 (m, 10 H, 2 Ph*H*), 5.50 (d, 1 H, $J_{2,1}$ 5.0 Hz, H-1), 5.06, 4.80 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.87, 4.55 (2 d, 2 H, *J* 10.8 Hz, PhCH_2), 4.61 (dd, 1 H, $J_{2,3}$ 2.4, $J_{4,3}$ 7.9 Hz, H-3), 4.35, 4.31 (2 d, 2 H, *J* 7.5 Hz, H-6′a, 6′b), 4.33 (dd, 1 H, $J_{1,2}$ 5.0, $J_{3,2}$ 2.4 Hz, H-2), 4.25 (d, 1 H, $J_{2',1'}$ 3.2 Hz, H-1′), 4.22 (dd, 1 H, $J_{3,4}$ 7.9, $J_{5,4}$ 1.8 Hz, H-4), 4.07 (dd, 1 H, $J_{1',2'}$ 3.2, $J_{3',2'}$ 11.0 Hz, H-2′), 4.01 (m, 1 H, H-5), 3.74 (dd, 1 H, $J_{2',3'}$ 11.0, $J_{4',3'}$ 8.1 Hz, H-3′), 3.65 (m, 1 H, H-5′), 3.60 (dd, 1 H, $J_{3',4'} = 8.1$, $J_{5',4'} = 10.5$ Hz, H-4′), 3.52 (d, 2 H, $J_{5,6}$ 4.8 Hz, H-6a,6b), 2.02 (s, 3 H, COCH_3), 1.52, 1.50, 1.48, 1.47 (4 s, 12 H, 4 CCH_3). Anal. Calcd for $C_{34}H_{44}O_{12}$: C, 63.35; H, 6.83. Found: C, 65.53; H, 6.32.

5-O-*Acetyl-3,6-di*-O-*benzyl-1,2*-O-*isopropylidene*-α-D-*glucofuranose* (**32**).—Acetylation of **31** (8.6 g, 21.5 mmol) with Ac_2O (15 mL) in C_5H_5N (20 mL) at rt for 4 h gave compound **32** in a quantitative yield as a syrup: $[\alpha]_D - 26°$ (*c* 5.3, $CHCl_3$); ^{1}H NMR: δ 7.40–7.20 (m, 10 H, 2 Ph*H*), 5.92 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.33 (m, 1 H, H-5), 4.65–4.41 (m, 6 H, H-2, 4, 2 PhCH_2), 3.97 (d, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 3.85 (dd, 1 H, $J_{5,6}$ 2.0, $J_{6,6'}$ 12.0 Hz, H-6), 3.72 (dd, 1 H, $J_{5,6'}$ 6.0, $J_{6,6'}$ 12.0 Hz, H-6′), 1.96 (s, 3 H, COCH_3), 1.50, 1.34 (2 s, 6 H, 2 CCH_3). Anal. Calcd for $C_{25}H_{30}O_7$: C, 67.83; H, 6.82. Found: C, 67.87; H, 6.79.

5-O-*Acetyl-3,6-di*-O-*benzyl*-D-*glucofuranose* (**33**).—A solution of **32** (5.2 g, 11.7 mmol) in 50% AcOH (60 mL) was refluxed with stirring for 5 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated to a syrup. The crude product was purified by column chromatography with 1:1 petroleum ether–EtOAc as the eluent. Compound **33** was obtained as a syrupy anomeric mixture (4.4 g, 92%, α:β 1:1): $[\alpha]_D - 36°$ (*c* 6.5, $CHCl_3$); ^{1}H NMR: δ 7.40–7.20 (m, 10 H, 2 Ph*H*), 5.41 (d, 0.5 H, $J_{1,2}$ 3.8 Hz, H-1 of α anomer), 5.28 (m, 1 H, H-5), 5.14 (s, 0.5 H, H-1 of β anomer), 4.63–4.38 (m, 4 H, 2 PhCH_2), 4.19–3.67 (5 H, H-2, 3, 4, 6, 6′), 1.96 (s, 3 H, COCH_3). Anal. Calcd for $C_{22}H_{26}O_7$: C, 65.67; H, 6.48. Found: C, 65.84; H, 6.53.

