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A Reinvestigation of the Tritylation of Maltose[1)]

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Treatment of β-maltose with 2 molar equivalents of trityl chloride in pyridine at 100°C for 1 h afforded trityl 6,6′-di-*O*-trityl-β-maltoside (**1**), 2,6′-di-*O*-trityl-α-maltose (**2**), trityl 6′-*O*-trityl-β-maltoside (**3**), 6,6′-di-*O*-tritylmaltose (**4**), and a mixture of 6- and 6′-*O*-tritylmaltoses (**6**). The ratios of **1**, **2**, **3**, and **6** to the main product, **4** were estimated to be 6, 9, 11, and 31: 100, respectively, by thin-layer chromatogram spectrophotometry at 260 nm. Each trityl ether was isolated by column chromatography (CC) and then acetylated individually. After acetylation, **6** was separated by CC to give 6-*O*-tritylmaltose heptaacetate (**6A**) and 6′-*O*-tritylmaltose heptaacetate (**7A**). The structures of all trityl ethers were established by means of ^{1}H-nuclear magnetic resonance (NMR) and ^{13}C-NMR analyses, optical rotation measurements, *etc.* The trityl ethers of maltose were compared with those of cellobiose, and the relationship between their conformations and their reactivities or chromatographic behavior is discussed.

Keywords——maltose; tritylation; trityl 6,6′-di-*O*-trityl-β-maltoside; trityl 6′-*O*-trityl-β-maltoside; 6,6′-di-*O*-tritylmaltose; 2,6′-di-*O*-trityl-α-maltose; 6-*O*-tritylmaltose; 6′-*O*-tritylmaltose; ^{1}H-NMR; ^{13}C-NMR

Previously, tritylation of the primary hydroxyl groups of maltose and subsequent acetylation yielded the six possible derivatives (α- and β-anomers of 6- and 6′-mono-, and 6,6′-di-*O*-tritylmaltose peracetates), and all six products were isolated by column chromatography (CC) on silica gel and by precise fractional crystallization.[2)] On the other hand, treatment of cellobiose with 2 molar equivalents of trityl chloride (TrCl) at 100°C afforded three unusual ditrityl ethers, which were tritylated at C-1 and C-6 or C-6′, and at C-2 and C-6′, in addition to the expected 6,6′-ditritylate.[3)]

Our interest in the formation of these unusual ditritylates of cellobiose led us to reinvestigate the tritylation of maltose.

Results and Discussion

Treatment of maltose with 2 molar equivalents of TrCl in pyridine at 100°C for 1 h afforded a mixture of six trityl ethers [**1**—**6**, in order of decreasing mobility on silica gel by thin-layer chromatography (TLC)]. CC on a Lobar prepacked column (E. Merck) separated **1**—**4** with solvent B and **5**—**6** with solvent C, and fractional crystallization or repeated semipreparative high-performance liquid chromatography afforded all six products as pure crystals. The molar absorptivity at 260 nm and the ^{13}C-nuclear magnetic resonance (NMR) spectra of these products suggested that **1** was a tritrityl ether, **2**, **3**, and **4** were ditrityl ethers, and **6** was a mixture of monotrityl ethers. Although **5** crystallized from ethanol, it seemed to be a mixture of mono- and ditrityl ethers according to the elemental analyses and ^{13}C-NMR data, and moreover its amount was so small that we could not investigate it in further detail. The ratios of **1**, **2**, **3**, and **6** to the main product, **4** were estimated to be 6, 9, 11, and 31: 100, respectively, by TLC spectrophotometry at 260 nm. Either increasing the quantity of reagent, TrCl, or decreasing the volume of solvent, pyridine, resulted in increasing yields of tritritylate (**1**) and decreasing yields of monotritylate(**6**), but the relative yields of the three ditritylates (**2**, **3**, and **4**) were almost constant under various conditions.

