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Fluorescent Pyrrolinone-modified Cyclodextrins as a Chemo-sensor for Organic Guests

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Abstract. Fluorescent pyrrolinone-modified β- and γ-cyclodextrins (β-1 and γ-1, respectively) have been synthesized as a fluorescent chemo-sensor for organic compounds such as terpenoids and bile acids. The host compounds show a pure monomer fluorescence around 472 nm, the intensity of which decreased when 1-adamantanecarboxylic acid, *p*-aminobenzoic acid, benzoic acid, phthalic acid or cyclohexanecarboxylic acid were used as a guest in an aqueous solution of pH 5.90. On the other hand, in Menzel buffer solution of pH 9.09, the fluorescent intensity is increased by accommodation of these guest molecules. The increase was seen with other guests such as terpenoids, amino compounds and sodium bile acid salts in a Menzel buffer solution. The extent of fluorescence variation with a guest is employed to display the chemo-sensor ability of these hosts. The sensing parameter ($\Delta I/I^0$) was used to show the sensing ability of those hosts. Hosts β-1 and γ-1 exhibit higher sensing ability for amines in a host solution of pH 5.90 than those in a host solution of Menzel buffer. It is probably caused by some hydrogen bonding between the carboxylic anion of the hosts and quaternary ammonium type guests.

Key words: modified cyclodextrin, chemo-sensor, hydrogen bonding, sodium bile acid salt.

1. Introduction

Cyclodextrins are torus-shaped cyclic oligomers of D-glucopyranose, which can accommodate a variety of guests in their cavity and have attracted much interest as model compounds for studies of enzymes. The modification of cyclodextrins with chromophores has aroused considerable interest because the modification can be expected to improve or alter their host-guest properties [1]. The fluorescent active cyclodextrins have recently received increasing attention because these compounds exhibit fluorescent sensor abilities for organic guest [2]. Recently, we reported a fluorescent host-guest sensing system using cyclodextrins modified with a fluorescent moiety [3]. Fluorescamine has been introduced as a novel reagent which reacts almost instantaneously with primary amino compounds to give highly fluorescent pyrrolinone [4]. Many biologically active peptides, including oxytocin, vasopressin, bradykinin, angiotensin, substance P, insulin, and glucagon, yield highly fluorescent derivatives with fluorescamine. The modification of cyclodextrin

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with fluorescamine can lead to a good receptor, in which the fluorescent pyrrolinone moiety can act as a fluorescent probe and as a hydrophobic cap to elevate the guest-binding ability of the cyclodextrins. For further extension of our fluorescent sensor system of modified cyclodextrin analogues, we would like to report the chemo-sensor ability of the titled compounds. β- and γ-Cyclodextrins capped by fluorescamine (β-1 and γ-1, respectively) were prepared and the ability of a fluorescent host-guest sensing system of these host molecules in an aqueous solution was studied.

2. Experimental

2.1. PREPARATIONS OF PYRROLINONE-MODIFIED β- AND γ-CYCLODEXTRIN ANALOGUES (β-1 AND γ-1, RESPECTIVELY)

Amino β-cyclodextrin (340 mg, 0.30 mM) and 100 mg of fluorescamine (0.36 mM) was added to a mixture of 10 mL of DMF and 3 mL of pyridine, and the reaction mixture was stirred at 50 °C for 1 h under a nitrogen atmosphere. The mixture was evaporated in vacuo to give an oily material, which was poured into 300 mL of ethylacetate. The resulting precipitates were filtered and dried. The crude product was dissolved in a small amount of water, which was chromatographed on a CM-Sephadex C-50 column (2 $\times$ 80 cm) eluted with water. The fractions containing β-1 were collected and evaporated in vacuo to give an oily material, which was poured into acetone. The resulting precipitates were rechromatographed on Sephadex G-15 (3 $\times$ 110 cm) eluted with water. The fractions indicating 0.5 Rf value on TLC plate (1-butanol : ethanol : water 5 : 4 : 3 by volume), were collected and evaporated in vacuo to afford 0.107 g (25.3% isolated yield) of pure β-1. ^{1}H-NMR (DMSO-d_6) = 8.67 (1H, s, –COOH), 8.00-7.90 (1H, m, aromatic-H), 7.66 (2H, t, J = 9, 2Hz, aromatic-H), 7.30-7.20 (3H, m, aromatic-H), 7.18-6.90 (3H, m, aromatic-H), 6.20-5.40 (15H, m, O_2H, O_3H of cyclodextrin and methine proton of pyrrolinone), 5.20-5.40 (12H, m, O_6H, C_1H of cyclodextrin), 4.00-3.00 (42H, m, C_2–C_6H of cyclodextrin). Calcd. for $C_{59}H_{81}0_{38}N \cdot 10H_2O$: C, 44.50; H, 6.39; N, 0.88%. Found C, 44.35; H, 6.03; N, 0.86%. MS(FAB): 1434 ([M + Na]$^+$). Compound γ-1 was prepared by the same procedure. The crude product of γ-1 was applied to a reversed-phase column (S-343-15S). After stepwise elution from 100 mL of 10 vol.-% aqueous MeOH, 200 mL of 20 vol.-% and 800 mL of 30 vol.-% aqueous MeOH was applied to give pure γ-1. Yield: 38.9%. Rf 0.49 (1-butanol:ethanol: water 5 : 4 : 3 by volume). ^{1}H-NMR (DMSO-d_6) = 8.67 (1H, s, –COOH), 8.00-7.80 (1H, m, aromatic-H), 7.74-7.57 (2H, m, aromatic-H), 7.40-7.00 (6H, m, aromatic-H), 6.20-5.20 (17H, m, O_2H, O_3H of cyclodextrin and methine proton of pyrrolinone), 5.05-3.95 (15H, m, O_6H, C_1H of cyclodextrin), 3.90-3.00 (48H, m, C_2-C_6H of cyclodextrin). Calcd. for $C_{65}H_{91}0_{43}N \cdot 10H_2O$: C, 44.49 H, 6.38; N, 0.80%. Found C, 44.61; H, 6.22; N,0.79%. MS(FAB): 1596 ([M + Na]$^+$).

