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A Facile Synthetic Approach for Alkyl α-Glycosides of Reducing Disaccharides

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Methanolysis and benzyl alcoholysis of β-cellobiosyl, β-lactosyl, or β-maltosyl N,N-dimethyldithiocarbamate in the presence of mercuric chloride and cadmium carbonate were investigated. Methyl and benzyl glycosides formation proceeded in good yield under mild conditions, in which formation of α-anomer was always predominant over that of β-anomer: in methanolysis, the ratios of α- and β-anomers were about 4: 1 and in benzyl alcoholysis, 2: 1, respectively. Using this method methyl α-cellobioside, α-lactoside, and α-maltoside were synthesized. The procedure is a facile synthetic method for appropriate alkyl α-glycosides of reducing disaccharides.

Keywords——β-glycosyl N,N-dimethyldithiocarbamates; methyl glycosides formation of reducing disaccharides; benzyl glycosides formation of reducing disaccharides; methyl α-lactoside; benzyl α-maltoside heptaacetate; GLC analysis of anomeric glycosides; NMR

Alkyl β-glycosides of reducing disaccharides are not so difficult to synthesize. Namely, reaction of acylated halogenoses with alcohols in the presence of mercury or silver salts gives rise to acylated β-glycosides, and their conversions into free β-glycosides are easily carried out by deacylation. But syntheses of alkyl α-glycosides of reducing disaccharides are more difficult compared to those of alkyl α-glycosides of monosaccharides: the simplest method for syntheses of glycosides by heating a mixture of monosaccharides with appropriate alcohols in the presence of hydrogen chloride is not suitable to disaccharides, mainly with regard to the possibility of the glycosidic bond cleavage in acid solution.

Alkyl α-glycosides of reducing disaccharides are important compounds in enzyme-mechanistic studies, useful starting materials for syntheses of disaccharide derivatives, and models for polysaccharides. But lack of practical, facile synthetic method of alkyl α-glycosides has limited the use of these compounds. Although stereospecific synthetic methods of α-glycosidic linkage have been designed by several workers,[2] those methods are not nesecssarily suitable for syntheses of alkyl α-glycosides of common alcohols.

Tejima and Ishiguro[3] reported previously that when β-D-glucopyranosyl N,N-dimethyldithiocarbamate was treated with mercury salts in methanol, a stereospecific methanolysis proceeded to yield methyl α-D-glucopyranoside in good yield. β-Glycosyl N,N-dialkyldithiocarbamates are easily available as stable crystals by deacetylation of acetylated β-glycosyl N,N-dialkyldithiocarbamates, synthesized from acetylated glycosyl bromides with sodium N,N-dialkyldithiocarbamates. Thus, alcoholysis of β-cellobiosyl, β-lactosyl, or β-maltosyl N,N-dimethyldithiocarbamate (**3**, **6**, or **9**) was studied to establish a facile, general synthetic method for alkyl α-glycosides of reducing disaccharides. In this paper, the results are described.

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Treatment of heptaacetyl α-cellobiosyl bromide (1)[4] with sodium N,N-dimethyldithiocarbamate dihydrates as reported previously for the syntheses of the corresponding lactosyl[3] and maltosyl analogs[5] yielded β-cellobiosyl N,N-dimethyldithiocarbamate heptaacetate (2) in 87% yield. The nuclear magnetic resonance (NMR) spectra and elemental analytical data indicated the assigned structure. Deacetylation of **2** afforded free carbamate (3) as white granules, which were easily recrystallized from methanol.

