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# Self-Assembling Properties of 6-O- and 6'-O-Alkylsucrose Mixtures Having Different Chain Lengths Under Aqueous Conditions

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The self-assembling properties of the 6-O- and 6'-O-alkylsucrose mixtures with different chain lengths including octyl, decyl, dodecyl, and tetradecyl under aqueous conditions were studied and compared with those of the 6-O- and 6'-O-hexadecylsucrose mixture previously reported. The title compounds were synthesized from sucrose in five steps. The results of scanning and transmission electron microscopes, powder Xray diffraction, and dynamic light scattering measurements indicated that the selfassembling properties of octyl, decyl, and dodecyl derivatives were completely different from those of the 6-O- and 6'-O-hexadecylsucrose mixture. The three derivatives reported here primarily formed lamellar planes, which further induced the formation of vesicle-type particles under aqueous conditions, whereas the previous derivatives primarily formed spherical micelles in water, which further assembled according to face-centered cubic organization by a drying process from the aqueous dispersion. It was also found that the 6-O- and 6'-O-tetradecylsucrose mixture showed concentrationinduced micelle-lamellar transition behavior in an aqueous dispersion. Furthermore, the mixing of a regioisomer, 6'-O-hexadecylsucrose, with 6-O-hexadecylsucrose induced different self-assembling properties from that of 6-O-hexadecylsucrose alone, but this effect did not appear in the self-assembling of the 6-O- and 6'-O-octylsucrose mixture.

Keywords Sucrose; Monoalkyl ether; Self-assembly; Micelle; Lamellar

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### INTRODUCTION

Amphiphilic molecules, so-called amphiphiles, possess antagonistic hydrophilic and hydrophobic moieties in the same molecule. In aqueous media, such molecules self-assemble or self-organize into diverse aggregate morphologies, such as spherical micelles, cylindrical micelles, spherical vesicles, planer bilayers, and tubes, depending on the molecular shape and solution conditions.<sup>[1]</sup> Because glycolipids, which are natural amphiphiles composed of carbohydrates as a hydrophilic part, exhibit important in vivo functions in living systems,<sup>[2]</sup> synthetic carbohydrate-based amphiphiles have been extensively studied to exhibit a large variety of self-assembling morphologies.<sup>[1]</sup>

In the practical application field, synthetic carbohydrate-based amphiphiles have been specifically employed as additives in various food industries in the form of emulsifiers.<sup>[3]</sup> One of the most effective food additives, practically employed, is the sucrose fatty acid ester, which is composed of a sucrose residue, as a hydrophilic part, and long-alkyl fatty acid moieties, as a hydrophobic part.<sup>[4]</sup> The self-assembling properties of sucrose fatty acid esters change depending on the lengths and types of fatty acid chains and have been investigated extensively.<sup>[5]</sup> In comparison, self-assembling studies of sucrose ether amphiphiles carrying long-alkyl chains attached by ether linkages to the sucrose residue have been less reported. As one of the examples, the effect of molecular shape on the liquid crystal properties of mono-O-(2-hydroxydodecyl)sucroses was reported.<sup>[6]</sup> In the previous paper, we reported the following self-assembling process of a mixture of 6-O- and 6'-O-hexadecylsucroses (C16-mixture) under aqueous conditions.<sup>[7]</sup> The mixture primarily formed spherical micelles with a diameter of approximately 5–7 nm in water, which hierarchically organized according to a face-centered cubic (FCC) structure during the drying process from the aqueous dispersion to construct nanoparticles with a diameter of approximately 50 nm. Moreover, several nanoparticles further assembled to form larger aggregates. In the subsequent investigation, furthermore, we synthesized homogeneous 6-O-hexadecylsucrose and evaluated its self-assembling property under aqueous conditions.<sup>[8]</sup> It was found that the self-assembling process of the pure molecule was completely different from that of its mixture containing the regioisomer, 6'-O-hexadecylsucrose (i.e., the C16 mixture), in which the pure molecule showed a hierarchical self-assembling process based on the primary formation of lamellar planes, leading to vesicle-type particles. It was also revealed that another 6-O-alkylsucrose with a different chain length (i.e., 6-O-octylsucrose) was found to show the same self-assembling process as that of 6-O-hexadecylsucrose. These results indicated that the self-assembling properties of monoalkylsucroses are different depending on the subtle change of their molecular shapes.

