Amphiphilic Cycloinulohexaose: Preparation, Surface-Active Properties, and Complexing Abilities toward Various Metal Chlorides

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Mono-6-*O*-acylated cycloinulohexaoses **1** and mono-6-*O*-alkylated cycloinulohexaoses **2** were prepareds by the reaction of cycloinulohexaose with long-chain acyl chlorides and long-chain alkyl bromides, respectively. These amphiphilic cycloinulohexaoses showed good water solubilities. The critical micelle concentration (cmc) of each amphiphilic compound, which was determined by a dye method, decreased along with an increase in the alkyl chain length. The micelle-forming ability of compound **2** was higher than that of compound **1** bearing the same carbon number in the hydrophobic part. The aggregation numbers of mono(6-*O*-tetradecanoyl)cycloinulohexaose **1b** and mono(6-*O*-tetradecyl)cycloinulohexaose **2b**, which were obtained with fluorescence measurements, were 4.8 and 6.5, respectively. The cmcs of compounds **1b** and **2b** were increased by the addition of either KCl, RbCl, or $BaCl_2$, though they were decreased by the addition of LiCl or NaCl. These results indicate that compounds **1b** and **2b** complex with K^+, Rb^+, or Ba^{2+} in water, but negligibly with Li^+ or Na^+.

Cyclodextrins are a class of cyclic oligosaccharides consisting of several α-(1,4)-linked D-glucopyranose units and have a cone-shaped cavity. Their abilities to form inclusion complexes with a wide range of organic guests have found applications in many areas.[1] Recently, cyclic oligosaccharides other than cyclodextrins have attracted much attention as new host compounds.[2—7] Cycloinulohexaose,[2] which is a β-(2, 1)-linked cyclohexaose of D-fructofuranose, is among them (Fig. 1). This compound is prepared from inulin by using cycloinulo-oligosaccharide fructanotransferase. The molecule possesses a chiral 18-crown-6 skeleton. The chemical modification using an appropriate reagent is expected to afford a promising artificial receptor. Indeed, cycloinulohexaose has been reported to have a high complexing ability toward Ba^{2+}.[8,9] Additionally, Sawada et al. have found that permethylated cycloinulohexaose has selectivity toward K^+ and Ba^{2+} among alkali metal and alkaline earth metal cations, like that of 18-crown-6.[10]

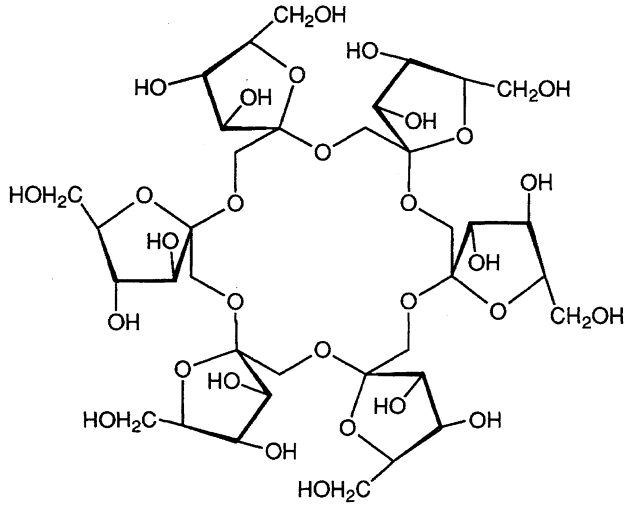


Fig. 1. Structure of cycloinulohexaose.

In this paper we describe the preparation of amphiphilic cycloinulohexaoses by the reaction of cycloinulohexaose with long-chain acyl chloride or long-chain alkyl bromide, their surface-active properties, and their complexing abilities toward metal cations, such as Li^+, Na^+, K^+, Rb^+, and Ba^{2+}. Similarly to amphiphilic cyclodextrins[11] and amphiphilic crown ethers,[12] both of which have been extensively studied up to now, the amphiphilic cycloinulohexaoses or their aggregates are potentially useful as carriers of ions or organic compounds in membrane systems and as sensors for a variety of chemical species. To the best of our knowledge, this is the first example of an amphiphilic compound bearing cycloinulohexaose as a hydrophilic part.

