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

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Methanolyis and benzyl alcoholysis of β-cellobiosyl, β-lactosyl, or β-maltosyl N,N-dimethylthioglycosides 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 methanolyis, 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-dimethylthioglycosides; 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 deacetylation. 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, those methods are not necessarily suitable for syntheses of alkyl α-glycosides of common alcohols.

Tejima and Ishiguro reported previously that when β-D-glucopyranosyl N,N-dimethylthiohexoside was treated with mercury salts in methanol, a stereospecific methanolysis proceeded to yield methyl α-D-glucopyranoside in good yield. β-Glycosyl N,N-dialkylthiohexosides are easily available as stable crystals by deacetylation of acetylated β-glycosyl N,N-dialkylthiohexosides, synthetized from acetylated glycosyl bromides with sodium N,N-dialkylthiohexosides. Thus, alcoholsysis of β-cellobiosyl, β-lactosyl, or β-maltosyl N,N-dimethylthiohexosides (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.

1) Location: Tanabe-dori, Misuku-ku, Nagoya, 467, Japan.
Treatment of heptaacetyl α-celllobiosyl bromide (1) with sodium N,N-dimethylthio-carbamate dihydrates as reported previously for the syntheses of the corresponding lactosyl(3) and maltosyl analogs(8) yielded β-celllobiosyl N,N-dimethylthiocarbamate 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-celllobioside 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-celllobioside heptaacetate (4b), synthesized according to the method of Zemplén and Gerecs,(6) and the other to the α-methoxyl by comparison with methyl α-celllobioside heptaacetate (4a) which is mentioned below. From the ratio of the individual intensity, the α-anomer comprised 79% of the anomic 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 α-glucopyranoside or methyl hexaacetyl maltoside, respectively, by intensity of the corresponding methoxyl proton signal.

From the anomic 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-celllobioside (5) in 84% yield.

Methanalysis of β-lactosyl or β-maltosyl N,N-dimethylthiocarbamate (6 or 9) and sequential acetylation of the methanalysis mixture gave the corresponding anomic 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 [α]D +64.3° (CHCl₃). In the NMR spectrum, the seven acetyl 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°, [α]D +115.1° (H₂O), 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 anomic 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-maltotriose heptaacetate (10a) as a homogeneous powder, from which methyl α-maltotriose (11) was prepared by deacetylation. Methyl β-maltotriose was isolated as a colorless sirup which was crystallized as heptaacetate (10b).

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<tr>
<th>Table I. Elution of Methyl Maltoses from Dowex 1 (OH⁻) Resin Column</th>
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<td>Fraction No.</td>
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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-maltotriose 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-dimethylmorpholinocarbamate, 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 anomic 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>
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<th>Table II. Yield and Ratio of Methyl Glycosides</th>
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(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 anomic mixture in 44—68% yield. The ratio

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 CDCl₃. 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 about 30 min before injection. The following columns, (A) and (B) were used: (A), a stainless steel column (2 m x 3 mm) packed with 9% JXR on Gas-Chrom Q (100–120 mesh) at 220° with a flow rate of 20 ml/min of N₂; (B), a stainless steel column (2 m x 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 N₂. TLC on Kieselgel GF₂₅₄ (E. Merck, Darmstadt, Germany) activated at 110° was performed with solvent combination (v/v): (A), CH₃Cl₂-acetone (9:1); (B), 70% iso-PrOH-AcOEt (2:1). Detection was effected with H₂SO₄ 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-Celllobiosyl N,N-Dimethyldithiocarbamate Heptaacetate (2)** — A mixture of sodium N,N-dimethyldithiocarbamate dibromides (8.7 g, 48.5 mmol) and 10 (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-H₂O (2 l) containing HClO₄ (10 ml). The resulting white precipitate was collected by filtration, dried in the air, and recrystallized from CHCl₃-EtOH (2:3, v/v) to give white needles (36 g, 87%), mp 249–250°, [α]D +8.8° (c = 1.36, CHCl₃), NMR (CDCl₃) δ: 2.00, 2.04, 2.06, 2.12 (2H, singlets, 7 OAc), 0.36, 3.56 (6H, singlets, N(CH₃)₂), 5.81 (1H, doublet, J₁,₂ = 9 Hz, H-1), TLC: RF 0.38 (solvent A). Anal. Calcd. for CₘHₙ₂₅N₂O₆S₂: C, 47.07; H, 5.58; N, 1.89. Found: C, 47.01; H, 5.67; N, 1.60.

