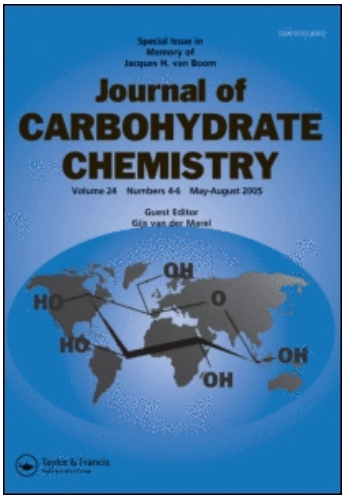

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Preparation of $6^{1}6^{X},6^{Y}$-Tris-*O*-(*tert*-butyldimethyl-silyl)-β-cyclodextrins, and Isolation and Regiochemical Determination of Five Positional Isomers

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PREPARATION OF $6^1,6^X,6^Y$-TRIS-*O*-(*TERT*-BUTYLDIMETHYLSILYL)-β-CYCLODEXTRINS, AND ISOLATION AND REGIOCHEMICAL DETERMINATION OF FIVE POSITIONAL ISOMERS

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ABSTRACT

Five positional isomers of $6^1,6^X,6^Y$-tris-*O*-(*tert*-butyldimethylsilyl)-cyclomaltoheptaose (β-cyclodextrin, βCD) were prepared by reaction of βCD with *tert*-butyldimethylsilyl chloride in pyridine, and were isolated by HPLC and characterized by ^{13}C NMR spectroscopy. The regiochemical determination of those positional isomers was carried out by the extended Körner's method, that is, by comparison with compounds obtained by additional monosilylation of $6^1,6^X$-bis-*O*-(*tert*-butyldimethylsilyl)-βCDs, and by conversion to the known compounds, $6^1,6^X,6^Y$-tri-*O*-(toluenesulfonyl)-βCDs.

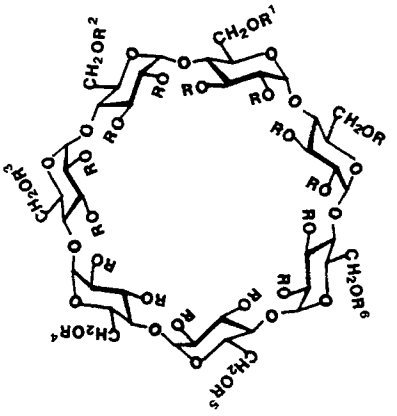
INTRODUCTION

Previously,[1] we had isolated four of five regioisomeric triglucosylcyclomaltoheptaoses (β-cyclodextrins, βCDs) from a mixture of glucosyl-βCDs which had been prepared by glucoamylolysis of a mixture of maltosyl-βCDs produced on an industrial scale from maltose and βCD through the reverse action of *Klebsiella pneumoniae* pullulanase. However, the regiochemical determination of these triglucosyl-βCDs by ^{13}C NMR spectrometry was not successful. So confirmation of their structures by chemical syntheses was attempted. However, suitable $6^1,6^X,6^Y$-tris-*O*-substituted derivatives of βCD which could be used as

intermediates for chemical syntheses of positional isomers of tribranched βCD had not been prepared.

In this paper, we report the synthesis of $6^1,6^X,6^Y$-tris-*O*-(*tert*-butyldimethylsilyl)-βCDs, a method of isolating five positional isomers of the tris-*tert*-butyldimethylsilyl derivative (trisilylate) as intermediates for chemical syntheses of authentic positional isomers of tribranched βCDs, and the regiochemical determination of those five positional isomers.

These regioisomeric trisilylates may be useful for syntheses of trigalactosylated or trimannosylated βCDs which might serve in studies on animal lectins as cluster ligands.