Experimental

^{1}H NMR spectra were recorded with a JEOL JNM-GSX-400 (400 MHz) spectrometer using DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal standard. IR spectra were measured on a Horiba FT-710 spectrometer. Mass spectra were measured on a JEOL JMS-DX-303 mass spectrometer. Elemental analyses were measured with a Yanagimoto CHN-Corder. Melting points were measured with a Yanaco MP-S3 apparatus. Cloud point (T_{cp}) were determined by the naked eye with a 1 wt% aqueous solution. Critical micelle concentrations (cmcs) were determined by a dye method using pinacyanol chloride as a dye probe.[13] Visible spectra of different concentrations of surfactant solutions including 5.0×10^{-6} M pinacyanol chloride (1 M = 1 mol dm^{-3}) were

measured with a Hitachi U-2000 spectrophotometer. Micellar aggregation numbers were determined by a static method in which pyrene and hexadecylpyridinium chloride (HPC) were used as a fluorescence probe and a quencher, respectively.[14] Fluorescence measurements were carried out on a Shimadzu fluorescence spectrophotometer (RF-1500). Fluorescence intensities of 1.0×10^{-7} M pyrene in 1.0×10^{-4} M surfactant solution were measured at 380 nm (excitation wavelength: 335 nm) as a function of the quencher concentration.

Materials. Cycloinulohexaose was obtained from Mitsubishi Kagaku Co. (Tokyo, Japan). Triethylamine, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were distilled before use. Pyrene and HPC were purified by recrystallization from ethanol and acetone, respectively, before use. All other reagents used were of commercially available reagent grade.

Mono(6-*O*-dodecanoyl)cycloinulohexaose (1a). Cycloinulohexaose (1.03 g, 1 mmol) was dissolved in DMF (50 mL) and the solution was concentrated to 30 mL in vacuo to eliminate water bonded to cycloinulohexaose. After triethylamine (0.70 mL, 5 mmol) was added to the solution, dodecanoyl chloride (0.22 g, 1 mmol) was dropped into this mixture at 0 °C; the mixture was then stirred for 2 h at room temperature. After DMF and triethylamine were removed under reduced pressure, the residue was purified by reversed-phase column chromatography (Column: ULTRA PACK$_{TM}$ ODS-A40B ϕ26×300 mm, Yamazen Co.) with methanol used as an eluent to give pure mono(6-*O*-dodecanoyl)cycloinulohexaose (0.30 g, 26% yield), mp 140—142 °C. ^{1}H NMR (DMSO-d_6) δ = 0.85 (t, 3H, CH_3), 1.24 (m, 16H, –(CH_2)$_8$–), 1.50 (m, 2H, CH_2CH$_2$C=O), 2.31 (t, 2H, CH_2C=O), 3.37—3.47 (m, 5H, H-6a′), 3.47—3.59 (m, 16H, H-1a+H-6b′+H-5′+H-1a′), 3.59—3.71 (m, 6H, H-1b+H-1b′), 3.71—3.77 (m, 1H, H-5), 3.77—3.86 (m, 6H, H-4+H-4′), 3.86—4.00 (m, 6H, H-3′+H-3), 4.04 (dd, 1H, J = 7 and 12 Hz, H-6a), 4.24 (dd, 1H, J = 2 and 12 Hz, H-6b), 4.43—4.50 (m, 4H, OH-3′), 4.57 (d, 1H, J = 6.2 Hz, OH-3′), 4.62 (d, 1H, OH-3, J = 6.2 Hz), 4.63—4.70 (m, 5H, OH-6′), 5.23 (d, 5H, J = 5.5 Hz, OH-4′), 5.44 (d, 1H, J = 5.5 Hz, OH-4). IR (KBr) 3380, 2925, 1724, 1030 cm^{-1}. FAB-MS *m*/*z* (rel intensity) 1177 [(M+Na)$^+$; 83], 89 (100). Found: C, 46.38; H, 7.07%. Calcd for $C_{48}H_{82}O_{31}\cdot5H_2O$: C, 46.30; H, 7.45%.

Mono(6-*O*-tetradecanoyl)cycloinulohexaose (1b). This compound was prepared and purified in the same manner as compound **1a**: Yield 30%. Mp 192—195 °C. ^{1}H NMR (DMSO-d_6) δ = 0.85 (t, 3H, CH_3), 1.24 (m, 20H, –(CH_2)$_{10}$–), 1.51 (m, 2H, CH_2CH$_2$C=O), 2.32 (t, 2H, CH_2C=O), 3.38—3.47 (m, 5H, H-6a′), 3.47—3.59 (m, 16H, H-1a+H-6b′+H-5′+H-1a′), 3.59—3.71 (m, 6H, H-1b+H-1b′), 3.71—3.77 (m, 1H, H-5), 3.77—3.86 (m, 6H, H-4+H-4′), 3.88—4.00 (m, 6H, H-3′+H-3), 4.04 (dd, 1H, J = 7 and 12 Hz, H-6a), 4.24 (dd, 1H, J = 2 and 12 Hz, H-6b), 4.43—4.50 (m, 4H, OH-3′), 4.57 (d, 1H, J = 6.2 Hz, OH-3′), 4.62 (d, 1H, J = 6.2 Hz, OH-3), 4.63—4.70 (m, 5H, OH-6′), 5.23 (d, 5H, J = 5.5 Hz, OH-4′), 5.44 (d, 1H, J = 5.5 Hz, OH-4). IR (KBr) 3380, 2925, 1728, 1030 cm^{-1}. FAB-MS *m*/*z* (rel intensity) 1205 [(M+Na)$^+$; 100]. Found: C, 48.94; H, 7.38%. Calcd for $C_{50}H_{86}O_{31}\cdot2H_2O$: C, 49.26; H, 7.44%.

