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Trityl Derivatives of Cellobiose. VII.¹⁾ Unusual Di-O-trityl Derivatives of Cellobiose²⁾

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Treatment of β -cellobiose with 2 molar equivalents of trityl chloride in pyridine at 100 °C for 1 h afforded three unusual ditritylates (**2**, **4**, and **5**) as well as the 6,6'-ditritylate (**3**) which was the expected product. The ratios of **2**, **4**, and **5** to **3** were approximately 2, 2, and 1 : 60, respectively. Each unusual ditritylate was isolated by column chromatography and was crystallized as needles. Their structures were established by the use of ¹H nuclear magnetic resonance (NMR), ¹³C-NMR, optical activity measurements, *etc.* It was concluded that **2** is trityl 6'-O-trityl- β -cellobioside, **4** is 2,6'-di-O-tritylcellobiose, and **5** is trityl 6-O-trityl- β -cellobioside.

Keywords—cellobiose; tritylation; unusual ditritylcellobiose; trityl 6-O-trityl- β -cellobioside; trityl 6'-O-trityl- β -cellobioside; 2,6'-di-O-tritylcellobiose; trideuterioacetyl analog; 2-O-tritylglucose; ¹H-NMR; ¹³C-NMR

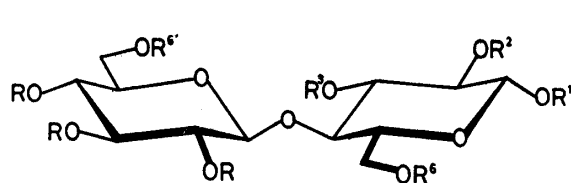
It is well known that in polyhydroxyl compounds containing both primary and secondary hydroxyl groups, the primary hydroxyl groups react preferentially with bulky triphenylmethyl (trityl) chloride.³⁾ Tritylation of D-glucose or D-galactose with one mole of trityl chloride in pyridine solution afforded the 6-trityl ether in a yield of only 30–50%.⁴⁾ If the hydroxyl group at C-1 was protected, as in methyl α - or β -D-glucosides, the reaction gave a much better yield.⁵⁾ These results suggest that the hemiacetal hydroxyl group at C-1, as well as the primary hydroxyl group at C-6, is probably tritylated. However, neither trityl D-glucoside nor trityl D-galactoside has been isolated after direct tritylation of D-glucose or D-galactose with trityl chloride. Zeile *et al.*⁶⁾ isolated 1,5-di-O-trityl-D-xylose, 1,5-di-O-trityl-L-arabinose, 1,5-di-O-trityl-D-ribose, 1,2,6-tri-O-trityl-D-fructose, and 1,2,6-tri-O-trityl-L-sorbose, in which all primary and hemiacetal hydroxyl groups were tritylated. Although they also obtained a monotrityl ether of D-xylose, which had the trityl group attached glycosidically at C-1, this compound must have had no primary hydroxyl group remaining untritylated, namely it was trityl D-xylopyranoside.

In our study on tritylation of β -cellobiose, we have found the production of unusual ditrityl ethers which were tritylated at C-1 and C-6 or C-6', and at C-2 and C-6'. Thus, we wish to report here this unusual example of ditritylation.

Results and Discussion

Ordinarily, treatment of β -cellobiose (**1**), with 2 molar equivalents or a small excess of trityl chloride in pyridine at room temperature for one to two days or at 100°C for one to two hours results in the displacement of two primary hydroxyl groups to give the 6,6'-ditritylate (**3**).⁷⁾ However, thin-layer chromatography (TLC) showed that the treatment afforded three ditritylates (**2**, **4**, and **5** in order of decreasing TLC mobility) in addition to **3** (Fig. 1). The ratios of **2**, **4**, and **5** to **3** were estimated to be 2, 2, and 1 : 60, respectively, by TLC spectrophotometry at 260 nm, and did not vary much in the range of reaction conditions mentioned above.

