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Supramolecular Polymers Formed by Modified Cyclodextrins

AKIRA HARADA*, YOSHINORI KAWAGUCHI and TAIKI HOSHINO
Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

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Abstract

6-Hydrocinnamoyl α-cyclodextrin (6-HyCiO-α-CD), 6-hydrocinnamoyl β-cyclodextrin (6-HyCiO-β-CD), 6-cinnamoyl α-cyclodextrin (6-CiO-α-CD), and 6-cinnamoyl β-cyclodextrin (6-HyCiO-β-CD) have been prepared. 6-HyCiO-β-CD formed an intramolecular complex in an aqueous solution. 6-HyCiO-α-CD formed weak intermolecular complexes. 6-CiO-α-CD formed intermolecular complexes to give supramolecular oligomers. 6-CiO-β-CD formed insoluble supramolecular complexes in the solid state. The structures of these complexes are discussed.

Introduction

Recently, much attention has been focused on the design and synthesis of interlocked molecules, such as rotaxanes and catenanes, because of their unique structures and properties [1]. Host–guest interactions are used for efficient preparation of such interlocked molecules. When a guest group is covalently attached to a cyclic host, the molecule may form an intramolecular complex [2] or intermolecular complexes to give supramolecular polymers [3]. When supramolecular polymers are treated with bulky stopper groups, they may form poly[2]rotaxanes [4]. Now we found that the α-cyclodextrin derivative which has a cinnamoyl group as a guest part on the 6-position of cyclodextrin forms oligomeric supramolecular structures in aqueous solutions and that the β-cyclodextrin derivative which has a cinnamoyl group as a guest part on the 6-position of cyclodextrin forms a supramolecular structure in the solid state.

We chose cyclodextrin(CD) as a cyclic host and a phenyl group as a guest moiety because a phenyl group is suitable for fitting in a cyclodextrin cavity. However, benzoyl CD did not form supramolecular polymers [5]. This result suggests that some spacer groups are required for efficient formation of intermolecular complexes. Therefore, we tested a hydrocinnamoyl group as a guest moiety. We have also tested cinnamoyl derivatives as a guest moiety.

Results and discussion

Cyclodextrin derivatives have been prepared by the reactions of 6-tosylcyclodextrin and sodium hydrocinnamate or sodium cinnamate (Scheme 1).

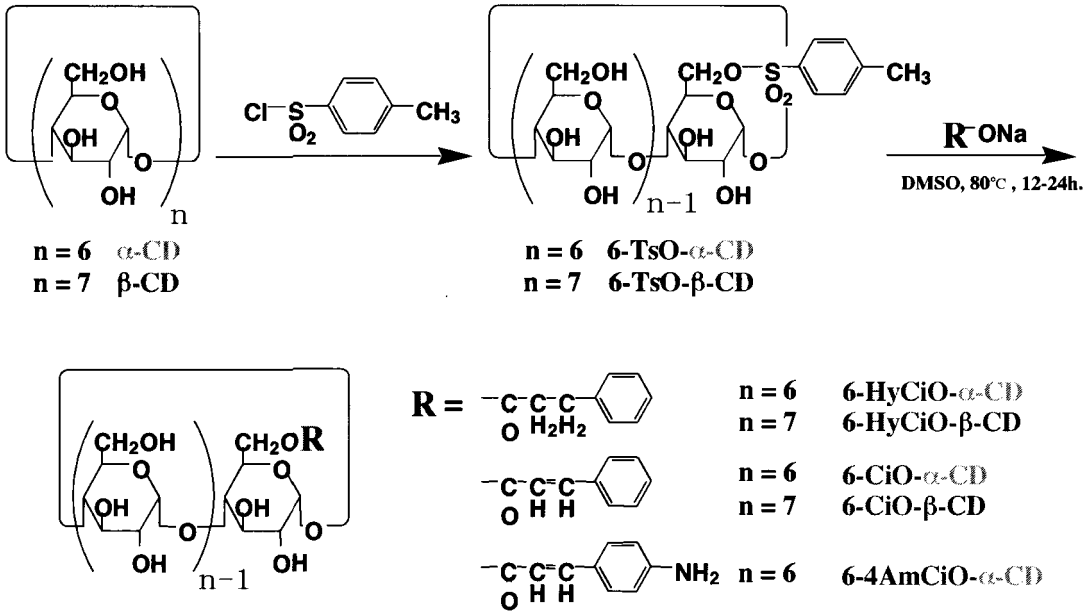
* Author for correspondence.

6-Hydrocinnamoyl β-CD (6-HyCiO-β-CD)

The ^{1}H NMR spectra of 6-hydrocinnamoyl β-CD (6-HyCiO-β-CD) in D_2O showed that the phenyl protons shifted in the same direction as those of ethylhydrocinnamate (a model compound) on addition of β-CD, indicating that the phenyl ring is included in a CD cavity. The shifts are independent of the concentrations, indicating that 6-HyCiO-β-CD forms intramolecular complexes in D_2O. The ROESY spectrum of 6-HyCiO-β-CD shows cross peaks between the phenyl signals and the CD signals, indicating that the phenyl ring is included in its own CD cavity. All the signals due to β-CD in the ^{1}H NMR spectrum of 6-HyCiO-β-CD are assigned by measuring various 2D NMR (COSY, TOCSY, ROESY, HMQC) (Figure 1). The C(3) and C(5) protons in the cavity shifted. When the glucose unit with a guest part is named the A ring, the protons of the glucose D and E rings showed large shifts indicating that the phenyl ring is included in the cavity sandwiched by ring A and rings D and E. A proposed structure of 6-HyCiO-β-CD in water is depicted in Figure 2a.

