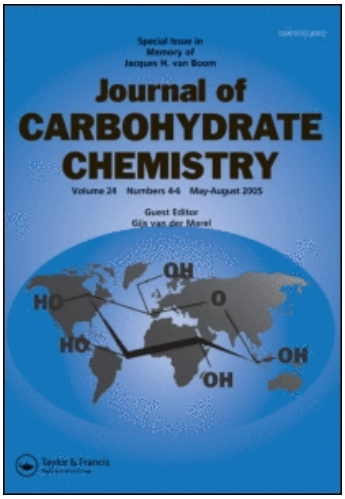

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THE APPLICATION OF THE TRICHLOROACETIMIDATE METHOD TO THE SYNTHESIS OF α-D-GLUCO- AND α-D-GALACTOPYRANOSIDES [1]

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ABSTRACT

The trichloroacetimidate method has been applied to the construction of α-D-galacto- and α-D-glucopyranosides. The readily available β-trichloroacetimidates of 2,3,4,6-tetra-O-benzyl-D-galacto- and glucopyranose (1-β and 3-β, respectively) have been employed in glycosidations with several monosaccharides (either A, B, C or D) under varying experimental conditions. With the galactose derivative 1-β as a donor and each of the monosaccharides A-D as acceptors, the corresponding disaccharides 1A-1D, were obtained in high yield and with good α-stereoselectivity when employing diethyl ether as solvent and either trimethylsilyl- or tert-butyldimethylsilyl trifluoromethane sulphonate as catalyst. Glycosidations with the glucose derivative 3-β, as donor, and with the monosaccharide acceptors A, B or D, gave the corresponding disaccharides 3A, 3B and 3D, in high yield but with somewhat lower α-diastereoselectivity than observed with the galactose derivative 1-β. The stereochemical outcome of the reactions is rationalised in terms of possible reaction mechanisms.

INTRODUCTION

α-D-Glucopyranosides are ubiquitious in nature and α-D-galactopyranoside moieties have been identified as constituents of many natural glycoconjugates. As a consequence, considerable attention has been paid to developing methods for the efficient chemical syntheses of glycosides of these particular sugars.

Amongst the most satisfactory approaches by which the required α-diastereoselectivity has previously been achieved, is through the use of the in-situ anomerisation procedure, i.e. by the reaction of an α-halogenose donor with an acceptor, in the presence of an appropriate catalyst.[2] An alternative method, by which have been claimed comparably good α-stereoselectivities, is that employing O-(ß-D-galactopyranosyl)-N-methyl-acetimidate as the donor, with p-toluene sulphonic acid as a catalyst.[3]

We were interested in examining the use of the trichloroacetimidate procedure as a possible alternative to these aformentioned approaches. The potential of O-glycosyl-trichloroacetimidates in glycosylation reactions under mild acidic catalysis conditions has been confirmed by many investigations.[4,5] The direct glycosylation of Brønsted acids as glycosyl acceptors is a particularly advantageous property of these glycosyl donors.[4,6] Alcohol components for reaction as O-nucleophiles generally require the presence of an acid catalyst. Boron trifluoride etherate in either dichloromethane or dichloromethane/hexane as solvents, at temperatures of between -40 °C and 25 °C have proved to be particularly good conditions under which to carry out these glycosidations with regard both to yield and diastereoselectivity. This is exemplified by various successful applications of the methodology to hexopyranoside syntheses.[4,5] These studies have shown that in general, with glycosyl donors bearing 2-O- or 2-N-protective groups capable of neighbouring group participation, glycosidations proceed to give the 1,2-trans-products. However, when donors bearing either the 2-O-benzyl protective group or the 2-azido-2-deoxy group have been used, products of opposite anomeric configuration to that of the starting trichloroacetimidates are preferentially obtained. It has therefore been possible, through use of the appropriately protected glycosyl donors, to obtain ß-glycopyranosides (1,2-trans configuration) of all the major D-hexoses.[4,5] Furthermore, the stronger catalyst system trimethylsilyl triflate ($CF_3SO_3SiMe_3$) has been found to lead to the formation of the thermodynamically more stable product,[7] and its use has led to the synthesis of α-glycopyranosides (1,2-cis-configuration) of D-glucosamine and D-galactosamine.

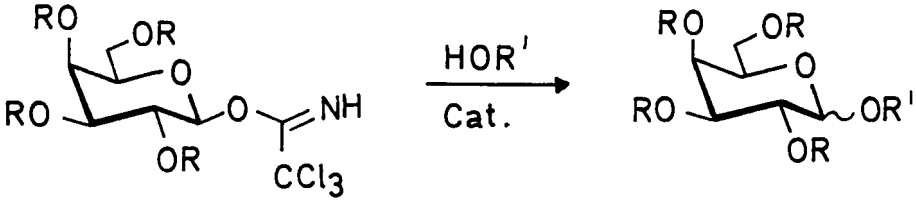
This paper describes in full detail [8,9] the utilisation of the trichloroacetimidate method in the syntheses of α-glycopyranosides (1,2-cis-configuration) of D-glucose and D-galactose, and demonstrates the general applicability of this methodology to the formation of these types of glycosidic bond.

RESULTS AND DISCUSSION

A. SYNTHESIS OF α-D-GALACTOPYRANOSIDES.

The readily available glycosyl donor O-(β-D-galactopyranosyl)trichloroacetimidate 1-β, and each of the monosaccharide derivatives A-D (each of which exhibit different acceptor properties) were reacted to give the corresponding α- and β-disaccharides (SCHEME 1).