A methanolic suspension of a mixture of 1 molar equivalent of 3, 2 molar equivalents of mercuric chloride, and 3 molar equivalents of cadmium carbonate as an acid acceptor was refluxed for 30 min. After the mercury and cadmium salts were removed from the reaction mixture, the solvent was evaporated to dryness which was acetylated in the usual way. The resulting acetate was purified by column chromatography on silica gel. Removal of the solvent from the fraction having *Rf* 0.26 on thin-layer chromatography (TLC) gave methyl α,β-cellobioside heptaacetates (**4a** and **4b**) as an amorphous powder in 90% yield. The anomers were indistinguishable in mobility on TLC. But the NMR spectrum showed two separate signals at δ 3.41 and 3.50 due to methoxyl proton: the addition of the intensity corresponded to three protons. The signal at the lower field was assigned to the β-methoxyl by comparison with an authentic methyl β-cellobioside heptaacetate (**4b**), synthesized according to the method of Zemplén and Gerecs,[6] and the other to the α-methoxyl by comparison with methyl α-cellobioside heptaacetate (**4a**) which is mentioned below. From the ratio of the individual intensity, the α-anomer comprised 79% of the anomeric mixture. Almost the same value, 80: 20, was obtained by gas chromatographic (GLC) analysis of the trimethylsilylated (TMS) derivative of the product. Ferrier, *et al.*[7] or Takeo[8] determined the ratio of the α- and β-anomers in methyl D-glucopyranoside or methyl hexaacetyl maltoside, respectively, by intensity of the corresponding methoxyl proton signal.

From the anomeric mixture, **4a** was isolated in 45% yield by fractional crystallization from ethanol. The melting point and specific rotation showed in good agreement with the published data[9] Deacetylation of **4a** afforded methyl α-cellobioside (5) in 84% yield.

Methanolysis of β-lactosyl or β-maltosyl N,N-dimethyldithiocarbamate (6 or 9) and sequential acetylation of the methanolysis mixture gave the corresponding anomeric glycoside acetates as white powder in 89 or 66% yield, respectively. In lactose series, α-anomer (**7a**) was isolated in 54% yield by fractional crystallization from aqueous methanol. The product crystallized as white needles having mp 161—162° and $[\alpha]_D^{25}+64.3°$ ($CHCl_3$). In the NMR spectrum, the seven acetyls appeared as four separate singlets, and the methoxyl proton appeared at δ 3.40 as three proton singlet. The elemental analysis was in good agreement with the assigned structure. Deacetylation of **7a** afforded methyl α-lactoside (8), mp 189—190°, $[\alpha]_D^{25}+115.1°$ (H_2O), which was crystallized as white microscopic needles. This is, so far as we know, the first reported example of methyl α-lactoside.

It was difficult to resolve the anomers of methyl maltoside heptaacetate (**10a** and **10b**) by fractional crystallization. Baddiley, *et al.*[10] showed that anomeric glycoside mixture of monosaccharide was resolved rapidly by chromatography on the hydroxide form of Dowex 1 resin. Therefore, we tested this type of separation.

Anomeric methyl maltoside mixture was applied to a column of Dowex 1 resin and chromatographed with water as eluent. Excellent separation of the α- and β-anomers were effected

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by this method; α-anomer was eluted more rapidly than β-anomer. Because the α-anomer was an amorphous powder, it was acetylated and purified by column chromatography to afford methyl α-maltoside heptaacetate (**10a**) as a homogeneous powder, from which methyl α-maltoside (**11**) was prepared by deacetylation. Methyl β-maltoside was isolated as a colorless sirup which was crystallized as heptaacetate (**10b**).

TABLE I. Elution of Methyl Maltosides from Dowex 1 (OH^-) Resin Column

Fraction No.	Methyl maltoside	Yield (mg)
5—7	Methyl α-maltoside	120
8—9	Methyl α-maltoside	290
10—11	Methyl α-maltoside	340
12—13	Methyl α-maltoside	150
14—20	Methyl β-maltoside	100

In the Koenigs-Knorr reaction, silver perchlorate has been shown to be a good catalyst for preparation of α-glycosidic linkage.[11] A mixture of pyridine and silver nitrate was also used as a successful acid acceptor in methyl α-maltotrioside synthesis.[12] Thus, instead of using mercuric chloride and cadmium carbonate, methanolysis in the presence of a mixture of silver salts and pyridine was investigated.