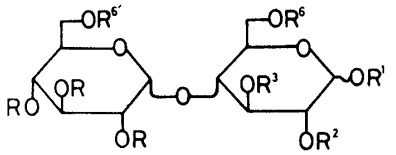
TABLE I. Trityl Derivatives of Maltose

Compd.	Rf[a] on TLC	mp (°C)	$[\alpha]_D^t$ in C_5H_5N (°) t(°) c(%)
1	0.87	157—158	+41.0 26 2.00
2	0.77	204—205	+89.1 18 1.75
3	0.73	148—149	+36.3 25 1.00
4	0.58	148—149	+74.0 18 2.00
5	0.37	170—171.5	
6	0.30	139—141.5	

a) Plates; TLC plates Silica gel 60 (0.25 mm) (E. Merck).
Solvent composition: $CHCl_3$-CH_3COCH_3-CH_3OH-H_2O =58 : 20 : 20 : 2.

Determination of Structures

Tritritylate 1——Compound **1** crystallized from methanol, did not show mutarotation, and was not colored with aniline hydrogen phthalate (AHP) reagent.[4] Treatment of **1** with acetic anhydride in pyridine afforded the peracetate(**1A**) which was a single anomeric product and crystallized from isopropanol–methyl ethyl ketone: mp 135—136°C, $[\alpha]_D^{26}$ +31.4° (c=1.75, $CHCl_3$), ^{1}H-NMR ($CDCl_3$) δ 4.27 (1H, d, $J_{1,2}$ =8.06 Hz, H-1). These data suggest that **1** is trityl β-maltoside. From the chemical shifts of triphenyl methyl carbons (-O$\underline{C}$Ph$_3$) in the ^{13}C-NMR spectrum of **1A**, the other two trityl groups of **1** were concluded to be at C-6 and C-6′; the signals of O$\underline{C}$Ph$_3$-6 and O$\underline{C}$Ph$_3$-6′ in the ^{13}C-NMR spectra of tritylmaltose peracetates appear at δ 87.2±1 and δ 86.7±2, respectively (see Table II). Thus, it was concluded that **1** is trityl 6,6′-di-*O*-trityl-β-maltoside.



1 : $R^1(\beta)=R^6=R^{6'}=Tr$, $R^2=R^3=R=H$
2 : $R^2=R^{6'}=Tr$, $R^1(\alpha)=R^3=R^6=R=H$
3 : $R^1(\beta)=R^{6'}=Tr$, $R^2=R^3=R^6=R=H$
4 : $R^6=R^{6'}=Tr$, $R^1=R^2=R^3=R=H$

1A : $R^1(\beta)=R^6=R^{6'}=Tr$, $R^2=R^3=R=Ac$
2A : $R^2=R^{6'}=Tr$, $R^1(\alpha)=R^3=R^6=R=Ac$
2A′ : $R^2=R^{6'}=Tr$, $R^3=H$, $R^1(\alpha)=R^6=R=Ac$
2A-d_3: $R^2=R^{6'}=Tr$, $R^3=Ac\text{-}d_3$, $R^1(\alpha)=R^6=R=Ac$
3A : $R^1(\beta)=R^{6'}=Tr$, $R^2=R^3=R^6=R=Ac$
4A : $R^6=R^{6'}=Tr$, $R^1=R^2=R^3=R=Ac$
6A : $R^6=Tr$, $R^1=R^2=R^3=R^{6'}=R=Ac$
7A : $R^{6'}=Tr$, $R^1=R^2=R^3=R^6=R=Ac$
7A-d_3: $R^{6'}=Tr$, $R^2=R^3=Ac\text{-}d_3$, $R^1(\alpha)=R^6=R=Ac$
8A : $R^2=R^{6'}=Tr$, $R^1(\beta)=Me$, $R^3=R^6=R=H$