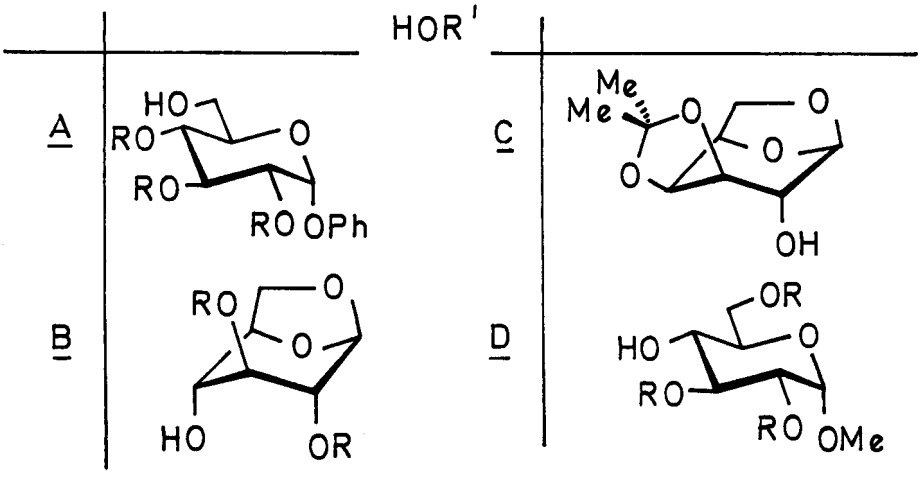
SCHEME 1



1-β : R = Bzl

1A-1D : R = Bzl
2A, 2D : R = Ac

HOR'



The identity of the products (1B-1D) was established by a comparison with known materials, and that of 1A and 1D on the basis of ^{13}C NMR data and full ^{1}H-NMR spectral analysis of compounds 2A-α and 2D-α (derived from 1A-α and 1D-α respectively, after their hydrogenolytic debenzylation and subsequent acetylation).

In glycosidations with 1-ß and A under the standard conditions used in the trichloroacetimidate method, i.e. boron trifluoride-ether as catalyst in dichloromethane as solvent, the corresponding disaccharides 1A-α and 1A-ß were obtained in high yields (α:ß = 2:1). The poor α-stereoselectivity was not improved through use of the alternative catalyst trimethylsilyl triflate ($CF_3SO_3SiMe_3$) in dichloromethane. Diethyl ether has been observed to be a suitable solvent in glycosidations using modifications of the Koenigs-Knorr procedure,[10] and an investigation of glycosidations using 1-ß and A in different solvents revealed that the α-stereoselectivity could be improved using $CF_3SO_3SiMe_3$ in diethyl ether at room temperature (TABLE 1, Exp. 1). Lower temperatures decreased the α-stereoselectivity. The alternative catalyst tert-butyldimethylsilyl triflate ($CF_3SO_3SiMe_2t$-Bu) gave slightly improved yields compared with $CF_3SO_3SiMe_3$ (Exp. 1 and Exp. 2, TABLE 2).

Excellent α-diastereoselectivities and yields were obtained with the less reactive acceptors 1,6-anhydro-glucose and -galactose (B and C, respectively), or the relatively unreactive 4-O-unprotected glucose derivative D, in glycosidations catalysed by either $CF_3SO_3SiMe_3$ or $CF_3SO_3SiMe_3$t-Bu in diethyl ether, to give the corresponding disaccharides 1B, 1C and 1D (TABLE 1, Exp. 3-7).

The stereochemical outcome of these reactions is consistent with a mechanism involving an intramolecular stabilisation by the 4-benzyloxy group of an intermediate anomeric oxocarbenium ion, followed by attack of a nucleophile on its less hindered α-face. An alternative explanation would involve reaction of the solvent diethyl ether, with an intermediate oxocarbenium ion leading to a ß-oxonium ion intermediate (of a type previously postulated [10]) followed by α-attack of a nucleophile on this species. The competing ß-disaccharide formation observ-

TABLE 1

Reaction of Trichloroacetimidate 1-β with the Glycosyl Acceptors A-D in Diethyl Ether as the Solvent. Formation of Disaccharides 1A-α - 1D-α and 1A-β - 1D-β.

Exp.	[1-β]:[HOR']:[Cat.]			Temp. [°C]	Time [h]	Yield[d] [%]	Product Ratio[d]
1	0.74	0.65	0.25[b]	RT	1.5	67	1A-α:1A-β = 5:1
2	0.37	0.32	0.1 [c]	RT	0.75	75	1A-α:1A-β = 5:1
3	0.74	0.62	0.25[a]	RT	1	67	1B-α:1B-β =29:1
4	0.74	0.64	0.2 [c]	RT	1	66	1B-α:1B-β =36:1
5	0.37	0.28	0.125[b]	RT	3.5	77	1C-α:1C-β = 8:1
6	0.37	0.29	0.1 [c]	0	6.5	75	1C-α:1C-β = 7:1
7	0.8	0.42	0.2[b]	RT	5.25	65	1D-α:1D-β = 8:1

[a] For HOR', see Scheme 1; [b] $CF_3SO_3SiMe_3$; [c] $CF_3SO_3SiMe_2t$-Bu.
[d] from isolated products.

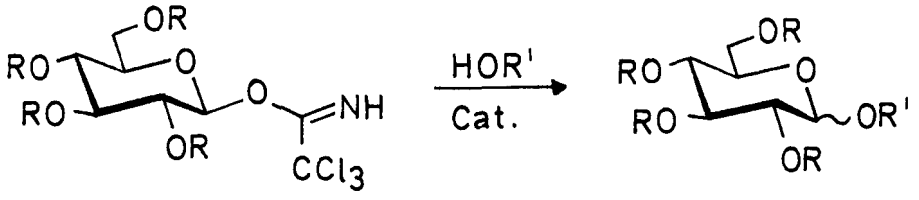
ed in other solvents may be due either to intramolecular stabilisation of an intermediate oxonium ion by the 2-benzyloxy group or by a competing S_Ni-type inversion reaction with the trichloroacetimidate group (as previously discussed for the formation of alkyl 1-thio-α-D-glucopyranosides.[11,12]

B. SYNTHESIS OF α-D-GLUCOPYRANOSIDES

The reaction of the O-(β-D-glucopyranosyl)trichloroacetimidate 3-β as donor with each of the monosaccharide acceptors A, B and D led to the formation of the corresponding disaccharides 3A, 3B and 3D (SCHEME 2).