On the basis of the above viewpoints, we synthesized in the present study a series of 6-O- and 6'-O-alkylsucrose mixtures having different chain lengths including octyl, decyl, dodecyl, and tetradecyl (C8 mixture, C10 mixture, C12 mixture, and C14 mixture, respectively) and evaluated their self-assembling properties under aqueous conditions. They were compared with those of the C16 mixture reported previously.<sup>[7]</sup> The first three derivatives showed different self-assembling properties from those of the C16 mixture but the same as that of 6-O-hexadecylsucrose as well as 6-O-octylsucrose. Interestingly, the C14 mixture exhibited different self-assembling properties depending on the concentrations of its aqueous dispersions.

#### **RESULTS AND DISCUSSION**

The 6-O- and 6'-O-alkylsucrose mixtures were synthesized from sucrose according to the same procedure as that described in our previous report (Sch. 1).<sup>[7]</sup> Thus, the common intermediate **3** having a hydroxy group at the 6- or 6'-position was first prepared by the successive tritylation at the 6- or 6'-position of sucrose, benzylation of the other hydroxy groups, and detritylation. Etherification of **3** with the corresponding alkyl bromides was then performed in the presence of sodium hydride in DMF at elevated temperatures. Debenzylation of the products was conducted by catalytic hydrogenation under the appropriate conditions to afford the C8 mixture, C10 mixture, C12 mixture, and C14 mixture, respectively. The structures of the materials were confirmed by <sup>1</sup>H NMR and MALDI-TOF MS measurements. The molar ratios of 6-ether to 6'-ether in the products, which were calculated from the integrated ratios of two H1 signals of the glucose residues, were almost 1:1 or higher, because of the higher reactivity of the 6-position than the 6'-position. The ratios are given in the Experimental section.

Then, the resulting products were subjected to the investigation of their self-assembly properties under aqueous conditions. In the scanning electron microscope (SEM) images of the samples on aluminum plates (Fig. 1), which were prepared by drying dispersions of the products in water  $(1 \times 10^{-5} \text{ mol/L})$ , particle-like nanoaggregates were seen. The average diameters of the particles from the C8 mixture, C10 mixture, C12 mixture, and C14 mixture samples were 169, 104, 173, and 156 nm, respectively (the values of the standard deviations are shown in Table 1). The values and morphologies were much different from those of the C16 mixture sample because nanoparticles with an average diameter of ~50 nm by hierarchical organization according to the FCC structure and larger aggregates, which were formed by further assembly of the nanoparticles probably due to their greater density, were observed in the SEM image of the C16 mixture sample (Fig. 1(e), Table 1). Moreover, the standard deviation in the diameters of the C16 mixture was much smaller than that in







Figure 1: SEM images of the samples prepared from dispersions of (a) C8 mixture, (b) C10 mixture, (c) C12 mixture, (d) C14 mixture, and (e) C16 mixture in water  $(1.0 \times 10^{-5} \text{ mol/L})$ .

the diameters of the other particles (4.34 and 16–45, respectively). To further confirm the hierarchical structures of the nanoparticles, transmission electron microscope (TEM) measurement of the selected samples was performed. Dispersions of the C8 mixture and C16 mixture in water ( $1.0 \times 10^{-5}$  mol/L) were placed on carbon film-coated grids. After completing the negative-straining technique, the TEM samples were prepared by drying the preparative materials. The TEM image of the C8 mixture sample (Fig. 2(a)) exhibited vesicle-type particles with diameters of approximately 100–150 nm, whereas in the TEM image of the C16 mixture sample (Fig. 2(b)), some particles with diameters