Tr=trityl, Ac=acetyl, Ac-d_3=trideuterioacetyl, Me=methyl

Chart 1

Ditritylates 2,3, and 4——The main product **4** crystallized from methanol and was colored with AHP reagent, but did not exhibit mutarotation. The ^{1}H-NMR spectrum of **4** obtained immediately after dissolving **4** in dimethyl sulfoxide-d_6 showed that **4** had crystallized as an equilibrium mixture of α- and β-anomers in the ratio of 3 : 1. Acetylation of **4** in the usual way gave a mixture of α- and β-anomers of the peracetate(**4A**). After chromatography, the α-anomer crystallized in needles, mp 224.6—225.4°C, $[\alpha]_D^{20}$ +98° (c=2, $CHCl_3$), and the β-anomer crystallized in plates, mp 126.4—126.8°C, $[\alpha]_D^{20}$ +59° (c=2, $CHCl_3$). Consequently, **4A** was identified as 6,6′-di-*O*-tritylmaltose hexaacetate.[2]

The unusual ditritylates **2** and **3** crystallized from ethanol and acetone-ligroin, respectively. Compound **3** had the trityl group attached glycosidically at C-1, since it showed no mutarotation and was not colored with AHP reagent. On the other hand, **2** had reducing power, so one of the two trityl substituents must be on a secondary hydroxyl group.

The peracetate(**3A**) of **3** was obtained in the usual way without difficulty and crystallized from ethanol: mp 117—118.5°C, $[\alpha]_D^{22}$ +59.2° (c=1.2, $CHCl_3$), ^{1}H-NMR ($CDCl_3$) δ 4.21 (1H, d, $J_{1,2}$=7.8 Hz, H-1). The signals at δ 88.9 and 86.6 in the ^{13}C-NMR spectrum of **3A** are assigned to -O$\underline{C}$Ph$_3$ at C-1 and at C-6′, respectively. All the data relating to the optical rotation,

^{1}H-NMR and ^{13}C-NMR of **3** and **3A** supported the conclusion that **3** is trityl 6′-*O*-trityl-β-maltoside.

Treatment of **2** with acetic anhydride in pyridine overnight at room temperature afforded a mixture of the pentaacetate(**2A′**) and the hexaacetate(**2A**), each of which was a single anomeric product, *i.e.*, the α-anomer.[5] It is noteworthy that **2A′** contains a polar hydroxyl group, but nevertheless has a higher *Rf* value than **2A** on a silica gel plate with solvent F: the *Rf* of **2A′** is 0.67 and that of **2A** is 0.65. This phenomenon is the same as that observed with the acetates of 2,6′-di-*O*-trityl-α-cellobiose.[3] The complete acetylation of **2A′** was very difficult, and required 40 h at 60°C. From the reaction mixture, **2A** was isolated by CC with solvent E, and crystallized from ethanol: mp 207—208°C, $[\alpha]_D^{22}$ +100.0° (c=1.0, $CHCl_3$), ^{1}H-NMR ($CDCl_3$) δ 5.26 (1H, d, $J_{1,2}$=3.9 Hz). It seemed that **2A** had a trityl group at C-6′, since one