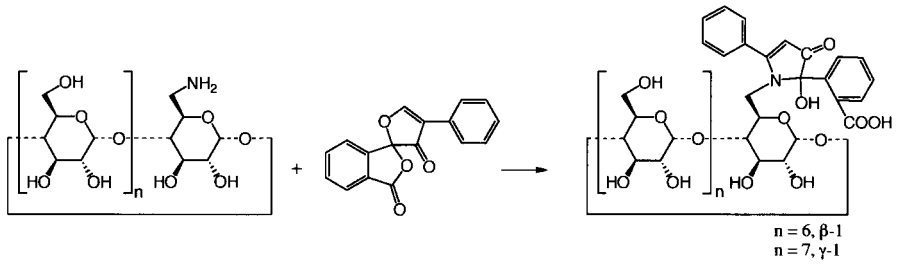


Figure 1. Preparations of β-1 and γ-1.

2.2. MEASUREMENT

Fluorescence, circular dichroism, and ultraviolet spectra were measured at 25 °C, with a Perkin Elmer LS 40B fluorescence spectrometer, a JASCO J-700 spectropolarimeter, and a Perkin Elmer Lambda 40 UV/VIS spectrophotometer, respectively. For the fluorescence measurements, the excitation wavelength of the fluorescence spectra was 382 nm and excitation and emission slits were 5 nm. Five microliters of guest species (0.5 and 0.05 M) in dimethyl sulfoxide (DMSO) or MeOH were injected into an aqueous solution of β-1 and γ-1 (2.5 mL) to make a sample solution with a host concentration of 2×10^{-6} M and a guest concentration of 0.1 and 1.0 mM, respectively. Carbonate buffer of pH 9.09 and distilled water (pH 5.90) were used as a solvent for β-1 and γ-1.

3. Results and Discussion

Hosts β-1 and γ-1 were prepared from amino β- and γ-cyclodextrins with excess of fluorescamine in DMF containing pyridine at 50 °C as shown in Figure 1. Fluorescamine reacts with primary amines to form fluorescence active pyrrolinone which upon excitation at 390 nm emits strong fluorescence at 475–490 nm [4]. The ^{1}H-NMR and elemental analyses supported the structures of β-1 and γ-1. Figure 2 shows fluorescence spectra of β-1 in an aqueous solution at pH 5.90, with and without sodium hyodeoxycholate. The spectrum of β-1, alone, exhibits a fluorescence peak at 475 nm, the intensity of which increases with increasing sodium hyodeoxycholate concentration. The fluorescence spectra of γ-1, alone or in the presence of sodium ursodeoxycholate show an almost similar pattern to those of β-1 in an aqueous solution at pH 5.90 with and without the guest molecule. The guest-induced fluorescence change suggests a movement of the appended moiety into a different polarity environment [5].

Upon the binding of a guest to a host site, a signal associated with the probe may change in response to direct interaction of the host molecule. To clarify the behavior of the host, induced circular dichroism (ICD) spectra of β-1 and γ-1 were recorded in an aqueous solution at pH 5.90, because an increase of ICD spectra is ascribed to the formation of a complex between achiral pyrrolinone and a chiral

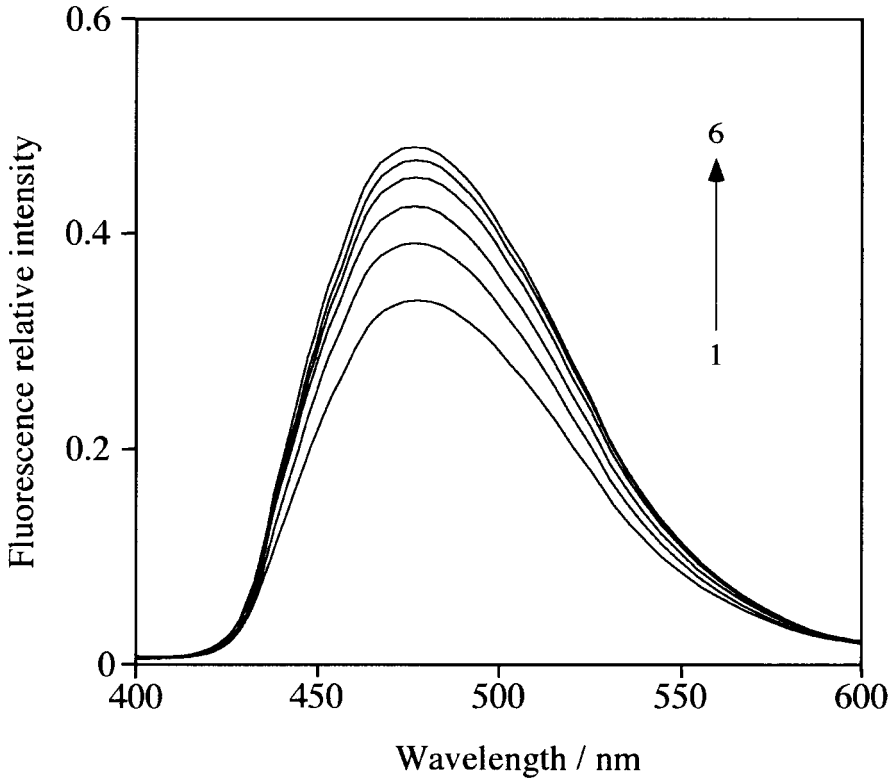


Figure 2. Fluorescence spectra of β-1 in aqueous solution (2.0×10^{-6} M, pH 5.90, 25 °C) at various concentration of sodium hyodeoxycholate (1: 0, 2: 4.0×10^{-6}, 3: 6.0×10^{-6}, 4: 1.0×10^{-5}, 5: 2.0×10^{-5}, 6: 8.0×10^{-5} M).

cyclodextrin [6]. The ICD spectra of β-1 show a negative band at around 280 nm and a positive band at around 380 nm, as shown in Figure 3. When sodium hyodeoxycholate was added as a guest, a guest-induced increase of the ICD bands in the 280 and 380 nm regions was observed. This suggests that the pyrrolinone moiety comes close to the interior of the hydrophobic cyclodextrin cavity from the outside bulk water environment when simultaneously a guest is included in the cyclodextrin cavity [7]. The ICD spectral pattern of γ-1 are almost similar to those of β-1 without the intensity of $[\theta]$. This suggests that the appended moiety is closer to or included in the cyclodextrin cavity because of the larger cyclodextrin cavity than that of β-cyclodextrin.