6-Hydrocinnamoyl α-CD (6-HyCiO-α-CD)

Figure 3 shows the ^{1}H NMR spectra of 6-hydrocinnamamoyl α-CD(6-HyCiO-α-CD) in various concentrations in D_2O. The ^{1}H NMR spectra showed that the phenyl protons shifted the same way as those of ethylcinnamate, indicating that the phenyl ring is included in a CD cavity. The shifts are slightly dependent on the concentrations in D_2O although they are independent of their concentrations in DMSO-*d6*, indicating that 6-HyCiO-α-CD forms weak intermolecular complexes in D_2O. The ROESY spectrum of 6-HyCiO-α-CD in D_2O shows cross peaks between the phenyl signals and CD signals, indicating that the phenyl



Scheme 1.

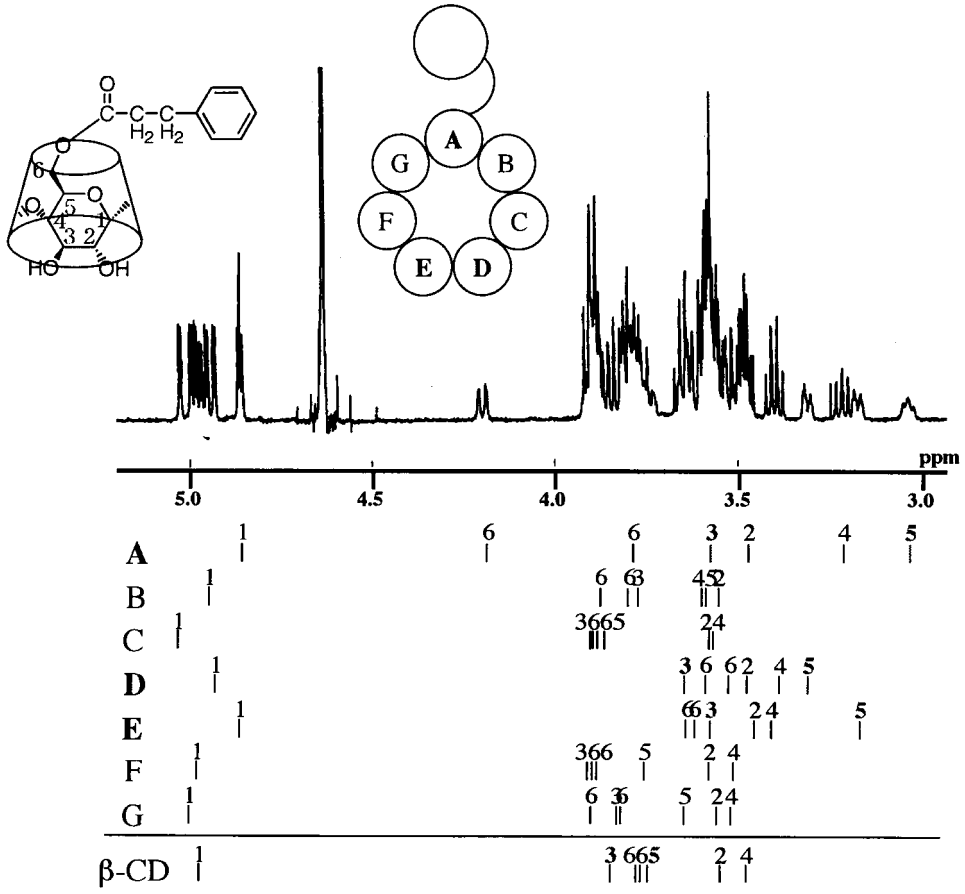


Figure 1. The 600 MHz ^{1}H NMR spectrum of 6-HyCiO-β-CD in D_2O.

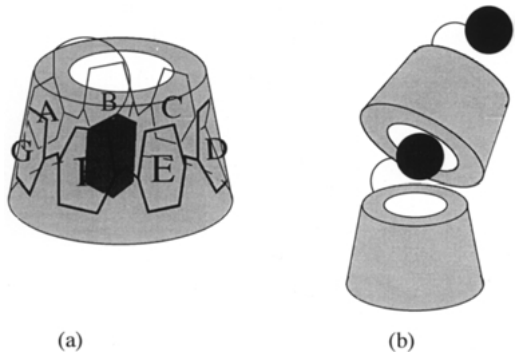


Figure 2. Proposed structures of (a) 6-HyCiO-β-CD and (b) 6-HyCiO-α-CD.

