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PREPARATION OF 8-METHOXYCARBONYLOCTYL GLYCOSIDES OF α-D-MANNOPYRANOSE, 2-*O*-α-MANNOPYRANOSYL-α-D-MANNOPYRANOSE, β-D-GALACTOFURANOSE, AND 3-*O*-β-D-GALACTOFURANOSYL-α-D-MANNOPYRANOSE*

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ABSTRACT

The 8-methoxycarbonyloctyl glycosides of α-D-mannopyranose, 2-*O*-α-mannopyranosyl-α-D-mannopyranose, β-D-galactofuranose, and 3-*O*-β-D-galactofuranosyl-α-D-mannopyranose were prepared as intermediates for the synthesis of complexes with the general structure mono-(or di-)saccharide–lipid spacer–protein having possible antigenic and immunogenic activity in respect to infection with *Trypanosoma cruzi*. Tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene) derivatives of D-mannopyranose and D-galactofuranose were treated with alcohols in the presence and absence of mercuric bromide to give orthoesters which rearranged into glycosides.

INTRODUCTION

The 8-methoxycarbonyloctyl glycosides of α-D-mannopyranose, 2-*O*-α-D-mannopyranosyl-α-D-mannopyranose, β-D-galactofuranose, and 3-*O*-β-D-galactofuranosyl-α-D-mannopyranose were prepared to be used as intermediates in the preparation of complexes of the type mono-(or di-)saccharide–lipid spacer–polylysine which may have immunogenic activity. These compounds may also be immobilized on solid supports in order to isolate specific antibodies from antisera of humans or laboratory animals infected with *Trypanosoma cruzi* (Chagas' disease). In these syntheses, suitable 1,2-orthoesters were treated with alcohol acceptors in nitromethane solution containing mercuric bromide and molecular sieve 4A, rather than by use of the Koenigs–Knorr reaction. The orthoester glycosidation method[1] is highly specific in terms of configuration of the product and gives high yields. The only complication is the possible formation of the alkyl glycoside from the alkyl

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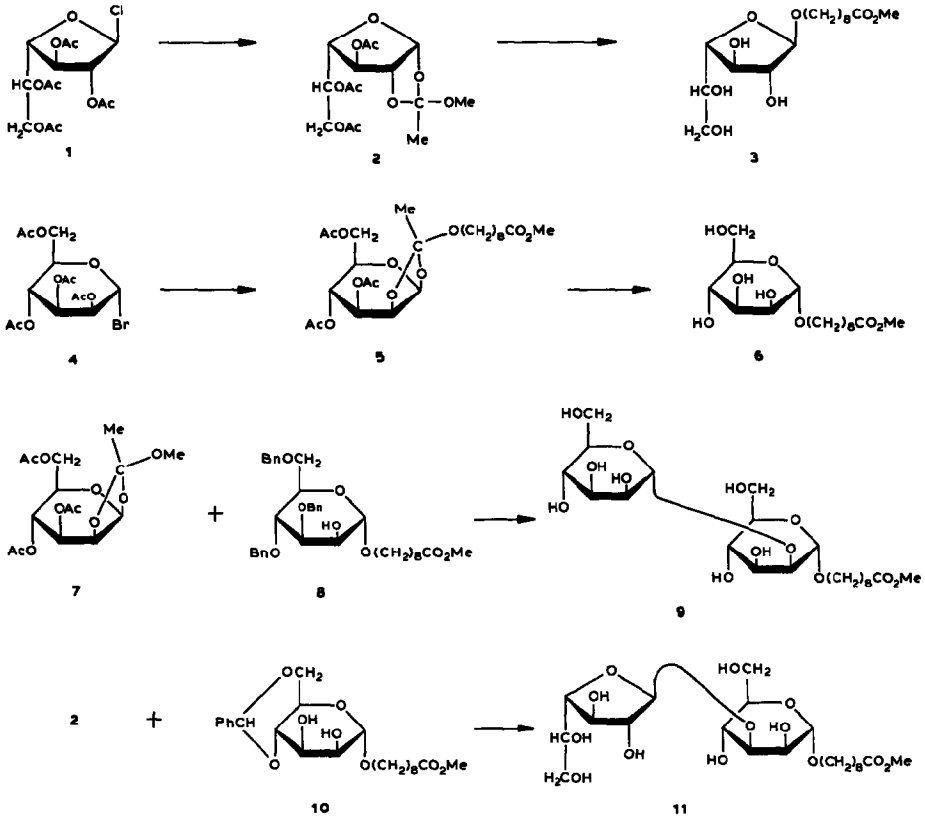
orthoester, instead of condensation of the orthoester with the alcohol acceptor which, *via* the orthoester of the acceptor alcohol, forms the desired alcohol glycoside[2,3]. In the formation of such glycosides, 2,6-dimethyl- and 3,4,6-trimethylpyridinium salts were used as reaction promotors[2] with chlorobenzene as solvent. Many orthoesters were prepared and further used by this and other methods[1,3]. In the present study, mercuric bromide in nitrobenzene was found to be superior to other catalysts and conditions for maximizing yields were determined.

