Polysulfonylated cyclodextrins. Part 11.[1] Preparation and structural validation of three isomeric pentakis(6-*O*-mesitylsulfonyl)cyclomaltoheptaoses †

Hatsuo Yamamura,*[,a] Daisuke Iida,[a] Shuki Araki,[a] Kyoko Kobayashi,[b] Ryoichi Katakai,[b] Kazuaki Kano[c] and Masao Kawai[a]

[a] *Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*
[b] *Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan*
[c] *Central Research Laboratories, Tsumura & Co., 3586 Yoshiwara, Inashiki-gun, Ibaraki 300-1192, Japan*

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Three isomers of cyclomaltoheptaose derivatives, **1a**–**c**, which possess five mesitylenesulfonyloxy groups on their C-6 atoms, were prepared. Assignment of the regiosiomers was performed by their conversion into compounds containing five 3,6-anhydroglucose units followed by ^{1}H NMR analyses. The structures of the pentakis(3,6-anhydro) derivatives were also confirmed by their derivation from the known bis(TBDMS) derivatives.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides composed of α(1 ⟶ 4)-linked glucose units. The most common are cyclomaltohexaose (α-cyclodextrin, α-CD), cyclomaltoheptaose (β-cyclodextrin, β-CD) and cyclomaltooctaose (γ-cyclodextrin, γ-CD) which are composed of six, seven and eight glucose units, respectively. They can include a variety of guest molecules.[2] Because of this feature, not only the CDs themselves but also their modified derivatives have been the subject of a great number of academic studies as well as industrial applications.[2] While mono- and per-modification of the hydroxy group(s) on CD molecules have been reported many times, there have not been so many polymodified CDs such as bis- and tris-modified derivatives reported because of difficulties in the preparation and structure determination of the regioisomers. In highly specialized molecules such as enzymes, several functional groups work co-operatively. In the case of CD derivatives, Breslow prepared derivatives possessing two imidazole groups as an artificial ribonuclease.[3] Multifunctionalized CD derivatives are considered to be quite useful in generating highly sophisticated functions such as those of enzymes and antibodies. For the purpose of regiospecific functionalization of CD, regiospecifically sulfonylated derivatives are versatile synthetic intermediates. As for the 6-*O*-sulfonylated α-CD derivatives, all of the thirteen possible sulfonates are available, including the regioisomers of three disulfonates, four trisulfonates and three tetrasulfonates.[4] However, in the case of β-CD, tetrasulfonates and pentasulfonates have not been reported among the seventeen possible 6-*O*-sulfonylated derivatives. Here we will describe the preparation of β-CD derivatives **1a**–**c** possessing five mesitylenesulfonyl groups on their O(6) atoms.

Results and discussion

β-CD **2** was subjected to sulfonylation by use of mesitylenesulfonyl chloride in pyridine and the reaction was monitored by RP-HPLC analysis (Fig. 1). As in the case of mesitylenesulfonylation of α-CD,[4] the reaction generated a mixture of 6-*O*-mesitylsulfonylated derivatives composed of mainly the tetrasulfonates **3**,‡ pentasulfonates **1** and hexasulfonate **4**. The

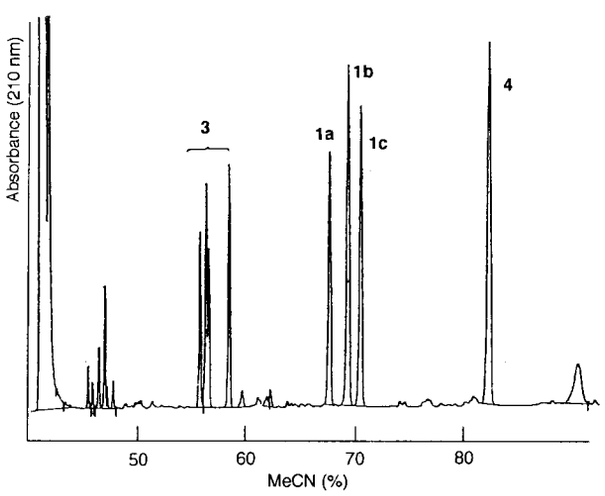
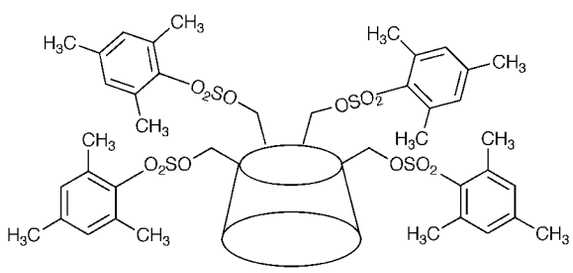


Fig. 1 RP-HPLC of the mixture obtained by the reaction of β-CD **2** with mesitylenesulfonyl chloride in pyridine. A linear gradient of MeCN was applied.