Mono(6-*O*-hexadecanoyl)cycloinulohexaose (1c). This compound was prepared and purified in the same manner as compound **1a**: Yield 26%. Mp 219—222 °C. ^{1}H NMR (DMSO-d_6) δ = 0.84 (t, 3H, CH_3), 1.22 (m, 24H, –(CH_2)$_{12}$–), 1.50 (m, 2H, CH_2CH$_2$C=O), 2.30 (t, 2H, CH_2C=O), 3.37—3.46 (m, 5H, H-6a′), 3.46—3.59 (m, 16H, H-1a+H-6b′+H-5′+H-1a′), 3.59—3.69 (m, 6H, H-1b+H-1b′), 3.69—3.75 (m, 1H, H-5), 3.75—3.86 (m, 6H, H-4+H-4′), 3.86—3.99 (m, 6H, H-3′+H-3), 4.04 (dd, 1H, J = 7 and 12 Hz, H-6a), 4.24 (dd, 1H, J = 2 and 12 Hz, H-6b), 4.40—4.50 (m, 4H, OH-3′), 4.53 (d, 1H, J = 6.2 Hz, OH-3′), 4.57 (d, 1H, J = 6.2 Hz, OH-3), 4.59—4.68 (m, 5H, OH-6′), 5.21 (d, 5H, J = 5.5 Hz, OH-4′), 5.43 (d, 1H, J = 5.5 Hz, OH-4). IR (KBr) 3390, 2925, 1728, 1030 cm^{-1}. FAB-MS *m*/*z* (rel intensity) 1233 [(M+Na)$^+$; 54], 89 (100). Found: C, 48.12; H, 7.44%. Calcd for $C_{52}H_{90}O_{31}\cdot5H_2O$: C, 47.99; H, 7.75%.

Mono(6-*O*-octadecanoyl)cycloinulohexaose (1d). This compound was prepared and purified in the same manner as compound **1a**: Yield 28%. Mp 164—166 °C. ^{1}H NMR (DMSO-d_6) δ = 0.85 (t, 3H, CH_3), 1.24 (m, 28H, –(CH_2)$_{14}$–), 1.51 (m, 2H, CH_2CH$_2$C=O), 2.32 (t, 2H, CH_2C=O), 3.37—3.47 (m, 5H, H-6a′), 3.47—3.59 (m, 16H, H-1a+H-6b′+H-5′+H-1a′), 3.59—3.70 (m, 6H, H-1b+H-1b′), 3.70—3.76 (m, 1H, H-5), 3.76—3.84 (m, 6H, H-4+H-4′), 3.84—3.99 (m, 6H, H-3′+H-3), 4.04 (dd, 1H, J = 7 and 12 Hz, H-6a), 4.24 (dd, 1H, J = 2 and 12 Hz, H-6b), 4.41—4.50 (m, 4H, OH-3′), 4.52 (d, 1H, J = 6.2 Hz, OH-3′), 4.57 (d, 1H, J = 6.2 Hz, OH-3), 4.58—4.68 (m, 5H, OH-6′), 5.21 (d, 5H, J = 5.5 Hz, OH-4′), 5.43 (d, 1H, J = 5.5 Hz, OH-4). IR (KBr) 3380, 2924, 1731, 1030 cm^{-1}. FAB-MS *m*/*z* (rel intensity) 1261 [(M+Na)$^+$; 63], 107 (100). Found: C, 49.17; H, 7.52%. Calcd for $C_{54}H_{94}O_{31}\cdot5H_2O$: C, 48.79; H, 7.89%.