The identity of the products (3B, 3D) was established by comparison with known material, and that of 3A on the basis of ^{13}C NMR data and a full analysis of ^1H NMR data of compounds 4A-α and 4A-β (derived from compounds 3A-α and 3A-β respec-

SCHEME 2



3 - β: R = Bzl

3A, 3B, 3D : R = Bzl
4A : R = Ac

For HOR', see SCHEME 1

tively, after their hydrogenolytic debenzylation and subsequent acetylation).

The α-stereoselectivities observed in these glycosidations (TABLE 2) were in general somewhat lower than observed in glycosidations with the galactopyranose donor 1-β (compare TABLES 1 and 2). This may be due to the electronic and/or steric influence of the function at C-4 of the glycosyl donor 3-β. Glycosidation with the 6-O-unprotected glucose acceptor A gave the corresponding disaccharides 3A in very good yield and with high α-stereoselectivity. This stereoselectivity was improved by using the catalyst $CF_3SO_3SiMe_2t$-Bu (TABLE 2, Exp. 1) instead of $CF_3SO_3SiMe_3$ (TABLE 2, Exp. 2). Although the overall yields of anomeric glycosides remained high in glycosidations with the less reactive acceptors B and D, the α-stereoselectivity fell (TABLE 2, exp. 3-6).

With the relatively unreactive acceptor D, use of dichloromethane instead of diethyl ether as solvent, led to an improved α-stereoselectivity (compare Exp. 5 and 6, TABLE 2). As a consequence, it was possible to improve the yield of 3D-α, through the use of dichloromethane, although the overall yield of anomeric disaccharides was lower than that in diethyl ether. The stereochemical outcome of these reactions supports a mecha-

TABLE 2

Reaction of Trichloroacetimidate 3-β with the Glycosyl Acceptors A, B, D. Formation of Disaccharides 3A-α/β, 3B-α/β, and 3D-α/β[a].

Exp.	[3-β] : [HOR'][b]:[Cat.]			Temp. [°]	Time [h]	Yield[f] [%]	Product Ratio[f]
1	0.37	0.31	0.1[c]	RT	2	83	3A-α:3A-β = 8:1
2	0.37	0.31	0.125[d]	-10	1.25	89	3A-α:3A-β = 5:1
3	0.74	0.47	0.25[d]	RT	5	95	3B-α:3B-β = 3:1
4	0.74[e]	0.45	0.25[d]	RT	5.5	82	3B-α:3B-β = 5:2
5	0.45	0.23	0.1[d]	RT	6	72	3D-α:3D-β = 3:1
6	0.58	0.29	0.15[d]	RT	6.75	50	3D-α:3D-β = 5:1

[a] Experiments 1 - 4 and 6 were carried out in diethyl ether; experiment 5 was carried out in dichloromethane; [b] For HOR', see Scheme; [c] $CF_3SO_3SiMe_2t$-Bu; [d] $CF_3SO_3SiMe_3$; [e] O-(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl)-trichloroacetimidate (3-α)[11]; [f] from isolated products.

nism which proceeds through the reaction of the starting trichloroacetimidate 3-β and an alcohol with simple inversion. However, participation by the solvent diethyl ether, is suggested by the fact that both the β-trichloroacetimidate 3-β and the corresponding α-analogue,[4,11] 3-α give simliar results in glycosidations under comparable reaction conditions (Exp. 3 and 4, TABLE 2).

Clearly, the synthesis of α-D-glucopyranosides using the trichloroacetimidate method needs to be explored more fully in order to rationalise these results. In order to obtain α-stereoselectivity the method needs detailed investigations in each case.

EXPERIMENTAL

General procedures. Melting points are uncorrected. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded in the solvents noted (Me_4Si, 0.00 ppm) with a Bruker "WM 250 Cryospec" and a JEOL "JNM-FX 90 Q". R_F values refer to TLC performed on silica gel (Merck) with the solvent systems noted. Column chromatography was performed under normal pressure with silica gel 60 (Merck, 70-230 mesh ASTM), and under medium pressure with silica gel (Merck, "LiChroprep" Si 60, 15-25 μm) with the solvent systems noted. For flash chromatography silica gel 60 (Merck, 230-400 mesh ASTM) was used. Optical rotations were determined with a Perkin Elmer 241 MC. The glycoside syntheses were performed under a dry nitrogen atmosphere with molecular sieve 4 Å. The solvents for chromatography were distilled. Petroleum ether was taken from bp 35-60 °C.

O-(2,3,4,6-Tetra-O-benzyl-ß-D-galactopyranosyl)trichloroacetimidate (1-ß).[14] To a solution of 2,3,4,6-tetra-O-benzyl-D-galactose[13] (5.2 g, 1 mmol) in 50 mL dry dichloromethane was added 5g potassium carbonate and 5 mL trichloroacetonitrile. The suspension was strongly stirred for 5 h at room temperature under a nitrogen atmosphere. The mixture was filtered over celite, washed with dichloromethane (10 mL), the filtrate concentrated under reduced pressure, and the oily residue crystallized from ethyl ether/petroleum ether = 1:1 (50 mL): yield 5.55 g (84 %); mp 87 °C from ethyl ether/petroleum ether = 1:1; $[\alpha]^{20}$ = +20.9° (c = 1, $CHCl_3$); TLC R_F = 0.55 (petroleum ether/ethyl ether = 1:1; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.62 (s, 1H, NH), 7.37-7.25 (m, 20H, $4C_6H_5$), 5.75 (d, 1H, H-1; $J_{1,2}$ = 7.9 Hz), 4.97-3.58 (m, 14H); IR (KBr) 3100 cm^{-1} (N-H), 1670 cm^{-1} (C=N).

