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# Synthesis and photostability of methoxycinnamic acid modified cyclodextrins

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ABSTRACT

Various cyclodextrins, alpha, beta and gamma, were esterified with 4-methoxy-, 2,4,5- and 2,4,6-trimethoxycinnamic acids. Upon esterification with β-cyclodextrin, the photostability of 2,4,5-trimethoxycinnamate increased while no improvement was observed for 4-methoxycinnamate and 2,4,6-trimethoxycinnamate. However, increase in the photostability of 4-methoxycinnamoyl moiety could be observed when esterified with α-CD and that of 2,4,6-trimethoxycinnamoyl moiety could be observed after being esterified with γ-CD. These photostability data together with the 2D NMR analyses indicated that the 4-methoxycinnamoyl, 2,4,5-trimethoxycinnamoyl and 2,4,6-trimethoxy cinnamoyl moieties could enter the α-CD, the β-CD, and the γ-CD cavities, respectively.



## 1. Introduction

Skin damage by effects of sunlight has been known for many years and it has been well accepted that skin cancer, photoimmunsuppresion and aging of the skin are caused by UV radiation. UVB is directly absorbed by DNA in the skin resulting in DNA damage by dimeric photoproducts between pyrimidine bases [1] while UVA can trigger the generation of reactive oxygen species which are harmful to many biomolecules including DNA [2].

The most popular organic UV absorber, 2-ethylhexyl-4-methoxycinnamate (EHMC), is commonly used as a UVB filter in commercial sunscreens and many cosmetic formulations. The photoisomerization of *trans*-EHMC to *cis*-EHMC causing a decrease of absorption efficiency was studied both in solutions and formulations [3]. Several studies suggested ways to improve the photostability of cinnamates [4]. Encapsulation of EHMC into nanoparticles consisting of polyvinylalcohol was studied for example [5–8]. Other cinnamic acid derivatives such as 2,4,5- and 2,4,6-trimethoxycinnamate have also been reported as potential UVA/B filters [9].

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6–8 glucopyranoside units (Fig. 1). Many literatures reported the increased photostability of organic UV-filters by forming inclusion complexes with CDs [10–12]. Scalia et al. reported that the stability of EHMC was increased to 26.1% after forming an inclusion complex with β-CD (compared to free EHMC which was 35.8%) [13].

An inclusion complex of 4-hydroxy-3-methoxycinnamic acid (ferulic acid) in α-cyclodextrin not only significantly improved the stability of ferulic acid against UVB but also slowed down the skin penetration of the material [14,15]. However, the inclusion complexes described above, are only held by several intermolecular noncovalent forces, thus, may easily be dissociated under appropriate conditions. The designing and synthesis of modified CDs have been shown to improve the original binding ability and increase the molecular selectivity of parent CDs [16,17]. Coulston et al. reported a molecular machine, β-cyclodextrin modified with *trans*- and *cis*-cinnamide, in which only one isomer exhibited the molecular recognition and performed work, so the photoisomerization turns the machine on and off [18]. In our previous work, we reported the synthesis and photostability of a novel UVB/A filter, 2-ethylhexyl-2,4,5-trimethoxycinnamate [9].

In this paper, we report the syntheses of modified CDs by functionalization of their primary hydroxyl rims with various methoxycinnamoyl moieties including 4-methoxycinnamoyl, 2,4,5-trimethoxycinnamoyl and 2,4,6-trimethoxycinnamoyl moieties. The behavior of these methoxycinnamoyl moieties was observed by 2D NMR (ROESY experiment). The effect of CD cavity size to the photostability of methoxy cinnamoyl moiety was investigated.

## 2. Experimental

### 2.1. Instruments

UV–vis spectra were recorded in a quartz cell (light path 10 mm) on a UV–vis spectrophotometer (PerkinElmer, CT, USA). All $^1$H

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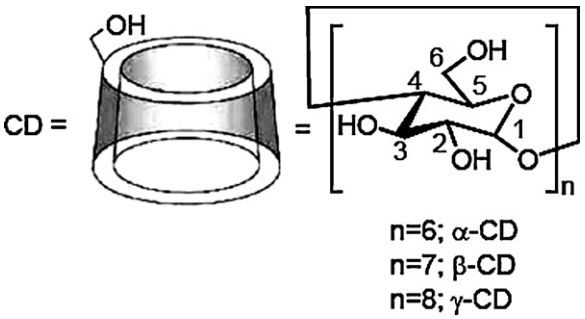



**Fig. 1.** General structure of cyclodextrins.

NMR spectra were obtained in $D_2O$ or DMSO-$d_6$ on a Varian Mercury NMR spectrometer, which operated at 400.00 MHz for $^1H$ and 100.00 MHz for $^{13}C$ nuclei (Varian Company, CA).