The reaction mixture was chromatographed on a prepacked silica gel column with chloroform-methanol (9:1) as an eluant. The ditritylate **5** was isolated as needles from fractions



- 1: $R^1=R^2=R^3=R^6=R^6'=R=H$
 2: $R^1=R^6'=Tr$, $R^2=R^3=R^6=R=H$
 3: $R^6=R^6'=Tr$, $R^1=R^2=R^3=R=H$
 4: $R^2=R^6'=Tr$, $R^1=R^3=R^6=R=H$
 5: $R^1=R^6=Tr$, $R^2=R^3=R^6'=R=H$
 6: $R^6'=Tr$, $R^1=R^2=R^3=R^6=R=H$
 7: $R^6=Tr$, $R^1=R^2=R^3=R^6'=R=H$
 1-A: $R^1=R^2=R^3=R^6=R^6'=R=Ac$
 2-A: $R^1=R^6'=Tr$, $R^2=R^3=R^6=R=Ac$
 3-A: $R^6=R^6'=Tr$, $R^1=R^2=R^3=R=Ac$
 4-A: $R^2=R^6'=Tr$, $R^1=R^3=R^6=R=Ac$
 5-A: $R^1=R^6=Tr$, $R^2=R^3=R^6'=R=Ac$
 6-A: $R^6'=Tr$, $R^1=R^2=R^3=R^6=R=Ac$
 7-A: $R^6=Tr$, $R^1=R^2=R^3=R^6'=R=Ac$
 8-A: $R^6'=Tr$, $R^2=R^3=Ac-d_3$, $R^1=R^6=R=Ac$

Tr=trityl, Ac=acetyl

Chart 1

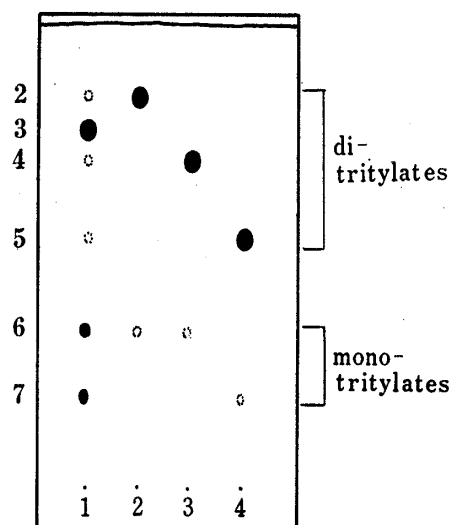


Fig. 1. TLC on Silica Gel

1, reaction mixture.
 2, fraction containing 2.
 3, fraction containing 4.
 4, fraction containing 5.
 Solvent system; chloroform-acetone-methanol-water (58:20:20:2).

containing the slower moving ditritylates without the need for rechromatography, and recrystallized from methanol-acetone, mp 155.5–156.0°C, $[\alpha]_D^{25} -41.0^\circ$ ($c=1.0$, CH_3OH), no mutarotation. Fractions containing the faster moving ditritylates 2 and 3 were combined and rechromatographed with benzene-methanol (9:1) as an eluant. Ditritylate 2 in the first fraction was isolated as needles, which were recrystallized from acetone-benzene, mp 193.0–194.0°C, $[\alpha]_D^{25} -10.8^\circ$ ($c=0.74$, CH_3OH), no mutarotation. Ditritylate 4 was isolated as needles from a fraction contaminated with a little of the preceding ditritylate (3) which was obtained by several repetitions of column chromatography (CC) using benzene-ethanol (10:1) as an eluant. Recrystallization from methanol gave pure 4, mp 156.0–157.0°C, $[\alpha]_D^{25} +11.0^\circ \rightarrow +3.0^\circ$ after 18 h ($c=1.0$, CH_3OH).