The extent of variation of the fluorescence intensity of β-1 and γ-1 with a guest is different when a different guest is used, even at the same concentration. Since the fluorescence intensity of modified cyclodextrins is affected by the presence of guest molecules, they can be used as fluorescence sensors of molecules. To calculate the sensing abilities of β-1 and γ-1, the $\Delta I/I^0$ value was used as the sensitivity factor [7]. Here ΔI is $I\text{-}I^0$, where I^0 is the fluorescence intensity of the host alone at 477

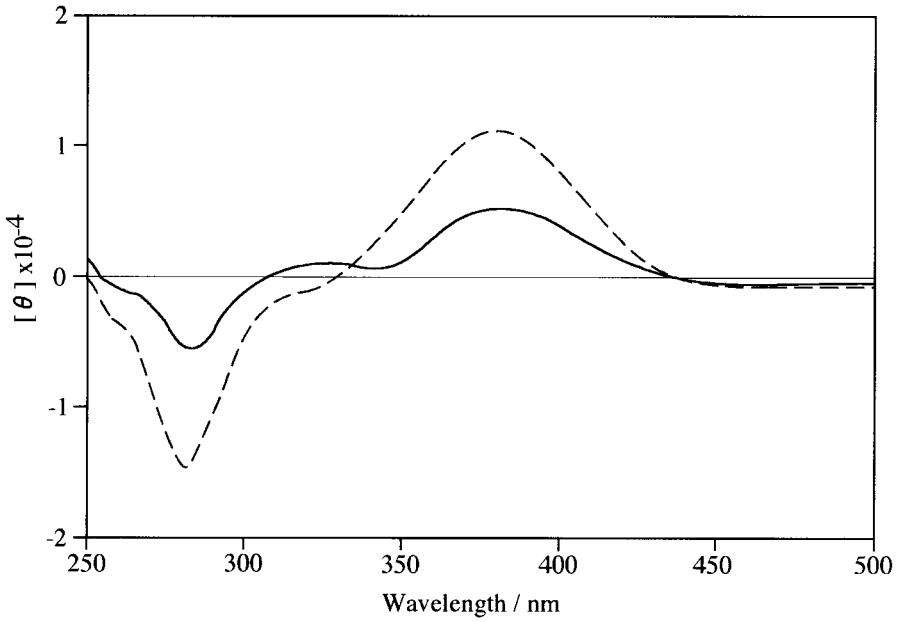
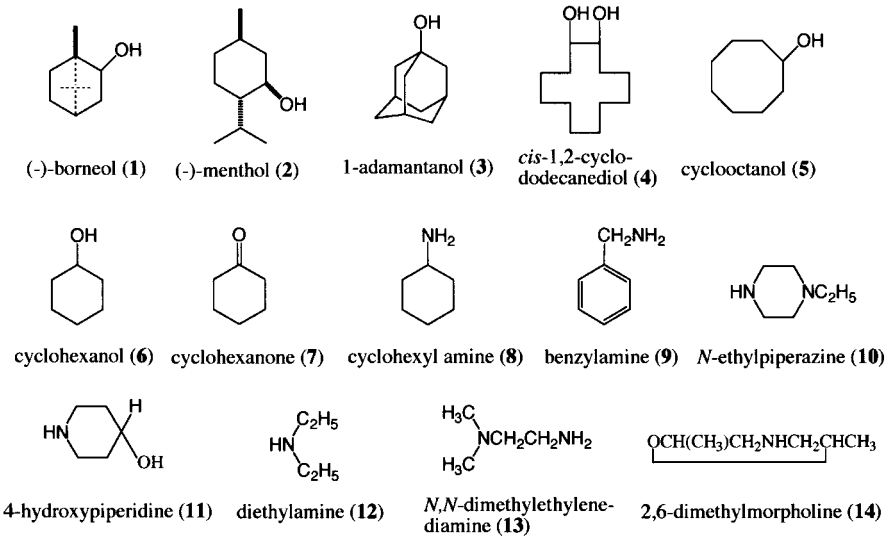
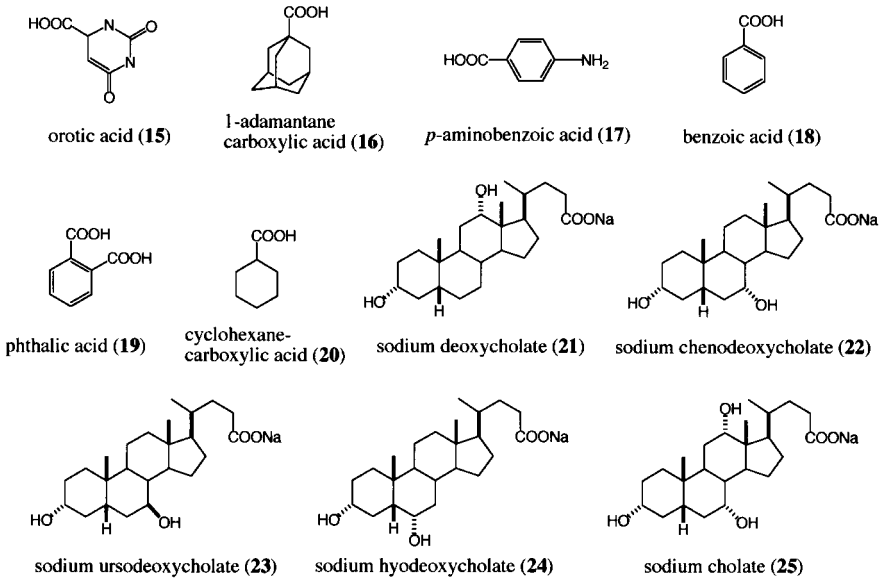


Figure 3. Induced circular dichroism spectra of β-1 in aqueous solution (10^{-4} M: —-, pH 5.90, 25 °C) and containing sodium hyodeoxycholate (10^{-4} M: – –).