	R	R^1	R^2	R^3	R^4	R^5	R^6
1	H	X	H	X	H	X	H
2	H	X	X	H	H	X	H
3	H	X	X	H	H	H	X
4	H	X	X	H	X	H	H
5	H	X	X	X	H	H	H
6	Ac	X	Ac	X	Ac	X	Ac
7	Ac	X	X	Ac	Ac	X	Ac
8	Ac	X	X	Ac	Ac	Ac	X
9	Ac	X	X	Ac	X	Ac	Ac
10	Ac	X	X	X	Ac	Ac	Ac
11	Ac	H	Ac	H	Ac	H	Ac
12	Ac	H	H	Ac	Ac	H	Ac
13	Ac	H	H	Ac	Ac	Ac	H
14	Ac	H	H	Ac	H	Ac	Ac
15	Ac	H	H	H	Ac	Ac	Ac

X : *t*-$BuMe_2Si$ Ac : $COCH_3$

RESULTS AND DISCUSSION

Preparation and Isolation. In the same manner as described previously,[2] *tert*-butyldimethylsilyl (*t*-$BuMe_2Si$) derivatives of βCD were prepared by reaction of dry βCD with 3.5 mol equivalent of *tert*-butyldimethylsilyl chloride (*t*-$BuMe_2SiCl$) in pyridine. Products were obtained as a powdery mixture. Trisilylates were separated from the mixture by semi-preparative HPLC using an ODS column (250 × 20 mm i.d., 10 μm) with methanol−water (9:37) as the eluent. The yield of combined trisilylates was about 40%. Figure 1 shows elution profiles of the regioisomeric $6^1,6^X,6^Y$-tris-*O*-(*t*-$BuMe_2Si$)-βCDs. The relative ratios of **1**, **2**, **3** and **4**, and **5**, calculated from the peak areas in the chromatogram, were approximately 2:1:2:1. The components **1**, **2** and **5** were isolated by repeated chromatography on an ODS column (250 × 20 mm i.d., 5 μm) with methanol−water (93:7−91:9). While the components **3** and **4** could not be separated with methanol−water, the use of 1-propanol−water (38:62) as an eluent made their separation possible.

^{13}C NMR. Figure 2 shows the ^{13}C NMR spectra of tris-*O*-(*t*-$BuMe_2Si$)-βCDs (**1** − **5**) in C_5D_5N. The relative intensities of signals for C-1 at δ 103 ppm, C-6 substituted with *t*-$BuMe_2SiO$ group at δ 62−63 ppm which shifted downfield by 1−2 ppm from the other C-6s at δ ~61ppm, and methyl carbon attached to silicon ($SiCH_3$) at δ-4 − -5 ppm were 7:3:6. The assignments of two kinds of C-6 were confirmed by the distortionless enhancement by polarization transfer (DEPT) method.[3] These results proved that all five compounds were indeed trisilyl substituted derivatives. Although the spectra of **1** − **5** are similar, comparison of the *t*-$BuMe_2Si$ substituted C-6 signals in these five spectra, suggests that **1** and **5** may be $6^1,6^3,6^5$-tris-*O*-(*t*-$BuMe_2Si$)-βCD and $6^1,6^2,6^3$-tris-*O*-(*t*-$BuMe_2Si$)-βCD, respectively.

Characterization of five positional isomers. The methods for the determination of substituted positions of di- (and poly-)substituted CD had been studied by Fujita *et al.*, where combination of the extended Körner's method,[4] the hydrolysis by Taka amylase A[5] and 3,6-anhydration[6] had been used. We carried out additional *tert*-butyldimethylsilylation of the known compounds, $6^1,6^X$-bis-*O*-(*t*-$BuMe_2Si$)-βCD.[2] Theoretically, additional monosilylation of $6^1,6^2$-, $6^1,6^3$- and $6^1,6^4$- disilylates should give a mixture of $6^1,6^2,6^3$-, $6^1,6^2,6^4$-, $6^1,6^2,6^5$- and $6^1,6^2,6^6$-trisilylates, a mixture of