**β-Celllobiosyl 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°, [α]D +54.3° (c = 2.26, H₂O), TLC: RF 0.51 (solvent B). Anal. Calcd. for CₙHₐ₂₅N₂O₆S₂: C, 40.36; H, 6.10; N, 3.14. Found: C, 40.20; H, 5.88; N, 3.44.

**Methyl α-Celllobioside Heptaacetate (4a)** — A mixture of 3 (1 g, 2.25 mmol), H₂C₅Cl (1.22 g, 4.49 mmol), and CdCO₃ (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 H₂S 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 Ac₂O (5 ml) and pyridine (5 ml). After keeping overnight at room temperature, the mixture was poured into ice-H₂O (100 ml), and extracted with CH₂Cl₂ (15 ml x 3). The combined extracts were washed with H₂O, dil. H₂SO₄, satd. NaHCO₃, and H₂O, dried (Na₂SO₄), and concentrated to dryness. The residue was dissolved in CH₂Cl₂ and chromatographed on a column of silica gel with CH₂Cl₂-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 (CDCl₃) δ: 3.41 (2.37H, singlet, O-Me), 3.50 (0.63H, singlet, β-OMe). After deacetylation, GLC analysis (column A) indicated that 4a comprised about 80% of the total cellulobiidoside fraction.

Pure 4a was prepared from the anomeric mixture by repeated recrystallizations from EtOH as white needles (660 mg, 45%), mp 185–186°, [α]D +55.4° (c = 1.1, CHCl₃), NMR (CDCl₃) δ: 2.00, 2.03, 2.05, 2.07, 2.10, 2.14 (2H, singlets, 7 OAc), 3.41 (3H, singlet, OMe), TLC: RF 0.26 (solvent A). Anal. Calcd. for C₈H₉₅O₅: C, 49.84; H, 5.88. Found: C, 49.72; H, 6.00. (lit. 19a) mp 185–186°, [α]D +55.7° (c = 1.2, CHCl₃); lit. 200 mp 185–186°, [α]D +57.8°.

**Methyl β-Celllobioside Heptaacetate (4b)** — Authentic 4b was obtained according to the method of Zemplen and Gerecs. NMR (CDCl₃) δ: 1.98, 2.01, 2.03, 2.08, 2.12 (2H, singlets, 7 OAc), 3.48 (3H, singlet, OMe).

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°, [x]D +97.8° (c=1, H2O), TLC: Rf 0.39 (solvent B). (lit.) mp 144—145°, [x]D +96.8° (c=1, H2O); lit.29 [x]D +106°.

Methyl α-Lactoside Heptacetate (7a)—Treatment of β-lactosyl N,N-dimethyldithiocarbamate (6b) (2 g, 4.50 mmol) with HgCl2 (2.42 g, 8.91 mmol) and CdCO3 (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 (CDCl3) 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—H2O (1:1, v/v) as colorless needles (1.57 g, 54%), mp 161—162°, [x]D +64.3° (c=1.25, CHCl3), NMR (CDCl3) δ: 1.96, 2.06, 2.13, 2.16 (2H, singlets, 7 OAc), 3.40 (3H, singlet, OMe), TLC: Rf 0.25 (solvent A). Anal. Calcd. for C27H34O16: C, 49.84; H, 5.88. Found: C, 49.69; H, 5.94.