### 2.2. Materials

α-Cyclodextrin was purchased from Sigma–Aldrich (Steinheim, Germany). β-Cyclodextrin and γ-cyclodextrin were purchased from Thai Isekyi Co. Ltd. All benzaldehydes, pyridine and malonic acid were purchased from Fluka Chemical Company (Buchs, Switzerland). Piperidine and 4-(dimethylamino) pyridine (DMAP) were purchased from Sigma (Sigma Chemical Co., Steinheirg, Germany). Solvents used in syntheses and spectroscopic techniques were reagent or analytical grades purchased from Labscan (Bangkok, Thailand).

### 2.3. Synthesis

All five cyclodextrin-methoxy cinnamates were carried out using the modified method of Chan et al. [16]. Trans-methoxycinnamic acid (75 mM) was prepared as previously described [19] and the obtained acid was dissolved in dichloromethane (25 mL) under a nitrogen atmosphere. The suspension was cooled in an ice bath before oxalylchloride (80 mM) was added. The reaction mixture was heated up to room temperature and stirred for 1 h. Then the solvent was removed under reduced pressure. Crude cinnamoyl chloride was added dropwise to a 25 mL anhydrous DMF solution containing CD (5 mM), 4-(dimethylamino)-pyridine (1 mM) and distilled pyridine (7.5 mL) at 0 °C under a nitrogen atmosphere and stirred overnight. Then the reaction mixture was added dropwise to cold acetone (300 mL), while stirring. A white precipitate was collected by filtration. The white solid was then dissolved in water (5 mL) and added dropwise to MeOH (300 mL). This procedure was repeated one more time and a white precipitate was again collected by filtration and dried under vacuum.

α-Cyclodextrin-4-methoxycinnamate (**1**): (15% yield) white solid; $^1H$ NMR (400 MHz, $D_2O$) $\delta$ 7.80–7.77 (d, $J$ = 8.8 Hz, 2H), 7.79–7.75 (d, $J$ = 16.0 Hz, 1H), 7.21–7.19 (d, $J$ = 8.0 Hz, 2H), 6.46–6.42 (d, $J$ = 16.0 Hz, 1H), 5.06–5.05 (d, $J$ = 4.0 Hz, 1H), 3.97–3.87 (t, 24H), 3.68–3.64 (t, 6H), 3.58–3.57 and 3.56–3.55 (d, $J$ = 4.0 MHz, 12H); EIMS calculated for [**1**−$Na^+$] 1156.00 found: 1155.524.

β-Cyclodextrin-4-methoxycinnamate (**2**): (55% yield) white solid; $^1H$ NMR (400 MHz, 50% DMSO-$d_6$:$D_2O$) $\delta$ 7.91–7.86 (d, $J$ = 16.8 Hz, 1H), 7.87–7.85 (d, $J$ = 8.0 Hz, 2H), 7.30–7.28 (d, $J$ = 8.0 Hz, 2H), 6.71–6.67 (d, $J$ = 16.0 Hz, 1H), 5.21–5.20 (d, $J$ = 4.0 Hz, 7H), 4.11 (s, 3H), 4.03–3.91 (m, 28H), 3.79–3.72 (m, 14H); EIMS calculated for [**2**−$Na^+$] 1318.14 found: 1317.50.

β-Cyclodextrin-2,4,5-trimethoxycinnamate (**3**): (73% yield) pale yellow solid; $^1H$ NMR (400 MHz, $D_2O$) $\delta$ 7.84–7.80 (d, $J$ = 16.0 Hz, 1H), 7.06 (s, 1H), 6.67 (s, 1H), 6.36–6.32 (d, $J$ = 16.0 Hz, 1H), 5.10–5.09 (d, $J$ = 4.0 Hz, 7H), 3.96–3.82 (m, 28H), 3.70–3.60 (m, 14H); EIMS calculated for [**3**−$Na^+$] 1378.20 found: 1377.677.

β-Cyclodextrin-2,4,6-trimethoxycinnamate (**4**): (16% yield) white solid; $^1H$ NMR (400 MHz, $D_2O$) $\delta$ 7.04–7.02 (d, $J$ = 10.8 Hz, 1H), 6.33–6.32 (d, $J$ = 4.0 Hz, 2H), 6.12–6.09 (d, $J$ = 12.4 Hz, 1H), 4.01–3.39 (m, 28H), 3.70–3.60 (m, 14H); EIMS calculated for [**4**−$Na^+$] 1378.20 found: 1378.199.

γ-Cyclodextrin-2,4,6-trimethoxycinnamate (**5**): (30% yield) white solid; $^1H$ NMR (400 MHz, $D_2O$) $\delta$ 7.82–7.77 (d, $J$ = 16.0 Hz, 1H), 6.56–6.52 (d, $J$ = 16.0 Hz, 1H), 6.22 (s, 2H), 5.15–5.14 (d, $J$ = 4.0 Hz, 8H), 3.99–3.88 (m, 41H), 3.71–3.63 (m, 16H); EIMS calculated for [**5**−$Na^+$] 1540.34 found: 1539.617.