5-O-*Acetyl-3,6-di*-O-*benzyl-2*-O-*(*p-*toluenesulfonyl)*-D-*glucofuranose* (**34**).—To a solution of compound **33** (3.4 g, 6.1 mmol) in CH_2Cl_2 (40 mL) was added TsCl (1.75 g, 9.2 mmol), TBAHS (150 mg, 0.44 mmol) and 5% aq NaOH (15.0 mL). The solution was stirred at rt for 15 h, and then diluted with CH_2Cl_2 and washed with cold water. The organic phase was dried over Na_2SO_4, then evaporated un-

der diminished pressure to give **34** (2.4 g, 71%) as an α,β mixture in the ratio of 1:6, along with recovered starting material **3** (0.6 g). Data for 34: $[\alpha]_D$ −18° (*c* 7.3, $CHCl_3$); ^1H NMR: δ 7.80 (d, 2 H, Ph–*H* of Ts), 7.39–7.19 (m, 12 H, Ph*H*), 5.43 (d, 0.14 H, $J_{1,2}$ 4.2 Hz, H-1 of α anomer), 5.28 (m, 1 H, H-5), 5.08 (s, 0.86 H, H-1 of β anomer), 4.77 (s, 0.86 H, H-2 of β anomer), 4.68 (dd, 0.14 H, $J_{1,2}$ 4.2, $J_{2,3}$ 3.6 Hz, H-2 of α anomer), 4.62–4.40 (5 H, 2 PhCH_2, H-4), 4.20 (m, 1 H, H-3), 3.82–3.64 (2 H, H-6, 6′), 2.44 (s, 3 × 0.86 H, PhCH_3 of β anomer), 2.42 (s, 3 × 0.14 H, PhCH_3 of α anomer), 1.87 (s, 3 × 0.14 H, COCH_3 of α anomer), 1.86 (s, 3 × 0.86 H, COCH_3 of β anomer). Anal. Calcd for $C_{29}H_{32}O_9S$: C, 62.59; H, 5.76. Found: C, 62.41; H, 5.81.

5-O-*Acetyl-1,2-anhydro-3,6-di*-O-*benzyl-β*-D-*mannofuranose* (**35**).—To a solution of **34** (560 mg, 1.01 mmol) in dry THF (6 mL) was added *t*-BuOK (124 mg, 1.11 mmol), and the mixture was stirred at rt for 10 min, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the starting material had disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether–EtOAc. Concentration of the combined extracts yielded 35 as a syrup (372 mg, 96%): $[\alpha]_D$ +23.7° (*c* 2.9, $CHCl_3$); ^1H NMR: δ 7.42–7.20 (m, 10 H, 2 Ph*H*), 5.38 (ddd, 1 H, $J_{4,5}$ 6.6, $J_{5,6}$ 2.4, $J_{5,6'}$ 5.6 Hz, H-5), 5.13 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 4.70, 4.62 (ABq, 2 H, *J* 11.7 Hz, PhCH_2), 4.63 (dd, 1 H, $J_{3,4}$ 8.1, $J_{4,5}$ 6.6 Hz, H-4), 4.53, 4.48 (ABq, 2 H, *J* 11.2 Hz, PhCH_2), 4.40 (dd, 1 H, $J_{2,3}$ 2.0, $J_{3,4}$ 8.1 Hz, H-3), 3.84 (dd, 1 H, $J_{5,6}$ 2.4, $J_{6,6'}$ 11.5 Hz, H-6), 3.73 (dd, 1 H, $J_{5,6'}$ 5.6, $J_{6,6'}$ 11.5 Hz, H-6′), 3.62 (t, 1 H, $J_{1,2} = J_{2,3} = 2.0$ Hz, H-2), 2.03 (s, 3 H, COCH_3).