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† Various NMR spectra for compounds **5a**–**c** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/1999/3111, otherwise available from BLDSC (SUPPL. No. 57645, 13 pp.) or the RSC library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

‡ This is a regioisomeric mixture. The number of mesitylsulfonyl groups was determined by its ^{1}H NMR spectrum. The data are not shown.

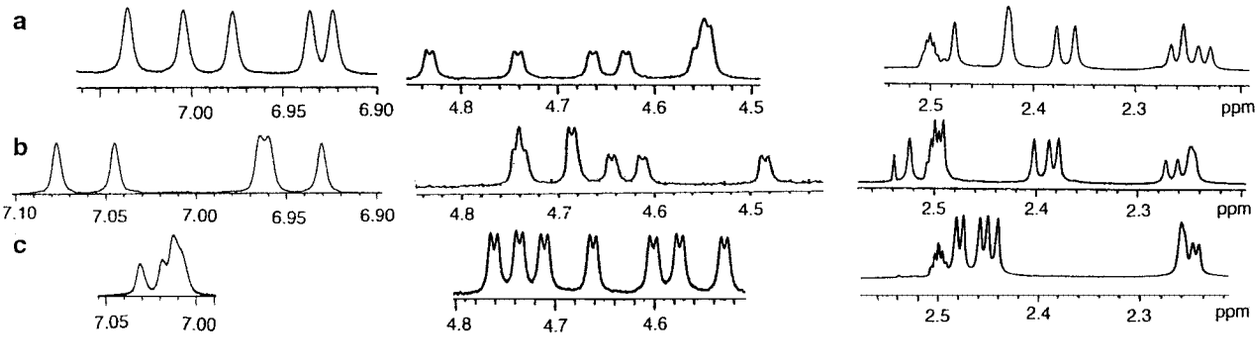
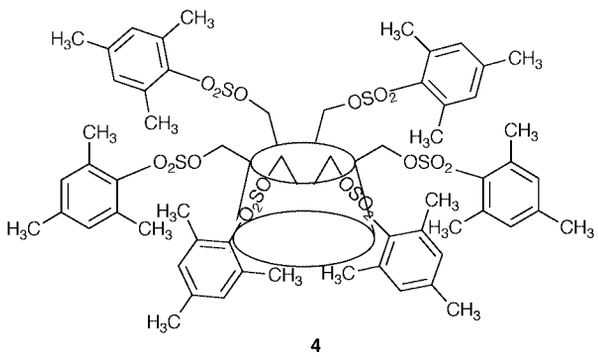


Fig. 2 ^{1}H NMR (500 MHz; [$^2H_6$]DMSO) spectra of the pentakis(6-*O*-mesitylsulfonyl) derivatives **1a** (a), **1b** (b) and **1c** (c).