Anal. Calcd for $C_{36}H_{36}Cl_3NO_6$ (685.03): C, 63.12; H, 5.30; N, 2.04. Found: C, 63.02; H, 5.18; N, 1.91.

Phenyl 6-O-(2,3,4,6-Tetra-O-benzyl-α- and -ß-D-Galactopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (1A-α and 1A-ß). Experiment 1 in TABLE 1: Compound 1-ß (500 mg, 0.74 mmol) and phenyl 2,3,4-tri-O-benzyl-α-D-glucopyranoside[15] (340 mg, 0.65 mmol) were dissolved in 15 mL of dry ethyl ether at room temperature. Trimethylsilyl triflate (0.25 mmol) was added. After 1.5 h the reaction mixture was treated with excess solid

sodium hydrogen carbonate and then with ethyl ether/ sodium hydrogen carbonate solution in water. The ethyl ether extract was washed with water, dried with sodium sulfate, and then concentrated. The oily residue was chromatographed on silica gel (chloroform/ethyl ether = 20:1, normal pressure). The pure mixture of compounds 1A-α and 1A-β was chromatographed on silica gel: petroleum ether/ethyl ether 1:1 (medium pressure); total yield of 1A-α and 1A-β 410 mg (67 %); yield 346 mg of compound 1A-α as an oil; $[\alpha]^{20}$ = +73.2° (c = 1, $CHCl_3$); $[\alpha]^{20}$ = +70.0° (c = 1, $CHCl_3$); TLC R_F = 0.64 (chloroform/ethyl ether = 20:1); TLC R_F = 0.62 (petroleum ether/ethyl ether = 1:1); ^1H NMR (250 MHz, $CDCl_3$) δ 7.39-6.95 (m, 40H, $8C_6H_5$), 5.37 (d, 1H, H-1; $J_{1,2}$ = 3.4 Hz), 5.04-3.43 (m, 27H, $7CH_2$-C_6H_5 + H-1'); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 98.12 (C-1'), 95.76 (C-1); yield 64 mg of compound 1A-β as a colourless syrup; $[\alpha]^{20}$ = +37.4° (c=1, $CHCl_3$); $[\alpha]^{20}$ = +36.1° (c = 1, $CHCl_3$); TLC R_F = 0.45 (chloroform/ethyl ether = 20:1); TLC R_F = 0.51 (petroleum ether/ethyl ether = 1:1); ^1H NMR (250 MHz, $CDCl_3$) δ 7.35-6.92 (m, 40H, $8C_6H_5$), 5.45 (d, 1H, H-1; $J_{1,2}$ = 3.4 Hz), 5.05-3.44 (m, 27H, $7CH_2$-C_6H_5 + H-1'); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 104.21 (C-1')), 95.81 (C-1).

Anal. Calcd for $C_{67}H_{68}O_{11}$ (1049.27): C, 76.69; H, 6.53.
Found: 1A-α: C, 76.84; H, 6.44
1A-β: C, 75.99; H, 6.40

Experiment 2 in TABLE 1 was carried out as described above.

Phenyl 6-O-(2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl)-2,3,4-tri-O-acetyl-α-D-glucopyranoside (2A-α). Compound 1A-α (396 mg, 0.38 mmol) was dissolved in 10 mL of dry ethyl acetate and 10 mL of dry methanol. 100 mg palladium on carbon were added. After 3.5 h of hydrogenolysis the reaction mixture was filtered and the solutions were concentrated to dryness. The debenzylated compound [TLC R_F = 0.40 (chloroform/methanol = 7:5)] was stirred with 10 mL of dry pyridine and 5 mL of dry acetic acid anhydride under a calcium chloride seal at room temperature overnight. Solvents were evaporated, remaining pyridine was removed by repeated evaporation with toluene and the residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 1:2, normal pressure): yield 233 mg (86 %) white powder of compound 2A-α; mp 75-77 °C from ethyl

ether; $[\alpha]^{20}$ = +185° (c = 1, $CHCl_3$); $[\alpha]^{20}$ = +177.7° (c = 1, $CHCl_3$); TLC R_F = 0.70 (petroleum ether/ethyl acetate = 1:2); ^1H NMR (250 MHz, $CDCl_3$) δ 7.38-7.06 (m, 5H, C_6H_5), 5.72 (dd, 1H, H-3; $J_{2,3} = J_{3,4}$ = 9.9 Hz); 5.68 (d, 1H, H-1; $J_{1,2}$ = 3.7 Hz), 5.43 (dd, 1H, H-4'; $J_{3',4'}$ = 2.4, $J_{4',5'}$ = 1 Hz), 5.28 (dd, 1H, H-3'; $J_{2',3'}$ = 10.4 Hz, $J_{3',4'}$ = 2.4 Hz), 5.15 (d, 1H, H-1'; $J_{1',2'}$ = 3.7 Hz), 5.14 (dd, 1H, H-4; $J_{3,4} = J_{4,5}$ = 9.8 Hz), 5.08 (dd, 1H, H-2'; $J_{1',2'}$ = 3.7 Hz, $J_{2',3'}$ = 10.4 Hz), 4.98 (dd, 1H, H-2; $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.4 Hz), 4.21-3.99 (m, 4H, H-5 + H-5'+ $H6^{A'}$ + $H\text{-}6^{B'}$), 3.76-3.47 (m, 2H, $H\text{-}^{6A}$ + $H\text{-}6^{B}$), 2.14 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.06 (s, 3H, CH_3) 2.06 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.00 (s, 3H, CH_3).

Anal. Calcd for $C_{32}H_{40}O_{18}$ (712.65): C, 53.93; H, 5.66. Found: C, 53.78; H, 5.77.