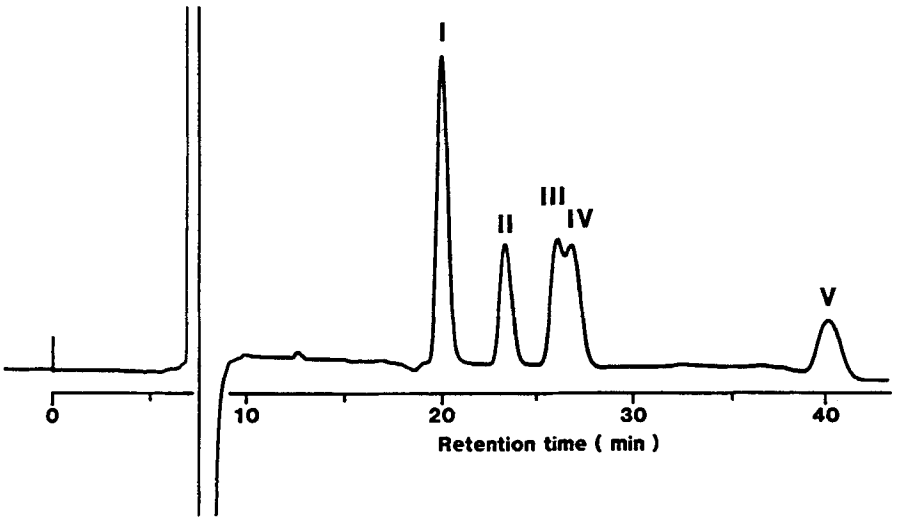


Fig. 1. Elution profiles of $6^1,6^X,6^Y$-tris-*O*-(*tert*-butyldimethylsilyl)-βCDs. I, $6^1,6^3,6^5$-tris-*O*-(*t*-$BuMe_2Si$)-βCD (**1**); II, $6^1,6^2,6^5$-tris-*O*-(*t*-$BuMe_2Si$)-βCD (**2**); III, $6^1,6^2,6^6$-tris-*O*-(*t*-$BuMe_2Si$)-βCD (**3**); IV, $6^1,6^2,6^4$-tris-*O*-(*t*-$BuMe_2Si$)-βCD (**4**); V, $6^1,6^2,6^3$-tris-*O*-(*t*-$BuMe_2Si$)-βCD (**5**). Chromatographic conditions: column, YMC-Pack SH-343-7 ODS (250 × 20 mm i.d.); eluent, 1-propanol − water (38:62); flow rate, 3.3 mL/min; temperature, 35 ℃.

$6^1,6^2,6^3$-, $6^1,6^2,6^4$-, $6^1,6^2,6^6$- and $6^1,6^3,6^5$-trisilylates, and a mixture of $6^1,6^2,6^4$-, $6^1,6^2,6^5$-, $6^1,6^2,6^6$- and $6^1,6^3,6^5$-trisilylates, respectively (Table 1). Figure 3 shows the results of HPLC analysis of the mixture obtained from the additional monosilylation of each disilylate. Consequently, it was confirmed that components **1**, **2** and **5** were $6^1,6^3,6^5$-, $6^1,6^2,6^5$- and $6^1,6^2,6^3$-tris-*O*-(*t*-$BuMe_2Si$)-βCDs, respectively. However, this method could not determine whether **3** and **4** were $6^1,6^2,6^4$- or $6^1,6^2,6^6$-tris-*O*-(*t*-$BuMe_2Si$)- βCD.

Further evidence for structural assignment of the trisilylates, according to the procedure of our previous paper,[2] was by conversion to the known compounds, $6^1,6^X,6^Y$-tri-*O*-(toluenesulfonyl)-βCDs.[7] The comparison of elution order of the tritosylates obtained and that of the tritosylates appearing in the report of Fujita *et al.*[7] under the chromatographic condition A in Fig. 4, suggested that the components **3** and **4** were $6^1,6^2,6^6$- and $6^1,6^2,6^4$-tris-*O*-(*t*-$BuMe_2Si$)-βCDs, respectively. It was noted that component **1**