Determination of the Structure

TLC of each ditritylate fraction suggested that some partial detritylation occurred on the silica gel plate (see Fig. 1). The resulting monotritylate spots on TLC gave a clue as to the position substituted by one of the trityl groups; these spots corresponded to those of 6'- and 6-mono-O-tritylcellobioses⁷⁾ (6 and 7, respectively). Therefore, ditritylates 2 and 4 were suggested to be 6'-substituted derivatives and 5 to be a 6-substituted one.

(a) **Ditritylates 2 and 5**—Both 2 and 5 had the trityl group attached glycosidically at C-1, since they showed no mutarotation and were colored with aniline hydrogen phthalate reagent.⁸⁾

Treatment of 2 and 5 with acetic anhydride in pyridine afforded their peracetates (2-A and 5-A), each of which was a single anomeric product: 2-A, mp 189.0–190.0°C, $[\alpha]_D^{25} +2.0^\circ$ ($c=1.0$, $CHCl_3$), 1H -NMR δ ($CDCl_3$) 4.17 (1H, d, $J_{1,2}=7.8$ Hz, H-1); 5-A, mp 245.5–247.0°C, $[\alpha]_D^{25} -65.0^\circ$ ($c=1.0$, $CHCl_3$), 1H -NMR δ ($CDCl_3$) 4.10 (1H, d, $J_{1,2}=8.1$ Hz, H-1). The above 1H -nuclear magnetic resonance (1H -NMR) data, which were determined at 200 MHz, showed that both 2-A and 5-A were the β -anomers. Moreover, the optical activities supported their β -anomeric structures in comparison with those of a series of trityl ethers (cf. 6'-O-trityl- α -cellobiose peracetate, $[\alpha]_D^{25} +53.3^\circ$; its β -anomer, $[\alpha]_D^{25} +14.5^\circ$; 6-O-trityl- α -cellobiose peracetate, $[\alpha]_D^{25} +24.0^\circ$; its β -anomer, $[\alpha]_D^{25} -28.0^\circ$).⁷⁾ Consequently, it was inferred that 2 and 5 were trityl β -cellobiosides.

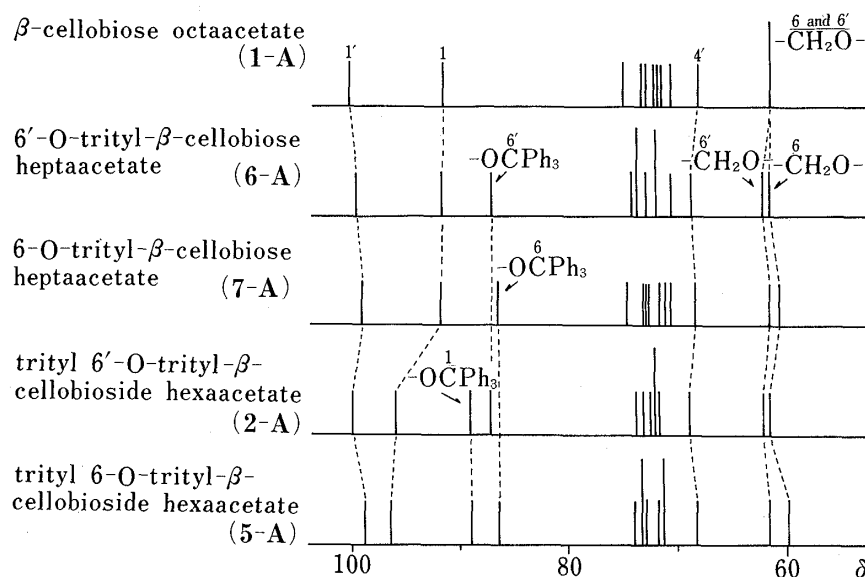


Fig. 2. ^{13}C -NMR Spectra of β -Cellobiose Octaacetate (1-A) and Tritylated β -Cellobiose Peracetates (2-A, 5-A, 6-A, and 7-A in CDCl_3)