### 2.4. Photostability test

The photostability of each compound was tested in 10% DMSO–$H_2O$. The fresh sample solution was irradiated by using a broadband UVB lamp (Daavlin, OH) at room temperature. UV intensity was measured by using a UVB power meter (Optix Tech, Ltd., DC). UV absorption profiles of the irradiated samples were analyzed on a UV/vis spectrometer. Photostability of each compound was expressed as percent relative absorbance at the maximum absorption wavelength of the compound. All experiments were done in triplicate. Percent photostability was calculated as follows:$\%\,\text{Photostability} = 100 \times \left(\frac{\text{absorbance of irradiated sample}}{\text{absorbance of unirradiated sample}}\right)$

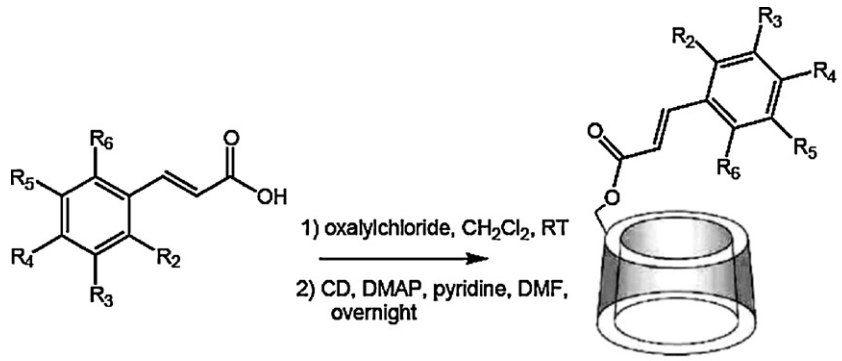
## 3. Results and discussion

### 3.1. Synthesis

Five cinnamoyl modified CDs, including 4-methoxycinnamoyl-α-cyclodextrin (**1**), 4-methoxycinnamoyl-β-cyclodextrin (**2**), 2,4,5-trimethoxycinnamoyl-β-cyclodextrin (**3**), 2,4,6-trimethoxycinnamoyl-β-cyclodextrin (**4**) and 2,4,6-trimethoxycinnamoyl-γ-cyclodextrin (**5**) were successfully obtained by esterification reaction between cinnamoyl chloride and cyclodextrin (Scheme 1) [16]. The crude products were easily purified by recrystallization in acetone (see the characterization details in Section 2). It has been known that the CDs' hydroxyl group at the 6-position is a primary hydroxyl group and the most basic (and often most nucleophilic) while the hydroxyl group at the 2-position is the most acidic, and that at the 3-position is the most inaccessible and under normal circumstances, an electrophilic reagent should be attacked from the 6-position of the hydroxyl group [16,17,21]. In this work, it was, thus, assumed that all esterification were localized at the 6-hydroxyl groups of the CDs [20–22].

### 3.2. UV absorption of cinnamoyl modified cyclodextrins

The absorption properties of all cinnamoyl modified CDs were similar to their parent cinnamic acids. The UVB (280–320 nm) absorption was observed in **1**, **2**, **4** and **5** while both UVA (320–400 nm) and UVB absorptions were detected in **3** (350 and 290 nm) (Fig. 2). The orientation of each cinnamoyl moiety could be interpreted from how the solvents affected its light absorption profile. The UV absorption spectra of **4** in 10% aqueous DMSO showed a slight red shift compared to that in the DMSO solution, suggesting that 2,4,6-trimethoxycinnamoyl moiety was outside the β-CD cavity, thus was stabilized by a more polar solvent (water). In contrast, the absorption of **1**, **2**, **3** and **5** in 10% aqueous DMSO showed a blue shift compared to those in the DMSO solution. As a result, it was speculated that these methoxycinnamoyl moieties were located inside the CD cavities which were of more hydrophobicity environment. In the case of **2**, the similarity between the absorption spectrum in DMSO and that in 10%DMSO suggested that the 4-




**1**; $R_2=R_3=R_5=R_6=H$, $R_4=OCH_3$, CD = α-CD
**2**; $R_2=R_3=R_5=R_6=H$, $R_4=OCH_3$, CD = β-CD
**3**; $R_2=R_4=R_5=OCH_3$, $R_3$, $R_6=H$, CD = β-CD
**4**; $R_2=R_4=R_6=OCH_3$, $R_3$, $R_5=H$, CD = β-CD
**5**; $R_2=R_4=R_6=OCH_3$, $R_3$, $R_5=H$, CD = γ-CD

**Scheme 1.** Synthesis pathway of **1**–**5**.

methoxycinnamoyl moiety probably kept moving in and out the β-CD cavity. This was because a large size of β-CD cavity did not fit to 4-methoxycinnamoyl moiety.