Methyl β-Lactoside Heptacetate (7b)—Authentic 7b was obtained according to the method of Smith and Van Cleve.14 NMR (CDCl3) δ: 1.96, 2.05, 2.11, 2.15 (2H, 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°, [x]D +115.1° (c=1.03, H2O), TLC: Rf 0.30 (solvent B). Anal. Calcd. for C27H34O16: C, 43.82; H, 6.78. Found: C, 43.76; H, 6.79.

Methyl α-Maltoside Heptacetate (10a)—Treatment of β-maltosyl N,N-dimethyldithiocarbamate (9b) (2 g, 4.50 mmol) with HgCl2 and CdCO3 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 (CDCl3) 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 H2O. The solution was applied to a column (18 x 1.7 cm) of Dowex 1 (OH−) resin, and chromatographed with H2O as eluent. The eluate was collected in fraction (10 ml), and the glycosides were eluted as shown in Table I. The fraction (5—13) was evaporated to give an amorphous powder, which was acetylated with Ac2O (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, [x]D +137.2° (c=1.74, CHCl3) δ: 1.98, 2.00, 2.03, 2.08, 2.12 (2H, singlets, 7 OAc), 3.40 (3H, singlet, OMe), TLC: Rf 0.33 (solvent A). Anal. Calcd. for C27H34O16: C, 49.84; H, 5.88. Found: C, 49.55; H, 5.76. (lit.) colorless glass, [x]D +136° (c=0.7, CHCl3).

Methyl β-Maltoside Heptacetate (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°, [x]D +56.3° (c=1.23, CHCl3), NMR (CDCl3) δ: 2.00, 2.02, 2.04, 2.08, 2.13 (2H, singlets, 7 OAc), 3.49 (3H, singlet, OMe), TLC: Rf 0.32 (solvent A). The product was indistinguishable from an authentic sample6 by mixed mp, NMR, and TLC. (lit.) mp 128—129°, [x]D +53°.

Methyl α-Maltoside (11)—Deacetylation of 10b (200 mg) as described above for 5 yielded an amorphous powder (102 mg, 93%), [x]D +177.7° (c=0.91, H2O), TLC: Rf 0.38 (solvent B). (lit.) colorless sirup, [x]D +174° (c=0.9, H2O).

Methanalysis of Glycosyl N,N-Dimethyldithiocarbamate (3, 6, or 9) in the Presence of Silver Salts—One of the representative of the procedures, methanalysis 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 AgClO4 (700 mg, 3.37 mmol) for 30 min under reflux. The mixture was treated as described above for 4a to give anomeric acetylated methyl cellobioside 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 AgClO4, AgNO3 (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 Heptacetates (12a and 12b)—A mixture of 9 (1 g, 2.24 mmol), HgCl2 (1.22 g, 4.49 mmol), and CdCO3 (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

saturated with H₂S and the resulting solution was filtered again. The solvent was evaporated in vacuum at 100° to dryness to afford a syrupy residue which was acetylated with Ac₂O (10 ml) and pyridine (10 ml). Treatment of the acetylation mixture as described above for 4a afforded a syrupy 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 anomic mixture with warm MeOH–H₂O (5:3, v/v), colorless needles (196 mg, 12%), mp 122–124°, [α]₁₀° D +28.8° (c=0.03, CHCl₃), NMR (CDCl₃) δ: 2.01, 2.04, 2.11, 2.17 (2H, singlets, 7 OAc), 7.37 (5H, singlet, aromatic protons), TLC: Rf 0.41 (solvent A). The product was indistinguishable from an authentic sample by mixed mp, TLC, and NMR. (lit. mp 125°, [α]₀° 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%), [α]₁₀° D +153° (c=2.30, CHCl₃), NMR (CDCl₃) δ: 2.02, 2.04, 2.08, 2.11, 2.17 (2H, singlets, 7 OAc), 7.42 (5H, singlet, aromatic protons), TLC: Rf 0.42 (solvent A). Anal. Calcd. for C₃₃H₄₄O₁₆: 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 C₃₃H₄₄O₁₆: 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.

**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 C₃₃H₄₄O₁₆: 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.

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