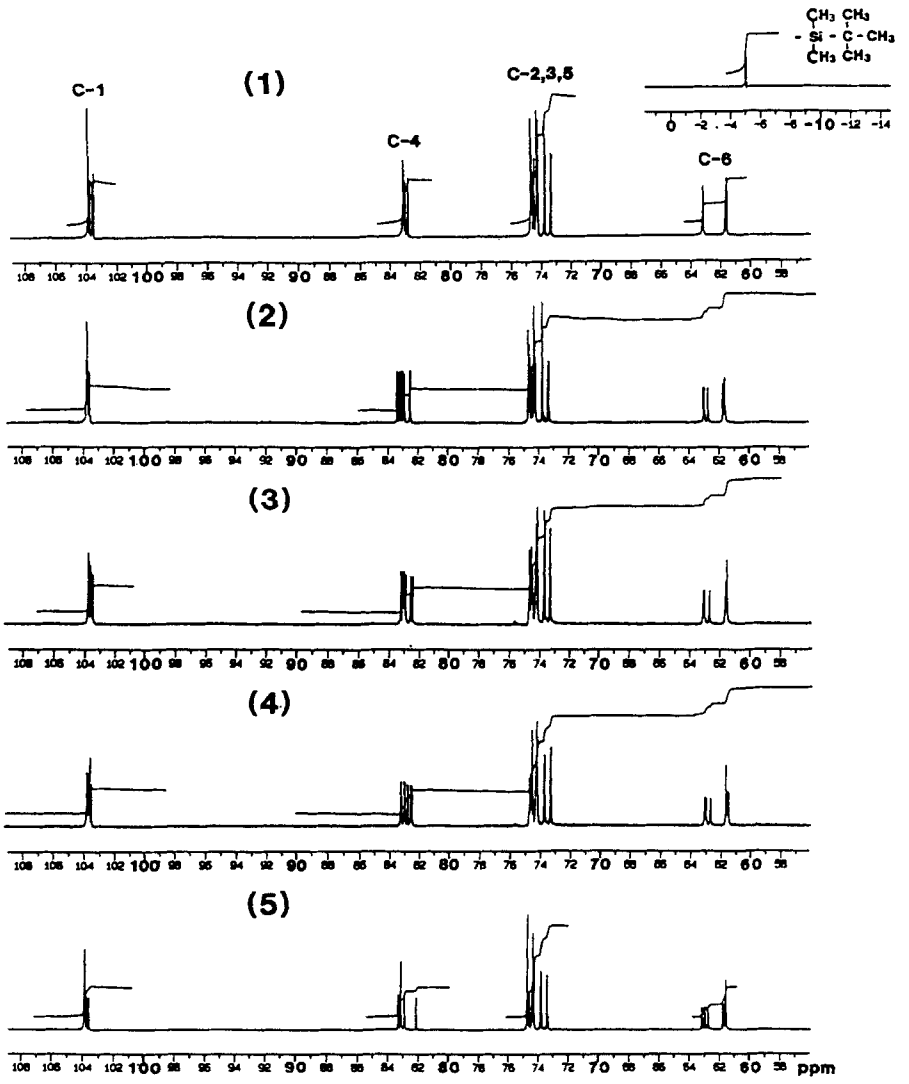
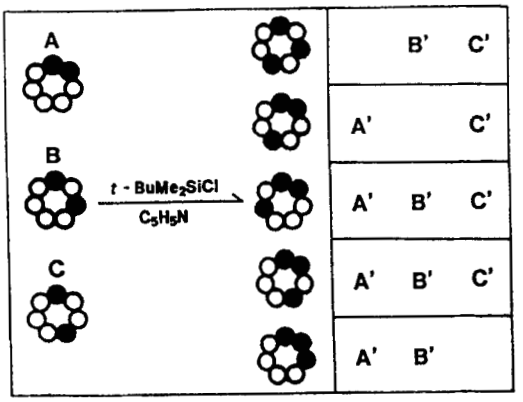
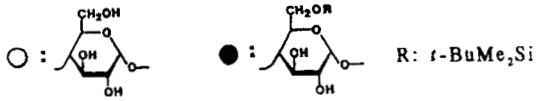


Fig. 2. ^{13}C NMR spectra of tris-*O*-(*tert*-butyldimethylsilyl)-βCDs in C_5D_5N at 125.65 MHz.

TABLE 1. Products of additional mono-*tert*-butyldimethylsilylation of $6^1,6^X$-bis-*O*-(*tert*-butyldimethylsilyl)-βCDs, A, B and C.