Mono(6-*O*-dodecyl)cycloinulohexaose (2a). Dodecyl bromide (0.37 g, 1.5 mmol)/DMSO (10 mL) was dropped into a mixture of cycloinulohexaose (1.03 g, 1 mmol) and NaH (60%) (0.07g net, 3 mmol) in DMSO (40 mL) at 60 °C under an argon atmosphere. The mixture was stirred at 60 °C for 8 h. After methanol was added into this reaction system to deactivate the unreacted NaH, the solvent was removed under reduced pressure. The residue was purified by reversed-phase column chromatography (Column: ULTRA PACK$_{TM}$ ODS-A-40B ϕ26×300 mm, Yamazen Co.) with methanol–H_2O (1 : 1, v/v) as an eluent to give pure mono(6-*O*-dodecyl)cycloinulohexaose (0.22 g, 19% yield). Mp 168—170 °C. ^{1}H NMR (DMSO-d_6) δ = 0.85 (t, 3H, CH_3), 1.23 (m, 18H, –(CH_2)$_9$–), 1.48 (m, 2H, CH_2CH$_2$O), 3.36—3.47 (m, 7H, CH_2O+H-6a′), 3.47—3.62 (m, 19H, H-6a+H-6b+H-6b′+H-5+H-5′+H-1a+H-1a′), 3.62—3.72 (m, 6H, H-1b+H-1b′), 3.71—3.85 (m, 6H, H-4+H-4′), 3.85—3.96 (m, 6H, H-3+H-3′), 4.40—4.52 (m, 6H, OH-3+OH-3′), 4.58—4.69 (m, 5H, OH-6′), 5.21 (d, 5H, J = 5.5 Hz, OH-4′), 5.29 (d, 1H, J = 5.5 Hz, OH-4). IR (KBr) 3380, 2927, 1026 cm^{-1}. FAB-MS *m*/*z* (relative intensity) 1179 [(M+K)$^+$; 100]. Found: C, 47.87; H, 7.29%. Calcd for $C_{48}H_{84}O_{30}\cdot4H_2O$: C, 47.52; H, 7.64%.

Mono(6-*O*-tetradecyl)cycloinulohexaose (2b). This compound was prepared and purified in the same manner as compound **2a**: Yield 19%. Mp 172—176 °C. ^{1}H NMR (DMSO-d_6) δ = 0.84 (t, 3H, CH_3), 1.23 (m, 22H, –(CH_2)$_{11}$–), 1.47 (m, 2H, CH_2CH$_2$O), 3.35—3.47 (m, 7H, CH_2O+H-6a′), 3.47—3.62 (m, 19H, H-6a+H-6b+H-6b′+H-5+H-5′+H-1a+H-1a′), 3.62—3.72 (m, 6H, H-1b+H-1b′), 3.73—3.86 (m, 6H, H-4+H-4′), 3.86—3.97 (m, 6H, H-3+H-3′), 4.42—4.56 (m, 6H, OH-3+OH-3′), 4.60—4.71 (m, 5H, OH-6′), 5.22 (d, 5H, J = 5.5 Hz, OH-4′), 5.30 (d, 1H, J = 5.5 Hz, OH-4). IR (KBr) 3380, 2927, 1026 cm^{-1}. FAB-MS *m*/*z* (rel intensity) 1207 [(M+K)$^+$; 100]. Found: C, 47.84; H, 7.56%. Calcd for $C_{50}H_{88}O_{30}\cdot5H_2O$: C, 47.69; H, 7.84%.

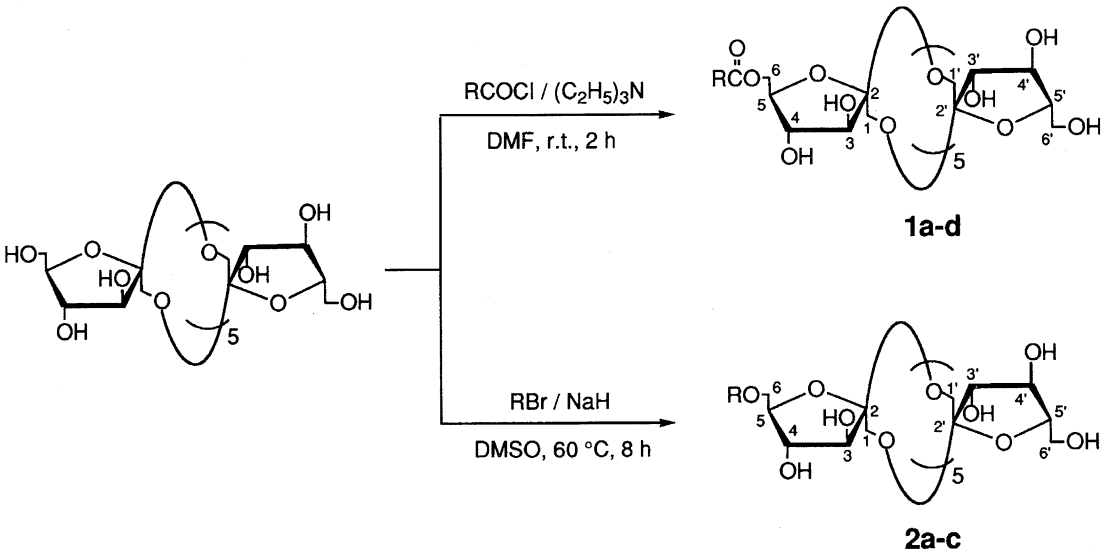
Mono(6-*O*-hexadecyl)cycloinulohexaose (2c). This compound was prepared and purified in the same manner as compound **2a**: Yield 15%. Mp 176—179 °C. ^{1}H NMR (DMSO-d_6) δ = 0.85 (t, 3H, CH_3), 1.23 (m, 26H, –(CH_2)$_{13}$–), 1.48 (m, 2H, CH_2CH$_2$O), 3.36—3.47 (m, 7H, CH_2O+H-6a′), 3.47—3.62 (m, 19H, H-6a+H-6b+H-6b′+H-5+H-5′+H-1a+H-1a′), 3.62—3.70 (m, 6H, H-1b+H-1b′), 3.73—3.84 (m, 6H, H-4+H-4′), 3.86—3.96 (m, 6H,