The ^{13}C -NMR spectra of 2-A and 5-A provided important information about their structures. Fig. 2 schematically represents parts of the ^1H -noise-decoupled ^{13}C FT NMR spectra of β -cellobiose octaacetate (1-A), 6'-O-trityl- β -cellobiose heptaacetate⁷⁾ (6-A), 6-O-trityl- β -cellobiose heptaacetate⁷⁾ (7-A), 2-A, and 5-A. In all cases, the acetate carbonyl carbons resonate at δ 168–170 and the methyl resonances appear at δ 20.4–20.8. The phenyl-ring carbons in trityl groups resonate at δ 143.4–144.2 (carbons bearing no hydrogen) and δ 127.3–129.4 (the other ring carbons). Gagnaire *et al.*⁹⁾ have already assigned the ^{13}C signals of 1-A, and the ^{13}C signals of 6-A and 7-A were assigned by Utamura *et al.*¹⁰⁾ In the spectrum of each of the 6-trityl substituted derivatives 5-A and 7-A, the C-1' signal exhibits a slight upfield shift. It is possible to differentiate the C-1 α and C-1 β resonances of acetylated cellobioses, since the chemical shift of the former (δ 89) was observed to be distinctly higher than that of the latter (δ 92).⁹⁾ The C-1 signals of the tritylated derivatives, 6-A and 7-A, were observed at δ 92, in agreement with their β -anomeric structure. A replacement of the acetyl group at C-1 by a trityl group (*e.g.*, 6-A $\rightarrow$ 2-A or 7-A $\rightarrow$ 5-A) causes a downfield shift by about 4 ppm in the resonances of C-1. The signals near δ 68.5 are assigned to C-4'. In 6'-trityl substituted derivatives, 2-A and 6-A, a slight downfield shift was observed in the C-4' signals. Although the C-6 and C-6' resonances in 1-A overlap at the highest field in Fig. 2, one of the signals in the 6-O-trityl derivatives 5-A and 7-A is shifted upfield, while in the 6'-O-trityl derivatives 2-A and 6-A it is shifted downfield. The quaternary carbon signals of the trityl groups at C-6, C-6', and C-1 appear at δ 86.7, 87.2, and 89.2 ± 0.1 , respectively.

As a result, it was concluded that 2 is trityl 6'-O-trityl- β -cellobioside and that 5 is trityl 6-O-trityl- β -cellobioside.

The β -configuration of the trityl group attached glycosidically at C-1 in ditritylate 5 is very interesting, for 5 has another trityl group at C-6. However, the ^1H -NMR data suggest that there is no interaction between two trityl groups at C-1 and at C-6: the acetoxyl group resonances in the spectrum of 5-A are almost the same as those in the spectrum of 7-A, except that the 1-acetoxyl group signal is absent. In this connection, signals of acetoxyl groups other than these at C-3' and C-4' in the spectrum of 2-A exhibit upfield shifts compared with those in the spectrum of 6-A. It appears that the orientation of the trityl group at C-1 in 5-A is different from that in 2-A.

(b) **Ditritylate 4**—Another ditritylate **4** was colored with aniline hydrogen phthalate and showed downward mutarotation. These findings suggest that the hydroxyl group at C-1 of **4** is unsubstituted, and therefore one of the two trityl substituents of **4** must be on a secondary hydroxyl group.

Treatment of **4** with acetic anhydride in pyridine overnight at room temperature afforded an α - and β -anomer mixture in which the α -anomer predominated. The $^1\text{H-NMR}$ spectrum of the α -anomer (isolated by CC) showed that the compound was the pentaacetate of **4** (**4-A'**), having one free hydroxyl group. The complete acetylation of **4-A'** was very difficult and this difficulty made it necessary to employ a prolonged reaction time (several days) and an elevated temperature (up to 50°C). The reaction mixture was chromatographed to isolate the peracetate (**4-A**). It is noteworthy that **4-A'** contains a polar hydroxyl group but has nevertheless a higher R_f value than **4-A** on a silica gel plate using benzene-ethyl acetate (3:1) as the developing solvent: R_f of **4-A'** is 0.44 and R_f of **4-A** is 0.38. Similar phenomena were previously observed in studies of the selective acetylation of **3**¹¹⁾ and **6**,¹²⁾ both having a trityl group at C-6', namely the partially acetylated derivative having one unacetylated hydroxyl group at C-3 showed a higher R_f value than the corresponding peracetate.