Methyl 5-O-*acetyl-3,6-di*-O-*benzyl*-α-D-*mannofuranoside* (**36**).—Compound **35** (120 mg, 0.31 mmol) was dissolved in anhyd MeOH (5 mL) and kept for 1 h at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **36** quantitatively as a syrup: $[\alpha]_D$ +37.2° (*c* 1.8, $CHCl_3$); ^1H NMR: δ 7.38–7.24 (m, 10 H, 2 Ph*H*), 5.38 (m, 1 H, H-5), 4.82 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 4.57, 4.54 (ABq, 2 H, *J* 12 Hz, PhCH_2), 4.53, 4.49 (ABq, 2 H, *J* 11.8 Hz, PhCH_2), 4.40–4.25 (m, 2 H, H-3, 4), 4.05 (dd, 1 H, $J_{1,2}$ 1.0, $J_{2,3}$ 4.8 Hz, H-2), 3.84 (2 d, 1 H, $J_{5,6}$ 4.0, $J_{6,6'}$ 11.0 Hz, H-6), 3.72 (2 d, 1 H, $J_{5,6'}$ 5.2, $J_{6,6'}$ 11.0 Hz, H-6′), 3.31 (s, 3 H, OCH_3), 2.02 (s, 3 H, COCH_3). Anal. Calcd for $C_{23}H_{28}O_7$: C, 66.35; H, 6.73. Found: C, 66.50; H, 6.77.

5-O-*Acetyl-3,6-di*-O-*benzyl*-α-D-*mannofuranosyl*-(1→6)-*1,2:3,4*-*di*-O-*isopropylidene*-α-D-*galactopyranose* (**37**).—To a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (130 mg, 0.50 mmol) in anhyd CH_2Cl_2 (4 mL) was added 4-Å molecular sieves (1 g) and $ZnCl_2$ (0.5 g). The mixture was stirred for 10 min at rt, and a solution of **35** (156 mg, 0.41 mmol) in CH_2Cl_2 (3 mL) was added. The mixture was stirred at rt for 12 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that **35** had disappeared. The suspension was filtered to remove solid material, and the filtrate was washed with water (3 × 50 mL), dried over Na_2SO_4, and concentrated to a syrup. The crude product was purified by column chromatography with 1:2 petroleum ether–EtOAc as the eluent. Compound **37** was obtained as a syrup (213 mg, 84%): $[\alpha]_D$ +1.2° (*c* 2.7, $CHCl_3$); ^1H NMR: δ 7.40–7.20 (m, 10 H, 2 Ph*H*), 5.51 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 5.37 (m, 1 H, H-5′), 4.99 (d, 1 H, $J_{1',2'}$ 1.2 Hz, H-1′), 4.59–4.51 (m, 5 H, H-3, 2 PhCH_2), 4.44–4.28 (m, 3 H, H-2, 3′, 4′), 4.21 (dd, 1 H, $J_{3,4}$ 7.6, $J_{4,5}$ 2.1 Hz, H-4), 4.13 (dd, 1 H, $J_{1',2'}$ 1.2, $J_{2',3'}$ 5.0 Hz, H-2), 3.96 (m, 1 H, H-5), 3.82 (dd, 1 H, $J_{5',6'a}$ 3.9, $J_{6'a,6'b}$ 11.2 Hz, H-6′a), 3.76–3.64 (m, 3 H, H-6′b, 6a, 6b), 2.55 (bs, 1 H, O*H*), 2.03 (s, 3 H, COCH_3), 1.55, 1.46, 1.35, and 1.34 (4 s, 12 H, 4 CCH_3). Anal. Calcd for $C_{32}H_{44}O_{12}$: C, 62.01; H, 7.06. Found: C, 61.94; H, 7.10.

5,6-Di-O-*benzoyl-3*-O-*benzyl-2*-O-(p-*toluenesulfonyl*)-D-*glucofuranose* (**39**).—To a solution of 5,6-di-*O*-benzoyl-3-*O*-benzyl-D-glucofuranose (**38**)[17] (2.1 g, 4.39 mmol) in CH_2Cl_2 (40 mL) was added TsCl (1.17 g, 6.14 mmol), TBAHS (75 mg, 0.22 mmol) and 5% aq NaOH (12.0 mL). The solution was stirred at rt for 15 h, and then diluted with CH_2Cl_2 and washed with cold water. The organic phase was dried over Na_2SO_4, then evaporated under diminished pressure to give **39** (1.9 g, 69%) as an α,β mixture in the ratio of 1:3, along with recovered starting material **38** (0.2 g).

