Preparation and Properties of New Surfactants Containing D-Glucosamine as the Building Block

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ABSTRACT: Three types of new surfactants were prepared by using *N*-acetyl-D-glucosamine as a starting material. The first type of surfactant, sodium methyl 4,6-*O*-alkylidene-2-(carboxylatomethylamino)-2-deoxy-D-glucopyranoside, was prepared successively by the following treatments: methyl glucosidation of *N*-acetyl-D-glucosamine, transacetalization with an appropriate aldehyde dimethyl acetal, deacetylation, and finally reaction of the resulting methyl-4,6-*O*-alkylidene-2-amino-2-deoxy-D-glucopyranoside (2-amino precursor) with bromoacetic acid. The reaction of this 2-amino precursor with methyl iodide yielded the second type of surfactant, methyl 4,6-*O*-alkylidene-2-deoxy-2-(trimethylammonio)-D-glucopyranoside iodide, in excellent yield. The last type of compound, sodium methyl 2-acetamide-4,6-*O*-alkylidene-3-*O*-[1-(carboxylato)-ethyl]-2-deoxy-D-glucopyranoside, was synthesized by the reaction of methyl 2-acetamide-4,6-*O*-alkylidene-2-deoxy-D-glucopyranoside with 2-chloropropionic acid. Concerning the two carboxylate types of surfactants, the compounds containing a C_9 or C_{11} hydrophobic chain in the alkylidene part showed higher water solubility than the corresponding compounds containing a C_7 hydrophobic chain. Both the micelle-forming property and the ability to lower the surface tension of these carboxylate types of compounds increased with an increase in the length of the hydrophobic chain in the alkylidene part. These compounds can be applied to new acid-decomposable types of cleavable surfactants because they contain an acetal group. The acetal bond of the ammonium type of compound was cleaved more slowly than that of the corresponding carboxylate types of surfactants in 2% aqueous HCl solution. The biodegradabilities of these compounds were also determined.
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KEY WORDS: Acetalization, acid decomposition properties, biodegradability, D-glucosamine, surface-active properties.

We have been studying various types of new amphiphiles, bearing a carbohydrate structure as the hydrophilic part, which can be easily prepared and have additional functions, as well as excellent surface-active properties. Recently, we have synthesized two types of surfactants by acetalization of glucono-1,5-lactone with a long-chain alkyl aldehyde or ketone, followed by hydrolysis under alkaline conditions (1) or amidation with an appropriate amine (2). These compounds can be used as acid-cleavable surfactants (3–12) because they show good surface- active properties under neutral or alkaline conditions. However, they decompose into nonsurface-active species under acidic conditions and lose their surface active properties.

D-Glucosamine is one of the most common compounds in the saccharide family, as its structure is found in chitin and it is a main component of peptidoglycan, which is the backbone of the cell wall of numerous bacteria. Therefore, surfactants derived from D-glucosamine are expected not only to be useful from an ecological point of view but also to be applicable to the biological and the medical fields. Several studies have been reported on the D-glucosamine-derived surfactants (13–18). For example, Matsumura *et al.* (18) reported a synthetic method for the surfactants bearing amine hydrochloride as a hydrophilic group from *N*-acetyl-D-glucosamine, their surface-active properties, and antimicrobial activities. In all these reports, hydrophobic groups have been introduced onto the D-glucosamine structure mainly by *N*-acylation or glucosidation.

In this work, we have developed another methodology for the preparation of a new D-glucosamine-derived surfactant in which the introduction of a hydrophobic alkyl chain onto D-glucosamine as an alkylidene part is included. According to this methodology, we have prepared three types of new surfactants, sodium methyl 4,6-*O*-alkylidene-2-(carboxylatomethylamino)-2-deoxy-D-glucopyranoside (**4**), methyl 4,6-*O*-alkylidene-2-deoxy-2-(trimethylammonio)-D-glucopyranoside iodide (**5**) and sodium methyl 2-acetamide-4,6-*O*-alkylidene-3-*O*-[1-(carboxylato)ethyl]-2-deoxy-D-glucopyranoside (**6**), by using *N*-acetyl-D-glucosamine as a starting material. Here we report the synthetic method for these surfactants, their surface-active properties, acid-decomposition properties, and biodegradabilities.

EXPERIMENTAL PROCEDURES

Materials. All reagents were commercially available and were used without further purification, except for methanol and tetrahydrofuran (THF), which were distilled before use.