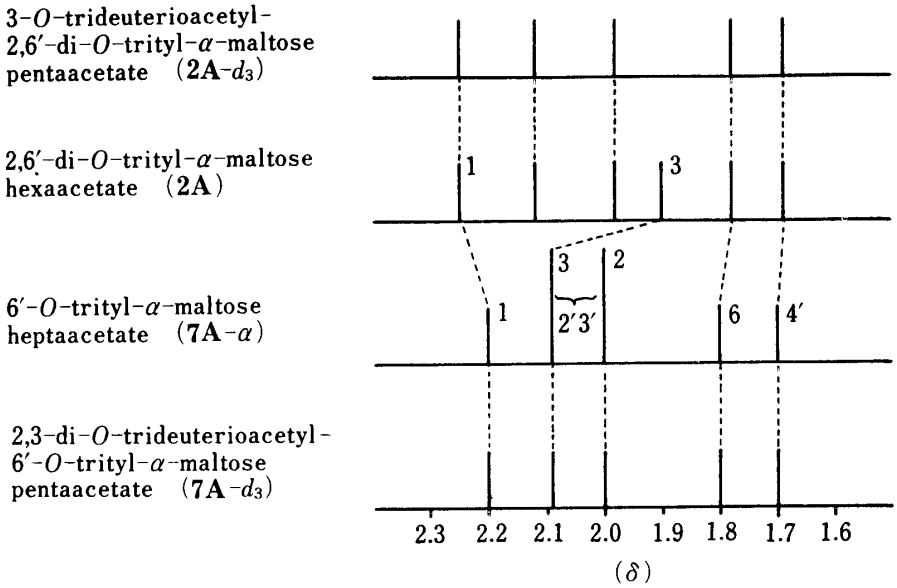


Fig. 1. Correlation of the Acetoxyl Resonances in the 200 MHz ^{1}H-NMR Spectra of **2A**, **2A**-d_3, **7A**-α, and **7A**-d_3

of the two $-OCPh_3$ signals appeared at δ 86.7. On the other hand, **2A′** was acetylated with acetic anhydride-d_6 in pyridine at 60°C for 40 h and then fractionated by CC to give an analog (**2A**-d_3) of **2A** together with an analog(**7A**-d_3) of 6′-*O*-trityl-α-maltose heptaacetate (**7A**-α), which was produced by trideuterioacetylation of partially detritylated **2A′** and had two acetyl-d_3 groups. Compound **7A**-d_3 gave a ^{1}H-NMR spectrum identical with that of **7A**-α, except that two of the acetoxyl group (–OAc) signals (δ 2.00, 2.09) were absent. The signal at δ 2.09 was already assigned to the OAc-3[6] by the method of specific spectral assignments for –OAc resonances using trideuterioacetyl analogs.[7] The unusual ditritylate of maltose **2** resembles 2,6′-di-*O*-tritylcellobiose[3] very closely in the following properties; they have one trityl group at C-6′ and one hydroxyl group that resists acetylation, and the *Rf* of the pentaacetate is higher than that of the hexaacetate. Consequently, it seems reasonable to assume that **2** had one trityl group at C-2 and that this trityl group hindered acetylation of the hydroxyl group at C-3, and that partial detritylation occurred at C-2. The missing –OAc signal of **7A**-d_3 at δ 2.00 could thus be assigned to the OAc-2. As a result, it was concluded that **2** is 2,6′-di-*O*-trityl-α-maltose and **2A′** is 1,6,2′,3′,4′-penta-*O*-acetyl-2,6′-di-*O*-trityl-α-maltose.

Fig. 1 shows the correlation of the –OAc resonances in the ^{1}H-NMR spectra of **2A** and related acetyltritylmaltoses. The chemical shifts of OAc-1, OAc-6, and OAc-4′ of **7A**-α could be assigned by analogy with those of **7A**-β, which have already been assigned unambiguously.[8] In the spectra of 6′-trityl-substituted maltose derivatives, OAc-4′ and OAc-6 resonate at abnor-

mally high field. Compound **2A**-d_3 gave a ^{1}H-NMR spectrum identical with that of **2A** except that one of the –OAc signals was absent, and this missing signal at δ 1.90 can be unambiguously assigned to OAc-3. By comparison of the spectrum of **2A** with that of methyl 2,6′-di-*O*-trityl-β-maltoside pentaacetate(**8A**), which was synthesized by tritylation of methyl β-maltoside and subsequent acetylation, the signal at δ 2.25 in the spectrum of **2A** could be assigned to OAc-1. A replacement of the acetyl group at C-2 by a trityl group (*e.g.*, **7A**-$\alpha\rightarrow$**2A**) causes an upfield shift in the resonance of OAc-3 and a downfield shift in the resonance of OAc-1, as in the case of cellobiose derivatives.[9] The signals of OAc-6 in the spectra of **2A** and **7A**-α are shifted upfield because the protons on OAc-6 are in the shielding region of the trityl group at C-6′. Therefore, the upfield shift of the OAc-6 signal on replacement of the acetyl group at C-2 by a trityl group seems to be much smaller than that in the case of cellobiose derivatives.