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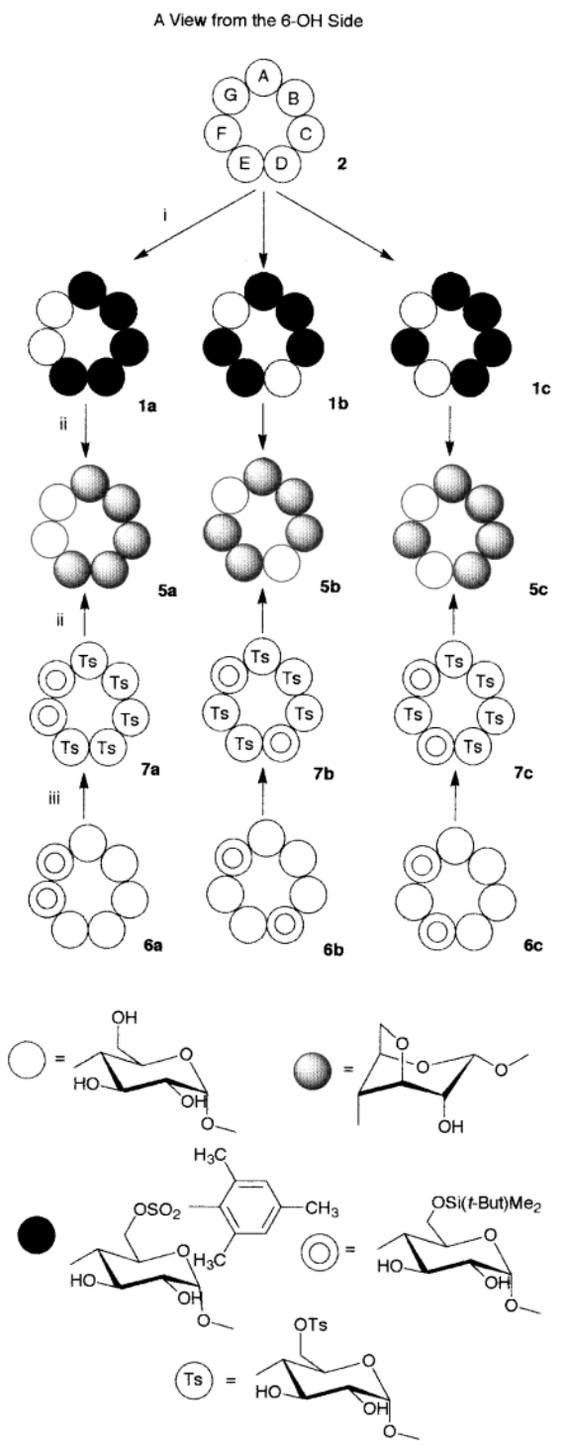
reaction mixture was applied to RP chromatography with increasing amounts of MeCN in water, which accomplished the isolation of the three possible isomeric pentasulfonates, **1a**–**c**, in yields of 5.8%, 6.6% and 5.8%, respectively. The elemental analyses and MS spectra of **1a**–**c** are consistent with the pentakis-mesitylsulfonylated structure. The ^{1}H NMR spectra of compounds **1a**–**c** confirmed the existence of five mesitylenesulfonyl groups. As shown in Fig. 2, spectral patterns of the three isomers are significantly different from each other especially in the regions of C(1)H (δ 4.4–4.9) and mesitylenesulfonyl groups [δ 2.2–2.6 (Me) and 6.9–7.1 (ArH)]. Regioisomeric assignment of **1a**–**c** was unsuccessful due to poor separation of the signals of glucose residues.

For the purpose of determining the structures of each isomer, the three pentamesitylenesulfonates **1a**–**c** were converted into the corresponding pentakis(3,6-anhydro) derivatives **5a**–**c**, respectively, by treatment with KOH in aq. MeOH followed by RP chromatographic purification (Scheme 1). The conversion of the 6-*O*-sulfonylated glucose unit into the 3,6-anhydroglucose unit is known to bring about a marked change in the ^{1}H NMR signals because of the unusual $^4C_1$ conformation of the 3,6-anhydroglucose.[5] The proton signals of the bicyclic 3,6-anhydroglucose unit are more deshielded than those of the normal glucose units. The change in the shape of the signals is also remarkable: much smaller equatorial–equatorial couplings replace vicinal axial–axial couplings commonly observed for protons of a normal glucose unit. Unlike those of the starting materials **1a**–**c**, the 500 MHz ^{1}H NMR spectra of **5a**–**c** in D_2O showed well separated signals, as expected. In order to assign the A,B,C,D,E-, A,B,C,D,F- and A,B,C,E,F-isomeric structures to the pentakis(anhydro) derivatives **5a**–**c**, relationship of the two unmodified glucose units in each isomer must be revealed. Neighbouring relationships between a glucose unit and the other glucose or 3,6-anhydroglucose unit can be studied by the observation of interunit NOE between the corresponding C(1)H and C(4)H. In the case of compound **5a**, ^{1}H–^{1}H DQF-COSY and HOHAHA† experiments enabled the assignment of the important signals, namely C(5)H (δ 4.13) and C(4)H (δ 3.64) of one of the two unmodified glucose units and C(1)H (δ 5.18) of the other glucose unit. The ROESY spectrum of **5a** showed cross-peaks corresponding to neighboring



Scheme 1 *Reagents*: i, mesitylenesulfonyl chloride, pyridine; ii, KOH; iii, TsCl, pyridine.