### 3.3. Photostability studies

Photostability of cinnamoyl moieties of the inclusion complexes was conducted in a 10% aqueous DMSO solution (Fig. 3). Compound **3** was more photostable than free 2,4,5-trimethoxycinnamic acid, thus, implying that the 2,4,5-trimethoxycinnamoyl moiety was inside the β-CD cavity. Compounds **1** and **5** were also more photostable than their corresponding free 4-methoxycinnamic acid and 2,4,6-trimethoxycinnamic acid, thus suggesting that both 4-methoxycinnamoyl moiety and 2,4,6-trimethoxycinnamoyl moiety in **1** and **5** were inside the α-CD cavity and γ-CD cavity, respectively. In contrast, the facts that no improvement was observed in **2** and **4** comparing to their corresponding free 4-methoxycinnamic acid and free 2,4,5-trimethoxycinnamic acid, implied that both 4-methoxycinnamoyl and 2,4,5-trimethoxycinnamoyl moieties in **2** and **4** were not in the β-CD cavity.

In addition to the use of photostability information to speculate the configuration of cinnamoyl moieties in compounds **1**–**5**, ROESY experiments were performed. The ROESY spectrum of 4-methoxy-cinnamoyl-α-CD (**1**), in a $D_2O$ solution, displayed clear NOE correlations between the H3 protons of α-CD and the $H_b/H_b'$ proton of 4-methoxycinnamoyl moiety (cross-peaks A), as well as between the H5 protons of α-CD and both $H_a/H_a'$ and $H_b/H_b'$ protons of the 4-methoxycinnamoyl moiety (cross-peaks C and B, Fig. 4a). These correlations indicated that the ring of 4-methoxycinnamoyl moiety entered the CD cavity (Fig. 4b), thus confirming the above conclusion which was drawn from the photostability information.

Because of the poor solubility in water of 4-methoxycinnamoyl-β-CD (**2**), the conformation could not be investigated by using the ROESY spectrum even in the presence of 10% DMSO.

The ROESY spectrum of **2** in DMSO-$d_6$ showed no appreciable NOE correlations between interior protons of the β-CD cavity and the protons of the 4-methoxycinnamoyl moiety, indicating that the 4-methoxy-cinnamoyl moiety was entirely located outside of the β-CD cavity. Thus the interaction in water could not be concluded with the present information. In fact, DMSO has been shown to act as a competing guest molecule and could decrease the formation of inclusion complexes through non-specific solvent effects [23].

The ROESY spectrum of 2,4,5-trimethoxy-cinnamoyl-β-CD (**3**) in a $D_2O$ solution (Fig. 5a) showed a NOE correlation between the H3 proton of β-CD and the $H_b$ proton of 2,4,5-trimethoxycinnamoyl moiety (cross-peak B). In the same way, cross-peak A was assigned

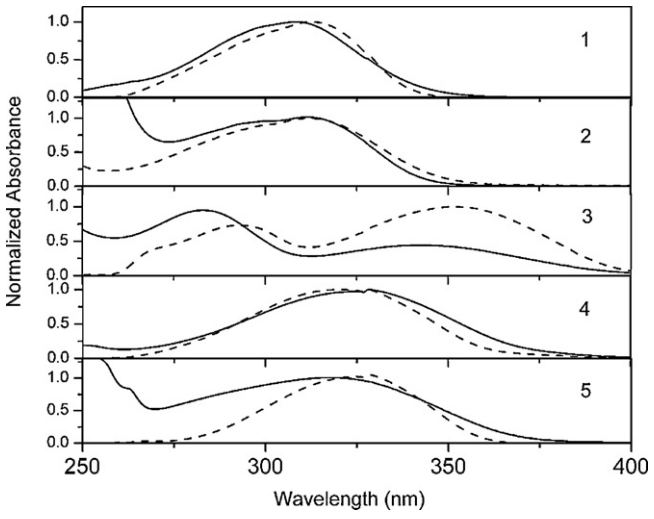



**Fig. 2.** Absorption spectrum of **1**–**5** ($1 \times 10^{-5}$ mM) in 10% DMSO (solid line) and DMSO (dashed line).

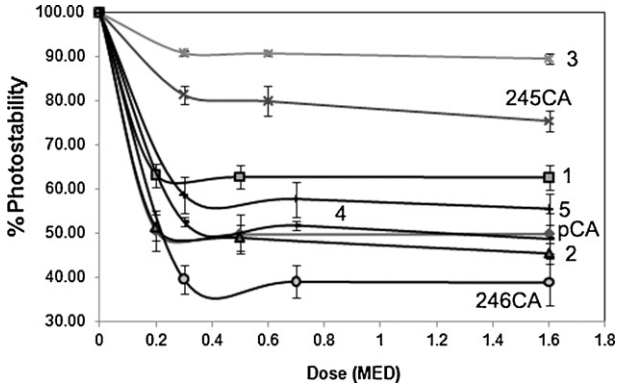



**Fig. 3.** Photostability of $1 \times 10^{-5}$ M **1**–**5** in a 10% DMSO solution compared to their parent cinnamic acids; pCA = 4-methoxycinnamic acid, 245CA = 2,4,5-trimethoxycinnamic acid and 246CA = 2,4,6-trimethoxycinnamic acid.