A methanolic suspension of 1 molar equivalent of glycosyl N,N-dimethyldithiocarbamate, 3 molar equivalents of silver salts, and a small amount of pyridine was refluxed for 30 min. After removal of the silver salts and the solvent, the residue was acetylated to afford an anomeric mixture of acetylated methyl glycosides in 70—91% yield except for one example: although the reason is not yet clear, when silver nitrate was used in maltosyl carbamate the yield was low. The ratio of anomer was determined by the NMR analysis, or the GLC analysis of the TMS glycosides. Thus, a mixture of silver perchlorate and pyridine, or silver nitrate and pyridine is applicable as a catalyst to α-glycoside formation.

TABLE II. Yield and Ratio of Methyl Glycosides

Starting compound	Catalyst	Product	Ratio of anomer (α: β)	Total yield[a] (%)
3	$AgClO_4$	Methyl cellobioside	85:15	91
6	$AgClO_4$	Methyl lactoside	67:33	79
9	$AgClO_4$	Methyl maltoside	83:17	70
3	$AgNO_3$	Methyl cellobioside	75:25	81
6	$AgNO_3$	Methyl lactoside	72:28	71
9	$AgNO_3$	Methyl maltoside	71:29	47

a) Yield based on heptaacetate.

Benzyl glycosides of disaccharides are versatile starting materials for syntheses of disaccharide derivatives. But only β-glycosides have been reported for cellobiose, maltose, and lactose. To synthesize α-glycosides, benzyl alcoholysis of glycosyl dithiocarbamates in the presence of mercuric chloride and cadmium carbonate was studied.

Using the same procedure as in methanolysis except that methanol was substituted for benzyl alcohol and removal of the solvent was carried out at 100° under vacuum, the resulting glycosides was isolated as acetylated anomeric mixture in 44—68% yield. The ratio

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of anomer was almost 2: 1, in which α-anomer was predominant. In maltose series, benzyl β-maltoside heptaacetate (**12b**) was isolated from the anomeric mixture as colorless needles. From the mother liquor, α-anomer was separated as a homogeneous heptaacetate. But in cellobiose and lactose series, attempt to separate the anomers by column chromatography failed, and further studies are now progressing.

Experimental

Melting points were determined by a Yanagimoto micro melting point apparatus and uncorrected. Solutions were evaporated in a rotary evaporator below 40° under vacuum unless otherwise indicated. Optical rotations were measured with a Unikon Giken Co., Ltd., automatic digital polarimeter, Model PM-201, in a 0.5 dm tube. NMR spectra were recorded at 100 MHz with a Jeol Model JNM-MH-100 spectrometer. Tetramethylsilane was used as the internal standard in $CDCl_3$. Chemical shifts were given in the δ scale. Shimadzu chromatograph, Model GC-4BPTF, equipped with a hydrogen flame ionization detector, was employed for GLC analysis. Hydroxyl derivatives were converted into TMS ethers[13] about 30 min before injection. The following columns, (A) and (B) were used: (A), a stainless steel column (2 m × 3 mm) packed with 3% JXR on Gas-Chrom Q (100—120 mesh) at 220° with a flow rate of 20 ml/min of N_2; (B), a stainless steel column (2 m × 3 mm) packed with 0.5% OV-1 on Gas-Chrom Q (100—120 mesh) at 170—240° (2°/min) with a flow rate of 28 ml/min of N_2. TLC on Kieselgel GF_{254} (E. Merck, Darmstadt, Germany) activated at 110° was performed with solvent combination (v/v): (A), CH_2Cl_2–acetone (9: 1); (B), 70% iso-PrOH–AcOEt (2: 1). Detection was effected with H_2SO_4 or UV light (short wave length). Column chromatography was performed on a column of Wakogel C-200 as the adsorbent, with 1 g of the mixture to be separated per 20 g of adsorbent.