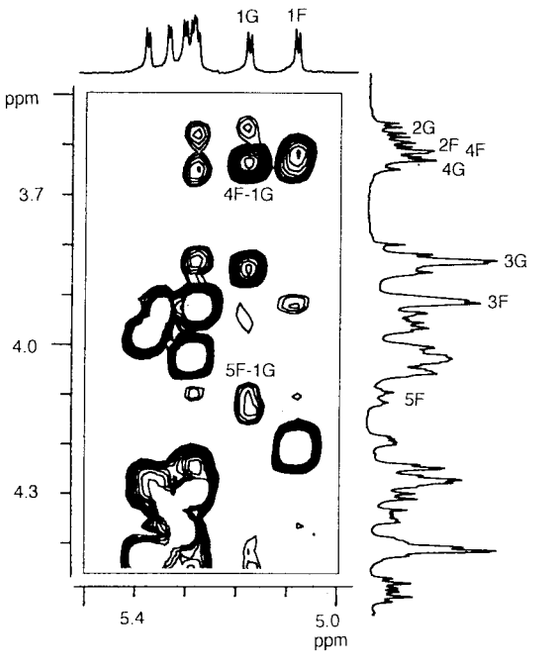


Fig. 3 Observed NOE cross-peaks between the protons of two glucoses in the ROESY spectrum of **5a** in D_2O.

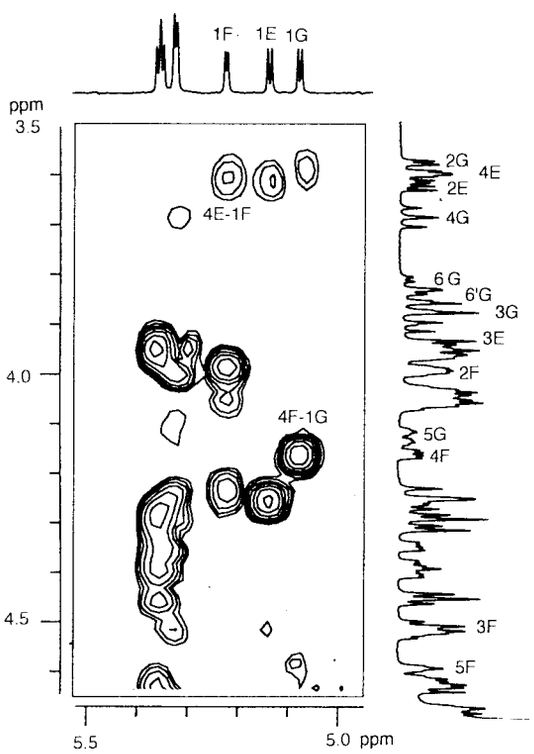


Fig. 4 Observed NOE cross-peaks between the protons of two glucoses in the ROESY spectrum of **5c** in D_2O.

[C(1)H:C(4)H] and [C(1)H:C(5)H] pairs as shown in Fig. 3, revealing that the two unmodified glucose units are directly linked by a C(1)–O–C(4) glycoside linkage. In the ROESY spectrum of **5c**, the cross-peaks were observed between one 3,6-anhydroglucose (unit F) and the two glucose units (unit E and G), namely [C(1)^{G}H (δ 5.07):C(4)^{F}H (δ 4.17)] and [C(1)^{F}H (δ 5.22):C(4)^{E}H (δ 3.61)], which revealed the sequential relationship of the three residues, as shown in Fig. 4. Thus, we established the structure of **5a** to be A,B,C,D,E-pentakis(3,6-anhydro)-β-CD and the structure of **5c** to be that of the A,B,C,D,F-isomer. Accordingly the structure of the remaining regioisomer **5b** was determined to be the A,B,C,E,F-isomer.

In order to confirm the structural assignment of the pentakis(3,6-anhydro) derivatives **5a–c** independently, a chemical correlation was then attempted with the bis(TBDMS) derivatives whose structures had been already established.[6] The AD-bis(6-*O*-TBDMS) derivative **6b** was treated with TsCl in pyridine to sulfonylate the five 6-OHs. RP-HPLC analysis showed that this reaction generated a mixture of the desired product **7b** and by-products with smaller and larger t_R-values. The by-products were assumed to be less-tosylated derivatives and those in which the 2-OH(s) were also sulfonylated since bulky TBDMS groups might make further sulfonylation of 6-OHs somewhat difficult. RP chromatographic purification gave the tosylate compound **7b** (19.1%). Each of the isomers, **7a** and **7c**, was prepared similarly from **6a** and **6c**, in yields of 14.4% and 15.7%, respectively. In the ^{1}H NMR spectra of products **7a–c**, the signals for five Ts groups [δ 2.3–2.6 (Me) and 7.3–7.8 (ArH)] appeared in addition to those of two TBDMS groups.§ The structures of **7a–c** were also confirmed by their elemental analyses and mass spectra.