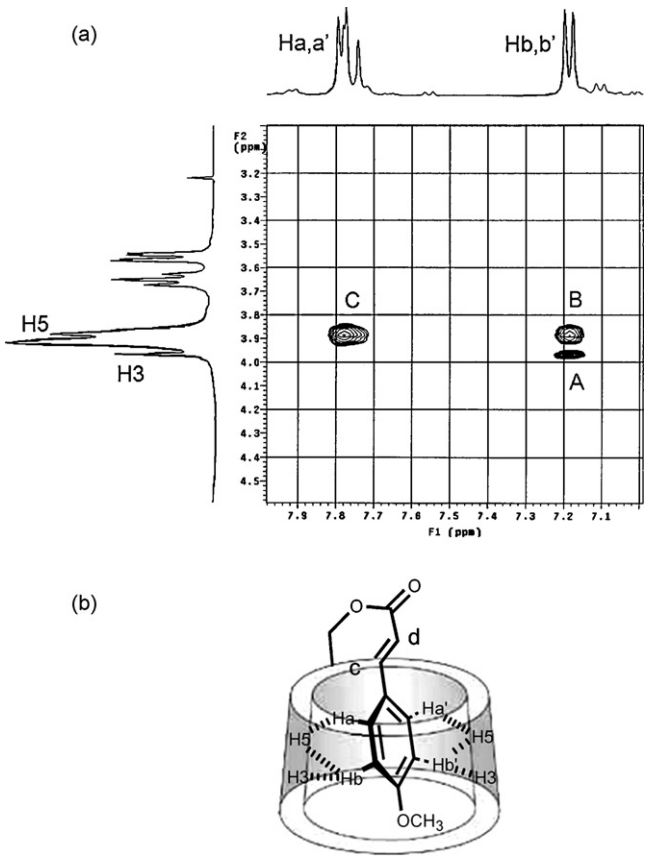



**Fig. 4.** (a) $^1$H ROESY spectrum of **1** (0.03 mM) in a 10% DMSO-$d_6$-$D_2O$ solution at 27 °C with a mixing time of 800 ms. (b) Possible structure of **1**.

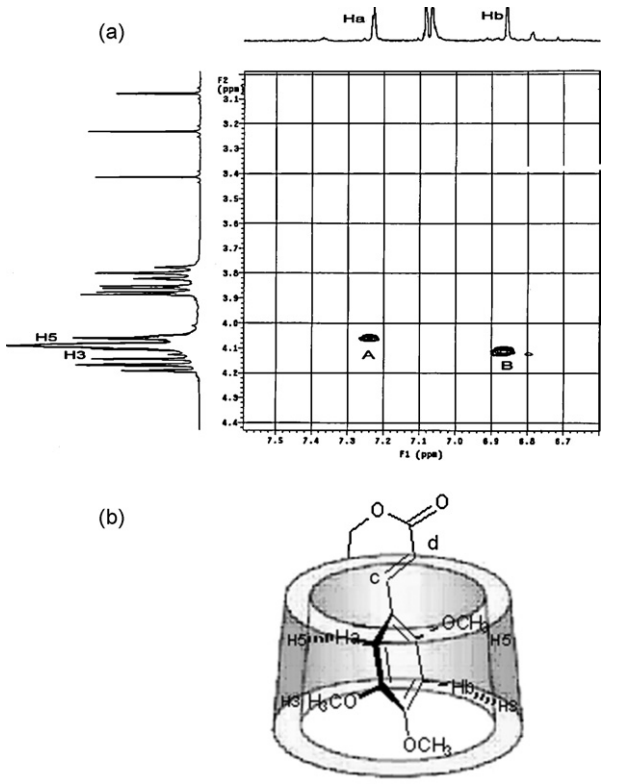



**Fig. 5.** (a) $^1$H ROESY spectrum of **3** (0.03 mM) in a $D_2O$ solution at 27 °C with a mixing time of 800 ms. (b) Possible structure of **3**.

to the intermolecular NOE correlation between the H5 proton of β-CD and the $H_a$ proton of 2,4,5-trimethoxycinnamoylmoiety. This indicated a good intramolecular inclusion complexation (Fig. 5b).

The concentration dependent of NMR was studied for **3** in $D_2O$ (Fig. 6). The upfield shift of all cinnamoyl protons were detected over the range of the concentrations tested. This result indicated that an intermolecular complexation *via* the cinnamoyl group could be formed at higher concentrations [24,25]. The concentration dependence NMR experiments of **1** and **3** were also investigated in DMSO-$d_6$ at even higher concentrations (due to a better solubility of the materials in DMSO, see supporting information, Figs. S18–19). The upfield shift of all cinnamoyl protons and the broad-