nm, and I is a mixture of a host and a guest. The $\Delta I/I^0$ values of β-1 and γ-1 in an aqueous solution at pH 5.90 and pH 9.09 obtained with 25 guests are summarized in Table 1. Small guests such as terpenoids or amino derivatives (guests **1** to **20**) were added at 1.0 mM. Because of the poor solubility in pure water, bile acids (guests **21** to **25**) were examined at 0.1 mM. Some of the results are shown in Figures 4 and 5. Figure 4 show the $\Delta I/I^0$ values obtained from β-1 and γ-1 in an aqueous solution at pH 5.90 or 9.09 at the guest concentration of 1.0 mM (guests **1** to **20**). The sensing behaviors of β-1 and γ-1 at pH 5.90 and 9.09 are not the same. Those hosts show almost the same sensing ability for neutral guests such as (-)-borneol (**1**), (-)-menthol (**2**), 1-adamantanol (**3**), and cyclohexanol (**6**), but in a host solution of pH 5.90, β-1 and γ-1 detect amine with a higher ability than in a Menzel buffer solution of pH 9.09. When 1.0 mM of cyclohexylamine was added to these host solutions of pH 5.90, the pH value changed to 10.62. It is suggested that the structure of the appended moiety of the cyclodextrin was ionized to a carboxylic anion type. The higher binding ability of β-1 and γ-1 for amines at pH 10.62 could be ascribed to the effect of the hydrogen bonding between the carboxylic acid anion of these hosts and a quaternary ammonium type guest, which leads to deep inclusion of the amino guest in the cyclodextrin cavity, as shown in Scheme 2. Host β-1 detects amine with a much higher sensitivity than γ-1. It seems that the cavity size of β-1 fits with these amino guests better than that of γ-1. The absorption spectra of β-1 with or without cyclohexylamine are shown in Figure



Scheme 1.1. Guest molecules (**1**–**14**).



Scheme 1.2. Guest molecules (**15**–**25**).

6. Isosbestic points are observed at 345 nm, 280 nm and 240 nm. A computer simulation using the absorption intensity as a function of guest concentration fitted the Benesi-Hildebrand equation for 1 : 1 type complexing, giving evidence for a 1 : 1 complex formation of the host.

Hosts β-1 and γ-1 also display different binding patterns for carboxylic acids such as 1-adamantanecarboxylic acid (**16**), *p*-aminobenzoic acid (**17**), benzoic acid

Table I. $\Delta I/I^0$ Values for β-1 and γ-1 in aqueous solution (2.0×10^{-6} M, 25°C) at pH 5.90 and 9.09 for all guests examined.

Guest	β-1		γ-1	
	pH 5.90	pH 9.09	pH 5.90	pH 9.09
(−)-borneol (**1**)	0.160	0.134	0.176	0.178
(−)-menthol (**2**)	0.251	0.281	0.052	0.038
1-adamantanol (**3**)	0.114	0.211	0.000	0.072
cis-1,2-cyclododecanediol (**4**)	−0.004	−0.004	0.040	0.034
Cyclooctanol (**5**)	0.060	0.069	0.034	0.046
Cyclohexanol (**6**)	0.053	0.106	0.027	−0.002
Cyclohexanone (**7**)	0.102	0.154	0.148	0.114
cyclohexylamine (**8**)	0.230	0.025	0.063	0.027
Cenzylamine (**9**)	0.117	0.031	0.063	0.008
N-ethylpiperazine (**10**)	0.075	0.028	0.029	0.008
4-hydroxypiperidine (**11**)	0.065	0.032	0.086	0.048
Diethyamine (**12**)	0.094	0.030	0.082	0.018
N,*N*-dimethylethylenediamine (**13**)	0.094	0.007	−0.007	0.009
2,6-dimethylmorpholine (**14**)	0.059	0.032	0.039	0.012
Orotic acid (**15**)	0.008	0.035	0.000	0.019
1-adamantanecarboxylic acid (**16**)	−0.140	0.201	−0.030	0.004
p-aminobenzoic acid (**17**)	−0.160	0.224	−0.083	0.003
Benzoic acid (**18**)	−0.277	0.004	−0.076	0.020
Phthalic acid (**19**)	−0.324	0.002	−0.123	0.013
Cyclohexanecarboxylic acid (**20**)	−0.253	0.054	−0.078	0.010
Sodium deoxycholate (**21**)	0.065	0.103	0.137	0.100
Sodium chenodeoxycholate (**22**)	0.327	0.361	0.373	0.413
Sodium ursodeoxycholate (**23**)	0.398	0.442	0.632	0.587
Sodium hyodeoxycholate (**24**)	0.441	0.453	0.846	0.656
Sodium cholate (**25**)	0.032	0.089	0.059	0.032

(**18**), phthalic acid (**19**), and cyclohexanecarboxylic acid (**20**) at a different pH. When these hosts are in a solution of pH 5.90, acidic guests are detected with negative parameter values, indicating that the pyrrolinone moiety of the cyclodextrin moves out from the cyclodextrin cavity, whereas in buffer solution of pH 9.09, β-1 and γ-1 show positive parameter values for these guests, in which the appended moiety is getting closer to the cyclodextrin cavity upon guest addition. It seems that the binding mechanism of these hosts in the acidic or alkaline solutions are different. When used in a Menzel buffer solution, a guest could be present as the sodium salt, which is much more hydrophilic than that of the free acid, the appended moiety is also the sodium salt. In this case, the host-guest binding behavior