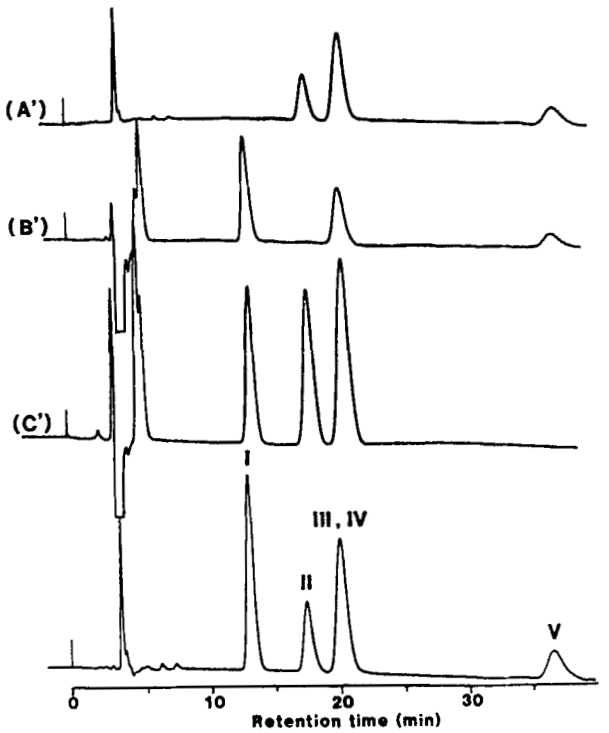


Fig. 3. Comparison of elution profiles of five positional isomers of tris-*O*-(*t*-$BuMe_2Si$)-βCD and those of mixtures of tris-*O*-(*t*-$BuMe_2Si$)-βCDs, (A'), (B'), and (C'), produced by additional mono *tert*-butyldimethylsilylation of bis-*O*-(*t*-$BuMe_2Si$)-βCDs, (A), (B) and (C), respectively. Chromatographic conditions:column, YMC-Pack AL-302 (150 × 4.6 mm i.d.); eluent, methanol–water (85:15); flow rate, 0.8 mL/min; temperature, ambient.

