CHEMISTRY LETTERS, pp. 1059-1062, 1989.

Host-Guest Sensory System for Detecting a Variety of Organic Compounds by Variations in Pyrene Excimer and Monomer Fluorescence Intensities

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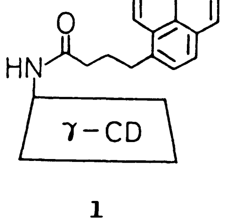
Pyrene-appended γ-cyclodextrin in solution changes pyrene excimer and monomer fluorescence intensities associated with the conversion from its dimer into host-guest complexes. This fluorescence variation was used to detect a variety of organic compounds, and this system has been shown to be sensitive particularly to some steroid compounds.

Cyclodextrins are torus-shaped oligosaccharides named as α, β, and γ for six-, seven-, and eight-glucose members, all of which have a central cavity capable of accommodating a variety of organic molecules in aqueous solution.[1)] Although they are spectroscopically inert, they can be converted into spectroscopically active hosts by modification by chromophores. On this basis, we have shown many examples of guest-induced spectral variations with cyclodextrins possessing one or two arene groups.[2)] In continuation of these works, we have recently prepared pyrene-appended γ-cyclodextrin (**1**) and found that **1** forms an association dimer (A), in which pyrene excimer is formed.[3)] The association dimer can be converted into 1:1 host-guest complexes (B), which show only monomer fluorescence, as shown by the following equilibria.

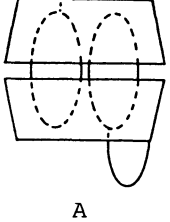
$$\mathbf{1} + \mathbf{1} \rightleftharpoons \mathbf{1}_2$$

$$\mathbf{1} + \text{guest} \rightleftharpoons \mathbf{1}\,.\,\text{guest}$$

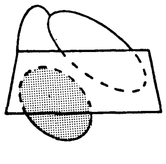
Consequently, many guest substances are expected to be detected by fluorescence variations of **1**. We wish to report here that this fluorescence method is very useful for detecting a variety of guest substances with high degrees of sensitivity and selectivity.



1



A



B

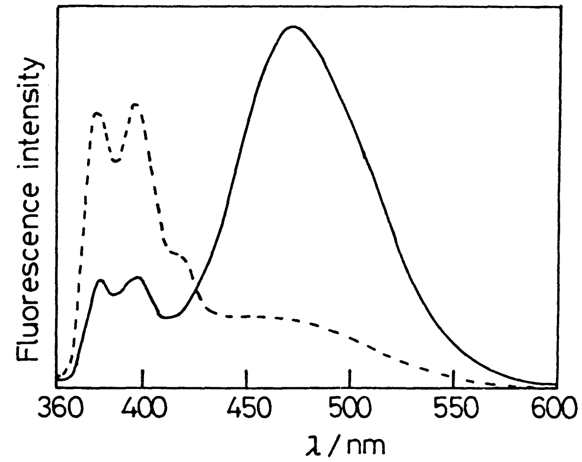
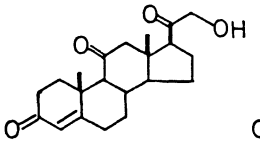


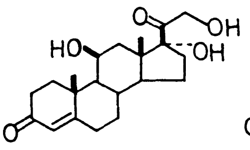
Fig. 1. Fluorescence spectra of **1** in aqueous 10% dimethyl sulfoxide solution (3.01×10^{-5} M) in the absence (——) and presence of l-borneol (---, 3.33×10^{-3} M).

Figure 1 shows fluorescence spectra of **1** in aqueous 10% dimethyl sulfoxide solution in the presence and absence of l-borneol. The spectrum of **1**, alone, exhibits excimer fluorescence at 470 nm in addition to monomer fluorescence, which has peaks at 378 and 397 nm. The excimer intensity decreases with increasing l-borneol concentration, resulting in promoted monomer fluorescence. Now excimer intensity ratio, r, is defined as follows

$$r = I_{ex}/(I_{ex} + I_m)$$

where I_{ex} and I_m are excimer (470 nm) and monomer (378 nm) fluorescence intensities, respectively. When the r value is abbreviated as r_o for **1**, alone, and r_g for a mixture of **1** and guest, $r_o - r_g$ can be used as a factor reflecting the sensitivity of the system to guest substances. Figure 2 shows the $r_o - r_g$ values obtained with a variety of guest substances at the concentrations of 2.0 and 0.2 mM (M=mol dm^{-3}). Many compounds, which are similar to or smaller than cyclohexanol in molecular size, caused negligible variations in the fluorescence of **1** at such guest concentrations. Among the guests examined at the concentration of 2.0 mM, **1** exhibits the best sensitivity to l-borneol. Since different $r_o - r_g$ values were obtained for a group of guest substances with molecular weight of 154 such as l-borneol, geraniol, nerol, d-fenchone, l-fenchone, d-camphore, and 1-adamantanol, it is obvious that the sensitivity of **1** remarkably depends on molecular structure of the guests.