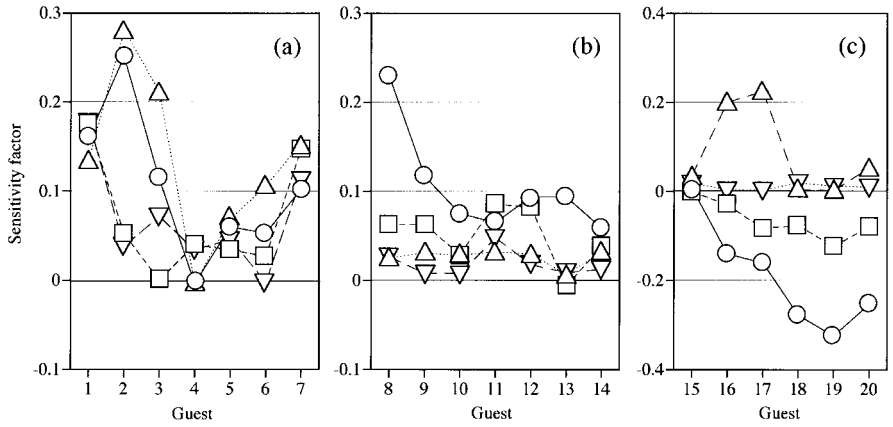
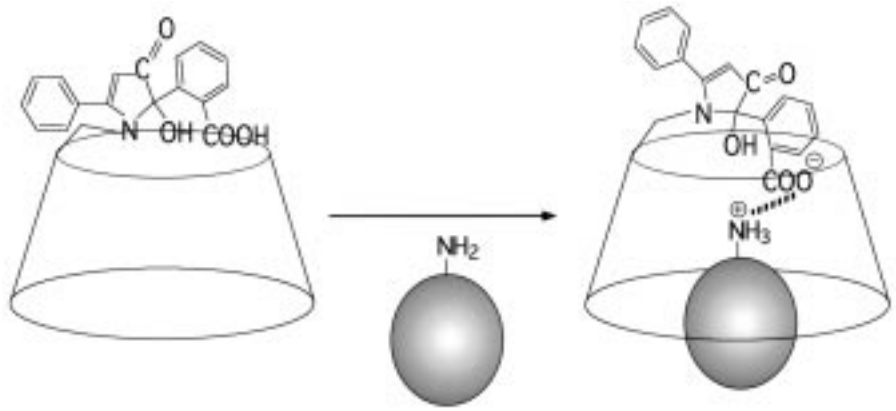


Figure 4. Sensitivity factors of β-1 in aqueous solution (pH 5.90: —○—, pH 9.09: - - -△ - - -) and γ-1 (pH 5.90: - - -□- - -, pH 9.09: - -▽- -) at 25 °C for small guests examined (a: guests 1–7, b: guests 8–14, c: guests 15–20).



Scheme 2. Host–guest complex formation of the carboxylic acid anion of β-1 with the quaternary ammonium type of the guest via the hydrogen bonding.

is different from that of the acidic solution because of its hydrophilicity. When an acidic guest such as cyclohexylcarboxylic acid was added to a host solution of pH 5.90, the pH value was 3.97. Scheme 3 shows host-guest binding behavior between quaternary ammonium type of appended moiety of the cyclodextrin and the carboxylic acid moiety of the guest. In this case, the appended moiety moves out from the cavity easily by accommodation with a guest because the hydrophobic interaction between the polarized appended moiety and cyclodextrin cavity is decreased. The absorption spectra of β-1 in a solution at pH 5.90 with or without cyclohexylcarboxylic acid are shown in Figure 7. Isosbestic points are observed at 410 nm and 260 nm. The spectral pattern is different from that when amine was used as a guest (Figure 6). It is clearly indicated that the host-guest binding

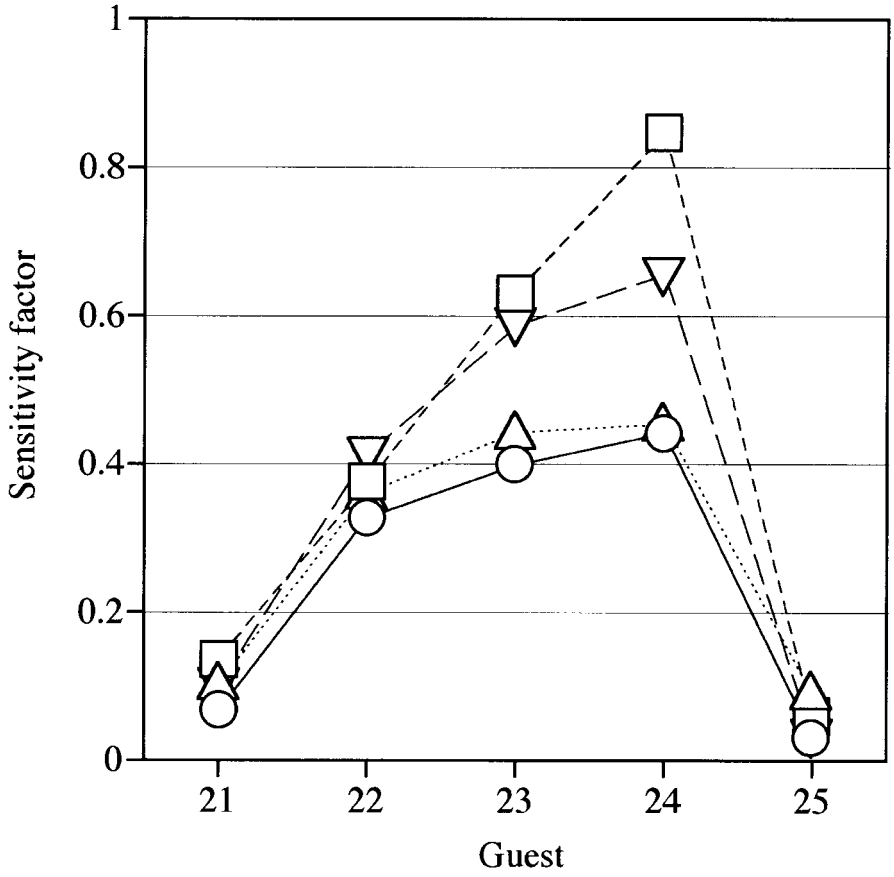


Figure 5. Sensitivity factors of β-1 in aqueous solution (pH 5.90: —○—, pH 9.09: - - -△- - -) and γ-1 (pH 5.90: - - -□- - -, pH 9.09: - -▽- -) at 25 °C for large guests examined.

mechanisms are different between amine and carboxylic acid guests in an acidic solution.