1,6-Anhydro-4-O-(2,3,4,6-tetra-O-benzyl-α- and -β-D-galactopyranosyl)-2,3-di-O-benzyl-β-D-glucopyranose (1B-α and 1B-β). Experiment 4 in TABLE 1: Compound 1-β (500 mg, 0.74 mmol) and 1,6-anhydro-2,3-di-O-benzyl-β-D-glucopyranose [16] (221 mg, 0.64 mmol) were dissolved in 25 mL of dry ethyl ether at room temperature. Tert-butyldimethylsilyl triflate (0.2 mmol) was added. After 1 h the reaction mixture was treated with solid sodium hydrogen carbonate as described for compounds 1A-α and 1A-β. Most of 1B-α could be crystallized as colourless needles from the oily residue by addition of ethyl ether. The mother liquor containing 1B-β and little traces of 1B-α was concentrated to dryness and the remaining oil was chromatographed for further separation on silica gel (chloroform/ethyl ether = 5:1, normal pressure); total yield of 1B-α and 1B-β 367 mg (66 %); yield 357 mg of compound 1B-α as colourless needles; mp 89-90 °C from methanol (lit. [16] 88-89 °C from methanol); $[\alpha]^{20}$ = +11.5° (c = 1, $CHCl_3$); $[\alpha]^{20}$ = +10.4° (c = 1, $CHCl_3$) (lit. [16] $[\alpha]^{20}$ = +11.5° (c = 1, $CHCl_3$)); TLC R_F = 0.56 (chloroform/ethyl ether = 5:1); TLC R_F = 0.60 (petroleum ether/ethyl ether = 1:3); ^1H NMR (250 MHz, $CDCl_3$) δ 7.37-7.19 (m, 30 H, $6C_6H_5$), 5.45 (s, 1H, H-1), 5.04-3.34 (m, 25H, $6CH_2$-C_6H_5 + H-1'); ^{13}C NMR (62.97 MHz, $CDCl_3$) δ 100.98 (C-1), 99.29 (C-1'); yield 10 mg of compound 1B-β as an oil which could be crystallized; mp 84-86 °C from ethyl ether; $[\alpha]^{20}$ = -26.7° (c = 0.93, $CHCl_3$); $[\alpha]^{20}$ = -25.0° (c = 0.93, $CHCl_3$) (lit. [16] $[\alpha]^{20}$ = -27.1° (c = 1,

$CHCl_3$); lit. [17] $[\alpha]^{22}$ = -27.2° (c = 1.02, $CHCl_3$)]; TLC R_F = 0.46 (chloroform/ethyl ether = 5:1); TLC R_F = 0.60 (petroleum ether/ethyl ether = 1:3); ^1H NMR (250 MHz, $CDCl_3$) δ 7.40-7.21 (m, 30H, $6C_6H_5$), 5.48 (s, 1H, H-1), 5.06-3.34 (m, 25 H, $6CH_2$-C_6H_5 + H-1'); ^{13}C NMR (62.97 MHz, $CDCl_3$) δ 102.85 (C-1'), 101.07 (C-1).

Experiment 3 in TABLE 1 was carried out as described above.

1,6-Anhydro-2-O-(2,3,4,6-tetra-O-benzyl-α- and -β-D-galactopyranosyl)-3,4-O-isopropylidene-β-D-galactopyranose (1C-α and 1C-β). Experiment 5 in TABLE 1: Compound 1-β (250 mg, 0.37 mmol) and 1,6-anhydro-3,4-O-isopropylidene-β-D-galactopyranose [18] (56 mg, 0.28 mmol) were dissolved in 20 mL of dry ethyl ether at room temperature. Trimethylsilyl triflate (0.125 mmol) was added. After 3.5 h the reaction mixture was treated with solid sodium hydrogen carbonate as described for compounds 1A-α and 1A-β. The oily residue was chromatographed on silica gel (chloroform/ethyl ether = 5:1, normal pressure). The pure mixture of compounds 1C-α and 1C-β was chromatographed on silica gel; petroleum ether/ethyl ether = 1:1 (medium pressure); total yield of 1C-α and 1C-β 154 mg (77 %): yield 137 mg colourless crystals of compound 1C-α; mp 122 °C from ethyl ether/petroleum ether (lit. [16] 121-122 °C from ethyl ether/petroleum ether); $[\alpha]^{20}$ = +19.5° (c = 1, $CHCl_3$); TLC R_F = 0.33 (petroleum ether/ethyl ether = 1:1); ^1H NMR (250 MHz, $CDCl_3$) δ 5.40 (s, 1H, H-1), 1.49 (s, 3H, isopropylidene), 1.24 (s, 3H, isopropylidene); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 108.36 (ketal-C), 99.53 (C-1), 98.34 (C-1'), 25.79 and 24.27 (CH_3-isopropylidene); yield 17 mg colourless crystals of compound 1C-β; mp 128-129 °C from ethyl ether/petroleum ether; $[\alpha]^{20}$ = -19.4° (c = 1, $CHCl_3$); TLC R_F = 0.37 (petroleum ether/ethyl ether = 1:1); ^1H NMR (250 MHz, $CDCl_3$) δ 5.58 (s, 1H, H-1), 1.49 (s, 3H, isopropylidene), 1.24 (s, 3H, isopropylidene); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 108.55 (ketal-C), 103.49 (C-1'), 100.72 (C-1), 25.79 and 24.27 (CH_3-isopropylidene); compounds 1C-α and 1C-β gave ^1H NMR spectral and optical rotation data identical with that reported for authentic material [16].

Experiment 6 in TABLE 1 was carried out as described above.

Anal. Calcd for $C_{43}H_{48}O_{10}$ (724.81): C, 71.26; H, 6.68. Found: 1C-α: C,71.33; H, 6.69. 1C-β: C, 71.14; H, 6.74.