H-3+H-3′), 4.37—4.50 (m, 6H, OH-3+OH-3′), 4.58—4.68 (m, 5H, OH-6′), 5.21 (d, 5H, $J=5.5$ Hz, OH-4′), 5.29 (d, 1H, $J=5.5$ Hz, OH-4). IR (KBr) 3390, 2927, 1026 cm^{-1}. FAB-MS *m/z* (rel intensity) 1235 [$(M+K)^+$; 100]. Found: C, 49.43; H, 7.54%. Calcd for $C_{52}H_{92}O_{30}\cdot 4H_2O$: C, 49.20; H, 7.94%.

Results and Discussion

Preparation of Amphiphilic Compounds Containing a Cycloinulohexaose as a Hydrophilic Moiety. Mono-6-*O*-acylated and mono-6-*O*-alkylated cycloinulohexaoses were prepared according to Scheme 1. It is noteworthy that the preparation of these amphiphilic cycloinulohexaoses was accomplished without protection and deprotection processes of the hydroxy groups in the cycloinulohexaose molecule. Mono-6-*O*-acylated cycloinulohexaose was prepared by the reaction of cycloinulohexaose with an equimolar amount of acyl chloride in the presence of triethylamine for 2 h at ambient temperature. Either prolonging the reaction time or raising the reaction temperature led to an increase of diacylated products. The mono-6-*O*-acylated product was isolated from the reaction mixture, which also included the diacylated product and unreacted cycloinulohexaose, by reversed-phase column chromatography with methanol used as an eluent. On the other hand, mono-6-*O*-alkylated cycloinulohexaose was prepared by the reaction of cycloinulohexaose with 1.5 molar amounts of alkyl bromide in the presence of sodium hydride as a base at 60 °C. The product was purified by reversed-phase column chromatography with methanol–H_2O (1 : 1, v/v) used as an eluent to give a pure mono-6-*O*-alkylated cycloinulohexaose. The structure of the obtained cycloinulohexaose derivatives, **1a—d** and **2a—c**, was confirmed by the ^{1}H NMR and ^{1}H-^{1}H COSY spectra. In the ^{1}H NMR spectra of compounds **1a—d**, for example, in the case of **1b**, two resonances at $\delta=4.04$ (dd, 1H) and 4.24 (dd, 1H) are present, as would be expected from the *O*-acylated methylene group, and the ^{1}H-^{1}H COSY spectrum showed that these resonances were associated with each other as well as the resonance at $\delta=3.73$, which can be assigned to H-5 of the same fructose residue. Compound **1b** was therefore assigned as mono(6-*O*-tetradecanoyl)cycloinulohexaose. In a similar manner, compounds **1a**, **1c**, and **1d** were assigned as the corresponding mono-6-*O*-acylated cycloinulohexaose. For compounds **2a—c**, a doublet (one OH proton) around $\delta=5.3$ is present, which can be assigned to OH-4 of the alkylated fructose residue on the basis of the assignment results of compounds **1a—d**. The assignment based on this resonance and the ^{1}H-^{1}H COSY spectrum proved that compounds **2a—c** are mono-6-*O*-alkylated cycloinulohexaoses.