The pentatosylated AD-bis(TBDMS) CD **7b** was treated with KOH in aq. MeOH for the purpose of conversion of the tosylated glucose units to 3,6-anhydroglucose units and also deprotection of the TBDMS groups.[7] RP chromatographic separation by gradient elution with increasing EtOH in water gave the desired pentakis(3,6-anhydro) derivative, which was identical to the pentakis(3,6-anhydro) derivative **5b** derived from **1b**, by comparing their ^{1}H NMR spectra (Scheme 1). Similarly, the isomers **7a** and **7c** were converted to the corresponding 3,6-anhydro derivatives which were identified as **5a** and **5c**, respectively. Consequently, parent compounds **1a**, **1b** and **1c** were determined unambiguously to be 6^{A},6^{B},6^{C},6^{D},6^{E}-, 6^{A},6^{B},6^{C},6^{E},6^{F}- and 6^{A},6^{B},6^{C},6^{D},6^{F}-pentakis(*O*-mesitylsulfonyl)-β-CDs, respectively.

Thus, three isomers of CD derivatives possessing five mesitylenesulfonyl groups on their primary hydroxy groups were prepared. This is a part of our research work of multi-sulfonylated CDs in order to establish a completely indexed 'library' of CD sulfonates for developing novel modified CDs. The study of other 6-*O*-sulfonates of β-CD, namely tetrasulfonates, and also those of γ-CDs including tri-, tetra-, penta- and hexasulfonates, are in progress.

Experimental

^{1}H NMR (500 MHz) spectra were recorded on a JEOL α 500. FAB mass measurements were carried out with a Shimadzu-Kratos Concept 32IH spectrometer. TLC was run on precoated silica gel plates (Art 5554, Merck) with the following solvent systems; PrOH–AcOEt–water [7:7:2 (v/v/v)] (solvent 1) or [7:7:5 (v/v/v)] (solvent 2). Spot detection was carried out by UV light and/or staining with 0.1% naphthalene-1,3-diol in EtOH–water–H_2SO_4 [200:157:43 (v/v/v)]. A prepacked ODS column [LiChroprep RP-18, size A (10 × 240 mm), or size B (25 × 310 mm), Merck] was used for low-pressure RP column chromatography. RP HPLC was carried out with a J'sphere ODS-M80 (4 μm; 4.6 × 150 mm or 2.0 × 150 mm, YMC Inc.) column.

Pentakis(6-*O*-mesitylsulfonyl)-β-CD 1a–c

Lyophilized β-CD **2** (300 mg, 2.65×10^{-4} mol) was treated with mesitylenesulfonyl chloride (3.60 g, 1.65×10^{-2} mol) in dry pyridine (30 cm^3) at 5 °C for 5 h. After addition of H_2O, pyridine was evaporated off and the residue was dissolved in 65% aq. MeCN (40 cm^3) and neutralized with $NaHCO_3$, and the mixture was subjected to low-pressure RP chromatography. Stepwise elutions with 65% aq. MeCN (500 cm^3), 68% aq. MeCN

§ Each of the compounds **7a–c** showed unique NMR signals which may enable isomeric discrimination (see Experimental section).

(500 cm^3), 71% aq. MeCN (500 cm^3), 74% aq. MeCN (1.5 dm^3) and gradient elution from 80% aq. MeCN (1.0 dm^3) to 100% MeCN (1.0 dm^3) were applied. The elution of 68% aq. MeCN gave the tetrasulfonates **3**‡ (88.3 mg, 19.1%). The 74% aq. MeCN elution gave the ABCDE-pentasulfonate **1a** (31.6 mg, 5.8%), ABCEF isomer **1b** (35.7 mg, 6.6%) and ABCDF **1c** (31.2 mg, 5.8%). The gradient elution gave hexasulfonate **4** (97.7 mg, 18.0%).