β-Cellobiosyl N,N-Dimethyldithiocarbamate Heptaacetate (2)——A mixture of sodium N,N-dimethyldithiocarbamate dihydrates (8.7 g, 48.5 mmol) and **1**[4] (41 g, 55.8 mmol) in acetone (200 ml) was warmed for 10 min to a boiling. The mixture was then allow to stand for 1 hr at room temperature, and poured into ice-H_2O (2 l) containing AcOH (10 ml). The resulting white precipitate was collected by filtration, dried in the air, and recrystallized from $CHCl_3$–EtOH (2: 3, v/v) to give white needles (36 g, 87%), mp 249—250°, $[\alpha]_D^{23}$ −8.8° (c=1.36, $CHCl_3$), NMR ($CDCl_3$) δ: 2.00, 2.04, 2.06, 2.12 (21H, singlets, 7 OAc), 3.36, 3.56 (6H, singlets, $N(C\underline{H}_3)_2$), 5.81 (1H, doublet, $J_{1,2}$=9 Hz, H-1), TLC: *Rf* 0.38 (solvent A). *Anal.* Calcd. for $C_{29}H_{41}NO_{17}S_2$: C, 47.07; H, 5.58; N, 1.89. Found: C, 47.01; H, 5.67; N, 1.60.

β-Cellobiosyl N,N-Dimethyldithiocarbamate (3)——To a suspension of **2** (10 g) in dry MeOH (100 ml) was added methanolic 1 N sodium methoxide (0.5 ml), and the mixture was stirred for 24 hr at room temperature. Dry Amberlite IR-120 (H^+) resin (0.5 g) was added, and the mixture was stirred for 30 min. Removal of the resin and evaporation of the solvent from the filtrate afforded an amorphous powder which crystallized from MeOH. Recrystallization from MeOH gave white granules (4.8 g, 80%), mp 245—246° (dec.), $[\alpha]_D^{21}$ −54.3° (c=2.26, H_2O), TLC: *Rf* 0.51 (solvent B). *Anal.* Calcd. for $C_{15}H_{27}NO_{10}S_2$: C, 40.36; H, 6.10; N, 3.14. Found: C, 40.20; H, 5.88; N, 3.44.

Methyl α-Cellobioside Heptaacetate (4a)——A mixture of **3** (1 g, 2.25 mmol), $HgCl_2$ (1.22 g, 4.49 mmol), and $CdCO_3$ (1.13 g, 6.55 mmol) in dry MeOH (15 ml) was stirred for 30 min under reflux. After cooling, the suspension was filtered. The residual mercury and cadmium salts in the filtrate were converted into the insoluble sulfide form by saturation with H_2S in the presence of pyridine (1 ml). The suspension was filtered again, and removal of the solvent from the filtrate afforded an amorphous powder which was acetylated with Ac_2O (5 ml) and pyridine (5 ml). After keeping overnight at room temperature, the mixture was poured into ice-H_2O (100 ml), and extracted with CH_2Cl_2 (15 ml × 3). The combined extracts were washed with H_2O, dil. H_2SO_4, satd. $NaHCO_3$, and H_2O, dried (Na_2SO_4), and concentrated to dryness. The residue was dissolved in CH_2Cl_2 and chromatographed on a column of silica gel with CH_2Cl_2–acetone (20: 1, v/v) as eluent. Removal of the solvent from the fraction having *Rf* 0.26 (TLC, solvent A) afforded an amorphous powder (1.31 g, 90%), NMR ($CDCl_3$) δ: 3.41 (2.37H, singlet, α-OMe), 3.50 (0.63H, singlet, β-OMe). After deacetylation, GLC analysis (column A) indicated that **4a** comprised about 80% of the total cellobioside fraction.