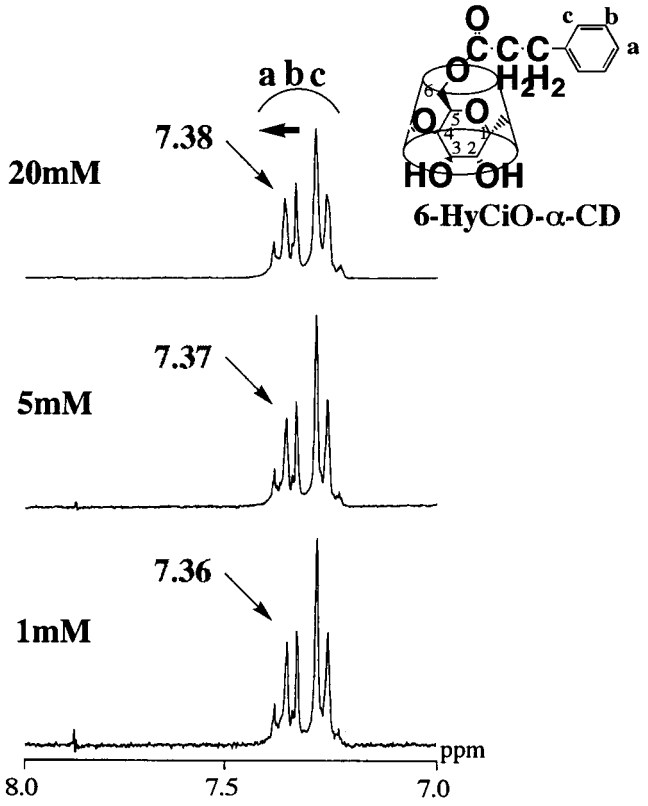


Figure 3. The 270 MHz ^{1}H NMR spectra of 6-HyCiO-α-CD in D_2O.

ring is included in the CD cavity. Although a part of the signals due to α-CD could be assigned, most of the signals could not be assigned because each signal is not well resolved. These results indicate that the interactions between the phenyl ring and the CD ring are weak. From these results, 6-HyCiO-α-CD has been found to form a weak intermolecular complex. A proposed structure is shown in Figure 2b.

6-HyCiO-β-CD formed intramolecular complexes and 6-HyCiO-α-CD formed weak intermolecular complexes. These results indicate that a hydrocinnamoyl group is too flexible to form intermolecular complexes. Therefore, we have decided to use a more rigid spacer like a cinnamoyl group having a double bond.

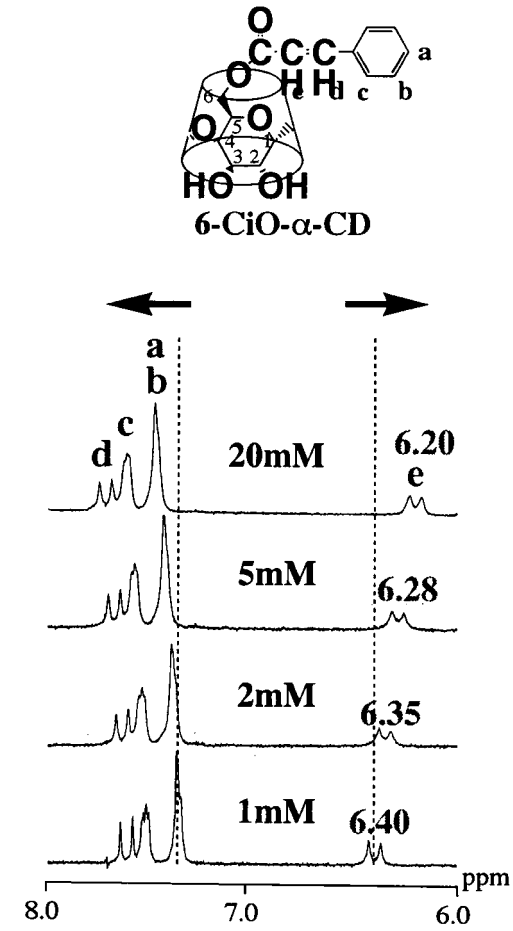


Figure 4. The 270 MHz ^{1}H NMR spectra of 6-CiO-α-CD in D_2O.

6-Cinnamoyl α-cyclodextrin (6-CiO-α-CD)

Figure 4 shows the ^{1}H NMR spectra of 6-cinnamamoyl-α-CD in the various concentrations in D_2O. The ^{1}H NMR spectra showed that the phenyl protons shifted the same way as those of methylcinnamate on addition of α-CD, indicating that the phenyl ring is included in a CD cavity. The shifts are dependent on the concentrations in D_2O, although they are independent of their concentrations in DMSO-*d6*, indicating that 6-CiO-α-CD forms intermolecular complexes in D_2O. The ROESY spectrum of 6-CiO-α-CD shows cross peaks between the phenyl signals and CD signals, indicating that the phenyl ring is included in the other CD cavity (Figure 5).

The molecular weight of 6-CiO-α-CD was measured by vapor pressure osmometry (VPO) at various concentrations in water. Figure 6 shows the results of the VPO measurements of the CD and their derivatives at various concentrations at 40 °C. Although α-CD showed no concentration dependency of the molecular weight, 6-CiO-α-CD showed a concentration dependence. The molecular weight increased with increase in the concentrations and the molecular weight reached saturation at about 3000. This result suggests that 6-CiO-α-CD forms an oligomer. At a higher temperature (at 70 °C) the molecular weight observed is lower than that observed at lower temperature (at 40 °C).