Compound **1a**, R_f (solvent 1) 0.42; t_R [column: J'sphere ODS-M80; gradient 40–90% aq. MeCN (100 min); flow rate 1.0 cm^3 min^{-1}] 52.2 min (Found: C, 48.71; H, 5.74; S, 7.27. Calc. for $C_{87}H_{120}O_{45}S_5{\cdot}5H_2O$: C, 48.91; H, 6.13; S, 7.48%); δ_H (500 MHz; [$^2H_6$]DMSO) 2.228, 2.240, 2.254, 2.265, 2.359, 2.378, 2.423 and 2.476 (15 H, Me), 4.520–4.570, 4.630, 4.662, 4.740 and 4.831 [7 H, C(1)H], 6.922, 6.935, 6.977, 7.004 and 7.034 (10 H, ArH); *m/z* (+FAB, LR) 2068.1 [(M + Na)$^+$], 2085.1 [(M + K)$^+$] (HR) 2067.561 10 [(M + Na)$^+$. $C_{87}H_{120}NaO_{45}S_5$ requires *m/z* 2067.560 33] (−FAB, LR) 2044.9 [(M)$^-$], 2197.7 [(M + nitrobenzyl alcohol)$^-$] 2243.3 [(M + mesitylenesulfonate)$^-$] (HR) 2243.612 89 [(M + mesitylenesulfonate)$^-$. $C_{87}H_{120}O_{45}S_5{\cdot}C_9H_{11}O_3S$ requires *m/z*, 2243.613 42].

Compound **1b**, R_f (solvent 1) 0.42; t_R 55.5 min (Found: C, 49.19; H, 5.68; S, 7.59. Calc. for $C_{87}H_{120}O_{45}S_5{\cdot}4H_2O$: C, 49.33; H, 6.09; S, 7.55%); δ_H (500 MHz; [$^2H_6$]DMSO) 2.249, 2.261, 2.273, 2.378, 2.389, 2.402, 2.492–2.503, 2.524 and 2.539 (15 H, Me), 4.487, 4.615, 4.647, 4.687 and 4.739 [7 H, C(1)H], 6.930, 6.960, 6.964, 7.045 and 7.078 (10 H, ArH); *m/z* (+FAB, LR) 2069.1 [(M + Na)$^+$], 2084.2 [(M + K)$^+$] (HR) 2067.559 86 [(M + Na)$^+$. $C_{87}H_{120}NaO_{45}S_5$ requires *m/z*, 2067.560 33] (−FAB, LR) 2044.9 [(M)$^-$], 2197.7 [(M + nitrobenzyl alcohol)$^-$], 2244.2 [(M + mesitylenesulfonate)$^-$] (HR) 2243.609 01 [(M + mesitylenesulfonate)$^-$. $C_{87}H_{120}O_{45}S_5{\cdot}C_9H_{11}O_3S$ requires 2243.613 42].

Compound **1c**, R_f (solvent 1) 0.42; t_R 57.7 min (Found: C, 48.92; H, 5.86; S, 7.55. Calc. for $C_{87}H_{120}O_{45}S_5{\cdot}5H_2O$: C, 48.91; H, 6.13; S, 7.48%); δ_H (500 MHz; [$^2H_6$]DMSO) 2.244, 2.250, 2.261, 2.441, 2.451, 2.459, 2.476 and 2.483 (15 H, Me), 4.533, 4.578, 4.605, 4.665, 4.714, 4.739 and 4.765 [7 H, C(1)H], 7.011, 7.018 and 7.030 (10 H, ArH); *m/z* (+FAB, LR) 2068.1 [(M + Na)$^+$], 2084.0 [(M + K)$^+$] (HR) 2067.559 11 [(M + Na)$^+$. $C_{87}H_{120}NaO_{45}S_5$ requires *m/z*, 2067.560 33] (−FAB, LR) 2043.9 [(M − H)$^-$], 2197.6 [(M + nitrobenzyl alcohol)$^-$], 2243.2 [(M + mesitylenesulfonate)$^-$] (HR) 2243.609 99 [(M + mesitylenesulfonate)$^-$. $C_{87}H_{120}O_{45}S_5{\cdot}C_9H_{11}O_3S$ requires *m/z*, 2243.613 42].