|                                       | SEM results              |                            |  |                |
|---------------------------------------|--------------------------|----------------------------|--|----------------|
| Sample                                | Average<br>diameter (nm) | Standard<br>devia-<br>tion | Average diameters (nm) by DLS results (1.0 $\times$ 10^{-3} mol/L) | XRD<br>results |
| C8 mixture                            | 169                      | 44.8                       | 106.4  | lamellar       |
| 6-O-octylsucrose <sup>a</sup>         | 117                      | 14.4                       | 105.9  | lamellar       |
| -                                     |                          |                            | $(1.0 \times 10^{-5} \text{ mol/L})$                               |                |
| C10 mixture                           | 104                      | 16.3                       | 126.5  | lamellar       |
| C12 mixture                           | 173                      | 26.2                       | 102.8  | lamellar       |
| C14 mixture                           | 156                      | 22.3                       | 6.8  | lamellar       |
|                                       |                          |                            | 82.0   |                |
|                                       |                          |                            | $(1.0 	imes 10^{-2} 	ext{ mol/L})$                                 |                |
| C16 mixture <sup><math>b</math></sup> | 50                       | 4.34                       | 7.1  | micelle        |
|                                       |                          |                            | $(1.0 \times 10^{-5} \text{ mol/L})$                               |                |
| 6-O-hexadecylsucrose <sup>a</sup>     | 51                       | 12.8                       | 99.8   | lamellar       |
|                                       |                          |                            | $(1.0 \times 10^{-5} \text{ mol/L})$                               |                |

Table 1: SEM, DLS, and XRD results of sucrose ethers

<sup>a</sup> Reference 8.

<sup>b</sup> Reference 7.

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Figure 2: TEM images of the samples prepared from dispersions of (a) C8 mixture and (b) C16 mixture in water  $(1.0 \times 10^{-5} \text{ mol/L})$ .

smaller than 50 nm were seen, which did not exhibit the vesicle-like morphology. The above SEM and TEM results indicated that the self-assembling processes of the present derivatives under aqueous conditions were completely different from those of the C16 mixture under the same conditions.

To confirm the self-assembling processes of these derivatives in the drying state from aqueous dispersions in even greater detail, the powder X-ray diffraction (XRD) measurement was conducted. Fig. 3 shows the XRD profiles of the C8 mixture, C10 mixture, C12 mixture, C14 mixture, and C16 mixture samples, which were prepared by drying their aqueous dispersions ( $1.0 \times 10^{-3}$ mol/L). As reported in our previous paper,<sup>[7]</sup> the XRD profile of the C16 mixture exhibited diffraction peaks ascribable to the (111), (200), (311/222), (400), and (600) Bragg reflections of the FCC structure based on the primary formation of spherical micelles. In the XRD profiles of the other derivatives, on the other hand, diffraction peaks due to (001) and (002) Bragg reflections of the lamellar patterns were observed. From the XRD patterns, it was found that the widths of each lamellar layer increased with an increase in the alkyl chain lengths and were calculated to be 3.00 nm for the C8 mixture, 3.37 nm for the C10 mixture, 3.76 nm for the C12 mixture, and 4.02 nm for the C14 mixture. These XRD results of the present four samples suggested that the lamellar planes probably with alternating hydrophilic sucrose and hydrophobic alkyl layers were primary formed, which further constructed the vesicle-type nanoparticles with the 100–150-nm diameters during the drying process from the aqueous dispersions as observed in the SEM and TEM images.

To evaluate the self-assembling properties of the above materials in aqueous dispersions, then, the dynamic light scattering (DLS) measurement was performed ( $1.0 \times 10^{-3}$  mol/L) (Fig. 4). In our previous paper, we reported the



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Figure 3: XRD profiles of the samples prepared from dispersions of (a) C8 mixture, (b) C10 mixture, (c) C12 mixture, (d) C14 mixture, and (e) C16 mixture in water  $(1.0 \times 10^{-3} \text{ mol/L})$ .

observation of a monomodal profile with the average diameter of ca. 7 nm corresponding to a spherical micelle (Fig. 5(b)) in the DLS profile of the aqueous dispersion of the C16 mixture as shown in Fig. 4(e).<sup>[7]</sup> On the other hand, the DLS results of the aqueous dispersions of the C8 mixture, C10 mixture, and C12 mixture showed the formation of the larger aggregates with the average diameters of 106.4, 126.5, and 102.8 nm, respectively (Figs. 4(a-c)), which probably corresponded to the vesicle-like particles formed from the lamellar planes (Fig 5(a)). The self-assembling processes of these samples were the same as those of 6-O-octylsucrose or 6-O-tetradecylsucrose alone.<sup>[8]</sup> On the other hand, the DLS profile of the aqueous dispersion of the C14 mixture in the same concentration showed the smaller particles with the average diameter of 6.8 nm (Fig. 4(d)) as similar to that of the C16 mixture. This result suggested that the C14 mixture formed the spherical micelles in this concentration in water, but that was not consistent with the self-assembling structure in solid state as observed in the XRD result, which indicated the formation of the lamellar planes. Interestingly, the average diameter increased to  $\sim$ 82 nm when the DLS measurement of the aqueous dispersion of the C14 mixture was conducted under the higher concentration conditions (1.0  $\times$  10 $^{-2}$  mol/L) (Fig. 4(d')). It was