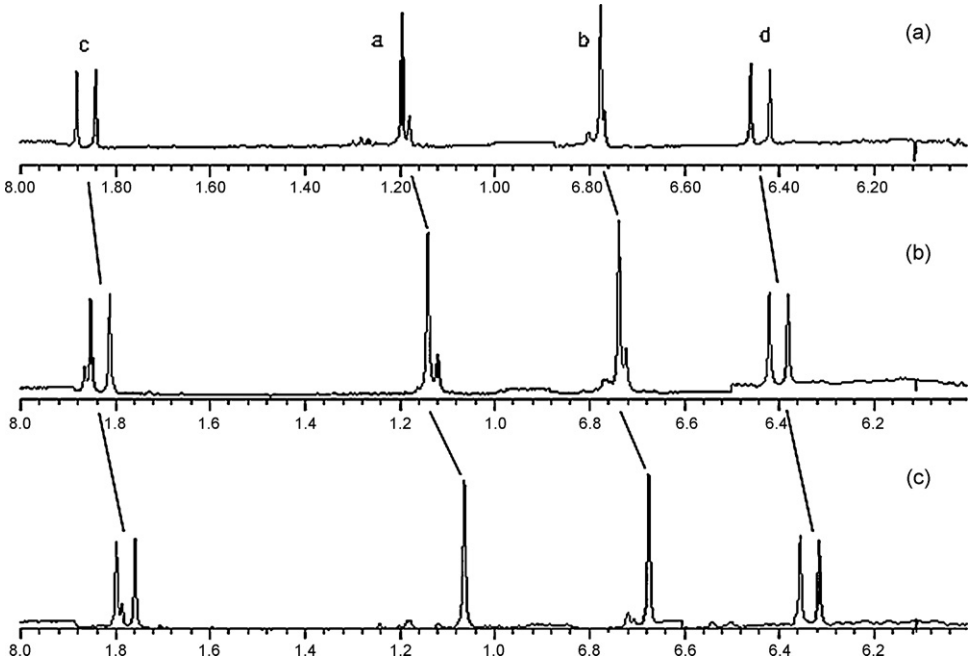



**Fig. 6.** $^1$H NMR spectra of **3**: (a) 0.07 (b) 0.15 and (c) 0.2 mM in 10% DMSO-$d_6$-$D_2O$ 27 °C.

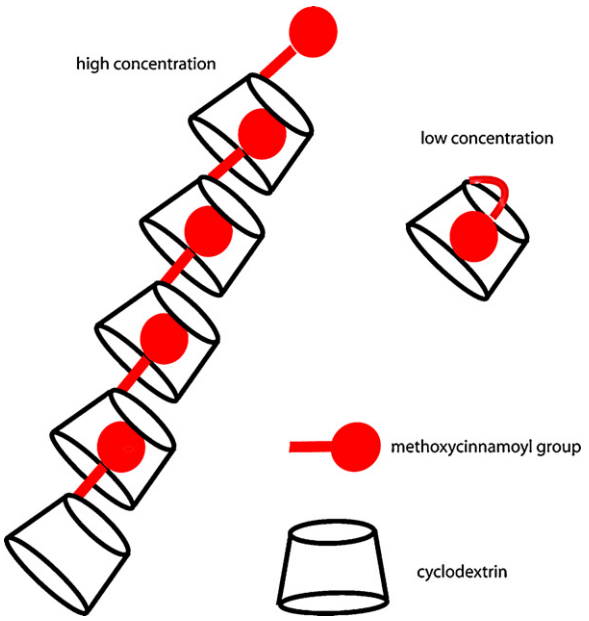



**Fig. 7.** Proposed structure of supramolecular structured of **1** and **3**.

ening of resonance peaks of CD protons were clearly observed over the range of the concentrations tested. This result indicated the formation of some intermolecular complexes or polymers in DMSO solution (Fig. 7). In fact, this intermolecular complexation has been proposed for 6-aminocinnamoyl-α-CD in aqueous solution [20].

However, the 2,4,6-trimethoxycinnamoyl-β-cyclodextrin (**4**) showed a particular NOE correlation (cross-peak A) between the $H_a$ and $H_{a'}$ protons of 2,4,6-trimethoxycinnamoyl moiety and the H5 proton of β-CD in an aqueous solution (Fig. 8a). This result suggested that only half of the aromatic ring of 2,4,6-trimethoxycinnamoyl moiety was inside the β-CD cavity (Fig. 8b). A simple calculation by semi-empirical AM1 indicated that the distance between the two methoxy substituents of 2,4,6-trimethoxycinnamoyl moiety (8.30 Å) was larger than the cavity size of β-CD. This explained why the whole cinnamoyl moiety could not fit into the β-CD cavity. In the case of 2,4,6-trimethoxycinnamoyl-γ-CD (**5**), 10% DMSO-$d_6$ was added to the $D_2O$ suspension due to its poor solubility. The ROESY of **5** in 10% DMSO-$d_6$-$D_2O$ showed no appreciable NOE correlation between the interior protons of the γ-CD cavity and the protons of the 2,4,6-trimethoxycinnamoyl moiety, suggesting poor inclusion complexation. However, it should be kept in mind that the spectrum was taken in a 10% DMSO-$d_6$-$D_2O$ mixture. The concentration dependence $^1$H NMR of **5** in 10% DMSO-$d_6$-$D_2O$ showed no change over the range of the concentrations tested, thus, indicating that **5** did not undergo any intermolecular complexation [24].