Pentakis(3,6-anhydro)-β-CD 5a–c

A solution of the pentasulfonate **1a** (79.5 mg, 3.89×10^{-5} mol) in 0.6 mol dm^{-3} KOH–85% aq. MeOH (50 cm^3) was kept at 85 °C for 1 day. The solution was neutralized with *d*-HCl and concentrated *in vacuo*. The residue was dissolved in water (30 cm^3) and subjected to low-pressure RP chromatography. After elution of water (200 cm^3), gradient elution from water (200 cm^3) to 20% aq. EtOH (200 cm^3) gave the ABCDE pentaanhydride **5a** (32.1 mg, 79.1%). Similarly, ABCEF anhydride **5b** and ABCDF anhydride **5c** were prepared similarly from **1b** and **1c** in 59.5% and 85.9% yield, respectively.

Compound **5a**, R_f (solvent 2) 0.05; δ_H (500 MHz; D_2O) 3.60 [dd, C(2)^{G}H], 3.64 [dd, C(2)^{F}H and t, C(4)^{F}H], 3.66 [t, C(4)^{G}H], 3.85 [t, C(3)^{G}H], 3.96 [t, C(3)^{F}H], 4.13 [dt, C(5)^{F}H], 5.09 [d, C(1)^{F}H] and 5.18 [d, C(1)^{G}H]; *m/z* (+FAB, LR) 1045.3 [(M + H)$^+$], 1067.3 [(M + Na)$^+$], 1083.3 [(M + K)$^+$] (−FAB, LR) 1043.3 [(M − H)$^-$] (HR) 1043.308 84 [(M − H)$^-$. $C_{42}H_{59}O_{30}$ requires *m/z*, 1043.309 12].

Compound **5b**, R_f (solvent 2) 0.05; δ_H (500 MHz; D_2O) 3.60 [dd, C(2)$^{D\text{ or }G}$H], 3.62 [dd, C(2)$^{G\text{ or }D}$H], 3.65 [t, C(4)$^{D\text{ or }G}$H], 3.77 [t, C(4)$^{G\text{ or }D}$H], 3.80 [dd, C(6)$^{G\text{ or }D}$H], 3.91 (C(3)$^{D\text{ or }G}$H], 3.98 [C(5)$^{G\text{ or }D}$H], 4.03 [C(3)$^{G\text{ or }D}$H], 4.08 [C(5)$^{D\text{ or }G}$H], 5.12 [C(1)$^{D\text{ or }G}$H] and 5.16 [C(1)$^{G\text{ or }D}$H]; *m/z* (+FAB, LR) 1045.3 [(M + H)$^+$], 1067.3 [(M + Na)$^+$], 1083.3 [(M + K)$^+$] (−FAB, LR) 1043.3 [(M − H)$^-$] (HR) 1043.309 31 [(M − H)$^-$. $C_{42}H_{59}O_{30}$ requires *m/z*, 1043.309 12].

Compound **5c**, R_f (solvent 2) 0.05; δ_H (500 MHz; D_2O) 3.60 [dd, C(2)^{G}H], 3.61 [t, C(4)^{E}H], 3.63 [dd, C(2)^{E}H], 3.70 [t, C(4)^{G}H], 3.83 [dd, C(6)^{G}H], 3.86 [dd, C(6)^{G}H′], 3.89 [t, C(3)^{G}H], 3.94 [t, C(3)^{E}H], 4.00 [t, C(2)^{F}H], 4.14 [dt, C(5)^{G}H], 4.17 [dd, C(4)^{F}H], 4.52 [t, C(3)^{F}H], 4.61 [t, C(5)^{F}H], 5.07 [d, C(1)^{G}H], 5.13 [d, C(1)^{E}H] and 5.22 [d, C(1)^{F}H]; *m/z* (+FAB, LR) 1045.3 [(M + H)$^+$], 1067.3 [(M + Na)$^+$], 1083.3 [(M + K)$^+$] (−FAB, LR) 1043.2 [(M − H)$^-$] (HR) 1043.309 55 [(M − H)$^-$. $C_{42}H_{59}O_{30}$ requires *m/z*, 1043.309 12].

Bis(6-*O*-*tert*-butyldimethylsilyl)-pentakis(6-*O*-*p*-tolylsulfonyl)-β-CD 7a–c

The AD bis(TBDMS) derivative **6b**[6] was treated with TsCl (901 mg, 4.73×10^{-3} mol) in dry pyridine (10 cm^3) on an ice–water-bath for 3.5 h. The work-up procedure gave the product in 60% aq. MeCN solution (20 cm^3), which was applied to a low-pressure RP chromatography column by use of 60% aq. MeCN (200 cm^3) and gradient elution from 60% aq. MeCN (700 cm^3) to 100% MeCN (700 cm^3) to give the tosyl ester **7b** (38.4 mg, 19.1%). Each of the other isomers, **7a** and **7c**, was prepared similarly from **6a**[6] and **6c**,[6] in 14.4% and 15.7% yield, respectively.