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Analytical methods. The infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer (Hitachi Co., Tokyo, Japan). ^{1}H Nuclear magnetic resonance spectra were measured with a JEOL JNM-GSX400 (400 MHz; JEOL Ltd., Tokyo, Japan) spectrometer with tetramethylsilane as an internal standard. Fast-atom bombardment mass spectra were recorded on a JEOL JMS-DX303 HF spectrometer. Gas–liquid chromatography (GLC) was performed with a Shimadzu GC-8APF (Shimadzu Ltd., Kyoto, Japan) equipped with a fused-silica capillary column (liquid phase, DB-1; film thickness, 0.25 μm; column dimensions, 5 m × 0.25 mm; J&W Scientific, Folsom, CA).

Synthesis of 1,1-dimethyoxydecane. This compound was synthesized according to a previously reported method (19). A mixture of decanal (15.6 g, 0.1 mol), methyl orthoformate (53.1 g, 0.5 mol), and anhydrous methanol (9.61 g, 0.3 mol) in the presence of *p*-toluenesulfonic acid monohydrate (0.95 g, 5 mmol) was refluxed for 20 h. After neutralization with Na_2CO_3 (1.04 g, 10 mmol), the methanol and the unreacted methyl orthoformate were removed *in vacuo*. The residue was extracted with H_2O (300 mL) and CH_2Cl_2 (300 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated. The resulting oil was purified by Kugelrohr distillation under reduced pressure to give the desired product (b.p. 60°C/0.05 Torr, 74% yield). IR (neat): 2930, 2850, 1120, 1060 cm^{-1}. 1,1-Dimethoxyoctane and 1,1-dimethoxydodecane were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and used without further purification.

*Synthesis of methyl 2-acetamide-4,6-*O*-alkylidene-2-deoxy-*D*-glucopyranoside (**2a–f**).* *N*-Acetyl-D-glucosamine (22.1 g, 0.1 mol) was stirred in anhydrous methanol (300 mL) under reflux conditions for 24 h in the presence of *p*-toluenesulfonic acid monohydrate (1.90 g, 0.01 mol). After evaporation of the methanol under reduced pressure, dimethylformamide (40 mL), an appropriate aliphatic aldehyde dimethyl acetal (0.12 mol), and *n*-hexane (40 mL) were added to the residue. The mixture was refluxed for 24 h in a round-bottom flask equipped with a Dean-Stark trap; a theoretical amount of methanol (8 mL) was collected in the Dean-Stark trap. After neutralization with Na_2CO_3 (2.12 g, 0.02 mol), the solvent was evaporated *in vacuo*. The resulting liquid was extracted with H_2O (300 mL) and CH_2Cl_2 (300 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was washed with *n*-hexane and then acetone to yield a white solid as a mixture of the corresponding α- and β-anomers. These isomers were separated by silica-gel column chromatography with a methanol/chloroform (0.5:99.5, vol/vol) eluent. Under these reaction conditions, the α-anomer was preferentially formed. The yields and analytical data are summarized in Table 1.

*Synthesis of methyl 4,6-*O*-alkylidene-2-amino-2-deoxy-*D*-glucopyranoside (**3a–d**).* Deacetylation of methyl 2-acetamide-4,6-*O*-alkylidene-2-deoxy-D-glucopyranoside (**2**) (0.02 mol) was carried out by refluxing for 24 h in 4 N aq. KOH (75 mL)/ethanol (75 mL). After evaporation of the ethanol, the resulting light-yellow solid was extracted with H_2O (300 mL) and Et_2O (300 mL). The ether layer was dried (anhydrous $MgSO_4$) and concentrated. The crude product was purified by silica-gel column chromatography with a methanol/chloroform (1:99, vol/vol) eluent to yield the corresponding compound **3**.

*Synthesis of sodium methyl 4,6-*O*-alkylidene-2-(carboxylatomethylamino)-2-deoxy-*D*-glucopyranoside (**4a–d**).* The mixture of methyl 4,6-*O*-alkylidene-2-amino-2-deoxy-D-glucopyranoside (**3**) (0.01 mol), bromoacetic acid (1.39 g, 0.01 mol), and Na_2CO_3 (5.30 g, 0.05 mol) was stirred in methanol (100 mL) under reflux conditions for 48 h. After evaporation of the solvent, chloroform was added to the residue, and the precipitate was filtered off through a Celite 545 short column. The filtrate was concentrated, and the crude product was purified by silica-gel column chromatography with a methanol/chloroform (3:97) eluent.