Pure **4a** was prepared from the anomeric mixture by repeated recrystallizations from EtOH as white needles (660 mg, 45%), mp 185—186°, $[\alpha]_D^{26}$ +55.4° (c=1.1, $CHCl_3$), NMR ($CDCl_3$) δ: 2.00, 2.03, 2.05, 2.07, 2.10, 2.14 (21H, singlets, 7 OAc), 3.41 (3H, singlet, OMe), TLC: *Rf* 0.26 (solvent A). *Anal.* Calcd. for $C_{27}H_{38}O_{18}$: C, 49.84; H, 5.88. Found: C, 49.72; H, 6.00. (lit.[9a] mp 185—186°, $[\alpha]_D^{20}$ +55.7° (c=1.2, $CHCl_3$); lit.[9b] mp 185—186°, $[\alpha]_D$ +57.8°).

Methyl β-Cellobioside Heptaacetate (4b)——Authentic **4b** was obtained according to the method of Zemplén and Gerecs.[6] NMR ($CDCl_3$) δ: 1.98, 2.01, 2.03, 2.08, 2.12 (21H, singlets, 7 OAc), 3.48 (3H, singlet, OMe).

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Methyl α-Cellobioside (5)——To a suspension of **4a** (500 mg) in dry MeOH (10 ml) was added 0.5 N methanolic sodium methoxide (0.2 ml). The solution was stirred for 5 hr at room temperature, neutralized with dry Amberlite IR-120 (H^+) resin (0.2 g) with stirring. After removal of the resin, the solvent was evaporated to give an amorphous powder which on recrystallization from EtOH gave microscopic needles (230 mg, 84%), mp 144—145°, $[\alpha]_D^{25}$ +97.3° (c=2, H_2O), TLC: *Rf* 0.39 (solvent B). (lit.[9a] mp 144—145°, $[\alpha]_D^{20}$ +96.8° (c=1, H_2O); lit.[9b] $[\alpha]_D$ +106°).

Methyl α-Lactoside Heptaacetate (7a)——Treatment of β-lactosyl N,N-dimethyldithiocarbamate (**6**)[3] (2 g, 4.50 mmol) with $HgCl_2$ (2.42 g, 8.91 mmol) and $CdCO_3$ (2.31 g, 13.4 mmol) in dry MeOH (30 ml), and sequential acetylation of the resulting sirup as described above for **4a** gave, after column chromatography, a mixture of anomeric acetylated methyl lactosides (**7a** and **7b**) as a white powder (2.61 g, 89%), TLC: *Rf* 0.25 (solvent A), NMR ($CDCl_3$) δ: 3.40 (2.34H, singlet, α-OMe), 3.49 (0.66H, singlet, β-OMe). After deacetylation, GLC analysis (column A) indicated that **7a** comprised about 84% of the total lactoside fraction.

Pure **7a** was separated from the anomeric mixture by repeated recrystallizations from MeOH–H_2O (1:1, v/v) as colorless needles (1.57 g, 54%), mp 161—162°, $[\alpha]_D^{25}$ +64.3° (c=1.25, $CHCl_3$). NMR ($CDCl_3$) δ: 1.96, 2.06, 2.13, 2.16 (21H, singlets, 7 OAc), 3.40 (3H, singlet, OMe), TLC: *Rf* 0.25 (solvent A). *Anal.* Calcd. for $C_{27}H_{38}O_{18}$: C, 49.84; H, 5.88. Found: C, 49.69; H, 5.94.

Methyl β-Lactoside Heptaacetate (7b)——Authentic **7b** was obtained according to the method of Smith and Van Cleve.[14] NMR ($CDCl_3$) δ: 1.96, 2.05, 2.11, 2.15 (21H, singlets, 7 OAc), 3.48 (3H, singlet, OMe).

Methyl α-Lactoside (8)——Deacetylation of **7a** (350 mg) was effected as described above for **5**. Recrystallization from EtOH gave **8** as white crystals (145 mg, 75%), mp 189—190°, $[\alpha]_D^{25}$ +115.1° (c=1.03, H_2O), TLC: *Rf* 0.30 (solvent B). *Anal.* Calcd. for $C_{13}H_{24}O_{11}$: C, 43.82; H, 6.78. Found: C, 43.76; H, 6.79.