cortisone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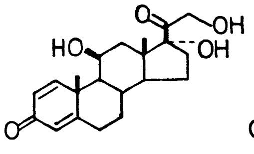
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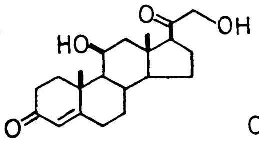
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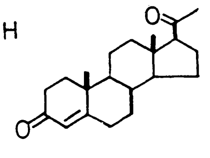
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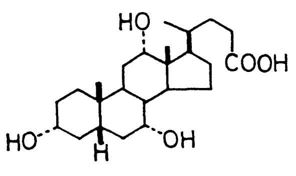
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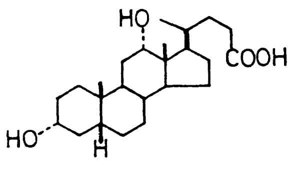
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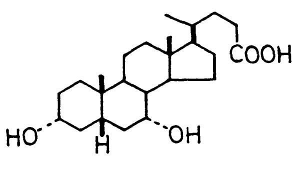
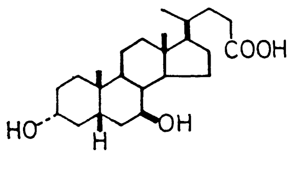

chenodeoxycholic acid


ursodeoxycholic acid

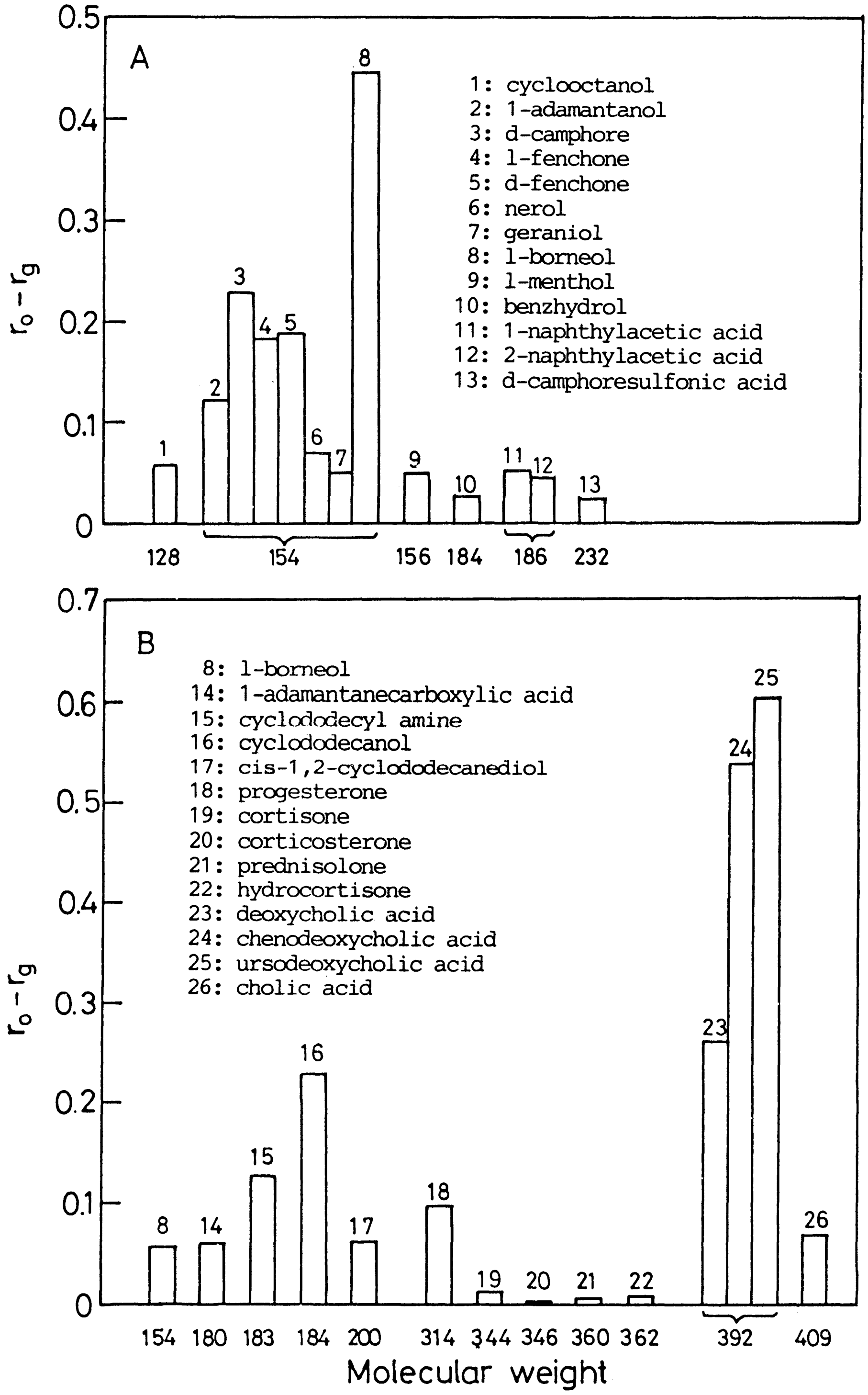


Fig. 2. The sensitivity factor $r_o - r_g$ of **1** (3.01×10^{-5} M) for various guests (A, 2.0 mM; B, 0.2 mM).

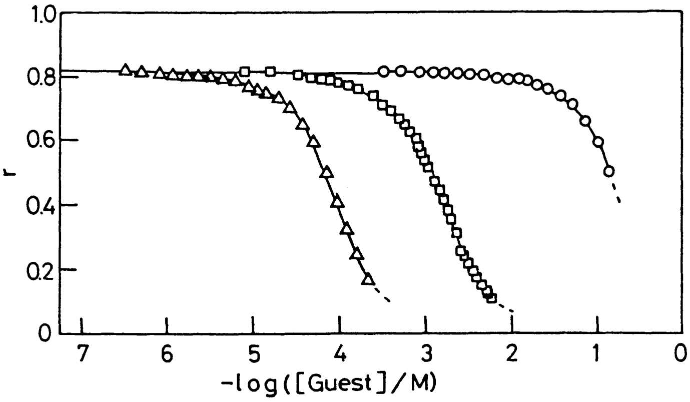


Fig. 3. The r value as a function of concentration of ursodeoxycholic acid (Δ), l-borneol (□), and cyclohexanol (o).

Detailed examination of the data indicates that bicyclic compounds exhibit higher $r_o - r_g$ values than acyclic compounds probably because of their good shapes to be accommodated in the cavity of **1**.

The data obtained at the guest concentration of 0.2 mM also substantiate the importance of molecular structure of guest compounds. Among nine steroid compounds examined, ursodeoxycholic acid and chenodeoxycholic acid were detected with high degrees of sensitivity. The important feature of substitution on steroid framework is seen in the observation that cholic acid was detected with remarkably lower sensitivity than deoxycholic acid in spite of the fact that the only difference between both compounds exists in the number of hydroxyl group, that is, cholic acid has one more hydroxyl group than deoxycholic acid.