Compound **7a**, R_f (solvent 1) 0.56; t_R [column: J'sphere ODS-M80; gradient, 70–100% aq. MeCN (30 min) and 100% MeCN (20 min); flow rate 0.2 cm^3 min^{-1}] 30.0 min (Found: C, 48.25; H, 5.96; S, 7.31. Calc. for $C_{89}H_{128}O_{45}S_5Si_2{\cdot}4H_2O$: C, 48.44; H, 6.22; S, 7.25%); δ_H (500 MHz; [$^2H_6$]DMSO) −0.095, −0.090, −0.043 and −0.010 (12 H, MeSi), 0.789, 0.829 and 0.841 (18 H, *t*-Bu), 2.366, 2.374, 2.380, 2.396 and 2.540 (15 H, Me of Ts group), 4.550–4.640, 4.675, 4.703, 4.745 and 4.782 [7 H, C(1)H], 7.359, 7.375, 7.389, 7.404, 7.651, 7.667, 7.680, 7.694, 7.711, 7.716, 7.731 and 7.747 (20 H, ArH); *m/z* (+FAB, LR) 2156.6 [(M + Na)$^+$], (−FAB, LR) 2131.6 [(M − H)$^-$] and 2304.6 [(M + toluenesulfonate)$^-$].

Compound **7b**, R_f (solvent 1) 0.56; t_R 25.7 min (Found: C, 48.17; H, 5.85; S, 7.41. Calc. for $C_{89}H_{128}O_{45}S_5Si_2{\cdot}4H_2O$: C, 48.44; H, 6.22; S, 7.25%); δ_H (500 MHz; [$^2H_6$]DMSO) −0.074, −0.060, −0.052 and −0.038 (12 H, MeSi), 0.812 and 0.824 (18 H, *t*-Bu), 2.373, 2.377, 2.382 and 2.390 (15 H, Me of Ts group), 4.614, 4.646, 4.662 and 4.738–4.750 [7 H, C(1)H], 7.354, 7.371, 7.386, 7.397, 7.408, 7.414, 7.650, 7.663, 7.667, 7.679, 7.696, 7.733, 7.749, 7.753 and 7.747 (20 H, ArH); *m/z* (+FAB, LR) 2156.6 [(M + Na)$^+$], (−FAB, LR) 2131.6 [(M − H)$^-$] and 2304.7 [(M + toluenesulfonate)$^-$].

Compound **7c**, R_f (solvent 1) 0.56; t_R 25.4 min (Found: C, 48.18; H, 6.04; S, 7.70. Calc. for $C_{89}H_{128}O_{45}S_5Si_2{\cdot}4H_2O$: C, 48.44; H, 6.22; S, 7.25%); δ_H (500 MHz; [$^2H_6$]DMSO) −0.081, −0.064, −0.055 and −0.048 (12 H, MeSi), 0.811 and 0.816 (18 H, *t*-Bu), 2.370, 2.380, 2.377 and 2.387 (15 H, Me of Ts group), 4.592, 4.622, 4.639, 4.728 and 4.766 [7 H, C(1)H], 7.362, 7.3795, 7.397, 7.415, 7.669, 7.686, 7.689, 7.701, 7.706, 7.710, 7.717, 7.726, 7.753 and 7.770 (20 H, ArH); *m/z* (+FAB, LR) 2156.6 [(M + Na)$^+$], 2084.0 [(M + K)$^+$] (−FAB, LR) 2132.6 [(M)$^-$] and 2286.6 [(M + nitrobenzyl alcohol)$^-$].

Conversion of 7a–c to 5a–c

A solution of the AD TBDMS tosyl ester **7b** (16.5 mg, 7.96×10^{-6} mol) in 1 mol dm^{-3} KOH–75% MeOH (10 cm^3) was kept at 70 °C for 1 day. After work-up procedure, the aqueous solution (20 cm^3) was subjected to low-pressure chromatography. Elution with water (100 dm^3) followed by gradient elution from water (200 cm^3) to 40% aq. EtOH (200 cm^3) gave the anhydride **5b** (6.5 mg, 80.5%). Similarly, **7a** and **7c** were converted to **5a** (94.8%) and **5c** (99.8%), respectively.

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