Methyl α-Maltoside Heptaacetate (10a)——Treatment of β-maltosyl N,N-dimethyldithiocarbamate (**9**)[5] (2 g, 4.50 mmol) with $HgCl_2$ and $CdCO_3$ in dry MeOH as described above for **4a** or **7a** gave a mixture of anomeric acetylated methyl maltosides (**10a** and **10b**) as a white powder (1.9 g, 66%), TLC: *Rf* 0.33 (solvent A), NMR ($CDCl_3$) δ: 3.40 (2.52H, singlet, α-OMe), 3.47 (0.48H, singlet, β-OMe). After deacetylation, GLC analysis (column A) indicated that **10a** comprised about 79% of the total maltoside fraction.

The product was deacetylated as described for **5** to give an amorphous powder (1 g, 97%), which was dissolved in a minimum quantity of H_2O. The solution was applied to a column (18×1.7 cm) of Dowex 1 (OH^-) resin, and chromatographed with H_2O as eluent. The eluate was collected in fraction (10 ml), and the glycosides were eluated as shown in Table I. The fraction (5—13) was evaporated to give an amorphous powder, which was acetylated with Ac_2O (12 ml) and pyridine (12 ml) as described above for **4a**. After purification by column chromatography on silica gel, **10a** (1.52 g, 80%) was obtained as a homogeneous powder, $[\alpha]_D^{24}$ +137.2° (c=1.74, $CHCl_3$) δ: 1.98, 2.00, 2.03, 2.08, 2.12 (21H, singlets, 7 OAc), 3.40 (3H, singlet, OMe), TLC: *Rf* 0.33 (solvent A). *Anal.* Calcd. for $C_{27}H_{38}O_{18}$: C, 49.84; H, 5.88. Found: C, 49.55; H, 5.76. (lit.[15] colorless glass, $[\alpha]_D^{20}$ +136° (c=0.7, $CHCl_3$)).

Methyl β-Maltoside Heptaacetate (10b)——Removal of the solvent from the fraction (14—20) of Dowex 1 mentioned above afforded an amorphous powder from which **10b** crystallized by treatment with EtOH. Recrystallization from EtOH gave white needles (160 mg, 8.4%), mp 127—128°, $[\alpha]_D^{23}$ +56.5° (c=1.23, $CHCl_3$), NMR ($CDCl_3$) δ: 2.00, 2.02, 2.04, 2.09, 2.13 (21H, singlets, 7 OAc), 3.49 (3H, singlet, OMe), TLC: *Rf* 0.32 (solvent A). The product was indistinguishable from an authentic sample[16] by mixed mp, NMR, and TLC. (lit.[17] mp 128—129°, $[\alpha]_D$ +53°).

Methyl α-Maltoside (11)——Deacetylation of **10a** (200 mg) as described above for **5** yielded an amorphous powder (102 mg, 93%), $[\alpha]_D^{23}$ +177.7° (c=0.91, H_2O), TLC: *Rf* 0.38 (solvent B). (lit.[15] colorless sirup, $[\alpha]_D^{20}$ +174° (c=0.9, H_2O)).

Methanolysis of Glycosyl N,N-Dimethyldithiocarbamate (3, 6, or 9) in the Presence of Silver Salts——One of the representative of the procedures, methanolysis of **3** is described. The yields and the ratios of anomers of the corresponding disaccharides are summarized in Table II.

Compound **3** (500 mg, 1.12 mmol) in dry MeOH (15 ml) containing pyridine (0.3 ml) was stirred with $AgClO_4$ (700 mg, 3.37 mmol) for 30 min under reflux. The mixture was treated as described above for **4a** to give anomeric acetylated methyl cellobiosides mixture (661 mg, 91%) as a crystalline powder. After deacetylation, GLC analysis (column A) indicated that **4a** comprised about 85% of the total cellobioside fraction.