RESULTS AND DISCUSSION

The starting material for the synthesis of D-mannopyranoside derivatives was 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose (**7**), which has already been prepared in good yield[4] and used in glycoside syntheses[5]. However, attempts to prepare the other starting material, 3,5,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-α-D-galactofuranose (**2**) by treatment of 2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranosyl chloride (**1**) with methanol in 2,6-dimethylpyridine[6] gave a low yield. Decomposition most likely occurred on washing the dichloromethane solution of the orthoester with aqueous silver nitrate, a process that could have resulted in the formation in only 17% yield of *N*-benzyloxycarbonyl-L-seryl-β-D-galactofuranoside in a similar synthesis[3]. An improved yield of the methyl orthoacetate was obtained on evaporation of the reaction mixture to a small volume, and addition of excess ether to precipitate the insoluble 2,6-dimethylpyridinium chloride, followed by filtration. Evaporation of ether gave a product which could be stored in the freezer and the remaining 2,6-dimethylpyridine could be removed by azeotropic distillation in the presence of xylene immediately prior to use. The only impurities present appeared to be partly *O*-deacetylated material, as shown by t.l.c.

In order to find an effective catalyst for the conversion of 1,2-orthoacetates into corresponding glycosides and to ascertain optimum reaction conditions for the best yields, the reactivity of 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(methoxycarbonyloctyloxy)-ethylidene]-β-D-mannopyranose (**5**) in the presence of mercuric bromide in nitromethane and 2,6-dimethylpyridinium perchlorate in chlorobenzene[2] was investigated. However, the latter method was not used as the reacion proceeded slowly with much decomposition and formation of partly acetylated by-products, as shown by t.l.c. A satisfactory procedure was reflux for 5 h of a nitromethane solution containing mercuric bromide at a concentration of 2.7 mol of catalyst per 20 mL of solvent (one sixth of this concentration resulted in the formation of partly acetylated by-products). The reaction was preferably carried out in the presence of molecular sieve 4A which removed the water that would also react with the orthoester.

In the case of reactions of 1,2-(methyl orthoacetates) with acceptors, the procedure used was somewhat different. For example, prior to reaction in the presence of mercuric bromide (as described above), 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose (**7**) and the acceptor were refluxed in nitromethane



in the presence of molecular sieve to form the orthoacetate of the acceptor. Methanol liberated by the reaction had to be removed by the molecular sieve before formation of the methyl glycoside. The orthoester exchange-reaction is known to take place under mild conditions without catalyst[7], and we found that the methyl orthoacetate **7**, and an equimolar amount of 8-methoxycarbonyloctanol in ($^2H_2$)chloroform gave rise to 40% of the 1,2-*O*-β-[1-(8-methoxycarbonyloctyloxy)-ethylidene] derivative **5** after 24 h at room temperature (n.m.r. data). In the present syntheses, mercuric bromide was added and slow distillation carried out for 5 h when starting with the D-mannose orthoacetate **7** and for 2 h when starting with the D-galactose orthoacetate **2**.