On the other hand, **4-A'** was partially detritylated when its solution in chloroform- d was allowed to stand overnight at 60°C . The reaction mixture was acetylated with acetic anhydride- d_6 in pyridine and then fractionated by CC to give an analog (**8-A**) of 6'-O-trityl- α -cellobiose heptaacetate (α -anomer of **6-A**). **8-A** gave a $^1\text{H-NMR}$ spectrum identical with that of the α -anomer of **6-A**, except that two of the acetoxy group signals were absent. The acetoxy group signals in the 100 MHz $^1\text{H-NMR}$ spectrum of the α -anomer of **6-A** were previously assigned as indicated in Fig. 3.¹⁾ The missing signals of **8-A** could thus be assigned to the 2- and 3-acetoxy groups (see Fig. 3).

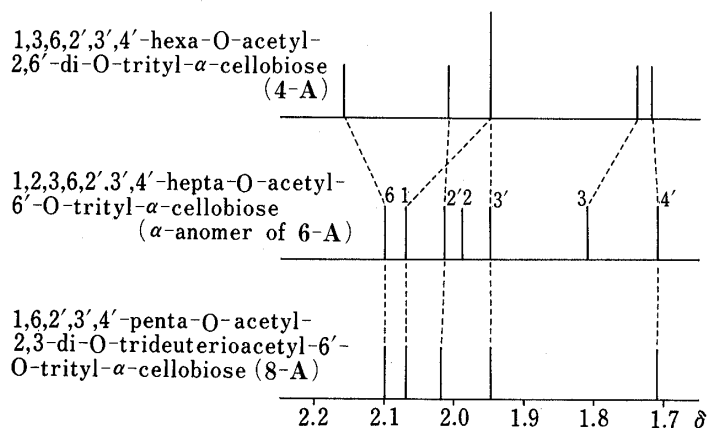


Fig. 3. Correlation of the Acetoxy Resonances in the 100 MHz $^1\text{H-NMR}$ Spectra of **4-A**, α -Anomer of **6-A**, and **8-A**

Previously,¹²⁾ it was confirmed that the originally low reactivity of the hydroxyl group at C-3 in the cellobiose molecule was further decreased to a great extent by the influence of the trityl group at C-6'.

From these results, it seemed that **4** had trityl groups at C-2 and C-6', and that these trityl groups hindered acetylation of the hydroxyl group at C-3. Thus, **4-A'** was 1,6,2',3',4'-penta-O-acetyl-2,6'-di-O-trityl- α -cellobiose.

Fig. 3 shows the correlation of the acetoxy group resonances in the $^1\text{H-NMR}$ spectra of **4-A** and the α -anomer of **6-A**. In both spectra, the chemical shifts of the 2'-, 3'-, and 4'-acetoxy groups are practically the same, since the non-reducing residues of both compounds are the same, 2,3,4-tri-O-acetyl-6-O-trityl- β -glucoside. A replacement of the acetyl group

at C-2 by a trityl group (*e.g.*, α -anomer of **6-A**→**4-A**) causes upfield shifts in the resonances of the acetoxy groups at C-1 and C-3, and causes a downfield shift in the resonance of the acetoxy group at C-6. These results suggest that the orientation of the benzene ring of the trityl group at C-2 is such that the protons on the 1- and 3-acetoxy groups are in the shielding region, whereas the protons on the 6-acetoxy group are in the deshielding region.

In addition, a very large upfield shift of the H-1 signal in the spectrum of **4-A** (δ 6.31→5.11) is observed. This characteristic upfield shift of the H-1 signal is similar to that observed in the spectrum of 2-O-trityl- α -D-glucose tetraacetate and therefore, the structure of **4-A**, having a trityl substituent on C-2, was confirmed.