Figure 3 shows r as a fuction of guest concentration for cyclohexanol, l-borneol, and ursodeoxycholic acid. The r value varies in the concentration ranges of $10^{-5} - 10^{-3}$, $10^{-4} - 10^{-2}$, and 10^{-2} M for ursodeoxycholic acid, l-borneol, and cyclohexanol, respectively. The result indicates that l-borneol as well as ursodeoxycholic acid can be selectively detected even if the solution contains a considerable amount of cyclohexanol.

In conclusion, the sensory system of **1** is very useful to detect a variety of organic compounds by variations of pyrene excimer and monomer emission intensities. The fact that this system is particularly sensitive to some steroid compounds promises future applications of this system as host-guest sensors capable of detecting many biological compounds with high degrees of molecular recognition.

This work was supported partly by Grant-in-Aid for Scientific Reseach on Priority Areas (636045070) from the Ministry of Education, Science and Culture of Japan.

References

1) M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry," Springer-Verlag (1978).
2) A. Ueno, F. Moriwaki, T. Osa, F. Hamada, and K. Murai, J. Am. Chem. Soc., 110, 4323 (1988), and references therein.
3) A. Ueno, I. Suzuki, and T. Osa, J. Chem. Soc., Chem. Commun., 1989, 1373.

(Received March 16, 1989)