Methyl 4-O-(2,3,4,6-Tetra-O-benzyl-α- and -β-D-galacto-pyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (1D-α and 1D-β). Experiment 7 in TABLE 1: Compound 1-β (550 mg, 0.8 mmol) and methyl 2,3,6-tri-O-benzyl-α-D-glucopyranoside,[19,20,21] (195 mg, 0.42 mmol) were dissolved in 25 mL of dry ethyl ether at room temperature. Trimethylsilyl triflate (0.2 mmol) was added. After 5.25 h the reaction mixture was treated with solid sodium hydrogen carbonate as described for compounds 1A-α and 1A-β. The oily residue was flash chromatographed on silica gel (petroleum ether/ethyl acetate = 8:2). The resulting glycoside fraction was chromatographed on silica gel (chloroform/ethyl ether = 20:1, normal pressure). A small amount of 1D-α was chromatographed on silica gel for microanalysis; petroleum ether/ethyl ether = 1:1 (medium pressure): total yield of 1D-α and 1D-β 270 mg (65 %); yield 240 mg of compound 1D-α as an oil; $[\alpha]^{20}$ = +41.5° (c = 1, $CHCl_3$); $[\alpha]^{20}$ = +40.1° (c = 1, $CHCl_3$); TLC R_F = 0.41 (petroleum ether/ethyl ether = 1:1); TLC R_F = 0.73 (chloroform/ethyl ether = 20:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.32-7.17 (m, 35H, $7C_6H_5$), 5.76 (d, 1H, H-1'; $J_{1',2'}$ = 3.7 Hz), 4.95-3.43 (m, 27H), 3.37 (s, 3H, OCH_3); yield 30 mg of compound 1D-β containing a slight impurity which could not be removed by chromatography; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.32-7.17 (m, 35H, $7C_6H_5$), 5.06-3.41 (m, 28H), 3.40 (s, 3H, OCH_3).

Anal. Calcd for $C_{62}H_{66}O_{11}$ (987.20): C, 75.43; H, 6.74. Found: 1D-α: C, 75.32; H, 6.67.

Methyl 4-O-(2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl)-2,3,6-tri-O-acetyl-α-D-glucopyranoside (2D-α). A mixture of 1D-α and 1D-β (717 mg, 0.73 mmol) was dissolved in 15 mL of dry ethyl acetate and 15 mL of dry methanol. 100 mg palladium on carbon were added. After 3.5 h of hydrogenolysis the reaction mixture was filtered and the solutions were concentrated to dryness. The debenzylated compounds [TLC R_F = 0.45 (chloroform/methanol = 1:1)] were stirred with 10 mL of dry pyridine and 5 mL of dry acetic acid anhydride under a calcium chloride seal at room temperature overnight. Solvents were evaporated, remaining pyridine was removed by repeated evaporation with toluene and the residue was chromatographed on silica gel (petro-

leum ether/ethyl acetate = 1:2, normal pressure); yield 406 mg (86 %) of the mixture. The mixture was chromatographed on silica gel (petroleum ether/ethyl acetate = 1:2, medium pressure) to obtain pure α-glycoside 2D-α as a white powder: mp 70-72 °C from ethyl ether/petroleum ether; $[\alpha]_D^{20}$ = +138.9° (c = 1, $CHCl_3$) $[\alpha]_D^{20}$ = +136.0° (c = 1, $CHCl_3$) [lit.[22] $[\alpha]_D^{24}$ = +137.2° (c = 1.74, $CHCl_3$); lit.[22] $[\alpha]_D^{20}$ = +136.0° (c = 0.7, $CHCl_3$)]; TLC R_F = 0.60 (petroleum ether/ethyl acetate = 1:2); ^1H NMR (250 MHz, $CDCl_3$) δ 3.42 (s, 3H, OCH_3), 2.13, 2.07, 2.06, 2.05, 2.02, 1.98 (s, 21H, $7CH_3$).

Anal. Calcd for $C_{27}H_{38}O_{18}$ (650.57): C, 49.84; H, 5.89. Found: 2D-α: C, 49.84; H, 5.86.

O-(2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl)trichloroacetimidate (3-β). Compound 3-β was prepared from 2,3,4,6-tetra-O-benzyl-D-glucose[23,24] according to ref.[14] 3-β can be obtained now according to the previously published procedure[14] as crystalline material from ethyl ether/petroleum ether = 1:1 in 90 % yield under a nitrogen atmosphere; mp 72-73°C.

Phenyl 6-O-(2,3,4,6-tetra-O-benzyl-α- and -β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (3A-α and 3A-β). Experiment 1 in TABLE 2: Compound 3-β (250 mg, 0.37 mmol) and phenyl 2,3,4-tri-O-benzyl-α-D-glucopyranoside[15] (163 mg, 0.31 mmol) were dissolved in 20 mL of dry ethyl ether at room temperature. Tert-butyldimethylsilyl triflate (0.1 mmol) was added. After 1.25 h the reaction mixture was treated with excess solid sodium hydrogen carbonate as described for compounds 1A-α and 1A-β. The oily residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 8:2, normal pressure). The pure mixture of compounds 3A-α and 3A-β was chromatographed for separation on silica gel (chloroform/ethyl ether = 20:1, normal pressure): total yield of 3A-α and 3A-β 269 mg (83 %). Small amounts of 3A-α and 3A-β were chromatographed on silica gel (medium pressure) for microanalysis: yield 238 mg of compound 3A-α as a colourless oil; $[\alpha]_D^{20}$ = +85° (c = 1, $CHCl_3$); $[\alpha]_D^{20}$ = +81.6° (c = 1, $CHCl_3$); TLC R_F = 0.73 (chloroform/ethyl ether = 20:1); TLC R_F = 0.62 (petroleum ether/ethyl ether = 1:1); ^1H NMR (250 MHz, $CDCl_3$) δ 7.38-6.94 (m, 40H, $8C_6H_5$), 5.37 (d, 1H, H-1; $J_{1,2}$ = 3.7 Hz), 5.06-3.47 (m, 27H, $7CH_2$-C_6H_5 + H-1'); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 97.28 (C-1'), 95.82 (C-1); yield 31 mg