*Synthesis of methyl 2-deoxy-4,6-*O*-dodecylidene-2-(trimethylammonio)-α-*D*-glucopyranoside iodide (**5c**).* The mixture of methyl 2-amino-2-deoxy-4,6,-*O*-dodecylidene-α-D-glucopyranoside (**3c**) (3.60 g, 10 mmol), Na_2CO_3 (2.65 g, 25 mmol), and methyl iodide (150 mL, 2.5 mol) was refluxed for 72 h. Methylene chloride was added to the resulting solids after removal of the methyl iodide. The insoluble solids were filtered off through a Celite 545 short column, and the filtrate was concentrated. The crude product was purified by recrystallization from benzene to yield the desired compound as a white solid (5.30 g, 100%).

*Synthesis of sodium methyl 2-acetamide-4,6-*O*-alkylidene-3-*O*-[1-(carboxylato)ethyl]-2-deoxy-α-*D*-glucopyranoside (**6a–c**).* Compounds **6a–c** were synthesized according to a previously reported method (20). Methyl 2-acetamide-4,6-*O*-alkylidene-2-deoxy-α-D-glucopyranoside (**2a–c**) (0.01 mol) was added to a suspension of sodium hydride (2.40 g net, 0.1 mol)/dry THF (80 mL), and the mixture was stirred at 60°C for 1 h. Next, 2-chloropropionic acid (2.17 g, 0.02 mol) was dropped into this suspension, and the mixture was stirred at 60°C for 24 h. The solvent was evaporated *in vacuo* after deactivation of the unreacted sodium hydride by addition of methanol. The resulting solids were dispersed in methylene chloride, and the precipitate was filtered off through a Celite 545 short column. The filtrate was concentrated, and the crude product was purified by silica-gel column chromatography with a methanol/chloroform (2:98, vol/vol) eluent.

The yields and analytical data of compounds **4, 5,** and **6** are shown in Table 2.

Surface-active properties. The Krafft point (T_{Kp}) was determined by the naked eye with a 1 wt% (or 0.1 wt%) aqueous solution. The surface tension of the surfactant solutions in the presence of swamping electrolyte (0.1 M NaCl for **4a–d** and **6a–c**, or 0.1 M NaI for **5c**) was measured at 20°C with a Wilhelmy tensiometer (Shimadzu ST-1; glass plate). The critical micelle concentration (CMC) was determined from the break point of each surface tension vs. concentration (on log scale) curve. The ability to lower surface tension (γ_{CMC}) is based on the surface tension at the CMC. The area per molecule at the liquid–gas interface (A) in nm^2 was calculated

TABLE 1
Yields and Analytical Data of Compounds 2a–f[a,b,c]