Monotritylate 6——Compound **6** crystallized from acetone and the elemental analyses data agreed with the calculated values for the monotrityl ether. Acetylation of **6** afforded a mixture of 6-*O*-tritylmaltose heptaacetate(**6A**) and 6′-*O*-tritylmaltose heptaacetate(**7A**). The main product was 6′-*O*-trityl-β-maltose heptaacetate(**7A**-β). The chromatographic behavior, mp, $[\alpha]_D$, and NMR data of these monotritylmaltose heptaacetates were consistent with those of the known compounds.[2]

Features of the NMR Spectra

The NMR data that provided important information about the structures of the trityl derivatives of maltose can be summarized as follows.

^{1}H-NMR——The anomeric proton signals of the trityl β-maltoside derivatives appear at much higher field than those of the corresponding acetyl β-maltose derivatives, namely, δ 4.27 for **1A** and δ 5.68 for **4A**-β, δ 4.21 for **3A** and δ 5.78 for **7A**-β. A replacement of the acetyl group at C-2 by a trityl group (*e.g.*, **7A**-$\alpha\rightarrow$**2A**) also causes an upfield shift by 1 ppm in the resonance of H-1. The effects of trityl groups on –OAc resonances are as follows: the –OAc signals in the ^{1}H-NMR spectra of α- and β-maltose octaacetates are concentrated in the region of δ 1.95—2.15, whereas the ^{1}H-NMR spectra of 6′-*O*-trityl-substituted maltose peracetates show two –OAc signals shifted to higher field (δ 1.65—1.71 and δ 1.78—1.80) than the others. The signal at δ 1.65—1.71 is assigned to OAc-4′ and the signal at δ 1.78—1.80 is assigned to OAc-6. The trityl group at C-2 causes an upfield shift by 0.2 ppm in the resonance of OAc-3, and the trityl group attached β-glycosidically at C-1 causes an upfield shift by 0.15 ppm in the resonance of OAc-6 (*e.g.*, δ 1.86 for **7A**-$\beta\rightarrow\delta$ 1.71 for **3A**).

TABLE II. ^{13}C Chemical Shifts[a] of the Signals in the Region of δ 80—100

Compd.	C-1′	C-1		Ph_3CO-[b]			
		α	β	at C-1	at C-2	at C-6	at C-6′
α-Maltose octaacetate	96.1	89.1					
β-Maltose octaacetate	95.8		91.3				
6-*O*-Trityl-α-maltose heptaacetate (**6A**-α)	95.5	89.2				87.3	
6-*O*-Trityl-β-maltose heptaacetate (**6A**-β)	95.2		91.7			87.3	
6′-*O*-Trityl-α-maltose heptaacetate (**7A**-α)	96.1	89.2					86.9
6′-*O*-Trityl-β-maltose heptaacetate (**7A**-β)	95.9		91.5				86.7
6, 6′-Di-*O*-trityl-α-maltose hexaacetate (**4A**-α)	95.3	89.2				87.1	86.6
6, 6′-Di-*O*-trityl-β-maltose hexaacetate (**4A**-β)	95.2		91.8			87.1	86.5
2, 6′-Di-*O*-trityl-α-maltose hexaacetate (**2A**)	95.7	90.3			88.3		86.7
Trityl 6′-*O*-trity-β-maltoside hexaacetate (**3A**)	95.5		95.5	88.9			86.6
Trityl 6, 6′-di-*O*-trity-β-maltoside pentaacetate (**1A**)	95.5		95.2	89.1		87.0	86.4

a) δ ppm from internal standard TMS in CDCl3; JEOL JNM-FX 200 spectrometer at 50.10 MHz; concentration, 2—3; temperature, ambient; micro cell. FT NMR conditions: spectral width, 12004 Hz; acquisition time, 0.682 s; pulse flipping angle, 45°; number of data points, 16384; number of recycles, 2000—25000.

b) Ph_3CO- = $(C_6H_5)_3CO$-.

