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Trityl Derivatives of Cellobiose. VII.[1] Unusual Di-O-trityl Derivatives of Cellobiose[2]

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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 ^{1}H nuclear magnetic resonance (NMR), ^{13}C-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; ^{1}H-NMR; ^{13}C-NMR

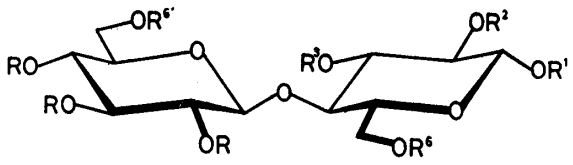
It is well known that in polyhydroxyl compounds containing both primary and secondary hydroxyl groups, the primary hydroxyl groups react preferentially with bulky triphenylmethyl (trityl) chloride.[3] Tritylation of D-glucose or D-galactose with one mole of trityl chloride in pyridine solution afforded 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 dityryl 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: $R^{6'}=Tr$, $R^2=R^3=Ac\text{-}d_3$, $R^1=R^6=R=Ac$

Tr=trityl, Ac=acetyl

Chart 1

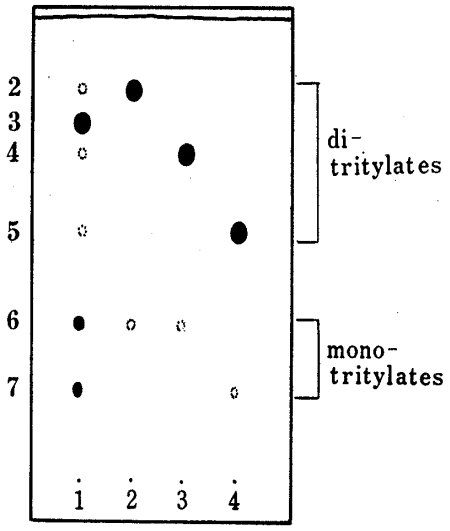


Fig. 1. TLC on Silica Gel

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, $[\alpha]_D^{21}$ −41.0° (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, $[\alpha]_D^{21}$ −10.8° (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°→ +3.0° 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-tritylcellobioses[7] (**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, $[\alpha]_D^{21}$ +2.0° (c=1.0, $CHCl_3$), ^{1}H-NMR δ ($CDCl_3$) 4.17 (1H, d, $J_{1,2}$=7.8 Hz, H-1): **5-A**, mp 245.5—247.0°C, $[\alpha]_D^{21}$ −65.0° (c=1.0, $CHCl_3$), ^{1}H-NMR δ ($CDCl_3$) 4.10 (1H, d, $J_{1,2}$=8.1 Hz, H-1). The above ^{1}H-nuclear magnetic resonance (^{1}H-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, $[\alpha]_D^{24}$ +53.3°; its β-anomer, $[\alpha]_D^{23}$ +14.5°; 6-O-trityl-α-cellobiose peracetate, $[\alpha]_D^{25}$ +24.0°; its β-anomer, $[\alpha]_D^{21}$ −28.0°).[7] Consequently, it was inferred that **2** and **5** were trityl β-cellobiosides.

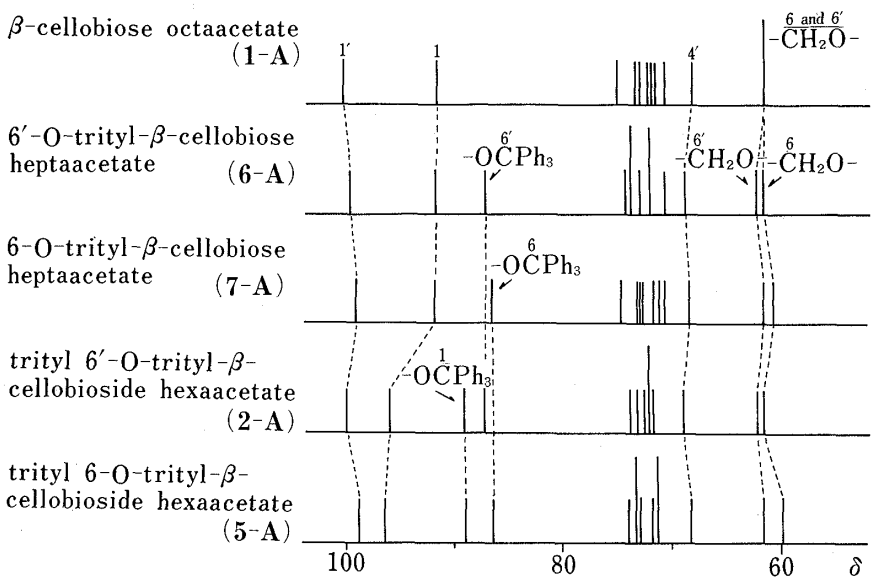


Fig. 2. ^{13}C-NMR Spectra of β-Cellobiose Octaacetate (**1-A**) and Tritylated β-Cellobiose Peracetates
(**2-A**, **5-A**, **6-A**, and **7-A** in $CDCl_3$)