Compound	Yield (%)	Melting point (°C)	^{1}H Nuclear magnetic resonance[d] (δ)
2a	35	174–175	0.87(*t*, 3H), 1.27–1.39(*m*, 10H), 1.64–1.68(*m*, 2H), 2.05 (*s*, 3H), 3.35(*dd*, 1H), 3.37(*s*, 3H), 3.47–3.50(*br*, OH), 3.55 (*dd*, 1H), 3.59–3.63(*m*, 1H), 3.77–3.83(*m*, 1H), 4.11(*dd*, 1H), 4.13–4.17(*dd*, 1H), 4.58(*t*, 1H), 4.68(*d*, 1H), 6.09(*d*, NH)
2b	55	171–172	0.88(*t*, 3H), 1.26–1.39(*m*, 14H), 1.62–1.67(*m*, 2H), 2.05 (*s*, 3H), 3.35(*dd*, 1H), 3.37(*s*, 3H), 3.47–3.50(*br*, OH), 3.53 (*dd*, 1H), 3.59–3.64(*m*, 1H), 3.78–3.84(*dd*, 1H), 4.12(*dd*, 1H), 4.13–4.17(*m*, 1H), 4.58(*t*, 1H), 4.68(*d*, 1H), 6.10(*d*, NH)
2c	54	162–163	0.88(*t*, 3H), 1.25–1.39(*m*, 18H), 1.62–1.68(*m*, 2H), 2.06 (*s*, 3H), 3.28–3.29(*br*, OH), 3.35(*dd*, 1H), 3.37(*s*, 3H), 3.53 (*dd*, 1H), 3.59–3.62(*m*, 1H), 3.80–3.83(*m*, 1H), 4.11(*dd*, 1H), 4.12–4.16(*m*, 1H), 4.57(*t*, 1H), 4.68(*d*, 1H), 5.99(*d*, NH)
2d	12	234–236	0.86(*t*, 3H), 1.24–1.32(*m*, 10H), 1.50–1.53(*m*, 2H), 1.81 (*s*, 3H), 3.15(*m*, 2H), 3.31(*s*, 3H), 3.43–3.47(*m*, 3H), 4.03 (*m*, 1H), 4.32(*d*, 1H), 4.55(*t*, 1H), 5.14(*br*, OH), 7.77(*d*, NH)
2e	9	119–222	0.86(*t*, 3H), 1.24–1.32(*m*, 14H), 1.50–1.53(*m*, 2H), 1.81 (*s*, 3H), 3.15(*m*, 2H), 3.30(*s*, 3H), 3.43–3.47(*m*, 3H), 4.03 (*dd*, 1H), 4.31(*d*, 1H), 4.55(*t*, 1H), 5.14(*d*, OH), 7.77(*d*, NH)
2f	18	222–223	0.88(*t*, 3H), 1.23–1.36(*m*, 18H), 1.55–1.68(*m*, 2H), 1.94 (*s*, 3H), 3.21–3.24(*m*, 4H), 3.42–3.59(*m*, 3H), 3.70(*m*, 1H), 4.10–4.12(*m*, 1H), 4.44(*d*, 1H), 4.53(*t*, 1H), 5.01(*br*, OH), 7.66(*d*, NH)

[a]Infrared spectra: **2a–c**: 3600–3000, 2900, 1620, 1540, 1100 cm^{-1}. **2d–f**: 3600–3000, 2900, 1650, 1570, 1100 cm^{-1}.
[b]Fast-atom bombardment mass spectra: *m/z* (rel. intens.): **2a**: 346[(M + 1)$^+$, 100], 314[26], 154[31], 136[24], 126[22]. **2b**: 374[(M + 1)$^+$, 100], 342[27], 126[22]. **2c**: 402[(M + 1)$^+$, 100], 370[24], 154[58], 136[43], 126[23]. **2d**: 346[(M + 1)$^+$, 100], 314[21], 154[63], 136[45]. **2e**: 374[(M + 1)$^+$, 100], 342[17], 154[60], 136[42]. **2f**: 402[(M + 1)$^+$, 100], 370[24], 154[58], 136[43], 126[23].
[c]Anal.: **2a**: Calcd. for $C_{17}H_{31}NO_6$: C, 59.11; H, 9.05; N, 4.05. Found: C, 59.17; H, 9.15; N, 4.02. **2b**: Calcd. for $C_{19}H_{35}NO_6$: C, 61.10; H, 9.45; N, 3.75. Found: C, 61.28; H, 9.55; N, 3.67. **2c**: Calcd. for $C_{21}H_{39}NO_6$: C, 62,82; H, 9.79; N, 3.49. Found: C, 62.67; H, 9.85; N, 3.38. **2d**: Calcd. for $C_{17}H_{31}NO_6 \cdot H_2O$: C, 56.19; H, 9.15; N, 3.85. Found: C, 56.01; H, 8.92; N, 3.93. **2e**: Calcd. for $C_{19}H_{35}NO_6 \cdot 0.5\ H_2O$: C, 59.66; H, 9.49; N, 3.66. Found: C, 59.35; H, 9.52; N, 3.77. **2f**: Calcd. for $C_{21}H_{39}NO_6$: C, 62.82; H, 9.79; N, 3.49. Found: C, 62.60; H, 9.78; N, 3.43.
[d]$CDCl_3$ for **2a–c** and DMSO (dimethyl sulfoxide)-d_6 for **2d–f** as a solvent. *s*: Singlet, *d*: doublet, *t*: triplet, *m*: multiplet, and *br*: broad.

from Equations 1 and 2 (21):

$$\Gamma = -(1/2.303RT)(\delta\gamma/\delta \log C)_T \quad [1]$$

$$A = 10^{21}/N\Gamma \quad [2]$$

where Γ is the surface excess concentration (mol/1000 m^2), R = 8.31 $Jmol^{-1}K^{-1}$, (δγ/δ log *C*) is the slope of the γ vs. log *C* curve below the CMC at constant temperature (*T*), and N = Avogadro's number. The foaming properties were measured by the semi-micro TK Method at 20°C (22). The surface-active properties of compounds **4a–d** and **6a–c** were measured at pH 11 (aq. NaOH), and those for compound **5c** were measured under neutral conditions (pH 6).