^{13}C-NMR——Table II shows the ^{13}C chemical shifts of the signals in the region of δ 80—100 in the spectra of maltose octaacetates and tritylmaltose peracetates. In the spectra of the trityl β-maltoside derivatives, **1A** and **3A**, the C-1(β) signal exhibits a large downfield shift by 4 ppm. A replacement of the acetyl group at C-2 by a trityl group (*e.g.*, **7A**-α→**2A**) also causes a downfield shift by 1 ppm in the resonance of C-1. The quaternary carbon signals of the trityl groups at C-1, C-2, C-6, and C-6′ are distinguishable, as shown in Table II.

Comparison of Maltose with Cellobiose

Maltose is much more soluble in pyridine, the solvent used in the tritylation, than cellobiose. The O-3···O-2′ hydrogen bond in the maltose molecule[10] seems to be one of the reasons, since the hydrogen bond will cause the polarity of the molecule to decrease. Although a O-3···O-5′ hydrogen bond is also present in the cellobiose molecule,[11] the hydrogen bond is less stable than the hydrogen bond in the maltose molecule and does not resist changes in the conformation around the interglycosidic linkage; namely, the tritylation at C-6 of methyl β-cellobioside caused rotation around the glycosidic bond.[12] On the other hand, the tritylation at C-6 of methyl β-maltoside caused no change in the torsion angles[13] unless the O-3···O-2′ hydrogen bond was broken by subsequent acetylation.[14] This means that the cellobiose molecule is more flexible than the maltose molecule. In addition, the relative orientation of

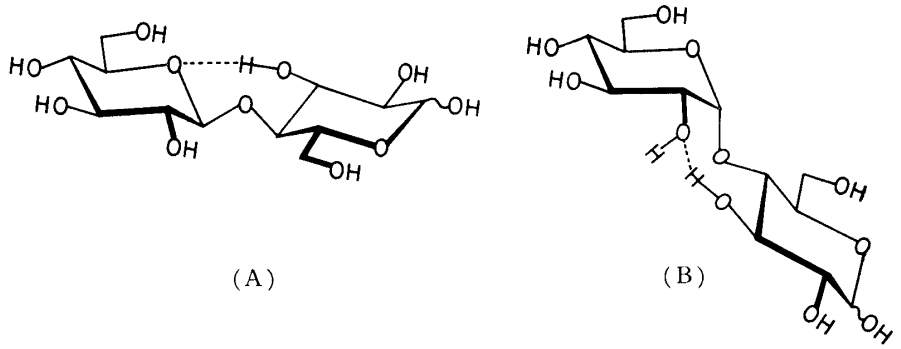


Fig. 2. Conformations of Cellobiose(A) and Maltose(B)

the two glucose residues of maltose is very different from that of cellobiose and the two $-CH_2OH$ groups of maltose are much closer to each other in space than those of cellobiose. Consequently, steric or proximity effects occur between the two glucose residues of maltose.[15] In contrast to cellobiose, the reactivity of the primary hydroxyl group at C-6 of maltose is much lower than that of the primary hydroxyl group at C-6′,[16] and the ratios of unusual ditritylates(**2** and **3**), having one trityl group at C-6′, to 6,6′-ditritylate(**4**) were consequently larger than those in the case of cellobiose, and trityl 6-*O*-tritylmaltoside was not formed.

The Chromatographic behavior of maltose tritylates on silica gel plates is very different from that of cellobiose tritylates. The mobilities of ditritylmaltoses decreases in the order of 2,6′-, 1,6′-, and 6,6′-ditritylates, whereas those of ditritylcellobioses decrease in the order of 1,6′-, 6,6′-, 2,6′-, and 1,6-ditritylates.[3] It seems that the polarity of ditritylates decreases with increasing distance between the two trityl groups in space. Unlike cellobiose monotritylates, 6- and 6′-monotritylmaltoses have the same mobilities on a silica gel plate. After cleavage of the O-3···O-2′ hydrogen bond in the maltose molecule by acetylation, 6- and 6′-monotritylmaltose heptaacetates show chromatographic behavior similar to that of 6- and 6′-monotritylcellobiose heptaacetates.