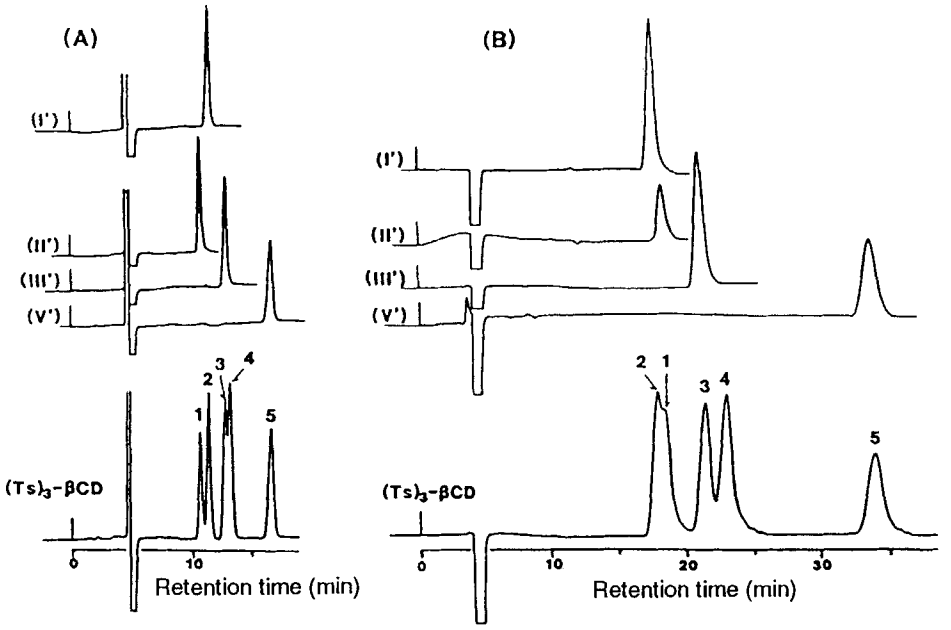


Fig. 4. Elution profiles of five positional isomers of tri-*O*-*p*-toluenesulfonyl-βCD, and tri-*O*-*p*-toluenesulfonyl-βCDs, (I'), (II'), (III') and (V'), converted from tris-*O*-(*tert*-butyldimethylsilyl)-βCDs, (I), (II), (III) and (V), respectively. Chromatographic conditions: (A) column, DAISO-PAK SP-120-5-ODS-A (150 × 6 mm i.d.) ; eluent, acetonitrile − water (38:62); flow rate, 0.6 mL/min; temperature, 35 ℃. (B) column, YMC-Pack A-212 C_8 (150 × 6 mm i.d.); eluent, ethanol − water (35:65); flow rate, 0.7 mL/min; temperature, 35 ℃. Peaks: 1 = $6^1,6^2,6^5$-, 2 = $6^1,6^3,6^5$-, 3 = $6^1,6^2,6^6$-, 4 = $6^1,6^2,6^4$-, 5 = $6^1,6^2,6^3$-tri-*O*-*p*-toluenesulfonyl-βCD, respectively.

eluted after **2** under another condition using a C_8-bonded silica column and ethanol − water as an eluent (Fig. 4B).

Thus the structures of five regioisomers of tris-*O*-(*t*-$BuMe_2Si$)-βCD have been unambiguously determined.

EXPERIMENTAL

General Procedures. Melting points were measured with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a JASCO digital polarimeter, model DIP 360. TLC was performed on Silica gel 60 TLC plates (Merck) with

appropriate developing solvents and with detection by spraying with sulfuric acid. A Harrison Centrifugal Thin Layer Chromatotron, model 7924 was used for centrifugal chromatography (Cen.C.). HPLC was performed with a JASCO 880-PU pump, a Waters U6K universal injector, a KNAUER refractive index monitor, and a column oven SSC-3510C (Senshu). The columns used were YMC-Pack SH-343 ODS (250×20 mm i.d.), YMC-Pack AL-302 ODS (150×4.6 mm i.d.), DAISO-PAK SP-120-5-ODS (150×6 mm i.d.) and YMC-Pack A-212 C_8 (150×6 mm i.d.). A Shimadzu Chromatopac C-R3A digital integrator was used for quantitative analyses. ^{13}C NMR spectra (125.65 MHz) were recorded with a JEOL GSX-500 spectrometer in C_5D_5N and $CDCl_3$ (internal Me_4Si).

$6^1,6^X,6^Y$-Tris-*O*-(*tert*-butyldimethylsilyl)-βCDs (1－5). To a stirred solution of dry βCD (3.4 g, dried over 4Å molecular sieves under reduced pressure at 100 ℃) in anhydrous pyridine (30 mL) was added *t*-$BuMe_2SiCl$ (1.63 g, 3.5 mol equiv.) at 2－3 ℃, and then the mixture was stirred at room temperature for 1 h. After addition of water, the solvent was evaporated and the residue was stirred in ice-water. The precipitate was collected by filtration and washed with water. The yield of silylated βCDs was 5.65 g. Separation from mono-, di-silylated and over-silylated βCDs by semi-preparative HPLC using a column of YMC-Pack SH-343-10 ODS (250×20 mm i.d.) with methanol－water (93:7) gave a mixture of trisilylated βCDs (ca. 40%). The mixture of regioisomeric trisilylates was repeatedly chromatographed on a column of YMC-Pack SH-343-5 ODS (250×20 mm i.d.) with methanol－water (91:9－93:7) and pure $6^1,6^3,6^5$-, $6^1,6^2,6^5$- and $6^1,6^2,6^3$-tris-*O*-(*t*-$BuMe_2Si$)βCDs (**1**,**2** and **5**) and a mixture of $6^1,6^2,6^6$- and $6^1,6^2,6^4$-tris-*O*-(*t*-$BuMe_2Si$)βCDs (**3** and **4**) were obtained. The regioisomers **3** and **4** were separated on a column of YMC-Pack SH-343-7 ODS (250×20 mm i.d.) with 1-propanol－water (38:62). **1**: mp 280 ℃ (dec.), $[\alpha]_D^{26}$ +112.8° (*c* 1.0, CH_3OH); ^{13}C NMR (C_5D_5N), δ 103.93－103.54 (C-1), 63.24, 63.22, 63.18 (C-6, *t*-$BuMe_2Si$-substituted), 61.71, 61.67, 61.64, 61.61 (C-6), -4.99, -5.02, -5.03, -5.06 ($SiCH_3$). **2**: mp 278 ℃ (dec.), $[\alpha]_D^{26}$+113.3° (*c* 1.0, CH_3OH), ^{13}C NMR (C_5D_5N), δ 103.87－103.60 (C-1), 63.06, 62.98, 62.74 (C-6, *t*-$BuMe_2Si$-substitutrd), 61.78, 61.70, 61.65, 61.61 (C-6), -4.90, -4.92, -4.97, -5.02, -5.04, -5.11 ($SiCH_3$). **3**: mp 288 ℃(dec.), $[\alpha]_D^{26}$ +109.6° (*c* 1.0, CH_3OH), ^{13}C NMR (C_5D_5N), δ 103.84－103.50 (C-1), 63.15, 63.02, 62.70 (C-6, *t*-$BuMe_2Si$-substituted), 61.63, 61.59, 61.54 (C-6), -4.95, -4.97, -5.01, -5.04, -5.07, -5.11 ($SiCH_3$).