Data for **39**: $[\alpha]_D$ −18° (*c* 7.3, $CHCl_3$); ^1H NMR: δ 7.80 (d, 2 H, Ph–*H* of Ts), 8.01–7.11 (m, 15 H, 3 Ph*H*), 5.75 (m, 0.75 H, H-5 of β anomer), 5.67 (m, 0.25 H, H-5 of α anomer), 5.52 (d, 0.25 H, $J_{1,2}$ 3.7 Hz, H-1 of α anomer), 5.12 (s, 0.75 H, H-1 of β anomer), 4.91 (dd, 0.75 H, $J_{5,6}$ 2.4, $J_{6,6'}$ 12.4 Hz, H-6 of β anomer), 4.86 (dd, 0.25 H, $J_{5,6}$ 2.8, $J_{6,6'}$ 11.9 Hz, H-6 of α anomer), 4.80 (s, 0.75 H, H-2 of β anomer), 4.72 (dd, 0.25 H, $J_{1,2}$ 3.7, $J_{2,3}$ 2.3 Hz, H-2 of α anomer), 4.63–4.56 (m, 2 H, H-4, 6′), 4.54, 4.39 (2 d, 2 H, *J* 12.4 Hz, PhCH_2), 4.30 (dd, 0.25 H, $J_{2,3}$ 2.3, $J_{3,4}$ 4.0 Hz, H-3 of α anomer), 4.25 (d, 0.75 H, $J_{3,4}$ 4.0 Hz, H-3 of β anomer), 2.47 (s, 3 × 0.75 H, PhCH_3 of β anomer), 2.45 (s, 3 × 0.25 H, PhCH_3 of α anomer). Anal. Calcd for $C_{34}H_{32}O_{10}S$: C, 64.55; H, 5.06. Found: C, 64.61; H, 5.10.

1,2-Anhydro-5,6-di-O-*benzoyl-3*-O-*benzyl-β*-D-*mannofuranose* (**40**).—To a solution of **39** (420 mg, 0.66 mmol) in dry THF (6 mL) was added *t*-BuOK (80.6 mg, 0.72 mmol), and the mixture was stirred at rt for 10 min, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the starting material had disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether–EtOAc. Concentration of the combined extracts yielded **40** as a syrup (294 mg, 97%): $[\alpha]_D$ +23.7° (*c* 2.9, $CHCl_3$); ^1H NMR: δ 8.09–7.24 (m, 15 H, 3 Ph*H*), 5.84 (m, 1 H, H-5), 5.20 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1), 4.83 (dd, 1 H, $J_{5,6}$ 2.7, $J_{6,6'}$ 12.2 Hz, H-6), 4.78–4.64 (m, 2 H, H-3, 4), 4.68, 4.58 (ABq, 2 H, *J* 12.0 Hz, PhCH_2), 4.46 (dd, 1 H. $J_{5,6'}$ 1.9, $J_{6,6'}$ 12.2 Hz, H-6′), 3.66 (t, 1 H, $J_{1,2} = J_{2,3} = 1.9$ Hz, H-2).

Methyl 5,6-di-O-*benzoyl-3*-O-*benzyl*-α-D-*mannofuranoside* (**41**).—Compound **40** (210 mg, 0.46 mmol) was dissolved in anhyd MeOH (5 mL) and kept for 1 h at rt. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **41** quantitatively as a syrup: $[\alpha]_D$ +37.2° (*c* 1.8, $CHCl_3$); ^1H NMR: δ 8.06–7.24 (m, 15 H, 3Ph*H*), 5.38 (ddd, 1 H, $J_{4,5}$ 7.4, $J_{5,6}$ 2.4, $J_{5,6'}$ 5.7 Hz, H-5), 4.91 (d, 1 H, $J_{1,2}$ 0.9 Hz, H-1), 4.90 (2 d, 1 H, $J_{5,6}$ 2.4, $J_{6,6'}$ 12.3 Hz, H-6), 4.69 (2 d, 1 H, $J_{5,6'}$ 5.7, $J_{6,6'}$ 12.3 Hz, H-6′), 4.54 (dd, 1 H, $J_{3,4}$ 5.6, $J_{4,5}$ 7.4 Hz, H-4), 4.53 (s, 2 H, PhCH_2), 4.36 (t, 1 H, $J_{2,3} = J_{3,4} = 5.6$ Hz, H-3), 4.10 (dd, 1 H, $J_{1,2}$ 0.9, $J_{2,3}$ 5.6 Hz, H-2), 3.33 (s, 3 H, OCH_3). Anal. Calcd or $C_{28}H_{28}O_8$: C, 68.29; H, 5.69. Found: C, 68.15; H, 5.61.

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