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl bromide (**4**) was treated with 2,6-dimethylpyridine containing 8-methoxycarbonyloctanol to give crystalline 3,4,6-tri-*O*-acetyl-1,2-*O*-[1-(8-methoxycarbonyloctyloxy)ethylidene]-β-D-mannopyranose (**5**) in 80% yield. This was treated, at reflux, with nitromethane containing mercuric bromide, 4A molecular sieve, and 8-methoxycarbonyloctanol and the resulting glycoside was *O*-deacetylated to give 8-methoxycarbonyloctyl α-D-mannopyranoside (**6**). 3,4,6-Tri-*O*-benzyl-1,2-*O*-(methoxyethylidene)-β-D-mannopyranose was prepared from 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose by a modification of the method of Borén *et al.*[8] and then treated

as described earlier to give 8-methoxycarbonyloctyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (**8**). This was treated with a threefold excess of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose (**7**) in nitromethane and the product deacetylated with methanolic sodium methoxide to give 8-methoxycarbonyloctyl 3,4,6-tri-*O*-benzyl-2-*O*-α-D-mannopyranosyl-α-D-mannopyranoside. *O*-Debenzylation by hydrogenolysis provided 8-methoxycarbonyloctyl 2-*O*-α-D-mannopyranosyl-α-D-mannopyranoside (**9**) in 24% yield, based on **8**. 3,5,6-Tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-α-D-galactofuranose (**2**) was treated with 8-methoxycarbonyloctanol to give, after *O*-deacetylating, crystalline **3** in 60% yield. For the synthesis of 8-methoxycarbonyloctyl 3-*O*-β-D-galactofuranosyl-β-D-mannopyranoside (**11**), 8-methoxycarbonyloctyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**10**) was synthesized (50% yield) from 8-methoxycarbonyloctyl α-D-mannopyranoside (**6**) by treatment with benzaldehyde and separated from the 2,3,4,6-di-*O*-benzylidene derivative (15% yield) by chromatography. 3,5,6-Tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-α-D-galactofuranose (**2**) was condensed with **10** as described for the synthesis of **9** except that a 2:1 ratio of reagents was used for obtaining the mono- rather than the di-*O*-substituted compound. An analogous reaction using methyl 4,6-*O*-benzylidene-α-D-mannopyranoside as acceptor resulted exclusively in 3-*O*-substitution[5]. After *O*-deacetylation, chromatography gave 8-methoxycarbonyloctyl 4,6-*O*-benzylidene-3-*O*-β-D-galactofuranosyl-α-D-mannopyranoside. The *O*-benzylidene group was removed with acetic acid and **11** obtained in 40% yield after chromatography.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were measured with an automatic polarimeter, Perkin–Elmer Model 141. ^{1}H-N.m.r. spectra for solutions in $CDCl_3$ or CD_3OD were recorded, with a Varian XL-100 spectrometer, relative to the resonance of Me_4Si measured in a separate experiment. Molecular sieve 4A was obtained from Merck of Canada. Silica gel (70–230 mesh), used in column chromatography, was supplied by Sigma Chemical Co., St. Louis, MO. T.l.c. was performed on 100-μ-thick precoated sheets of silica gel Eastman–Kodak Co., Rochester, NY) in solvents *A* (3:1, v/v, toluene–ethyl acetate), *B* (methanol), and *C* (1:1:1, v/v, dichloromethane–methanol–water); the spots were detected by spraying with 50% aqueous H_2SO_4, followed by heating at 110° for a few min.

3,5,6-Tri-O-acetyl-1,2-O-(1-methoxyethylidene)-α-D-galactofuranose (**2**). — This compound was obtained by a modification of the method of Kochetkov *et al.*[2]. 2,3,5,6-Tetra-*O*-acetyl-β-D-galactofuranosyl chloride[9] (**1**; 10.0 g) was dissolved in a mixture of methanol (50 mL) and 2,6-dimethylpyridine (10 mL), and, after 3 days, excess methanol was evaporated. On addition of excess ether (100 mL), a precipitate of hydrochloride formed which was removed by filtration and the filtrate evaporated. The remaining 2,6-dimethylpyridine was removed by several additions

and evaporations of xylene (50 mL) to yield **2** (9.79 g, 98%); ^{13}C-n.m.r. ($CDCl_3$; 85% of exo-isomer): δ 170.5, 170.0, 169.6 (3 C=O), 124.7 (tert. C), 105.0 (C-1), 84.7 (C-2), 83.1 (C-4), 76.5 (C-3), 69.9 (C-5), 62.8 (C-6), 50.0 (OMe), and 21.9, 20.8, 20.6 (3 $COCH_3$); (15% of endo-isomer) 126.0 (tert. C), 103.3 (C-1), 86.4 (C-2), 69.7 (C-5), 62.6 (C-6), and 51.0 (OMe).