4: mp 285 ℃ (dec.), $[\alpha]_D^{26}$ +108.9° (*c* 1.0, CH_3OH), ^{13}C NMR (C_5D_5N), δ 103.83 − 103.52 (C-1), 63.08, 62.96, 62.68 (C-6, *t*-$BuMe_2Si$-substituted), 61.65, 61.55, 61.49 (C-6), -4.96, -4.98, -5.06, -5.11, -5.15 ($SiCH_3$). **5**: mp 299 ℃ (dec.), $[\alpha]_D^{26}$+110.6° (*c* 1.0, CH_3OH), ^{13}C NMR (C_5D_5N), δ 103.88 − 103.56 (C-1), 63.15, 62.94, 62.73 (C-6, *t*-$BuMe_2Si$-substituted), 61.77, 61.66, 61.54 (C-6), -4.73, -4.85, -4.88, -4.92, -4.94, -4.96 ($SiCH_3$).

Additional monosilylation of disilylates. To a solution of each of positional isomers of $6^1,6^X$-bis-*O*-(*tert*-$BuMe_2Si$)-βCDs (30 mg) in pyridine (5 mL) was added *t*-$BuMe_2SiCl$ (7.5 mg, 2.0 mol equiv.). The mixture was stirred at 45 ℃ for 4 h, and processed as described for the preparation of **1** − **5**. The obtained reaction mixture was directly analyzed by HPLC.