Figure 5 shows the sensitivity parameter for bile acid sodium salts, such as sodium deoxycholate (**21**), sodium chenodeoxycholate (**22**), sodium ursodeoxycholate (**23**), sodium hyodeoxycholate (**24**), and sodium cholate (**25**). All parameters obtained from these guests are positive, which means the appended moiety comes close to the cyclodextrin cavity upon guest addition. In the case of γ-1, these guests, except for sodium chenodeoxycholate, were detected in the acidic solution of pH 5.90 with much higher sensitivity than that of a solution at pH 9.09. When 0.1mM of sodium hyodeoxycholate was added to the host solution, the pH value changed to 6.11. Figures 8a and 8b show that the absorption spectra of β-1 in a solution of pH 5.90 and buffer solutions with and without sodium hyodeoxycholate. In these spectra, isosbestic points are observed at 370 nm and 303 nm for β-1 in a solution of pH 5.90, and at 365 nm and 300 nm for β-1 in buffer solutions,

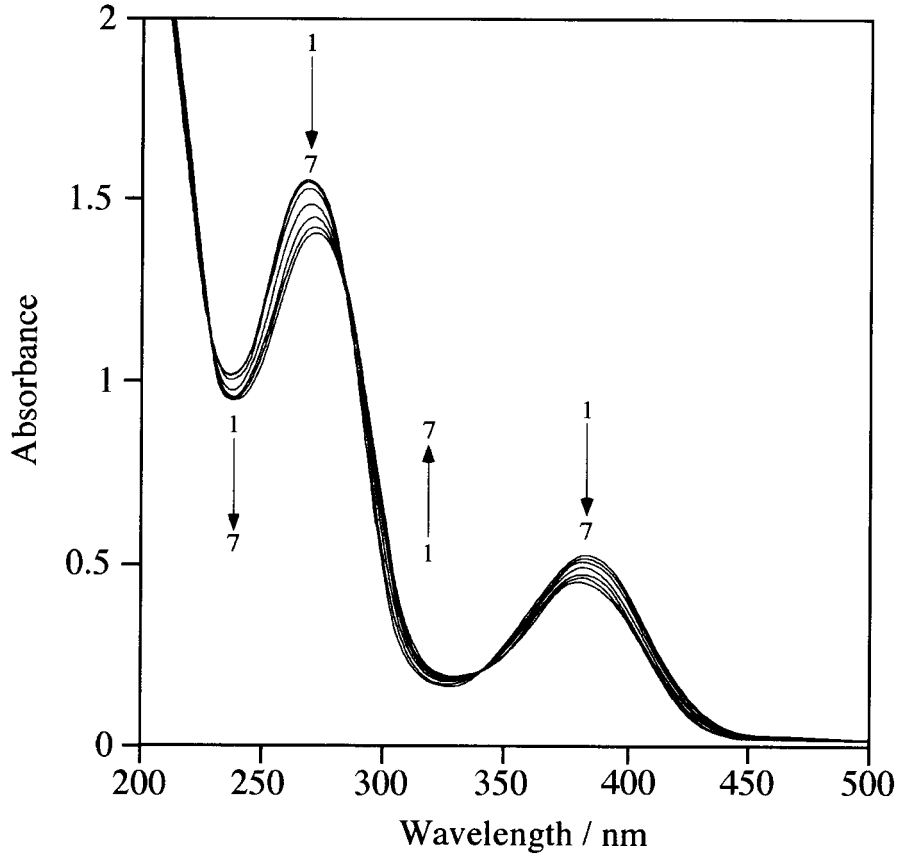
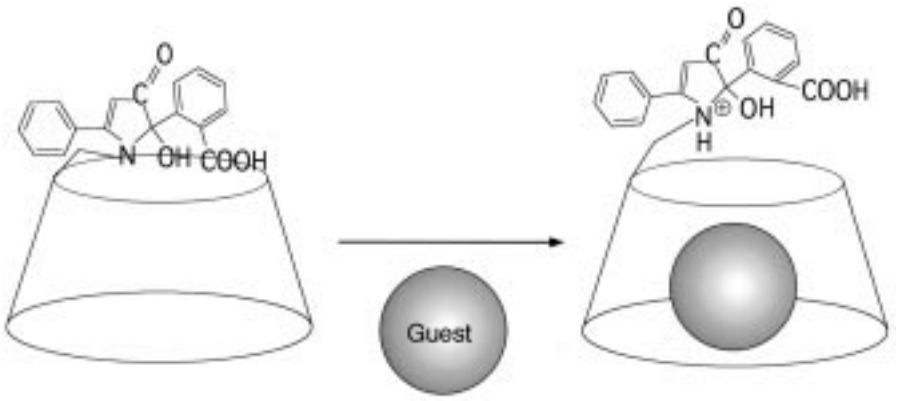


Figure 6. Absorption spectra of β-1 in aqueous solution (10^{-4} M, pH 5.90, 25 °C) at various concentration of cyclohexyl amine (1: 0, 2: 1.0×10^{-4}, 3: 4.0×10^{-4}, 4: 8.0×10^{-4}, 5: 1.2×10^{-3}, 6: 1.6×10^{-3}, 7: 2.0×10^{-3}).



Scheme 3. Host–guest binding between the quaternary ammonium type of appended moiety of β-1 and the guest.