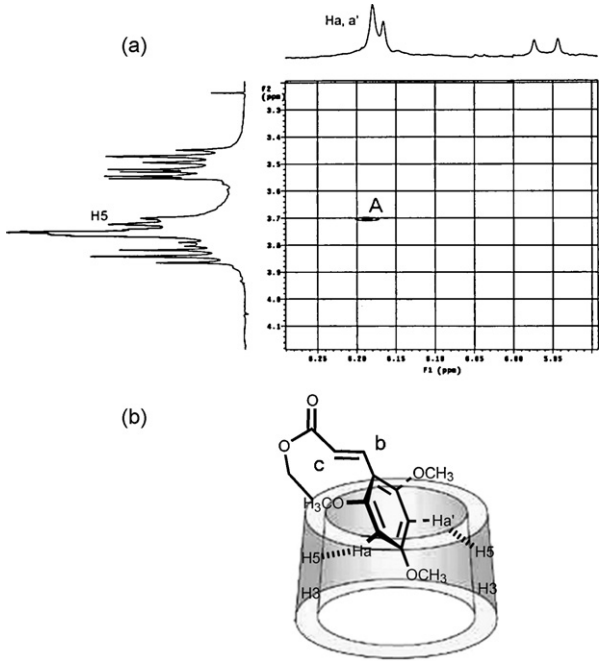



**Fig. 8.** (a) $^1$H ROESY spectrum of **4** (0.03 mM) in a $D_2O$ solution at 27 °C with a mixing time of 800 ms. (b) Possible structure of **4**.

Characterization of the complexes in a solid state by DSC showed that upon forming the inclusion complexes with CDs, the methoxycinnamic acids melting peak disappeared, suggesting no free methoxycinnamic acid remained in the products. On the contrary, a broad peak near 250 °C was prominent in the thermograms due to the cinnamoyl modified cyclodextrins melting.

## 4. Conclusion

Five modified CDs with different methoxycinnamoyl moieties (**1**–**5**) were synthesized in moderate yield. Their conformations were investigated by spectroscopic techniques. A photostability study of methoxycinnamoyl moieties attached to the cyclodextrins indicated that size matching played an important role in the molecular recognition process of the methoxy cinnamoyl modified cyclodextrins. In other words, the smallest 4-methoxycinnamoyl moiety was more photostable in the small α-CD cavity, while the largest 2,4,6-trimethoxy cinnamoyl was more photostable in the large γ-CD cavity. The 2,4,5-trimethoxycinnamoyl moiety best fitted into the moderate size of the β-CD cavity. Inclusion complexation could improve photostability of the cinnamoyl moieties in an aqueous solution. Moreover, these complexes have been evaluated for safety by using human cancer cells (see the result in supporting information). The results indicated that methoxycinnamoyl modified cyclodextrins are not cytotoxic compared to their parent methoxycinnamic acids and shows promise to be applied in cosmetic technology.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.03.016.

## References

[1] Y. Matsumura, H.N. Ananthaswamy, Toxic effects of ultraviolet radiation on the skin, Toxicol. Appl. Pharm. 195 (2004) 298–3082.
[2] N.S. Agar, G.M. Halliday, R.S. Barnetson, H.N. Ananthaswamy, M. Wheeler, A.M. Jones, The basal layer in human squamous tumors harbors more UVA than UVB fingerprint mutations: a role for UVA in human skin carcinogenesis, Proc. Natl. Acad. Sci. U.S.A. 101 (2004) 4954–4959.
[3] H.M. Chawla, S. Mrig, Simultaneous quantitative estimation of oxybenzone and 2-ethylhexyl-4-methoxycinnamate in sunscreen formulations by second order derivative spectrophotometry, J. Anal. Chem. 64 (2009) 585–592.