Surface-Active Properties. The cmcs of compounds **1** and **2** were determined by a dye method[13] with pinacyanol chloride used as a dye probe. Figure 2 shows plots of the wavelength of maximal absorption (λ_{max}) of pinacyanol chloride vs. the logarithm of concentration (log *C*) for compounds **1b** and **2b**. Since the λ_{max} of pinacyanol chloride shifts to a longer wavelength when it is incorporated into the hydrophobic region of micelles from the bulk phase, the break point on the $\lambda_{max}-\log C$ curve can be regarded as being the cmc of the surfactant. The cmcs and cloud points (T_{cp}) measured at 1 wt% concentration are summarized in Table 1. The cloud points of compounds **1** and **2** were more than 95 °C at 1 wt% concentration, which clearly show that they have good water solubility. As regards compounds **1a—c** and **2a—c**, the cmc decreased along with an increase in the carbon number of the alkyl chain. On the other hand, compound **1d** bearing 17 carbon atoms in the straight-chain



	1a	1b	1c	1d	2a	2b	2c
R :	$C_{11}H_{23}$	$C_{13}H_{27}$	$C_{15}H_{31}$	$C_{17}H_{35}$	$C_{12}H_{25}$	$C_{14}H_{29}$	$C_{16}H_{33}$

Scheme 1.

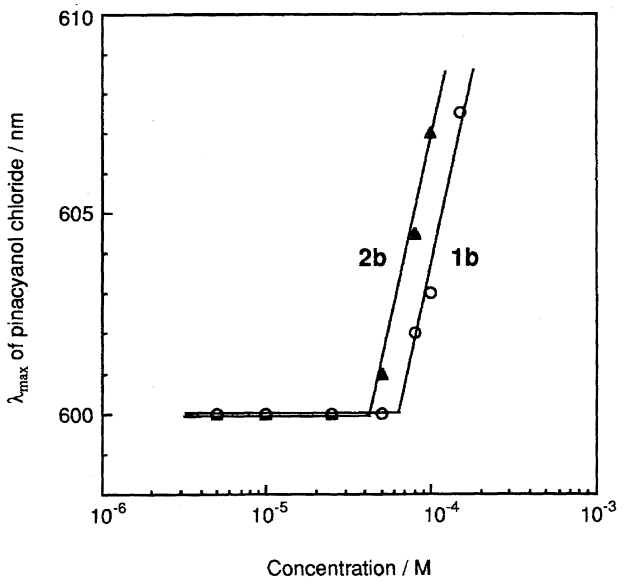


Fig. 2. Plots of wavelength of maximal absorption (λ_{max}) of pinacyanol chloride vs. concentration of compounds **1b** and **2b** at 20 °C.

Table 1. Surface-Active Properties of Compounds **1** and **2**

Compound	T_{cp}[a] (°C)	cmc[b] ($\times 10^{-5}$ mol dm^{-3})
1a (R = $C_{11}H_{23}$)	>95	21
1b (R = $C_{13}H_{27}$)	>95	6.6
1c (R = $C_{15}H_{31}$)	>95	1.8
1d (R = $C_{17}H_{35}$)	>95	2.2
2a (R = $C_{12}H_{25}$)	>95	14
2b (R = $C_{14}H_{29}$)	>95	4.1
2c (R = $C_{16}H_{33}$)	>95	1.4

a) T_{cp} = cloud point. Measured at 1 wt% concentration. b) At 20 °C.

hydrophobic group showed about the same cmc as that of compound **1c** which bears 15 carbon atoms. This result can be explained by coiling of the long C17 alkyl chain, similarly to the case of a conventional surfactant.[15] Meanwhile, the micelle-forming ability of monoalkylated cycloinulohexaose **2** was higher than that of monoacylated cycloinulohexaose **1** bearing the same carbon number in the hydrophobic part. The cmc value of mono(6-*O*-dodecyl)cycloinulohexaose **2a** was almost equal to that of dodecyl β-D-maltoside (1.6×10^{-4} M).[16]

Micellar Aggregation Number. The micellar aggregation number (N) was determined from the slope of the plot of the logarithm of I_0/I of pyrene vs. the quencher concentration as follows:

$$\ln(I_0/I) = [\mathrm{HPC}]N/\{[\mathrm{Surfactant}] - \mathrm{cmc}\}, \quad (1)$$

where I and I_0 are the fluorescence intensities of pyrene in a surfactant solution in the presence and absence of the quencher, respectively, and [HPC] and [Surfactant] are the concentrations of HPC and the surfactant, respectively.[14] Figure 3 shows that a linear relationship exists between $\ln(I_0/I)$ and [HPC] for each surfactant solution. The aggregation numbers of compounds **1b** and **2b** determined from this relation were 4.8 and 6.5, respectively. These values are much smaller than the aggregation numbers of octyl β-D-glucoside and dodecyl β-D-maltoside, which are 87[17] and 110,[18] respectively. This result may be attributed to the large molecular size of cycloinulohexaose as the hydrophilic part of compounds **1b** and **2b**, compared to the sizes of glucose and maltose.