Thus, it was concluded that **4** is 2,6'-di-O-tritylcellobiose. Finally, we believe that this is the first report of the isolation of trityl glycosides of a disaccharide having a primary hydroxyl group remaining untritylated by direct tritylation with trityl chloride. Furthermore, it is noteworthy that a disaccharide having two primary hydroxyl groups was ditritylated at a secondary hydroxyl group and at a primary hydroxyl group. On separation of the tritylation products by CC, several unusual ditritylates other than **2**, **4**, and **5** were also recognized on TLC as minor components.

The present study has confirmed that there is some possibility of preferential tritylation of the hemiacetal hydroxyl group at C-1 or even of secondary hydroxyl groups over the primary hydroxyl group at C-6 or C-6'.

Experimental

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-4 automatic polarimeter. TLC was performed on TLC plates, silica gel 60 (0.25 mm, E. Merck), with detection by spraying with anthrone-sulfuric acid. CC was carried out using Lobar prepacked columns, LiChroprep Si 60 (40–63 μ m) size B or C (E. Merck). The solvent systems (v/v) used for TLC and CC were as follows; (a) chloroform–acetone–methanol–water=58:20:20:2, (b) benzene–ethyl acetate=3:1, (c) benzene–ethyl acetate=5:1, (d) chloroform–methanol 9:1, (e) benzene–methanol=9:1, (f) benzene–ethanol=10:1 [(a), (b) for TLC, (b)–(f) for CC]. The ^1H -NMR spectra were recorded with a Varian HA-100 (100 MHz) spectrometer or a JEOL JNM-FX 200 (200 MHz) spectrometer in CDCl_3 with tetramethylsilane (TMS) as an internal standard. The 15.087-MHz ^{13}C FT NMR spectra were measured in CDCl_3 (about 0.5 M) with a Varian NV-14 FT NMR spectrometer at 60°C in 8 mm spinning tubes; δ (ppm downfield from internal TMS) $\pm$ 0.1 ppm. Quantitative analyses of the ditrityl ethers on TLC were conducted with a Shimadzu CS-920 high-speed TLC scanner, set at 260 nm.

Tritylation of Cellobiose—Well-dried and powdered cellobiose (2 g) was stirred in pyridine (200 ml) for 15–30 min at 100 °C and dissolved as far as possible. Then trityl chloride (3.2 g, 2 mol. equiv.) was added and the mixture was continuously stirred for 1 h at 100°C. The solvent was evaporated off under reduced pressure, the residue was dissolved in the minimum volume of methanol, and the solution was poured into ice-water. The precipitate was collected by filtration, washed with cold water, and dried to yield a mixture of trityl ethers as a powder (4.3 g). Unreacted cellobiose (0.4 g) was recovered from the aqueous mother liquor. TLC with solvent (a) indicated the presence of four ditritylated derivatives having *R_f* values of 0.86 (**2**), 0.79 (**3**), 0.72 (**4**), and 0.55 (**5**), and of two monotritylated derivatives having *R_f* values of 0.34 (**6**) and 0.20 (**7**). The mixture was separated by CC with solvent (d) to give six fractions; the 1st fraction contained **2** and **3**, the 2nd fraction mainly consisted of **3**, the 3rd fraction contained **3** and **4**, and the 4th, 5th and 6th fractions mainly consisted of **5**, **6**, and **7**, respectively. The tritylation of cellobiose and the separation of the products mentioned above were repeated several times, and from the appropriate pooled fractions, the ditritylated **2**, **4**, and **5** were isolated as needles.

Trityl 6'-O-Trityl- β -cellobioside (2)—*Anal.* Calcd for $\text{C}_{50}\text{H}_{50}\text{O}_{11}$: C, 72.62; H, 6.09. Found: C, 72.60; H, 6.14.