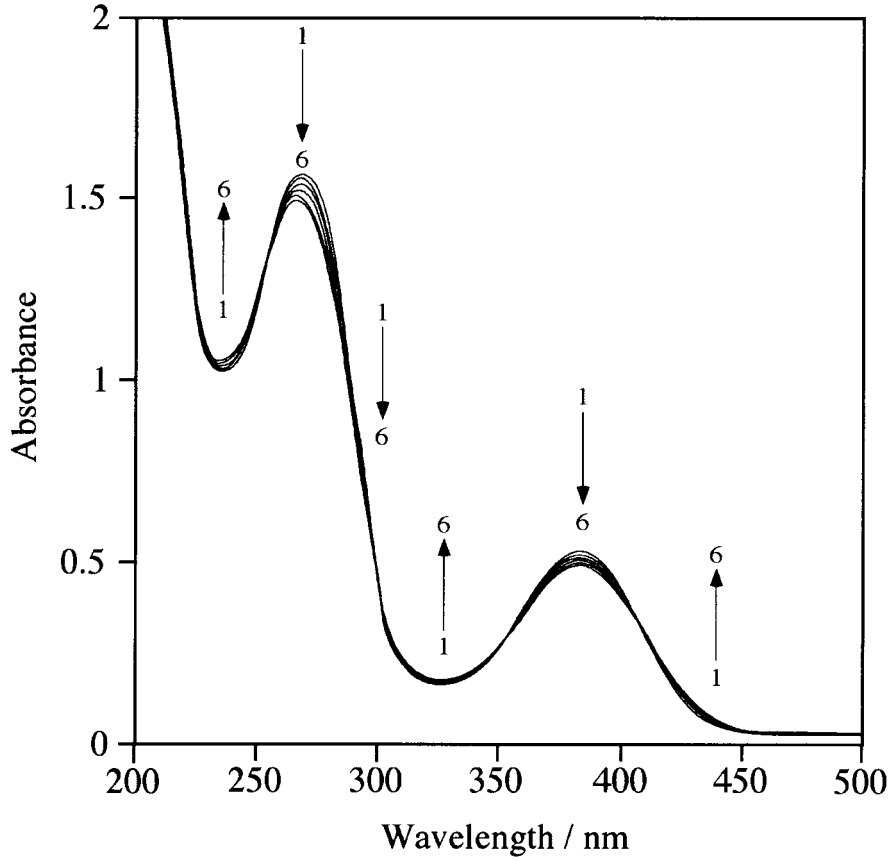


Figure 7. Absorption spectra of β-1 in aqueous solution (10^{-4} M, pH 5.90, 25 °C) at various concentration of cyclohexanecarboxylic acid (1: 0, 2: 1.0×10^{-4}, 3: 2.0×10^{-4}, 4: 6.0×10^{-4}, 5: 1.0×10^{-3}, 6: 1.4×10^{-3}).

respectively. The patterns of these spectra are almost the same, which suggests the host-guest binding behaviors should be similar. In these cases, the hydrogen bonding contribution for host-guest complexation formation as shown in the case of an amine guest in a host solution of pH 5.90 seems to be almost negligible. In this case, the appended moiety works as a hydrophobic cap to accelerate the host-guest binding ability of the host, in which the host-guest binding mechanism should be an induced-fit type complexation behavior as shown in Scheme 4. The response curves of β-1 and γ-1, at pH 5.90 and 9.09, for some guests, which are sodium deoxycholate (**21**), sodium chenodeoxycholate (**22**), and sodium hyodeoxycholate (**24**), are shown in Figure 9. Since these guests were detected with remarkably different responses by the host in the order of sodium hyodeoxycholate (**24**) > sodium chenodeoxycholate (**22**) > sodium deoxycholate (**21**), they are expected to have a different response range when the guest concentration is varied. All hosts

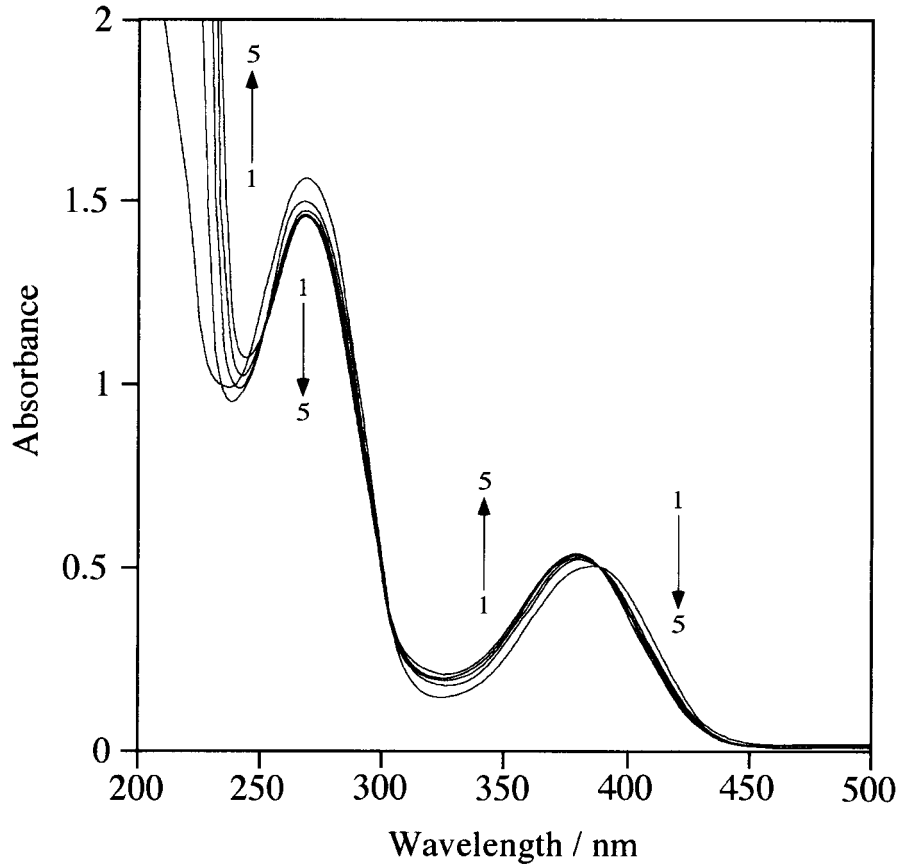


Figure 8A. Absorption spectra of β-1 in aqueous solution (10^{-4} M, pH 5.90, 25 °C) at various concentration of sodium hyodeoxycholate (1: 0, 2: 1.0×10^{-4}, 3: 4.0×10^{-4}, 4: 8.0×10^{-4}, 5: 1.2×10^{-3}).

give a clear concentration dependence for the guests, reflecting the sensitivities of the system for the guests with a response range of $10^{-5.5}$–$10^{-4.5}$, 10^{-5}–10^{-4} and above 10^{-4} M for sodium hyodeoxycholate, sodium chenodeoxycholate, and sodium deoxycholate, respectively.