*3,4,6-Tri-*O*-acetyl-1,2-*O*-[1-(8-methoxycarbonyloctyloxy)ethylidene]-β-*D*-mannopyranose* (**5**). — The procedure was similar to that for **2**, but with a reaction mixture containing 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (**4**; 10.0 g) in 2,6-dimethylpyridine (10 mL) containing 8-methoxycarbonyloctanol (5 mL). The product (10 g) crystallized and recrystallization from ether–hexane gave **5** (8.1 g, 80%). A further recrystallization gave material having m.p. 74–75°, $[\alpha]_D^{25}$ −5.5° (*c* 0.8, chloroform); t.l.c. (*A*) R_F 0.57.

Anal. Calc. for $C_{24}H_{38}O_{12}$: C, 55.59; H, 7.38. Found: C, 55.49; H, 7.32.

*3,4,6-Tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-β-*D*-mannopyranose.* —This compound was prepared according to the method of Borén *et al.*[8] with some modifications. 3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose (**7**; 8.0 g) was dissolved in 0.1M methanolic sodium methoxide (40 mL) and, after a few min, the solution was evaporated. The residue was dissolved in *N,N*-dimethylformamide (18 mL) and Ag_2O (30 g) was added and while this mixture was agitated vigorously at 0° in the dark, benzyl bromide (16 mL) was added dropwise over a period of 3 h. The mixture was maintained at 0° for a further 2 h prior to being kept overnight at room temperature. Methanol (10 mL) was added to destroy excess reagent and, after 2 h, the mixture was treated with dichloromethane (50 mL). The insoluble material was removed by filtration and the filtrate evaporated *in vacuo* at 50° to give a syrup which crystallized. The compound was recrystallized from ether–hexane (9.8 g, 88%), m.p. 76–77°, t.l.c. (*A*) R_F 0.78; lit.[8] m.p. 75–77°.

8-Methoxycarbonyloctyl α-D-mannopyranoside (**6**). — Compound **5** (10.0 g) was added to nitromethane (25 mL) containing molecular sieve 4A (2.0 g), $HgBr_2$ (1.0 g), and 8-methoxycarbonyloctanol (2 drops). The mixture was refluxed for 5 h, cooled to room temperature, and dichloromethane (100 mL) was added, followed by Ag_2CO_3 (3.0 g). The suspension was stirred in the dark overnight, the insoluble material filtered off and washed with dichloromethane, and the filtrate shaken successively with water, aqueous 10% KBr, and twice with water. The organic layer was dried (Na_2SO_4) and evaporated to a syrup, which was deacetylated with 0.2M methanolic sodium methoxide (100 mL). After a few min, the solution was made neutral with acetic acid and evaporated, the residue partitioned between ethyl acetate and water, and the ethyl acetate layer evaporated to a syrup. Chromatography on silica gel and subsequent elution with ethyl acetate gave 8-methoxycarbonyloctanol, and 23:2 ethyl acetate–methanol gave **6**, t.l.c. (*B*) R_F 0.62, which crystallized from ethyl acetate at −15° overnight (5.00 g, 74%); on recrystallization, m.p. 70–72°, $[\alpha]_D^{25}$ −47° (*c* 0.75, water); lit.[10] m.p. 81–82°, $[\alpha]_D^{25}$ +48°.

Anal. Calc. for $C_{16}H_{30}O_8$: C, 54.84; H, 8.60. Found: C, 54.90; H, 8.61.