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); detection was effected by spraying with anthrone-sulfuric acid, followed by heating. 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–ethanol=10: 1, (C) benzene–ethanol=5: 1, (D) benzene–ethyl acetate=10: 1, (E) benzene–ethyl acetate=7: 1, (F) benzene–ethyl acetate=3: 1, (G) chloroform–methanol=19: 1. ^{1}H-NMR spectra were recorded for 0.7—0.8% solutions in $CDCl_3$ or $(CD_3)_2SO$ (internal standard $(CH_3)_4Si$) with a JEOL JNM-FX 200 spectrometer (200 MHz). For ^{13}C-NMR, see the notes in Table II. A Shimadzu CS-920 high-speed TLC scanner, set at 260 nm, was used for quantitative analyses of the trityl ethers on TLC.

Tritylation of Maltose——Well-dried powdered maltose (1.05 g) was dissolved in dry pyridine (130 ml) and the solvent was distilled at atmospheric pressure until the boiling point of the distillate reached 114°C. The solution was made up to 100 ml with dry pyridine, TrCl (1.6 g, 2 mol eq) 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 (1.96 g). The mixture was separated by CC with solvent B, followed by solvent C.

Trityl 6,6′-Di-*O*-trityl-β-maltoside (1)——*Anal.* Calcd for $C_{69}H_{64}O_{11}\cdot H_2O$: C, 76.22; H, 6.12. Found: C, 76.23; H, 5.87.

2,6′-Di-*O*-trityl-α-maltose (2)——*Anal.* Calcd for $C_{50}H_{50}O_{11}\cdot H_2O$: C, 71.07; H, 6.20. Found: C, 71.40; H, 5.98.

Trityl 6′-*O*-Trityl-β-maltoside (3)——*Anal.* Calcd for $C_{50}H_{50}O_{11}\cdot H_2O$: C, 71.07; H, 6.20. Found: C, 71.24; H, 6.20.

6,6′-Di-*O*-tritylmaltose (4)——*Anal.* Calcd for $C_{50}H_{50}O_{11}\cdot CH_3OH$: C, 71.31; H, 6.34. Found: C, 71.82; H, 6.06.

Monotritylmaltose (6)——*Anal.* Calcd for $C_{31}H_{36}O_{11}\cdot H_2O$: C, 61.78; H, 6.36. Found: C, 61.43; H, 6.13.

Quantitative Analyses of the Trityl Ethers by TLC——On the basis of the molar extinction coefficients at 260 nm (ε_{260}) of mono-, di-, and tritrityl ethers (780.48, 1547.16, and 2340.35, respectively), the ratios of absorbance of di- and tritrityl ethers to that of monotrityl ether at the same concentration (%) were calculated to be 1.40 and 1.64: 1. The peak area of each spot on a silica gel plate with solvent (A) was measured with the TLC scanner and then corrected based on the absorbance ratios described above; **1**: **2**: **3**: **4**: **6**= 1748/1.64: 2254/1.40: 2716/1.40: 24887/1.40: 5549=6: 9: 11: 100: 31.

Trityl 2,3,2′,3′,4′-Penta-*O*-acetyl-6,6′-di-*O*-trityl-β-maltoside (1A)——**1** (100 mg) was acetylated with acetic anhydride (4 ml) and dry pyridine (5 ml) overnight at room temperature, then the mixture was concentrated to dryness. The residue (89 mg) was purified by CC on a Lobar column with solvent D to give an amorphous powder which was crystallized from isopropanol and methyl ethyl ketone, yield 73 mg (61.0%). ^{1}H-NMR ($CDCl_3$) δ: 2.05, 2.01, 1.99, 1.93, 1.65 (15H, s, $OCOCH_3\times5$), *Anal.* Calcd for $C_{79}H_{74}O_{16}$: C, 74.16; H, 5.83. Found: C, 73.90; H, 5.80.