2,6'-Di-O-tritylcellobiose (4)—*Anal.* Calcd for $\text{C}_{50}\text{H}_{50}\text{O}_{11}\cdot\text{H}_2\text{O}$: C, 71.07; H, 6.20. Found: C, 71.20; H, 6.02.

Trityl 6-O-Trityl- β -cellobioside (5)—*Anal.* Calcd for $\text{C}_{50}\text{H}_{50}\text{O}_{11}\cdot\text{H}_2\text{O}$: C, 71.07; H, 6.20. Found: C, 71.02; H, 6.15.

Trityl 2,3,6,2',3',4'-Hexa-O-acetyl-6'-O-trityl- β -cellobioside (2-A)—**2** (103 mg) was acetylated with acetic anhydride (3 ml) and dry pyridine (4 ml) overnight at room temperature. The product was crystallized from ethanol, yield 93 mg (69.2%), ^1H -NMR (200 MHz, 5% solution in CDCl_3) δ 4.17 (1H, d, $J_{1,2}=7.8$ Hz, H-1), 4.39 (1H, d, $J_{1',2'}=7.8$ Hz, H-1'), 1.99, 1.96, 1.95, 1.93, 1.78, 1.69 (18H, s, $\text{OCOCH}_3\times 6$), *Anal.* Calcd for $\text{C}_{62}\text{H}_{62}\text{O}_{17}$: C, 69.00; H, 5.79. Found: C, 68.73; H, 5.75.

Trityl 2,3,2',3',4',6'-Hexa-O-acetyl-6-O-trityl- β -cellobioside (5-A)—5 (68 mg) in dry pyridine (4 ml) was treated with acetic anhydride (2 ml) as described for 2. Crystallization of the resulting syrup from ethanol gave crystalline 5-A (81 mg, 91.3%), $^1\text{H-NMR}$ (200 MHz, 5% solution in CDCl_3) δ 4.10 (1H, d, $J_{1,2}=8.1$ Hz, H-1), 4.31 (1H, d, $J_{1',2'}=7.8$ Hz, H-1'), 2.08, 2.03, 2.02, 1.98, 1.91, 1.56 (18H, s, $\text{OCOCH}_3 \times 6$), *Anal.* Calcd for $\text{C}_{62}\text{H}_{62}\text{O}_{17} \cdot 1/2\text{C}_2\text{H}_5\text{OH}$: C, 68.65; H, 5.94. Found: C, 68.65; H, 5.97.

1,6,2',3',4'-Penta-O-acetyl-2,6'-di-O-trityl- α -cellobiose (4-A')—Acetylation of 4 (108 mg) in the same manner as mentioned above gave a mixture in which 4-A' was predominant. The mixture was fractionated on a Lobar column with solvent (c) and chromatographically homogeneous 4-A' (98 mg, 72.4%) was obtained together with small amounts of the β -anomer (7 mg, 5.2%, *Rf* on TLC with solvent (b) 0.48).

1,3,6,2',3',4'-Hexa-O-acetyl-2,6'-di-O-trityl- α -cellobiose (4-A)—A mixture of 4-A' (85 mg), acetic anhydride (2 ml), and dry pyridine (5 ml) was stirred for several days in an incubator kept at 45–50°C. From the resulting mixture, 4-A was isolated by CC with solvent (e) and crystallized from methanol, yield 38 mg (43.0%), mp 130–131°C, $[\alpha]_D^{25} +36.9^\circ$ ($c=1.3$, CHCl_3), $^1\text{H-NMR}$ (200 MHz, 5% solution in CDCl_3) δ 5.11 (1H, d, $J_{1,2}=3.9$ Hz, H-1), 4.42 (1H, d, $J_{1',2'}=8.1$ Hz, H-1'), 2.16, 2.00, 1.96, 1.95, 1.75, 1.71 (18H, s, $\text{OCOCH}_3 \times 6$), *Anal.* Calcd for $\text{C}_{62}\text{H}_{62}\text{O}_{17} \cdot \text{CH}_3\text{OH}$: C, 68.10; H, 5.99. Found: C, 68.37; H, 5.77.