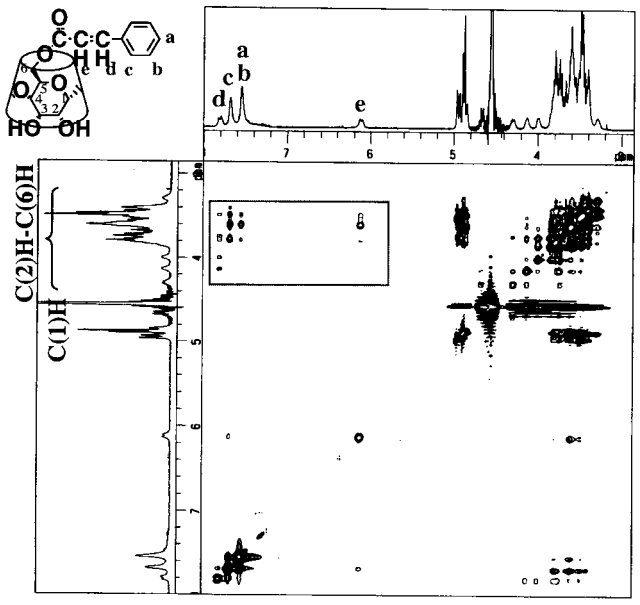


Figure 5. 500 MHz ROESY spectrum of 6-CiO-α-CD in D_2O.

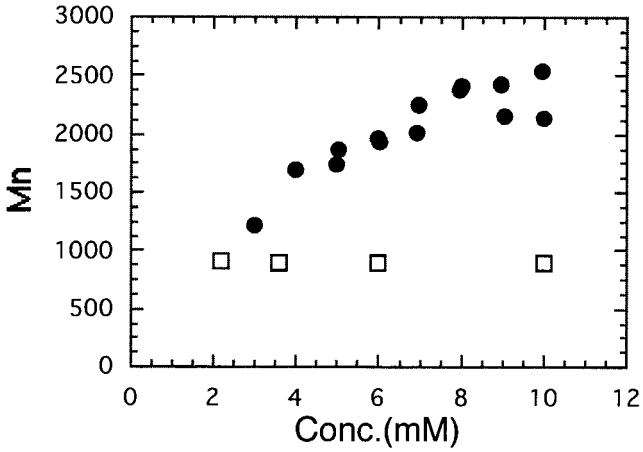


Figure 6. Concentration dependency of the number-averge molecular weight of α-CD (□) and 6-CiO-α-CD (•) in aqueous solutions measured by VPO.

A proposed structure of 6-CiO-α-CD in water is depicted in Figure 7.

6-Cinnamoyl β-cyclodextrin (6-CiO-β-CD)

6-CiO-β-CD is sparingly soluble in water, although most 6-substituted β-CDs are soluble. However, 6-CiO-β-CD is solubilized in water on the addition of *p*-iodoaniline or *p*-iodophenol which can be included in a β-CD cavity.

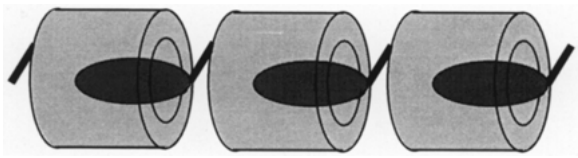


Figure 7. A proposed structure of 6-CiO-α-CD in aqueous soution.

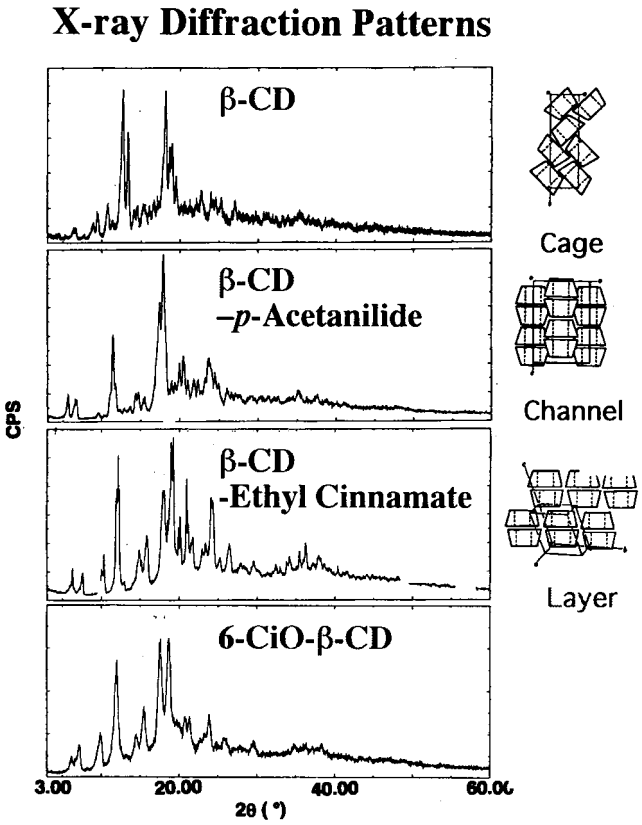


Figure 8. X-ray diffraction patterns for β-CD, the β-CD-*p*-acetanilide complex, the β-CD-ethyl cinnamate complex, and 6-CiO-α-CD.