Although the yield was a slight lower (590 mg, 81%), instead of $AgClO_4$, $AgNO_3$ (570 mg, 3.35 mmol) was available in the reaction. In this case, **4a** comprised about 75% of the total cellobioside fraction.

Benzyl α- and β-Maltoside Heptaacetates (12a and 12b)——A mixture of **9** (1 g, 2.24 mmol), $HgCl_2$ (1.22 g, 4.49 mmol), and $CdCO_3$ (1.13 g, 6.55 mmol) in benzyl alcohol (15 ml) was stirred for 30 min at 80°. The suspension was filtered and the residue was washed with MeOH. To the combined filtrate and washings were

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saturated with H_2S and the resulting suspension was filtered again. The solvent was evaporated in vacuum at 100° to dryness to afford a sirupy residue which was acetylated with Ac_2O (10 ml) and pyridine (10 ml). Treatment of the acetylation mixture as described above for **4a** afforded a sirupy residue (720 mg, 44%). After deacetylation, GLC analysis (column B) indicated that **12a** comprised about 57% of the total maltoside fraction.

The β-anomer (**12b**) crystallized by treatment of the anomeric mixture with warm MeOH–H_2O (5:3, v/v), colorless needles (196 mg, 12%), mp 122—124°, $[\alpha]_D^{18}$ $+28.9°$ ($c=0.93$, $CHCl_3$), NMR ($CDCl_3$) δ: 2.01, 2.04, 2.11, 2.17 (21H, singlets, 7 OAc), 7.37 (5H, singlet, aromatic protons), TLC: *Rf* 0.41 (solvent A). The product was indistinguishable from an authentic sample[18] by mixed mp, TLC, and NMR. (lit.[19] mp 125°, $[\alpha]_D$ $+27.6°$).

After separation of **12b** was completed, α-anomer (**12a**) was obtained by removal of the solvent from the filtrate as an amorphous powder (245 mg, 15%), $[\alpha]_D^{22}$ $+153°$ ($c=2.30$, $CHCl_3$), NMR ($CDCl_3$) δ: 2.02, 2.04, 2.08, 2.11, 2.17 (21H, singlets, 7 OAc), 7.42 (5H, singlet, aromatic protons), TLC: *Rf* 0.42 (solvent A). *Anal.* Calcd. for $C_{33}H_{48}O_{18}$: C, 54.52; H, 5.83. Found: C, 54.31; H, 5.74. After deacetylation, GLC analysis (column B) indicated that the product comprised about 99% of the α-anomer.

Benzyl α- and β-Cellobioside Heptaacetates——Benzyl alcoholysis and sequential acetylation of **3** (1 g) as described above for **12** yielded, after purification by column chromatography, benzyl α- and β-cellobioside heptaacetates (1.11 g, 68%), TLC: *Rf* 0.35 (solvent A), as an amorphous powder. *Anal.* Calcd. for $C_{33}H_{48}O_{18}$: C, 54.52; H, 5.83. Found: C, 54.34; H, 5.85. After deacetylation, GLC analysis (column B) indicated that the product comprised 63% of α- and 37% of β-anomers. Authentic benzyl β-cellobioside was prepared according to the method of Jayme and Demmig.[20]

Benzyl α- and β-Lactoside Heptaacetates——Compound **6** (1 g) was treated as described above for syntheses of benzyl cellobioside heptaacetates. Anomeric mixture of benzyl lactoside heptaacetates was obtained as an amorphous powder (0.8 g, 49%), TLC: *Rf* 0.34 (solvent A). *Anal.* Calcd. for $C_{33}H_{48}O_{18}$: C, 54.52; H, 5.83. Found: C, 54.23; H, 5.83. After deacetylation, GLC analysis (column B) indicated that the product comprised 66% of α- and 34% of β-anomers. Authentic benzyl β-lactoside was prepared according to the method of Richtmyer.[21]

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