1,6,2',3',4'-Penta-O-acetyl-2,3-di-O-trideuterioacetyl-6'-O-trityl- α -cellobiose (8-A)—When the ^{13}C FT NMR spectrum of 4-A' (98 mg) was measured in CDCl_3 (about 0.5 M solution) overnight at 60°C, partial detritylation occurred. The solution was dried *in vacuo* on a rotary evaporator. The residue was dissolved in dry pyridine and acetylated with acetic anhydride- d_6 at 40°C for a day. The resulting mixture (95 mg) was chromatographed on a Lobar column with solvent (b). 4-A' (50 mg), accompanied with a trace of the peracetate 4-A, was recovered from the faster moving fraction and concentration of the slower moving fraction yielded 35 mg of 8-A as a chromatographically homogeneous syrup. $[\alpha]_D^{25} +51.0^\circ$ ($c=1.0$, CHCl_3).

1,3,4,6-Tetra-O-acetyl-2-O-trityl- α -D-glucopyranose—2,6-Di-*tert*-butyl-4-methylpyridine (295 mg) and triphenylmethyl perchlorate¹³⁾ (500 mg) were added to a solution of 1,3,4,6-tetra-O-acetyl- α -D-glucopyranose¹⁴⁾ (300 mg) in dichloromethane (10 ml), and the mixture was stirred for 1.5 h at 40°C. Pyridine (0.05 ml) and methanol (0.05 ml) were then added, the mixture was concentrated, and the residue was poured into ice-water. Extraction with chloroform followed by concentration of the extract gave a syrup (890 mg) which was purified by CC with solvent (c). The pure syrup obtained was crystallized from ethanol, yield 264 mg (54.5%), mp 162°C, $[\alpha]_D^{25} +57.5^\circ$ ($c=2.0$, CHCl_3), $^1\text{H-NMR}$ (200 MHz, 6% solution in CDCl_3) δ 5.24 (1H, d, $J_{1,2}=3.7$ Hz, H-1), 2.24, 2.00, 1.99, 1.79 (12H, s, $\text{OCOCH}_3 \times 4$), *Anal.* Calcd for $\text{C}_{33}\text{H}_{34}\text{O}_{10}$: C, 67.11; H, 5.80. Found: C, 66.96; H, 5.74.

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References and Notes

- 1) Part VI: K. Koizumi and T. Utamura, *Chem. Pharm. Bull.*, **29**, 2791 (1981).
- 2) This work was presented in part at the 96th Annual Meeting of the Pharmaceutical Society of Japan, Nagoya, April, 1976.
- 3) B. Helferich, *Adv. Carbohydr. Chem.*, **3**, 79 (1948).
- 4) B. Helferich, L. Moog, and A. Jünger, *Chem. Ber.*, **58B**, 872 (1925).
- 5) B. Helferich and J. Becker, *Ann. Chem.*, **440**, 1 (1924).
- 6) K. Zeile and W. Kruckenberg, *Chem. Ber.*, **75**, 1127 (1942).
- 7) K. Koizumi and T. Utamura, *Yakugaku Zasshi*, **98**, 327 (1978).
- 8) S.M. Partidge, *Nature* (London), **164**, 443 (1949).
- 9) D.Y. Gagnaire, F.R. Taravel, and M.R. Vignon, *Carbohydr. Res.*, **51**, 157 (1976).
- 10) T. Utamura and K. Koizumi, *Yakugaku Zasshi*, **101**, 410 (1981).
- 11) K. Koizumi and T. Utamura, *Chem. Pharm. Bull.*, **29**, 2776 (1981).
- 12) K. Koizumi and T. Utamura, *Chem. Pharm. Bull.*, **29**, 2785 (1981).
- 13) H.J. Dauben, Jr., L.R. Honnen, and K.M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).
- 14) B. Helferich and J. Zirner, *Chem. Ber.*, **95**, 2604 (1962).