1,3,6,2′,3′,4′-Hexa-*O*-acetyl-2,6′-di-*O*-trityl-α-maltose (2A) and 1,6,2′,3′,4′-Penta-*O*-acetyl-2,6′-di-*O*-trityl-α-maltose (2A′)——A mixture of **2** (165 mg), acetic anhydride (5 ml), and dry pyridine (7 ml) was stirred for three days in an incubator kept at 45—50°C. TLC with solvent F gave two spots having *Rf* values of 0.67 and 0.65. The mixture (powder, 210 mg) was separated by CC with solvent E to give three fractions: the 1st fraction contained only **2A′** (19 mg), the 2nd fraction contained **2A′** and **2A** (114 mg), and the 3rd fraction mainly consisted of **2A** (49 mg). **2A** was purified by rechromatography of the 3rd fraction and crystallized from ethanol, ^{1}H-NMR ($CDCl_3$) δ: 2.25, 2.12, 1.98, 1.90, 1.78, 1.69 (18H, s, $OCOCH_3\times6$), *Anal.* Calcd for $C_{62}H_{62}O_{17}$: C, 69.00; H, 5.79. Found: C, 68.70; H, 5.76. **2A′** from the 1st fraction and additional **2A′**, obtained by refractionation of the 2nd fraction on a Lobar column with solvent E, were combined and used for the next experiment.

1,6,2′,3′,4′-Penta-*O*-acetyl-3-*O*-trideuterioacetyl-2,6′-di-*O*-trityl-α-maltose (2A-d_3) and 1,6,2′,3′,4′-Penta-*O*-acetyl-2,3-di-*O*-trideuterioacetyl-6′-*O*-trityl-α-maltose (7A-d_3)——**2A′** (63 mg) was dissolved in dry pyridine (2 ml) and acetylated with acetic anhydride-d_6 at 60°C for 40 h. At that time a part of **2A′** was partially detritylated and then trideuterioacetylated. The resulting mixture (69 mg) was chromatographed on a Lobar column with solvent E and chromatographically homogeneous **2A**-d_3 (19 mg) and **7A**-d_3 (24 mg) were obtained. **2A**-d_3: $[\alpha]_D^{22}$ +95.7° (c=1.4, $CHCl_3$), **7A**-d_3: $[\alpha]_D^{22}$ +128.3° (c=1.2, $CHCl_3$).

Trityl 2,3,6,2′,3′,4′-Hexa-*O*-acetyl-6′-*O*-trityl-β-maltoside (3A)——**3** (50 mg) in dry pyridine (4 ml) was acetylated with acetic anhydride (2 ml) and the product was post-treated as described for **1A**. Crystallization of the resulting syrup from ethanol gave crystalline **3A** (55.7 mg, 85.0%), ^{1}H-NMR ($CDCl_3$) δ: 2.06, 2.02, 2.01, 1.96, 1.71, 1.67 (18H, s, $OCOCH_3\times6$), *Anal.* Calcd for $C_{62}H_{62}O_{17}$: C, 69.00: H, 5.79. Found: C, 68.77; H, 5.78.

Methyl 3,6,2′,3′,4′-Penta-*O*-acetyl-2,6′-di-*O*-trityl-β-maltoside (8A)——Tritylation of methyl β-maltoside (2.41 g) with TrCl (3.37 g, 2 mol eq) under the same conditions as described for tritylation of maltose gave a complex mixture which was carefully and repeatedly separated by CC with solvent G. Chromatographically homogeneous methyl 2,6′-di-*O*-trityl-β-maltoside (18 mg) was acetylated with acetic anhydride (2 ml) and dry pyridine (3 ml) at 60°C for 45 h. After separation on a Lobar column with solvent E, **8A** (7 mg) was

obtained in a chromatographically pure state, ^{1}H-NMR ($CDCl_3$) δ: 2.93 (3H, s, CH_3), δ: 2.05, 1.98, 1.87, 1.79, 1.71 (15H, s, $OCOCH_3 \times 5$).

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References and Notes

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