8-Methoxycarbonyloctyl 4,6-O-benzylidene-α-D-mannopyranoside (**10**). — 8-Methoxycarbonyloctyl α-D-mannopyranoside (**6**; 10.0 g) was added to ethyl acetate (10 mL) containing benzylaldehyde (3.0 g) and zinc chloride (1.0 g). The mixture was stirred overnight and the organic layer washed successively with 10% aqueous $NaHSO_3$ (100 mL), 5% aqueous $NaHCO_3$ (100 mL), and water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel. Dichloromethane eluted 8-methoxycarbonyl 2,3,4,6-di-*O*-benzylidene-α-D-mannopyranoside (2.1 g, 15%), 49:1 dichloromethane–methanol eluted **10** (6.1 g, 50%), and 2:1 dichloromethane–methanol eluted unreacted **6** (3.0 g). Compound **10** was recrystallized twice from ether–hexane, m.p. 87–89°, $[\alpha]_D^{25}$ +37° (*c* 1.2, chloroform) t.l.c. (*B*) R_F 0.85; ^{13}C-n.m.r. ($CDCl_3$): δ 174.2 (=C=O), 137.4, 129.2, 128.3, 126.3 (4 C, Ph), 102.0 (=CH), 100.25 (C-1), 78.8, 71.1, 68.8, 68.6, 67.9, 63.1, 51.1 (OMe), 34.1, 29.4, 29.19, 29.11, 26.1, and 25.0.

Anal. Calc. for $C_{23}H_{32}O_8$: C, 62.99; H, 7.81. Found: C, 62.81; H, 7.75.

The unchanged starting material and di-*O*-benzylidene derivative could be recycled, the latter compound after partial hydrolysis with 80% aqueous acetic acid for 30 min at 100°.

General procedure for the condensation of 1,2-(methyl orthoacetates) of 3,5,6-tri-O-acetyl-α-D-galactofuranose and 3,4,6-tri-O-acetyl-β-D-mannopyranose with fatty acid glycoside and 8-methoxycarbonyloctanol. — As the 1,2-orthoacetates are more easily prepared than the fatty acid glycosides an excess of the former was used. The orthoacetate (10–60 mmol) and the glycoside acceptor ($^1/_3$–$^1/_2$ of molar equiv.) were dissolved in nitromethane (40 mL), molecular sieve 4A (10 g) was added, and the mixture stirred. Distillation at normal pressure promoted orthoester formation. When 5 mL of distillate had been obtained, $HgBr_2$ (0.5 g) was added and the distillation continued for 2 h until 20 mL more of nitromethane had been collected. In the case of the galactofuranose orthoacetate the reaction was complete, but in the mannopyranose series it was necessary to continue the distillation for a further 3 h with replacement of distilled nitromethane to maintain the volume of the reaction mixture. Where 8-methoxycarbonyloctanol was the acceptor, equimolar amounts of it and the 1,2-(methyl orthoacetate) were used in the reaction. The mixture was cooled and $HgBr_2$ was removed by addition of Ag_2CO_3 (1.50 g) and nitromethane (60 mL), stirring for 18 h in the dark, and filtration of insoluble material. The filtrate was washed with 10% aqueous KBr (25 mL), twice with water, and dried (Na_2SO_4). Evaporation gave a syrup which was dissolved in 0.2M methanolic sodium methoxide (50 mL). After 4 h at room temperature the solution was made neutral with acetic acid and evaporated. The residue was partitioned between ethyl acetate and water, and the material obtained from the organic layer chromatographed on silica gel.

8-Methoxycarbonyloctyl 3,4,6-tri-O-benzyl-α-D-mannopyranoside (**8**). — 3,4,6-Tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-β-D-mannopyranose (5.06 g) was treated with 8-methoxycarbonyloctanol (1.88 g) in nitromethane containing $HgBr_2$ (0.50 g) and molecular sieve 4A over a period of 5 h. On chromatography of the

crude deacetylated product, toluene–ethyl acetate eluted syrupy **8** (4.50 g, 73%) $[\alpha]_D^{25}$ +19° (*c* 2.8, chloroform), t.l.c. (*A*) R_F 0.35; ^{13}C-n.m.r. ($CDCl_3$): δ 174.3 (=C=O), 138.43, 138.36, 138.1, 128.5, 128.4, 128.0, 127.9, 127.7, 127.6 (9 C, arom.), 99.3 (C-1), 80.4 (C-3), 75.7, 74.5, 73.5, 72.0, 71.2, 69.15, 68.6, 67.8, 51.5 (OMe), 34.2, 39.5, 29.3 (2 superimposed signals), 29.15, 26.2, and 25.0.