of compound 3A-β as colourless crystals; mp 104-106°C from ethyl ether/petroleum ether; $[\alpha]^{20}$ = +45° (c = 0.5, $CHCl_3$); $[\alpha]^{20}$ = +42.8° (c = 0.5, $CHCl_3$); TLC R_F = 0.53 (chloroform/ethyl ether = 20:1); TLC R_F = 0.62 (petroleum ether/ethyl ether = 1:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.36-6.91 (m, 40H, $8C_6H_5$), 5.48 (d, 1H, H-1; $J_{1,2}$ = 3.4 Hz), 5.06-3.37 (m, 27 H, $7CH_2$-C_6H_5 + H-1'); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 103.65 (C-1'), 95.74 (C-1).

Anal. Calcd for $C_{67}H_{68}O_{11}$ (1049.27): C, 76.69; H, 6.53. Found: 3A-α: C, 76.44; H, 6.63. 3A-β C, 76.49; H, 6.68.

Experiment 2 in TABLE 2 was carried out as described above.

Phenyl 6-O-(2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-2,3,4-tri-O-acetyl-α-D-glucopyranoside (4A-α). Compound 3A-α (352 mg, 0.34 mmol) was dissolved in 10 mL of dry ethyl acetate and 10 mL of dry methanol. 100 mg palladium on carbon were added. After 2.5 h of hydrogenation the reaction mixture was filtered and the solutions were concentrated to dryness. The debenzylated compound [TLC R_F = 0.07 (chloroform/methanol = 7:3)] was stirred with 10 mL of dry pyridine and 5 mL of dry acetic acid anhydride under a calcium chloride seal at room temperature overnight. Solvents were evaporated, remaining pyridine was removed by repeated evaporation with toluene and the residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 1:2, normal pressure): yield 168 mg (70 %) white powder of compound 4A-α: mp 68-72 °C from ethyl ether/petroleum ether; $[\alpha]^{20}$ = +185.2° (c = 1, $CHCl_3$); $[\alpha]^{20}$ = +177.7° (c = 1, $CHCl_3$); TLC R_F = 0.69 (petroleum ether/ethyl acetate = 1:2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.39-7.06 (m, 5H, C_6H_5), 5.72 (dd, 1H, H-3; $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 9.8 Hz), 5.66 (d, 1H, H-1; $J_{1,2}$ = 3.7 Hz), 5.44 (dd, 1H, H-3'; $J_{2',3'}$ = 9.9 Hz, $J_{3',4'}$ = 9.8 Hz), 5.15-5.07 (m, 2H, H-1'+ H-4), 5.05 (dd, 1H, H-4'; $J_{3',4'}$ = $J_{4',5'}$ = 9.8 Hz), 4.97 (dd, 1H, H-2; $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.1 Hz), 4.84 (dd, 1H, H-2'; $J_{1',2'}$ = 3.7 Hz, $J_{2',3'}$ = 9.9 Hz), 4.25-3.49 (m, 6H, H-5 + H-5'+ $H\text{-}6^A$ + $H\text{-}6^B$ + $H\text{-}6^{A'}$ + $H\text{-}6^{B'}$), 2.09 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.01 (s, 3H, CH_3).

Anal. Calcd for $C_{32}H_{40}O_{18}$ (712.65): C, 53.93; H, 5.66. Found: C, 53.67; H, 5.76.

Phenyl 6-O-(2,3,4,6-Tetra-O-acetyl-ß-D-glucopyranosyl)-2,3,4-tri-O-acetyl-α-D-glucopyranoside (4A-ß). Compound 3A-ß (508 mg, 0.48 mmol) was dissolved in 10 mL of dry ethyl acetate and 10 mL of dry methanol. 100 mg palladium on carbon were added. After 3.5 h of hydrogenolysis the reaction mixture was filtered and the solutions was concentrated to dryness. The debenzylated compound [TLC R_F = 0.25 (chloroform/methanol = 7:3)] was stirred with 10 mL of dry pyridine and 5 mL of dry acetic acid anhydride under a calcium chloride seal at room temperature overnight. Solvents were evaporated. Remaining pyridine was removed by repeated evaporation with toluene. The residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 1:2, normal pressure); yield 258 mg (75 %) white powder of compound 4A-ß, which could be crystallized to colourless needles: mp 144 °C from ethyl ether/petroleum ether: mp 145-146 °C from ethanol; $[\alpha]_D^{20}$ = +88.4° (c = 1, $CHCl_3$); $[\alpha]_{546}^{20}$ = +84.6° (c = 1, $CHCl_3$); TLC R_F = 0.61 (petroleum ether/ethyl acetate = 1:2); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.31-6.99 (m, 5H, C_6H_5), 5.66 (d, 1H, H-1; $J_{1,2}$ = 3.4 Hz), 5.64 (dd, 1H, H-4; $J_{3,4}$ = $J_{4,5}$ = 10.4 Hz), 5.13 (dd, 1H, H-3; $J_{2,3}$ = 9.5 Hz; $J_{3,4}$ = 10.4 Hz), 5.06-4.90 (m, 4H, H-3' + H-4' + H-2 + H-2'), 4.46 (d, 1H, H-1'; $J_{1',2'}$ = 7.9 Hz), 4.19-4.02 (m, 3H, H-5' + H-$6^{A'}$ + H-$6^{B'}$), 3.89-3.47 (m, 3H, H-5 + H-6^A + H-6^B), 2.03 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.99 (s, 6H, 2 x CH_3), 1.97 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.93 (s, 3H, CH_3).