These results suggest that 6-CiO-β-CD forms supramolecular polymers in the solid state. The X-ray powder pattern of 6-CiO-β-CD is very similar to that of the complex between β-CD and ethyl cinnamate [6], in which the β-CDs form a layer structure (Figure 8). The pattern of 6-CiO-β-CD is different from those of β-CD and β-CD-*p*-acetamide which have been reported to have a cage type structure and a channel type structure, respectively, by single crystal X-ray structural analysis. A proposed structure of 6-CiO-β-CD is shown in Figure 9.

Control of Supramolecular Structures by Competitive Guests

6-CiO-α-CD and 6-CiO-β-CD form supramolecular oligomers and polymers. When guest molecules which bind strongly in a CD cavity are added, the modified CDs bind the competitive guest to give host-guest monomers.

Figure 9 shows the ^{1}H NMR spectra of 6-CiO-α-CD in the absence and presence of *p*-iodoaniline (Kc = 2800 M^{-1}) or *p*-iodophenol (Kc = 2300 M^{-1}). Protons of the guests shifted downfield with some broadening and signals of 6-CiO-α-CD also shifted with some sharpening. These results indicate that the guest molecules were included in a CD cavity and a cinnamoyl group was exposed to water.

6-CiO-β-CD is insoluble in water. This is due to intermolecular complexation through host-guest interactions. When an excess amount of adamantane-1-carboxylic acid

was added to the suspension of 6-CiO-α-CD, 6-CiO-β-CD was solubilized in water. The ^{1}H NMR spectra showed clearly 6-CiO-β-CD by the addition of adamantane carboxylic acid, indicating that adamantane carboxylic acid solubilizes 6-CiO-β-CD in D_2O.

Conclusion

Although 6-HyCiO-β-CD formed an intramolecular complex and 6-HyCiO-α-CD formed weak intermolecular complexes, 6-CiO-α-CD formed intermolecular complexes to give supramolecular oligomers and 6-CiO-β-CD formed insoluble supramolecular complexes in the solid state. These results indicate that flexible spacer groups allow formation of intramolecular complexes and rigid spacer groups are required for the formation of supramolecular polymers. Supramolecular structures can be controlled by the addition of suitable guest molecules.

Experimental section

Materials

α-CD was obtained from Wako Pure Chemical Industries. β-CD was obtained from Tokyo Kasei Inc. *p*-Toluenesulfonyl chloride and sodium hydroxide were obtained from Nacalai Tesque Inc. Hydrocinnamic acid (3-phenylpropionic acid) was obtained from Kanto Chemical Co., Inc. Ethyl hydrocinnamate (HyCiOEt) was obtained from Aldrich. Pyridine was obtained from Wako Pure Chemical Industries. DMSO-d_6 and D_2O used as solvents in the NMR measurements were obtained from Aldrich.

Measurements

HPLC was performed on a TOSOH CCP&8020 system (column: DAISOPAK SP-120-5-ODS-AP (150 mm × 4.6 mm^2), eluent: MeOH–H_2O (30 : 70 v/v), detector: RI, UV, flow rate: 1.00mL/min, at room temperature). Semipreparative HPLC was performed on a TOSOH CCP&8020 system (column: DAISOPAK SP-120-5-ODS-AP (250 mm × 20 mm^2), eluent: MeOH–H_2O (30 : 70 v/v), detector: RI and UV, flow rate: 3.00 mL/min, at room temperature). ^{1}H NMR spectra were recorded at 270 MHz on a JEOL JNM EX-270 NMR spectrometer. Chemical shifts were referenced to the solvent values (δ 2.50 ppm for DMSO and δ 4.70 ppm for HOD) or the internal standard (δ 2.06 ppm for CH_3CN in D_2O). ^{13}C NMR spectra were recorded at 67.8 MHz on a JEOL JNM EX-270 NMR spectrometer. Chemical shifts were referenced to the solvent values (δ 39.50 ppm for DMSO-d_6). 2D NMR (COSY, TOCSY, NOESY, ROESY, HMQC) experiments were obtained with D_2O as the solvent at 30 °C at 500 MHz on a JEOL JNM GX-500 NMR spectrometer or at 600 MHz on a VARIAN-UNITY-600 NMR spectrometer. FT-IR spectra were measured at JASCO FT/IR-410 spectrometer. Absorption spectra were recorded on a Shimadzu UV-2500PC spectrometer at room temperature.