[4] M. Centini, M. Maggiore, M. Casolaro, M. Andreassi, R.M. Facino, C.J. Anselmi, Cyclodextrins as cosmetic delivery systems, Incl. Phenom. Macrocycl. Chem. 57 (2007) 109–112.
[5] S. Pattanaargson, N. Hongchinnagorn, P. Hirunsupachot, Y. Sritana-anant, UV absorption and photoisomerization of *p*-methoxycinnamate grafted silicone, Photochem. Photobiol. 80 (2004) 322–325.
[6] S. Sasiwilaskorn, P. Klinubol, A. Tachaprutinun, T. Udomsup, S.P. Wanichwecharungruang, Oligoesters based on poly(p-alkoxycinnamate) and poly(pentaethylene glycol cinnamate) as potential UV filters, J. Appl. Polym. Sci. 109 (2008) 3502–3510.
[7] C. Luadthong, A. Tachaprutinun, S.P. Wanichwecharungruang, Synthesis and characterization of micro/nanoparticles of poly(vinylalcohol-co-vinylcinnamate) derivatives, Eur. Polym. J. 44 (2008) 1285–1295.
[8] P. Klinubol, P. Asawanonda, S.P. Wanichwecharungruang, Transdermal penetration of UV filters, Skin Pharmacol. Physiol. 21 (2008) 23–29.
[9] T. Monhaphol, B. Albinsson, S.P. Wanichwecharungruang, 2-Ethylhexyl-2,4,5-trimethoxycinnamate and di-(2-ethylhexyl)-2,4,5-trimethoxybenzalmalonate as novel broadband UV filters, J. Pharm. Pharmacol. 59 (2007) 279–288.
[10] S. Scalia, A. Molinari, A. Casolari, A. Maldotti, Complexation of the sunscreen agent, phenylbenzimidazole sulphonic acid with cyclodextrins: effect on stability and photo-induced free radical formation, Eur. J. Pharm. Sci. 22 (2004) 241–249.
[11] V. Saraveiya, J.F. Templeton, H.A.E. Benson, Inclusion complexation of the sunscreen 2-hydroxy-4-methoxy benzophenone (oxybenzone) with hydroxypropyl-β-cyclodextrin: effect on membrane diffusion, J. Incl. Phenom. Macro. Chem. 49 (2004) 275–281.
[12] E. Fenyvesi, K. Otta, I. Kolbe, Cs. Nova, J. Szejtli, Cyclodextrin complexes of UV filters, J. Incl. Phenom. Macro. Chem. 48 (2004) 117–123.
[13] S. Scalia, A. Casolari, A. Iaconinoto, S. Simeoni, Comparative studies of the influence of cyclodextrins on the stability of the sunscreen agent, 2-ethylhexyl-4-methoxycinnamate, J. Pharm. Biomed. Anal. 30 (2002) 1181–1189.
[14] C. Anselmi, M. Centini, M. Maggiore, N. Gaggelli, M. Andreassi, A. Buonocore, G. Beretta, R.M. Facino, Non-covalent inclusion of ferulic acid with alpha-cyclodextrin improves photo-stability and delivery: NMR and modeling studies, J. Pharm. Biomed. Anal. 46 (2008) 645–652.
[15] M. Centini, M. Maggiore, M. Casolaro, M. Andreassi, R.M. Facino, C. Anselmi, Cyclodextrins as cosmetic delivery systems, J. Incl. Macrocyclic. Chem. 57 (2007) 109–112.
[16] W.-K. Chan, W.-Y. Yu, C.-M. Che, M.K. Wong, A cyclodextrin-modified ketoester for stereoselective epoxidation of alkenes, J. Org. Chem. 68 (2003) 6576–6582.
[17] Y. Lui, Y.-L. Zhao, H.-Y. Zhang, Z. Fan, G.-D. Wen, F. Ding, Spectrophotometric study of inclusion complexation of aliphatic alcohols by β-cyclodextrins with azobenzene tether, J. Phys. Chem. B 108 (2004) 8836–8843.
[18] R.J. Coulston, H. Onagi, S.F. Lincoln, C.J. Easton, Harnessing the energy of molecular recognition in a nanomachine having a photochemical on/off switch, J. Am. Chem. Soc. 128 (2006) 14750–14751.
[19] J. Koo, M.S. Fish, G.N. Walker, J. Blake, 2,3-Dimethoxycinnamic acid, Org. Syn. Coll. 4 (1944) 327–328.
[20] M. Miyauchi, T. Hoshino, H. Yamaguchi, S. Kamitori, A. Harada, A [2]rotaxane capped by a cyclodextrin and a guest: formation of supramolecular [2]rotaxane polymer, J. Am. Chem. Soc. 126 (2005) 2034–2035.
[21] R.K. Abdul, F. Peter, J.S. Keith, T.D. Valerian, Methods for selective modifications of cyclodextrins, Chem. Rev. 98 (1998) 1977–1996.
[22] Y. Liu, Z.-X. Yang, Y. Chen, Syntheses and self-assembly behaviors of the azobenzenyl modified-cyclodextrins isomers, J. Org. Chem. 73 (2008) 5298–5304.
[23] T. Shikata, R. Takahashi, T. Onji, Y. Satokawa, A. Harada, Solvation and dynamic behavior of cyclodextrins in dimethyl sulfoxide solution, J. Phys. Chem. B 110 (2006) 18112–18114.
[24] M. Miyauchi, A. Harada, Construction of supramolecular polymers with alternating a-, b-cyclodextrin units using conformational change induced by competitive guests, J. Am. Chem. Soc. 126 (2004) 11418–11419.
[25] T. Hoshino, M. Miyauchi, Y. Kawaguchi, H. Yamaguchi, A. Harada, Daisy chain necklace: tris[2]rotaxane containing cyclodextrins, J. Am. Chem. Soc. 122 (2000) 9876–9877.