The ^{13}C-NMR spectra of **2-A** and **5-A** provided important information about their structures. Fig. 2 schematically represents parts of the ^{1}H-noise-decoupled ^{13}C FT NMR spectra of β-cellobiose octaacetate (**1-A**), 6′-O-trityl-β-cellobiose heptaacetate[7] (**6-A**), 6-O-trityl-β-cellobiose heptaacetate[7] (**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-1α and C-1β 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**→**2-A** or **7-A**→**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 ^{1}H-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}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 *Rf* value than **4-A** on a silica gel plate using benzene–ethyl acetate (3: 1) as the developing solvent: *Rf* of **4-A'** is 0.44 and *Rf* 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 *Rf* value than the corresponding peracetate.

On the other hand, **4-A'** was partially detritylated when its solution in chlororm-*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}H-NMR spectrum identical with that of the α-anomer of **6-A**, except that two of the acetoxyl group signals were absent. The acetoxyl group signals in the 100 MHz ^{1}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-acetoxyl groups (see Fig. 3).

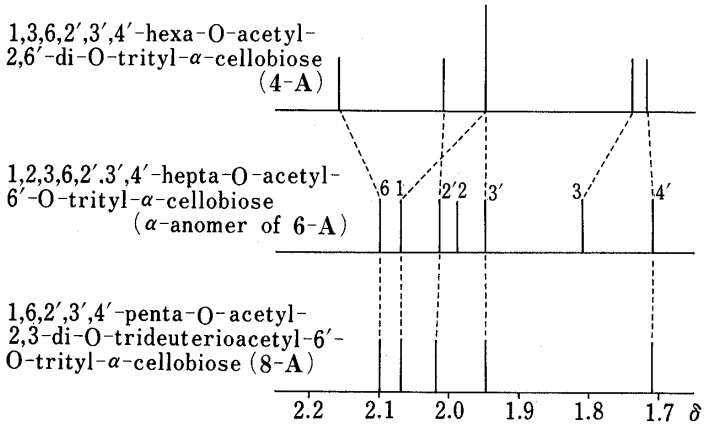


Fig. 3. Correlation of the Acetoxyl Resonances in the 100 MHz ^{1}H-NMR Spectra of **4-A**, α-Anomer of **6-A**, and **8-A**

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 acetoxyl group resonances in the ^{1}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'-acetoxyl 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 acetoxyl groups at C-1 and C-3, and causes a downfield shift in the resonance of the acetoxyl 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-acetoxyl groups are in the shielding region, whereas the protons on the 6-acetoxyl 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 μm) 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 ^{1}H-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) ± 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 *Rf* values of 0.86 (**2**), 0.79 (**3**), 0.72 (**4**), and 0.55 (**5**), and of two monotritylated derivatives having *Rf* 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 $C_{50}H_{50}O_{11}$: C, 72.62; H, 6.09. Found: C, 72.60; H, 6.14.

2,6′-Di-O-tritylcellobiose (**4**)——*Anal.* Calcd for $C_{50}H_{50}O_{11}\cdot H_2O$: C, 71.07; H, 6.20. Found: C, 71.20; H, 6.02.

Trityl 6-O-Trityl-β-cellobioside (**5**)——*Anal.* Calcd for $C_{50}H_{50}O_{11}\cdot H_2O$: 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%), ^{1}H-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, $OCOCH_3\times 6$), *Anal.* Calcd for $C_{62}H_{62}O_{17}$: 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}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, $OCOCH_3\times6$), *Anal.* Calcd for $C_{62}H_{62}O_{17}\cdot1/2C_2H_5OH$: 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, $[\alpha]_D^{22}$ +36.9° ($c=1.3$, $CHCl_3$), ^{1}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, $OCOCH_3\times6$), *Anal.* Calcd for $C_{62}H_{62}O_{17}\cdot CH_3OH$: 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. $[\alpha]_D^{21}$ +51.0° ($c=1.0$, $CHCl_3$).

1,3,4,6-Tetra-O-acetyl-2-O-trityl-α-D-glucopyranose——2,6-Di-*tert*-butyl-4-methylpyridine (295 mg) and triphenylmethyl perchlorate[13] (500 mg) were added to a solution of 1,3,4,6-tetra-O-acetyl-α-D-glucopyranose[14] (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, $[\alpha]_D^{23}$ +57.5° ($c=2.0$, $CHCl_3$), ^{1}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, $OCOCH_3\times4$), *Anal.* Calcd for $C_{33}H_{34}O_{10}$: C, 67.11; H, 5.80. Found: C, 66.96; H, 5.74.

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References and Notes

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