Preparation of mono (hydrocinnamoyl) substituted CDs

Mono-6-O-(hydrocinnamoyl)-α-CD (6-HyCiO-α-CD). 6-TsO-α-CD (370mg, 3.28×10^{-4} mol) was dissolved in DMSO (30 mL), and HyCiONa (283 mg, 1.64×10^{-3} mol) was added. The reaction was carried out with stirring at 80 °C for 24 h. After being cooled to room temperature, the solution was poured into acetone (300 mL). The resulting precipitate was dried under vacuum to give 550 mg of the crude product. The crude product (550 mg) was dissolved in MeOH–H_2O (30 : 70 v/v), and the solution was injected into a semipreparative HPLC column. UV absorption at 254 nm was monitored and the fraction containing the product was collected. The eluent after evaporation gave 30.7 mg of the desired product. Yield: 8.5%. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 7.30–17 (m, 5H, phenyl), 5.56–5.42 (m, 12H, O(2)H and O(3)H of α-CD), 4.81 (brs, 6H, C(1)H of α-CD), 4.50–4.28 (m, 7H, O(6)H and C(6′)H of α-CD), 3.81–3.29 (m, overlaps with HOD), 2.84 (t, J = 7.4 Hz, 2H, Ph–$CH_{2\_}$), 2.64 (t, J = 7.1 Hz, 2H, –CH_2–CO–); ^{13}C NMR (DMSO-d_6, 67.8 MHz): δ 175.37 (C=O), 140.46 (C-1 of phenyl), 128.59 (C-3 of phenyl), 128.31 (C-2 of phenyl), 126.34 (C-4 of phenyl), 101.41 (C(1) of α-CD), 101.14 (C(1′) of α-CD), 81.19 (C(4) of α-CD), 73.21 (C(3) of α-CD), 71.88 (C(5) of α-CD), 71.61 (C(2) of α-CD), 69.56 (C(5′) of α-CD), 63.81 (C(6′) of α-CD), 60.13 (C(6) of α-CD), 35.13 (Ph–$CH_{2\_}$), 30.30 (–CH_2–CO–); IR (KBr, cm^{-1}): 1731 (vs, $\nu_{C=O}$). Anal. Calcd for $C_{45}H_{68}O_{31}\cdot 5H_2O$: C, 45.23; H, 6.58. Found: C, 45.27; H,6.50.

Mono-6-O-(Hydrocinnamoyl)-β-CD (6-HyCiO-β-CD). 6-TsO-β-CD (3.04g , 2.36×10^{-3} mol) was dissolved in DMSO (100 mL), and HyCiONa (2.02 g, 1.18×10^{-2} mol) was added. The reaction was carried out with stirring at 80 °C for 12 h. After being cooled to room temperature, the solution was poured into acetone (1 L). The resulting precipitate was dried under vacuum to give 4.5 g of the crude product. The crude product (550 mg) was dissolved in water (100 mL), and the solution was made acidic with 1N HCl aqueous solution. The products precipitated were collected by filtration, washed with water, then dried under vacuum. The product was recrystallized from water to give 6-HyCiO-β-CD. Yield, 679 mg (23%), ^{1}H NMR (DMSO-d_6, 270 MHz): δ 7.30–17 (m, 5H, phenyl), 5.68 (brs, 12H, O(2)H and O(3)H of α-CD), 4.84 (brs, 6H, C(1)H of α-CD), 4.37–4.08 (m, 7H, O(6)H and C(6′)H of α-CD), 3.81–3.29 (m, overlaps with HOD), 2.84 (t, J = 7.3 Hz, 2H, Ph–$CH_{2\_}$), 2.64 (t, J = 7.4 Hz, 2H, –CH_2–CO–); ^{13}C NMR (DMSO-d_6, 67.8 MHz): δ 172.22 (C=O), 140.58 (C-1 of phenyl), 128.38 (C-3 of phenyl), 128.29 (C-2 of phenyl), 126.09 (C-4 of phenyl), 102.05 (C(1) of α-CD), 101.76 (C(1′) of α-CD), 81.66 (C(4) of α-CD), 73.14 (C(3) of α-CD), 72.49 (C(2) of α-CD), 72.13 (C(5) of α-CD), 69.06 (C(5′) of α-CD), 63.51 (C(6′) of α-CD), 60.02 (C(6) of α-CD), 34.94 (Ph–CH_2–), 30.28 (–CH_2–CO–). Anal. Calcd for $C_{51}H_{78}O_{36}\cdot 5.5H_2O$: C, 44.84; H, 6.57. Found: C, 44.75; H,6.53.