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**Figure 4:** DLS profiles of (a) C8 mixture, (b) C10 mixture, (c) C12 mixture, (d) C14 mixture, and (e) C16 mixture in water  $(1.0 \times 10^{-3} \text{ mol/L})$  and (d') C14 mixture in water  $(1.0 \times 10^{-2} \text{ mol/L})$ .

further confirmed by the DLS measurement that the diameters of the particles in the aqueous dispersions of the C14 mixture were reversibly changed as Figs. 4(d) and 4(d') depending on the concentrations. These results suggested that the C14 mixture showed the concentration-induced micelle–lamellar transition behavior in the aqueous dispersion as shown in Fig. 5.<sup>[9]</sup> Therefore, it was reasonably explained that the XRD profile of the C14 mixture sample in solid state prepared by drying the aqueous dispersion exhibited the lamellar pattern. Furthermore, the comprehensive results of our present and previous studies suggested that the mixing of the stereoisomer 6'-O-tetradecylsucrose



**Figure 5:** Plausible self-assembling processes of (a) C8 mixture, C10 mixture, C12 mixture, and C14 mixture (higher concentration) and (b) C14 mixture (lower concentration) and C16 mixture under aqueous conditions.

with 6-O-tetradecylsucrose (i.e., the C16 mixture) induced the different selfassembling property from that of 6-O-tetradecylsucrose alone, but the mixing did not affect the self-assembling property of the C8 mixture.<sup>[7,8]</sup> The reason for the difference in the self-assembling processes of the aforementioned derivatives is not yet clear, but it is obviously suggested that the subtle difference of their chemical structures strongly affects their self-assembling properties under aqueous conditions. More detailed studies using methods based on calculations that consider factors such as critical packing parameters are now in progress to further investigate the reasons for the difference in their selfassembling processes.

#### CONCLUSION

This study investigated the comparison of the characteristic self-assembling processes in the five 6-O- and 6'-O-alkyosucroses mixtures (C8 mixture, C10 mixture, C12 mixture, C14 mixture, and C16 mixture) with different chain lengths under aqueous conditions. The former four derivatives were presently synthesized from sucrose via the five reaction steps, whereas the latter one has already been synthesized in our previous study.<sup>[7]</sup> The self-assembling properties of the materials under aqueous conditions were evaluated by the SEM,

TEM, XRD, and DLS measurements. Consequently, the former three materials (C8 mixture, C10 mixture, and C12 mixture) primarily formed the lamellarlike planes in water, which further constructed the vesicle-type particles (Fig. 5(a)), whereas, as previously reported by us,<sup>[7]</sup> the C16 mixture formed the spherical micelles in water, which then assembled according to the FCC organization during the drying process from the aqueous dispersion to construct the nanoparticles with a size of approximately 50 nm (Fig. 5(b)). Interestingly, the C14 mixture showed the concentration-induced micelle-lamellar transition behavior in the aqueous dispersion as shown in Fig. 5, probably due to the intermediary nature between the C12 mixture and C16 mixture. Taking the previous results in addition to the present results into consideration as summarized in Table 1, furthermore, it was also confirmed that the mixing of the stereoisomer 6'-O-tetradecylsucrose with 6-O-tetradecylsucrose induced a different self-assembling property from that of 6-O-tetradecylsucrose alone, but the mixing effect was not observed in the self-assembling property of the C8 mixture.<sup>[7,8]</sup>

#### EXPERIMENTAL

#### General

The common intermediate **3** and C16 mixture were prepared from sucrose according to the literature procedure reported by us.<sup>[7]</sup> <sup>1</sup>H NMR spectra were recorded on a JEOL ECX400 spectrometer. MALDI-TOF MS measurements were carried out by using SHIMADZU Voyager Biospectrometry Workstation Ver. 5.1 with 2.5-dihydroxybenzoic acid as matrix containing 0.05% trifluoroacetic acid under positive ion mode. SEM images were obtained using a Hitachi S-4100H electron microscope. The average particle diameters and standard deviations were calculated on the basis of 50 objects for each SEM image. TEM measurements were operated using a Jeol JEM-3010 under 200 kV. XRD measurements were conducted using a PANalytical X'Pert Pro MPD with Nifiltered CuK $\alpha$  radiation ( $\lambda = 0.15418$  nm). DLS measurement was performed on a Zetasizer Nano ZS (Malvern Instruments).