4. Conclusion

Fluorescent pyrrolinone modified β- and γ-cyclodextrin derivatives (β-1 and γ-1) have been synthesized to investigate their fluorescent molecular sensing ability for organic guests including terpenoids and bile acids, which are biologically significant substances. These hosts show a pure monomer fluorescence, whose variation was used as a parameter to describe the sensing ability. In acidic or alkaline solution, these hosts show different binding behaviors for the guest molecules ex-

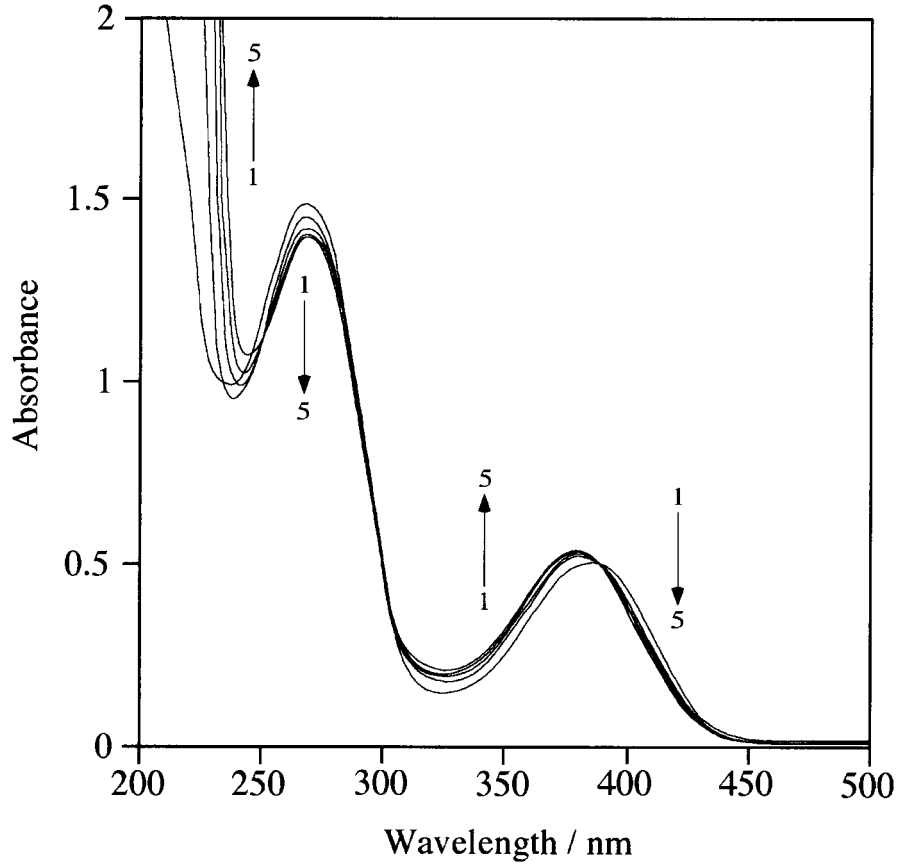
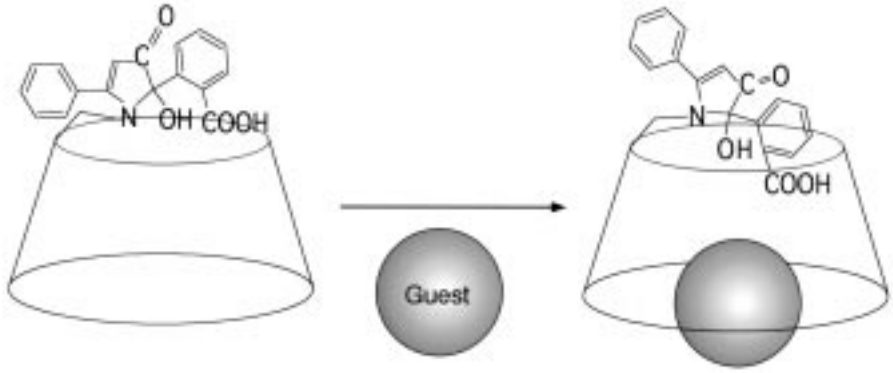


Figure 8B. Absorption spectra of β-1 in aqueous solution (10^{-4} M, pH 9.09, 25 °C) at various concentration of sodium hyodeoxycholate (1: 0, 2: 1.0×10^{-4}, 3: 4.0×10^{-4}, 4: 8.0×10^{-4}, 5: 1.2×10^{-3}).



Scheme 4. Induced-fit type complexaton behavior between β-1 and the guest.

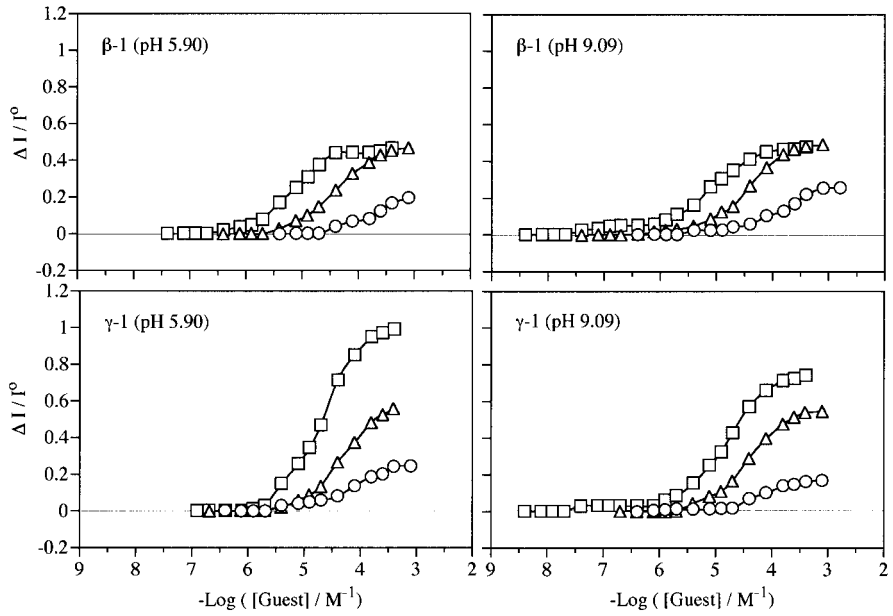


Figure 9. Fluorescence variations of β-1 and γ-1 in aqueous solution (2.0×10^{-6} M, pH 5.90 and 9.09, 25 °C) for sodium deoxycholate (○), sodium chenodeoxycholate (△), and sodium hyodeoxycholate (□) as a function of guest concentration.

amined, caused by hydrogen bonding interaction between a host and a guest. The appended moiety of the host, pyrrolinone, acts as a hydrophobic cap to increase the binding ability of the host. It is obvious that the fluorescent-sensory system using such modified cyclodextrins is a very convenient and useful method, because the chemical modification of a guest, which is even spectroscopically inert is not necessary; a guest can be examined directly in this system.

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