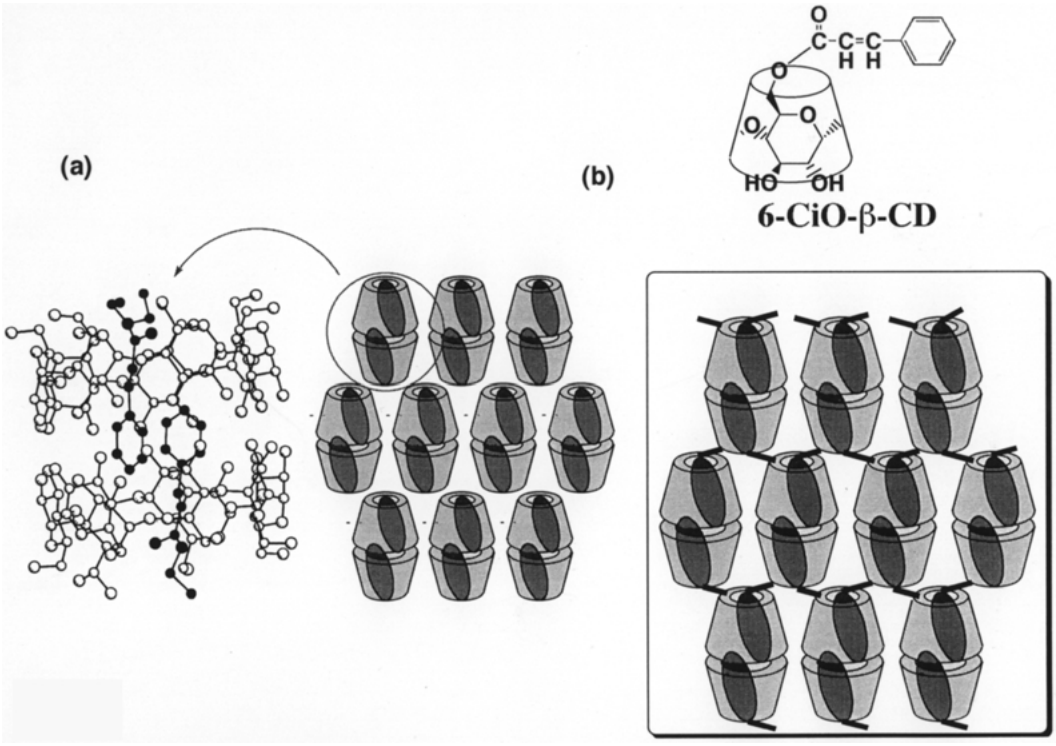


Figure 9. Crystal structure of the β-CD-ethyl cinnamate complex (a) and a proposed structure of 6-CiO-β-CD in the solid state.

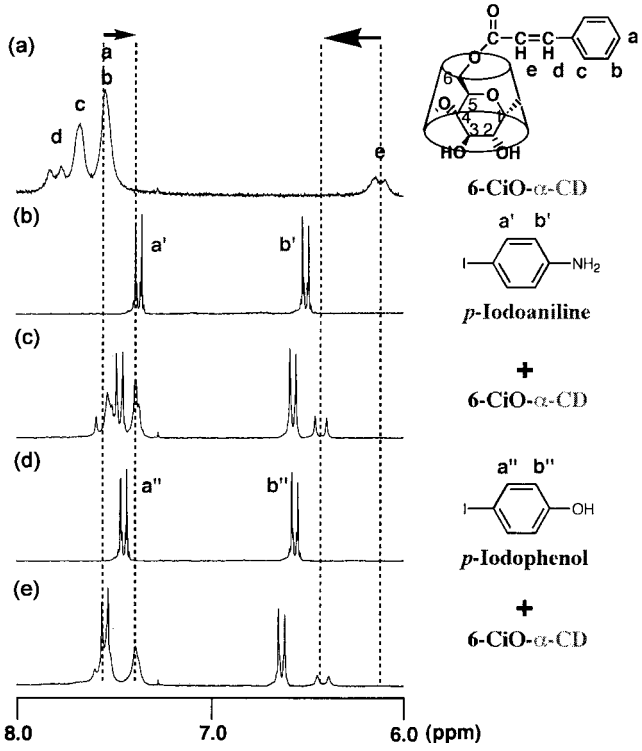


Figure 10. 270 MHz ^{1}H NMR spectra of 6-CiO-α-CD (a), *p*-iodoaniline (b), 6-CiO-α-CD + *p*-iodoaniline (c), *p*-iodophenol (d) and 6-CiO-α-CD + *p*-iodophenol (e) in D_2O. [6-CiO-α-CD] = [*p*-iodoaniline] = [*p*-iodophenol] = 5 mM.

Preparation of mono (cinnamoyl) substituted CDs

Cinnamic acid, sodium salt (CiONa). NaOH (2.75 g, 68.7 mmol) was dissolved in EtOH (200 mL). Cinnamic acid (10.17 g, 68.7 mol) was dissolved in EtOH (100 mL). The solution of NaOH was added to the above solution with stirring. The product precipitated was collected by centrifugion, washed with EtOH, then dried under vacuum up to 70 °C to give CiONa. Yield, 10.18 g (86%). ^{1}H NMR (D_2O, 270 MHz): δ 7.61–7.40 (m, 5H, phenyl), 7.36 (d, J = 16.2 Hz, ^{1}H, Ph–CH=), 6.49 (d, J = 16.2 Hz, ^{1}H, =CH–CO–); IR (KBr, cm^{-1}): 1547 (vs, $\nu_{C=O}$).

Mono-6-O-(cinnamoyl)-α-CD (6-CiO-α-CD). 6-TsO-α-CD (1.02g, 9.02×10^{-4} mol) was dissolved in DMSO (100 mL), and CiONa (829 mg, 5.00×10^{-3} mol) was added. The reaction was carried out with stirring at 80 °C for 24 h. After being cooled to room temperature, the solution was poured into acetone (2L). The resulting precipitate was dried under vacuum to give 1.29 g of the crude product. The crude product (1.29 g) was dissolved in MeOH–H_2O (30 : 70 v/v), and the solution was injected to a semipreparative HPLC column. UV absorption at 254 nm was monitored and the fraction containing the product was collected. The eluent after evaporation gave 289mg of the desired product. Yield: 32%. ^{1}H NMR (DMSO-d_6, 270 MHz): δ 7.74–7.70 (m, 3H, 3-H and 4-H of phenyl), 7.66 (d, J = 16.2 Hz, ^{1}H, Ph–CH=), 7.44–7.42 (m, 2H, 2-H of phenyl), 6.69 (d, J = 16.2Hz, ^{1}H, =CH–CO–), 5.56–5.42 (m, 12H, O(2)H and O(3)H of α-CD), 4.89–4.80 (m, 6H, C(1)H of α-CD), 4.60–4.30 (m, 7H, O(6)H and C(6′)H of α-CD), 3.78–3.29 (m, overlaps with HOD); IR (KBr, cm^{-1}): 1709 (vs, $\nu_{C=O}$), 1333 (s, nC = O). Anal. Calcd for $C_{45}H_{66}O_{31}\cdot 2.5H_2O$: C, 47.08; H, 6.23. Found: C, 47.07; H,6.38.