$6^1,6^X,6^Y$-Tris-*O*-(*tert*-butyldimethylsilyl)-βCD peracetates (6 − 10). Compound **1** (200 mg) was acetylated with acetic anhydride (8 mL) in anhydrous pyridine (20 mL) for 5 − 6 h at 100 ℃ and the solution then concentrated. The residue was extracted with chloroform, and the chloroform layer was washed succesively with water, aqueous sodium hydrogencarbonate, and water, then dried, and concentrated. Cen.C. with hexane − acetone (2:1) of the residue afforded **6** (275 mg, 90.9%). In the same manner as described above, compounds **7** (878 mg, 82.5%), **8** (484 mg, 85.1%), **9** (71 mg, before Cen.C.) and **10** (151 mg, 90.8%) were obtained from **2** (704 mg), **3** (376 mg), **4** (41 mg) and **5** (110 mg), respectively. **6**: $[\alpha]_D^{26}$ +100.1 (*c* 1.0, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ 63.10, 63.02 (C-6), 61.43, 61.35, 61.22 (C-6, *t*-$BuMe_2Si$-substituted), -5.19, -5.21, -5.25, -5.48, -5.54 ($SiCH_3$). **7**: $[\alpha]_D^{26}$ +106.0° (*c* 1.0, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ 62.96 (C-6), 61.60, 61.50, 61.32 (C-6, *t*-$BuMe_2Si$-substituted), -5.04, -5.11, -5.22, -5.26, -5.36, -5.47 ($SiCH_3$). **8**: $[\alpha]_D^{26}$+104.2° (*c* 0.77, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ 63.02, 62.98, 62.91 (C-6), 61.49, 61.43 (C-6, *t*-$BuMe_2Si$-substituted), -5.10, -5.15, -5.20, -5.33, -5.40, -5.49 ($SiCH_3$). **9**: $[\alpha]_D^{26}$ +104.2° (*c* 0.77, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ 63.02, 62.98, 62.91 (C-6), 61.49, 61.43 (C-6, *t*-$BuMe_2Si$-substituted) -5.12, -5.15, -5.20, -5.33, -5.38, -5.40 ($SiCH_3$). **10**: $[\alpha]_D^{27}$ + 100.3° (*c* 1.1, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ 63.00, 62.90, 62.76, 62.66 (C-6), 61.75, 61.71, 61.49 (C-6, *t*-$BuMe_2Si$-substituted), -4.91, -5.06, -5.15, -5.16, -5.37, -5.40 ($SiCH_3$).

Tris(2,3-di-*O*-acetyl)-tetrakis(2,3,6-tri-*O*-acetyl)-βCDs (11 − 15). Compound **6** (275 mg) was *O*-desilylated with 47% boron trifluoride etherate in ether (0.4 mL) in dichloromethane (10 mL) for 2 h at room temperature, diluted with dichloromethane, and poured into ice-water. The dichloromethane layer was separated, as described for preparation of **1** − **5**, followed by Cen.C. with benzene − acetone (2:1) of the residue, affording **11** (221 mg, 94.9%). In the same manner as described above, compounds **12** (587 mg, 85.0%), **13** (87 mg, 85.6%) and **15** (72 mg, 84.2%) were obtained from **7** (816 mg), **8** (120 mg) and **10** (101 mg), respectively. Compound **14** was obtained in total yields of 76.4% from **4** (41 mg). **11**: $[\alpha]_D^{26}$ + 103.4° (*c* 1.3, $CHCl_3$), ^{13}C NMR ($CDCl_3$), 63.28, 63.27, 63.14, 63.05, 61.57[a], 61.50[a], 61.40[a] (C-6). **12**: $[\alpha]_D^{26}$ + 112.9° (*c* 1.4, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ 63.24, 63.17, 63.08, 63.04, 61.53[a], 61.51[a] (C-6). **13**: $[\alpha]_D^{26}$ +100.9° (*c* 1.3, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ 63.43, 63.11, 63.03, 62.89, 61.65[a], 61.55[a], 61.52[a] (C-6). **14**: $[\alpha]_D^{27}$ +105.7 (*c* 1.1, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ 63.36, 63.20, 62.96, 62.93, 61.74[a], 61.56[a], 61.54[a] (C-6). **15**: $[\alpha]_D^{27}$ + 102.3 ° (*c* 1.1, $CHCl_3$), ^{13}C NMR ($CDCl_3$), 63.24, 62.93, 62.91, 62.75, 61.77[a], 61.64[a], 61.54[a] (C-6).

[a]: signal of C-6 on which free hydroxy group is bonded.

Sulfonylation of tris(2,3-di-*O*-acetyl)-tetrakis(2,3,6-tri-*O*-acetyl)-βCDs (11, 12, 13 and 15). To a solution of **11** (36 mg), **12** (48 mg), **13** (35 mg) or **15** (36 mg) in anhydrous pyridine (5 mL) was added *p*-toluenesulfonyl chloride (100 − 145 mg). The mixture was stirred at 45 ℃ over night. The residue was extracted with chloroform and treated with 0.05 N sodium methoxide (5 mL) for 1 h at room temperature. The methanol solution was neutralized with Amberlite IR-120 (H^+) resin, filtered and concentrated. The residue (**1'** − **3'** and **5'**) was directly analyzed by HPLC.

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