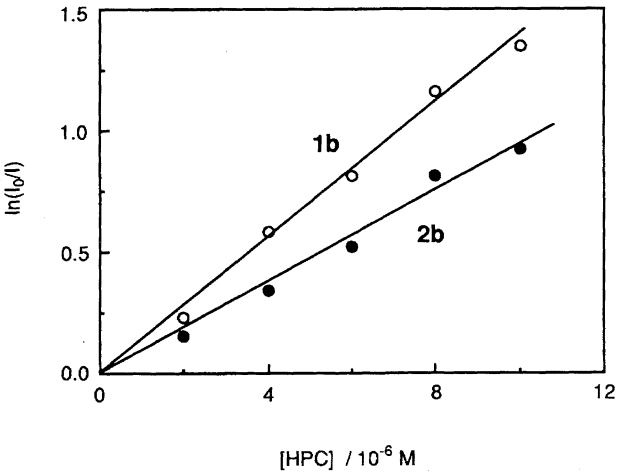


Fig. 3. Plots of $\ln(I_0/I)$ vs. [HPC] for 1.0×10^{-4} M surfactant aqueous solutions.

Complexation Properties. Previously, we reported that the cmcs of amphiphilic crown ethers were raised selectively by the addition of alkali metal salts when the crown ethers can strongly complex with the cations.[19] Based on this finding, the change in the cmcs was regarded to be an important method for estimating the complexing ability of the crown ethers in water toward alkali metal cations. According to this method for crown ethers, the complexation properties of compounds **1** and **2** with Li^+, Na^+, K^+, Rb^+, or Ba^{2+} in water were evaluated from the changes in their cmc values in the presence and absence of the corresponding metal chloride. Table 2 gives the cmc values of compounds **1b** and **2b**, together with those of Triton X-100 as a reference compound, both in the presence and absence of the above metal chlorides. It is well known that alkali metal or alkaline earth metal salts diminish the cmcs of polyoxyethylene-type non-

Table 2. Effect of Metal Chlorides on cmcs of Compounds **1b** and **2b**

	cmc ($\times 10^{-5}$ mol dm^{-3})		
Metal chloride[a]	**1b** (Δ[b])	**2b** (Δ[b])	Triton X-100 (Δ[b])
None	6.6	4.1	35
LiCl	6.0 (−0.6)	3.0 (−1.1)	28 (−7)
NaCl	5.0 (−1.6)	1.5 (−2.6)	19 (−16)
KCl	7.4 (+0.8)	5.0 (+0.9)	23 (−12)
RbCl	7.2 (+0.6)	4.6 (+0.5)	23 (−12)
$BaCl_2$	9.2 (+2.6)	5.5 (+1.4)	25 (−10)

a) Concentration of metal chloride = 0.1 M. b) Δ = (cmc in the presence of metal chloride) − (cmc in the absence of metal chloride).

ionic surfactants by a salting-out effect, except when special counter-anions are used.[20] Indeed, the cmc of Triton X-100 bearing a poly(oxyethylene) chain as the hydrophilic part was decreased by the addition of any of these metal chlorides, as reported. On the other hand, the cmc of compound **1b** was increased by the addition of either KCl or RbCl, and more greatly by the addition of $BaCl_2$, while it was decreased by the addition of either LiCl or NaCl. The cmc of compound **2b** in the presence of the metal chlorides also showed a tendency similar to the case of compound **1b**. These results can be explained by considering a salting-in effect due to complexation of the cycloinulohexaose ring, as the hydrophilic part of surfactants **1b** and **2b**, with K^+, Rb^+, or Ba^{2+}. On the other hand, surfactants **1b** and **2b** were salted out by the addition of Li^+ or Na^+ because of their low complexing abilities toward such cations. The observed complexation properties of the amphiphilic cycloinulohexaoses with alkali metal or alkaline earth metal cations are consistent with that of unsubstituted cycloinulohexaose in water, which has been estimated by Yoshie et al.[9] using the ^{1}H NMR titration method.

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References

1) G. Wenz, *Angew. Chem., Int. Ed. Engl.*, **33**, 803 (1994), and references therein.

2) M. Kawamura, T. Uchiyama, T. Kuramoto, Y. Tamura, and K. Mizutani, *Carbohydr. Res.*, **192**, 83 (1989); M. Sawada, T. Tanaka, Y. Takai, T. Hanafusa, K. Hirotsu, T. Higuchi, M. Kawamura, and T. Uchiyama, *Chem. Lett.*, **1990**, 2011; M. Sawada, T. Tanaka, Y. Takai, T. Hanafusa, T. Taniguchi, M. Kawamura, and T. Uchiyama, *Carbohydr. Res.*, **217**, 7 (1991).

3) M. Mori, Y. Ito, and T. Ogawa, *Carbohydr. Res.*, **192**, 131 (1989); M. Mori, Y. Ito, and T. Ogawa, *Tetrahedron Lett.*, **30**, 1273 (1989).