Anal. Calcd for $C_{32}H_{40}O_{18}$ (712.65): C, 53.93; H, 5.66. Found: C, 54.10; H, 5.72.

1,6-Anhydro-4-O-(2,3,4,6-tetra-O-benzyl-α- and -ß-D-glucopyranosyl)-2,3-di-O-benzyl-ß-D-glucopyranose (3B-α and 3B-ß). Experiment 3 in TABLE 2: Compound 3-ß (500 mg, 0.74 mmol) and 1,6-anhydro-2,3-di-O-benzyl-ß-D-glucopyranose [16] (162 mg, 0.47 mmol) were dissolved in 10 mL of dry ethyl ether at room temperature. Trimethylsilyl triflate (0.25 mmol) was added. After 5 h the reaction mixture was treated with excess solid sodium hydrogen carbonate as described for compounds 1A-α and 1A-ß. The oily residue was chromatographed on silica gel (chloroform/ethyl ether = 20:1, normal pressure) to give pure 3B-α.

Pure 3B-β was obtained by chromatography on silica gel (petroleum ether/ethyl ether = 1:3). Alternatively, 3B-α and 3B-β could be separated through the use of flash chromatography on silica gel (petroleum ether/ethyl ether = 1:1): total yield of 3B-α and 3B-β 388 mg (95 %); yield 293 mg of crystalline compound 3B-α; mp 75-76 °C from ethyl ether/petroleum ether (lit.[28] 77-78 °C, solvent not noted); $[\alpha]^{20}$ = +8.6° (c = 1, $CHCl_3$); $[\alpha]^{20}$ = +7.5° (c = 1, $CHCl_3$) [lit.[26,27] $[\alpha]^{20}$ = +9.6° (c = 1, $CHCl_3$); lit.[28] $[\alpha]^{22}$ = +7.66° (c = 2, $CHCl_3$)]; TLC R_F = 0.52 (chloroform/ethyl ether = 20:1); TLC R_F = 0.59 (petroleum ether/ethyl ether = 1:3); ^1H NMR (250 MHz, $CDCl_3$) δ 7.29-7.13 (m, 30H, $6C_6H_5$), 5.46 (s, 1H, H-1), 5.00 (d, 1H, H-1'; $J_{1',2'}$ = 3.7 Hz), 4.97-3.37 (m, 24H, $6CH_2$-C_6H_5); ^{13}C NMR (62.97 MHz, $CDCl_3$) δ 100.90 (C-1), 98.05 (C-1'); yield 95 mg of compound 3B-β as colourless needles; mp 86-87 °C from ethyl ether/petroleum ether (lit.[29] 86-87 °C from ethyl ether/petroleum ether); $[\alpha]^{20}$ = -17.5° (c = 1, $CHCl_3$); $[\alpha]^{20}$ = -16.7° (c = 1, $CHCl_3$); [lit.[26,27] $[\alpha]^{20}$ = -18.5° (c = 1, $CHCl_3$); lit.[29] $[\alpha]^{25}$ = -19.7° (c = 2.5, $CHCl_3$)]; TLC R_F = 0.37 (chloroform/ethyl ether = 20:1); TLC R_F = 0.53 (petroleum ether/ethyl ether = 1:3); ^1H NMR (250 MHz, $CDCl_3$) δ 7.39-7.14 (m, 30H, $6C_6H_5$), 5.48 (s, 1H, H-1), 5.09-3.34 (m, 25H, $6CH_2$-C_6H_5 + H-1').

Experiment 4 in TABLE 2 was carried out as described above with O-(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl) trichloroacetimidate 3-α.[11]

Methyl 4-O-(2,3,4,6-Tetra-O-benzyl-α- and -β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (3D-α and 3D-β). Experiment 5 in TABLE 2: Compound 3-β (310 mg, 0.45 mmol) and methyl 2,3,6-tri-O-benzyl-α-D-glucopyranoside[19,20,21] (108 mg, 0.23 mmol) were dissolved in 25 mL of dry dichloromethane at room temperature. Trimethylsilyl triflate (0.1 mmol) was added. After 6 h the reaction mixture was treated with solid sodium hydrogen carbonate as described for compounds 1A-α and 1A-β. The oily residue obtained was chromatographed on silica gel (chloroform/ethyl ether = 20:1, normal pressure): total yield of 3D-α and 3D-β 158 mg (72 %); yield 119 mg of compound 3D-α as an oil; $[\alpha]^{20}$ = +50.3° (c = 1, $CHCl_3$); $[\alpha]^{20}$ = +48.6° (c = 1, $CHCl_3$); [lit.[3] $[\alpha]^{20}$ = +48° (c = 1.05, $CHCl_3$); lit.[27] $[\alpha]^{20}$ = +39.5° (c = 1, $CHCl_3$); lit.[30] $[\alpha]^{20}$ = +45.4° (c =

0.82, $CHCl_3$)]; TLC R_F = 0.64 (chloroform/ethyl ether = 20:1), ^1H NMR (250 MHz, $CDCl_3$) δ 7.33-7.08 (m, 35H, $7C_6H_5$) 5.70 (d, 1H, H-1'; $J_{1',2'}$ = = 3.7 Hz), 5.22 (d, 1H, H-1; $J_{1,2}$ = 3.7 Hz), 5.06-3.40 (m, 26H), 3.37 (s, 3H, OCH_3); yield 39 mg of compound 3D-ß which was identical with authentic material [27, 30]. TLC R_F = 0.55 (chloroform/ethyl ether = 20:1). ^1H NMR (90 MHz, $CDCl_3$) δ 7.40-7.29 (m, 35H, $7C_6H_5$), 5.20-3.50 (m, 28 H, $7CH_2$-C_6H_5 + H-1 + H-1'), 3.40 (s, 3H, OCH_3).

Experiment 6 in TABLE 2 was carried out as described above.

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