## Synthesis of 6-O-octyl- and 6-O-octylsucuroses Mixture (C8 Mixture)

Under argon, to a dispersion of NaH (0.105 g, 4.36 mmol) in DMF (5.8 mL) was added a solution of **3** (0.556 g, 0.582 mmol) in DMF (11.6 mL) at rt and the mixture was stirred at that temperature for 30 min. After a solution of tetrabutylammonium bromide (small amount) in DMF (2.0 mL) and 1-bromooctane (0.36 mL, 2.04 mmol) were added to the mixture, the etherification was conducted at 80°C for 20 h. The reaction was stopped by addition of methanol

to the reaction mixture. After the resulting mixture was concentrated and diluted with chloroform, the solution was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The residue was subjected to column chromatography on silica gel (eluent; ethyl acetate:hexane = 1:50 (v/v)) to give 1',2,3,3',4,4,6'-hepta-O-benzyl-6-O-octyl- and 1',2,3,3',4,4,6-hepta-O-benzyl-6'-O-octylsucroses (**4-C8**, 0.101 g, 0.0928 mmol) in 15.9% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.86 (t, 3H, CH<sub>3</sub>, J = 4.8 Hz), 1.22–1.25 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-CH<sub>3</sub>), 1.54 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.20–4.20 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.35–4.95 (m, 14H, CH<sub>2</sub>-Ph), 5.69, 5.70 (2d, 1H, H-1, J = 5.2 and 3.6 Hz), 7.22–7.34 (m, 35H, aromatics).

To a solution of **4-C8** (0.101 g, 0.0928 mmol) in a mixed solvent of butanol, methanol, and water (2.14 mL, 10:1:0.25 (v/v/v)) was added 10% palladium on carbon (0.02 g) and the mixture was stirred at rt for 3.5 h under hydrogen atmosphere. After the reaction mixture was filtered and the filtrate was evaporated, the residue was subjected to column chromatography on silica gel (eluent; chloroform:methanol = 10:1) to give 6-*O*- and 6'-*O*-octylsucroses (C8 mixture, 0.023 g, 0.051 mmol, 6-ether : 6'-ether = 1:1) in 55.0% yield. <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$  0.86 (t, 3H, CH<sub>3</sub>, J = 4.8 Hz),  $\delta$  1.30–1.33 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>-CH<sub>3</sub>), 1.59 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.21–4.10 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 5.36, 5.39 (2d, 1H, H-1, J = 3.0 and 4.2 Hz). MALDI-TOF MS: Calcd [C<sub>20</sub>H<sub>38</sub>O<sub>11</sub>]Na<sup>+</sup>: m/z 477.2312. Found: m/z 477.4204.

## Synthesis of 6-O-decyl- and 6-O-decylsucuroses Mixture (C10 Mixture)

In the same way as **4-C8**, **4-C10** was prepared by the reaction of **3** with 3.5 equivalents of 1-bromodecane at 80°C for 20 h in 51.2% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.86 (t, 3H, CH<sub>3</sub>, J = 6.2 Hz), 1.22–1.25 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-CH<sub>3</sub>), 1.54 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.20–4.20 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.35–4.95 (m, 14H, CH<sub>2</sub>-Ph), 5.69, 5.70 (2d, 1H, H-1, J = 4.8 and 4.0 Hz), 7.22–7.34 (m, 35H, aromatics).

Then, synthesis of the C10 mixture was carried out in the same way as the C8 mixture from **4-C10** in 4.5% yield (6-ether:6'-ether = 1:1). <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$  0.87 (t, 3H, CH<sub>3</sub>, J = 6.2 Hz),  $\delta$  1.30–1.33 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>-CH<sub>3</sub>), 1.59 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.21–4.10 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 5.36, 5.39 (2d, 1H, H-1, J = 3.0 and 4.2 Hz). MALDI-TOF MS: Calcd [C<sub>22</sub>H<sub>42</sub>O<sub>11</sub>Na]<sup>+</sup>: m/z 505.2625. Found: m/z 505.3256.