Mono-6-O-(cinnamoyl)-β-CD (6-CiO-β-CD). 6-TsO-β-CD (1.29g, 1.00 × 10-3 mol) was dissolved in DMSO (100 mL), and CiONa (851 mg, 5.00×10^{-3} mol) was added. The reaction was carried out with stirring at 80 °C for 12 h. After being cooled to room temperature, the solution was poured into acetone (1.5 L). The resulting precipitate was dried under vacuum to give 2.0 g of the crude product. The crude product was recrystallized from *n*-BuOH-EtOH-H2O (5 : 4 : 3 v/v) and from water to give 6-CiO-β-CD. Yield, 420 mg (33%). Mp.: 220 °C(dec); Positive ion FAB-MS m/z 1265 (M+H+); ^{1}H NMR (DMSO-d_6, 270 MHz): δ 7.73–7.69 (m, 3H, 3-H and 4-H of phenyl), 7.66 (d, J = 16.2 Hz, ^{1}H, Ph–CH=), 7.44–7.42 (m, 2H, 2-H of phenyl), 6.68 (d, J = 16.2Hz, ^{1}H, =CH–CO–), 5.79–5.65 (m, ^{14}H, O(2)H and O(3)H of α-CD), 4.91–4.83 (m, 7H, C(1)H of α-CD), 4.52–4.20 (m, 8H, O(6)H and C(6′)H of α-CD), 3.93–3.29 (m, overlaps with HOD); ^{13}C NMR (DMSO-d_6, 67.8 MHz): δ 166.15 (C=O), 144.60 (Ph–CH=), 134.11 (C-1 of phenyl), 130.53 (C-4 of phenyl), 129.00 (C-3 of phenyl), 128.38 (C-2 of phenyl), 118.04 (=CH–CO–). 102.03 (C(1) of α-CD), 81.66 (C(4) of α-CD), 73.10 (C(3) of α-CD), 72.46 (C(2) of α-CD), 72.13 (C(5) of α-CD), 68.99 (C(5′) of α-CD), 63.67 (C(6′) of α-CD), 60.00 (C(6) of α-CD). Anal. Calcd for $C_{51}H_{76}O_{36}\cdot 6H_2O$: C, 44.61; H, 6.46. Found: C, 44.62; H,6.38.

Vapor pressure osmometry (VPO)

Measurements were performed using a KNAUER vapor pressure osmometer (No. A0280). α-CD, G1α-CD, and 6-TsO-α-CD were measured in water with concentration ranging from 2×10^{-3} to 2×10^{-2} M at 40 °C. 6-CiO-α-CD was measured in the same way at 40 °C and 70 °C. NaOH aqueous solution was used as the instrument standard.

References

1. D. B. Amabiliino and J. F. Stoddart, *Chem. Rev.* **95**, 2725 (1995): A. Harada, *Adv. Polym Sci.* **133**, 141 (1997): J.-P. Sauvage and C. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots*, Wiley-VCH, Weinheim (1999).
2. K. Hamasaki, H. Ikeda, A. Nakamura, A. Ueno, F, Toda, I. Suzuki, and T. Osa, *J. Am. Chem. Soc.* **115**, 5035 (1993): A, Ueno, S. Minato, I. Suzuki, M. Fukushima, M. Okubo, T. Osa, F. Hamada, and K. Mukai, *Chem. Lett.* 1990, 605: R. Corradini, A. Dossena, R. Marchelli, A. Panagia, G. Sartor, M. Saviano, A. Lomvardi, and V. Pavone, *Chem. Eur. J.* **2**, 373 (1996): R. Corradini, A. Dossena, G. Galaverna, R. Marchelli, A. Panagia, and G. Sartor, *J. Org. Chem.* **62**, 6283 (1997). Y. Wang, T. Ikeda, A. Ueno, and T. Toda, *Bull. Chem. Soc. Jpn.* **67**, 1589 (1999).
3. A. Zanotti-Gerosa, E. Solari, L. Chiesi-Villa, and C. Rissoli, *Chem. Commun.* 1996, 119: N. Yamaguchi, D. S. Nagvekar, and H.W. Gibson, *Angew. Chem. Int. Ed.* **37**, 2361 (1998).
4. P. R. Ashton, I. Baxter, S. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, D. J. Willams, and R. Wolf, *Angew. Chem. Int. Ed.* **37**, 1294 (1998): P. R. Ashton, I. W,. Parsons, F. M. Raymo, J. F. Stoddart, A. J. P. White, D. J. Willams, and R. Wolf, *Angew. Chem. Int. Ed.* **37**, 1913 (1998): S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White, and D. J. Willams, *Org. Lett.* **2**, 759 (2000).
5. L.-H. Tong, Z. -J. Hou, Y. Inoue, and A. Tai, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1253.
6. M. B. Hursthouse, C. Z. Smith, M. Thornton-Pet, and J. H. P. Utley, *J. Chem. Soc. Chem. Commun.* 1982, 881.