Anal. Calc. for $C_{37}H_{48}O_8$: C, 71.59; H, 7.79. Found: C, 71.20; H, 7.47.

8-Methoxycarbonyloctyl 2-O-α-D-mannopyranosyl-α-D-mannopyranoside (**9**). — Compound **7** (10.8 g, 0.03 mol) was treated with **8** (6.2 g, 0.01 mol) in nitromethane containing $HgBr_2$ (1.0 g) and molecular sieve 4A. The deacetylated product was chromatographed and ethyl acetate eluted unchanged **7** (0.8 g) and 9:1 ethyl acetate–methanol **9** (3.97 g). The latter was *O*-debenzylated in acetic acid (50 mL) by H_2 in the presence of 5% Pd–C at ambient temperature and pressure. After filtration and evaporation of the filtrate, the product was chromatographed. Elution with 4:1 ethyl acetate–methanol gave **9** (1.24 g, 24%), t.l.c. (*C*) R_F 0.76; ^{13}C-n.m.r. (CD_3OD): δ 175.95 (=C=O), 104.1 (C-1′), 99.9 (C-1), 80.6 (C-2), 74.9 and 74.6 (C-5 and C-5′), 72.4, 72.2, 71.85, (C-3,2′,3′), 69.1, 68.60, 68.64, [C-4,4′, –$OCH_2(CH_2)_7$], 63.0 (C-6,6′), 51.95 (OMe), 34.8, 30.6, 30.4, 30.3, 30.1, 27.2, and 26.0 [$(CH_2)_7$]. Peracetate, $[\alpha]_D^{25}$ +31° (*c* 2, chloroform).

Anal. Calc. for $C_{37}H_{56}O_{20}$: C, 54.13; H, 6.89. Found: C, 53.56; H, 6.80.

8-Methoxycarbonyloctyl β-D-galactofuranoside (**3**). — Compound **2** (3.6 g) was treated with 8-methoxycarbonyloctanol (1.88 g) in nitromethane containing $AgBr_2$ and molecular sieve 4A by distilling the solvent for 2 h at ambient pressure. The reaction mixture was processed as described for the preparation of **6** to give crystalline **3** (2.1 g, 60%), m.p. 83–84°, $[\alpha]_D$ −73° (*c* 0.6, ethanol); t.l.c. (*B*) R_F 0.72.

Anal. Calc. for $C_{16}H_{30}O_8$: C, 54.84; H, 8.60. Found: C, 55.64; H, 8.71.

8-Methoxycarbonyloctyl 3-O-β-D-galactofuranosyl-α-D-mannopyranoside (**11**). — Compound **2** (3.6 g, 0.01 mol) was condensed with **10** (2.19 g, 5 mmol) and the product chromatographed; 99:1 dichloromethane–methanol eluted unchanged **10** and 9:1 **11** (1.78 g). The *O*-benzylidene group was removed with 80% aqueous acetic acid (30 mL) at 100° for 25 min, the solution evaporated, and the residue fractionated on silica gel. 19:1 Ethyl acetate–methanol eluted **6** and 4:1 **11** (1.06 g, 40%), t.l.c. (*C*) R_F 0.78; ^{13}C-n.m.r. (CD_3OD): δ 175.9 (=C=O), 106.6 (C-1′), 101.2, (C-1), 85.4 (C-4′), 82.6 (C-2′), 78.9 (C-3′), 77.7 (C-3), 74.5 (C-5), 72.5 (C-5′), 68.9 and 68.6 [C-2 and –$OCH_2(CH_2)_7$–], 66.8 (C-4), 64.4 (C-6′), 62.9 (C-6), 51.95 (OMe), 30.5, 30.25, (2 superimposed signals), 30.1, 27.2, and 26.0 [$(CH_2)_7$]. Peracetate, $[\alpha]_D^{25}$ +31° (*c* 2, chloroform).

Anal. Calc. for $C_{37}H_{56}O_{20}$: C, 54.13; H, 6.19. Found: C, 54.38; H, 6.84.

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