## Synthesis of 6-O-dodecyl- and 6-O-dodecylsucuroses Mixture (C12 Mixture)

In the same way as 4-C8, 4-C12 was prepared by the reaction of 3 with 3.5 equivalents of 1-bromododecane at 80°C for 20 h in 39.4% yield. <sup>1</sup>H NMR

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(CDCl<sub>3</sub>)  $\delta$  0.87 (t, 3H, CH<sub>3</sub>, J = 6.8 Hz), 1.22–1.25 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub>), 1.54 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.20–4.20 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.35–4.95 (m, 14H, CH<sub>2</sub>-Ph), 5.69, 5.70 (2d, 1H, H-1, J = 4.8 and 3.6 Hz), 7.22–7.34 (m, 35H, aromatics).

Then, synthesis of the C12 mixture was carried out in the same way as the C8 mixture from **4-C12** in 7.28% yield (6-ether:6'-ether = 5:2). <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$  0.89 (t, 3H, CH<sub>3</sub>, J = 7.2 Hz),  $\delta$  1.30–1.33 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>-CH<sub>3</sub>), 1.59 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.21–4.10 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 5.36, 5.39 (2d, 1H, H-1, J = 3.0 and 4.2 Hz). MALDI-TOF MS: Calcd [C<sub>24</sub>H<sub>46</sub>O<sub>11</sub>Na]<sup>+</sup>: m/z 533.2938. Found: m/z 533.4521.

## Synthesis of 6-O-tetradecyl- and 6-O-tetradecylsucuroses Mixture (C14 Mixture)

In the same way as **4-C8**, **4-C14** was prepared by the reaction of **3** with 3.5 equivalents of 1-bromotetradecane at 80°C for 20 h in 26.5% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.88 (t, 3H, CH<sub>3</sub>, J = 6.8 Hz), 1.22–1.25 (m, 22H, -(CH<sub>2</sub>)<sub>11</sub>-CH<sub>3</sub>), 1.54 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.20–4.20 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 4.35–4.95 (m, 14H, CH<sub>2</sub>-Ph), 5.69, 5.70 (2d, 1H, H-1, J = 4.8 and 4.0 Hz), 7.22–7.34 (m, 35H, aromatics).

Then, synthesis of the C14 mixture was carried out in the same way as the C8 mixture from **4-C14** in 6.19% yield (6-ether:6'-ether = 5:3). <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$  0.89 (t, 3H, CH<sub>3</sub>, J = 7.2 Hz),  $\delta$  1.30–1.33 (m, 22H, -(CH<sub>2</sub>)<sub>11</sub>-CH<sub>3</sub>), 1.59 (m, 2H, -O-CH<sub>2</sub>-CH<sub>2</sub>-), 3.21–4.10 (m, 15H, H-1',2,3,3',4,4',5,5',6,6', -O-CH<sub>2</sub>-CH<sub>2</sub>-), 5.36, 5.39 (2d, 1H, H-1, J = 3.0 and 4.2 Hz). MALDI-TOF MS: Calcd [C<sub>26</sub>H<sub>50</sub>O<sub>11</sub>Na]<sup>+</sup>: m/z 561.3251. Found: m/z 561.4976.

#### Preparation of Samples for SEM Measurement

A dispersion of 6-O- and 6'-O-alkylsucroses mixture  $(1.0 \times 10^{-5} \text{ mol/L})$  was placed on an aluminum plate and it was left standing under ambient atmosphere until water was evaporated. Then, the resulting solid sample was subjected to the measurement.

#### Preparation of Samples for TEM Measurement

A dispersion of 6-O- and 6'-O-alkylsucroses mixture  $(1.0 \times 10^{-5} \text{ mol/L})$  was placed on a carbon film-coated copper grid. The negative-staining technique was used for TEM sample preparation. Then, the preparative material was left standing under ambient atmosphere until water was evaporated. Then, the resulting solid sample was subjected to the measurement.

#### Preparation of Samples for XRD Measurement

A dispersion of 6-O- and 6'-O-alkyl sucroses mixture ( $1.0 \times 10^{-3}$  mol/L) was placed on a sample plate and it was left standing under ambient atmosphere until water was evaporated. Then, the resulting solid sample was subjected to the measurement.

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