4) M. Nishizawa, H. Imagawa, Y. Kan, and H. Yamada, *Tetrahedron Lett.*, **32**, 5551 (1991); M. Nishizawa, H. Imagawa, Y. Kan, and H. Yamada, *Chem. Pharm. Bull.*, **42**, 1356 (1994).

5) P. R. Ashton, C. L. Brown, S. Menzer, S. A. Nepogodiev, J. F. Stoddart, and D. J. Williams, *Chem. Eur. J.*, **2**, 580 (1996).

6) F. W. Lichtenthaler and S. Immel, *Tetrahedron: Asymmetry*, **5**, 2045 (1994).

7) K. Fujita, H. Shimada, K. Ohta, Y. Nogami, K. Nasu, and T. Koga, *Angew. Chem., Int. Ed. Engl.*, **34**, 1621 (1995); Y. Nogami, K. Nasu, T. Koga, K. Ohta, K. Fujita, S. Immel, H. J. Lindner, G. E. Schmitt, and F. W. Lichtenthaler, *Angew. Chem., Int. Ed. Engl.*, **36**, 1899 (1997).

8) T. Uchiyama, M. Kawamura, T. Uragami, and H. Okuno, *Carbohydr. Res.*, **241**, 245 (1993).

9) N. Yoshie, H. Hamada, S. Takada, and Y. Inoue, *Chem. Lett.*, **1993**, 353.

10) Y. Takai, Y. Okumura, S. Takahashi, M. Sawada, M. Kawamura, and T. Uchiyama, *J. Chem. Soc., Chem. Commun.*, **1993**, 53; Y. Takai, Y. Okumura, T. Tanaka, M. Sawada, S. Takahashi, M. Shiro, M. Kawamura, and T. Uchiyama, *J. Org. Chem.*, **59**, 2967 (1994).

11) Y. Kawabata, M. Matsumoto, T. Nakamura, M. Tanaka, E. Manda, H. Takahashi, S. Tamura, W. Tagaki, H. Nakahara, and K. Fukuda, *Thin Solid Films*, **159**, 353 (1988); P. Zhang, H. P.-Lopez, P. Tchoreloff, A. Baszkin, C.-C. Ling, C. De Rango, and A. W. Coleman, *J. Phys. Org. Chem.*, **5**, 518 (1992); C.-C. Ling, R. Darcy, and W. Risse, *J. Chem. Soc., Chem. Commun.*, **1993**, 438; M. Tanaka, R. Azumi, H. Tachibana, T. Nakamura, Y. Kawabata, M. Matsumoto, T. Miyasaka, W. Tagaki, H. Nakahara, and K. Fukuda, *Thin Solid Films*, **244**, 832 (1994); D. P. Parazak, A. R. Khan, V. T. D'Souza, and K. J. Stine, *Langmuir*, **12**, 4046 (1996).

12) T. Kuwamura and T. Kawachi, *Yukagaku*, **28**, 195 (1979); Y. Moroi, E. Pramauro, M. Grätzel, E. Pelizzetti, and P. Tundo, *J. Colloid Interface Sci.*, **69**, 341 (1979); M. Okahara, P.-L. Kuo, S. Yamamura, and I. Ikeda, *J. Chem. Soc., Chem. Commun.*, **1980**, 586; S. Inokuma, S. Matsunaga, T. Negishi, T. Hayase, and T. Kuwamura, *J. Jpn. Oil Chem. Soc. (Yukagaku)*, **38**, 170 (1989); S. Yu Zaitsev, M. Belohradsky, J. Zavada, and D. Möbius, *Thin Solid Films*, **248**, 78 (1994).

13) T. Nakagawa, K. Tohri, and K. Kuriyama, *Nihon Kagaku Zasshi*, **77**, 1684 (1956).

14) E. Perez-Beeito and E. Rodenas, *J. Colloid Interface Sci.*, **139**, 87 (1990).

15) P. Mukerjee, *Adv. Colloid Interface Sci.*, **1**, 241 (1967).

16) H. Alpes, K. Allmann, H. Plattner, J. Reichert, R. Riek, and S. Schulz, *Biochim. Biophys. Acta*, **862**, 294 (1986).

17) K. Kameyama and T. Takagi, *J. Colloid Interface Sci.*, **137**, 1 (1990).

18) G. G. Warr, C. J. Drummond, F. Grieser, B. W. Ninham, and D. F. Evans, *J. Phys. Chem.*, **90**, 4581 (1986).

19) P.-L. Kuo, K. Tsuchiya, I. Ikeda, and M. Okahara, *J. Colloid Interface Sci.*, **92**, 463 (1983).

20) A. Ray and G. Nemethy, *J. Am. Chem. Soc.*, **93**, 6787 (1971).