Decomposition properties. The acid decomposition properties of the surfactants were evaluated by determining the quantity of liberated octanal (from **4a**), decanal (from **4b**), or dodecanal (from **4c, 4d, 5c,** and **6c**) with GLC under acidic conditions (2% aq. HCl). Typical procedures for compound **4c** are as follows: Compound **4c** (0.220 g, 0.5 mmol) was dissolved in 2% hydrochloric acid (20 mL) containing NaCl (6.0 g), and then *n*-hexane (3.5 mL) and *n*-tetradecane (50 mg, 0.25 mmol, as an internal standard) were added to this solution. The mixture was shaken at 20°C, and some of the solution was sampled from the *n*-hexane layer after a certain period. The quantity of liberated dodecanal into the *n*-hexane layer was determined by GLC calibration curve analysis.

Biodegradation test. A biodegradation test was carried out according to the provisions of Sub-Section 4 of Section 4 of the Law Concerning the Examination and Regulation of Manufacture, etc., of Chemical Substances (1973, Law No. 117, Japan) with activated sludge from a municipal sewage treatment plant in Osaka City. The biochemical oxygen demand (BOD) after one or two weeks was determined by the quantity (mg) of oxygen consumed. Biodegradability was calculated from the following formula:

$$\text{biodegradability (\%)} = \text{BOD/TOD} \times 100 \quad [3]$$

where TOD (mg) refers to the theoretical oxygen demand.

TABLE 2
Yields and Analytical Data of Compounds 4a–d, 5c and 6a–c[a,b,c]

Compound	Yield (%)	Melting point (°C)	^{1}H Nuclear magnetic resonance ($CDCl_3$) (δ)
4a	79	210[d]	0.87(*t*, 3H), 1.27–1.39(*m*, 10H), 1.62–1.65(*m*, 2H), 2.90–3.75 (*br*, 11H), 4.08(*m*, 1H), 4.57(*t*, 1H), 4.79(*d*, 1H)
4b	88	220[d]	0.88(*t*, 3H), 1.26–1.39(*m*, 14H), 1.62–1.68(*m*, 2H), 3.30–3.92 (*br*, 7H), 4.07(*m*, 1H), 4.10(*m*, 1H), 4.32(*br*, 2H), 4.56(*t*, 1H), 4.72(*d*, 1H)
4c	89	225[d]	0.88(*t*, 3H), 1.26–1.39(*m*, 18H), 1.61–1.68(*m*, 2H), 2.90–3.77 (*br*, 11H), 4.10(*m*, 1H), 4.57(*t*, 1H), 4.72(*d*, 1H)
4d	83	300[d]	0.88(*t*, 3H), 1.26–1.39(*m*, 18H), 1.61–1.68(*m*, 2H), 3.20–3.55 (*br*, 7H), 3.71(*m*, 1H), 4.11(*m*, 1H), 4.29(*br*, 2H), 4.39(*d*, 1H), 4.55(*t*, 1H)
5c	100	166–168	0.88(*t*, 3H), 1.26–1.40(*m*, 18H), 1.63–1.66(*m*, 2H), 3.47(*s*, 3H), 3.59(*dd*, 1H), 3.62(*dd*, 1H), 3.64(*s*, 9H), 3.68(*dd*, 1H), 3.80(*br*, OH), 4.11(*dd*, 1H), 4.33(*dd*, 1H), 4.43–4.44(*m*, 1H), 4.61(*t*, 1H), 5.31(*d*, 1H)
6a	76	106–107	0.87(*t*, 3H), 1.20–1.41(*m*, 13H), 1.60–1.62(*m*, 2H), 1.98(*s*, 3H), 3.30(*s*, 3H), 3.46–3.70(*m*, 5H), 3.92–4.20(*m*, 2H), 4.52(*t*, 1H), 4.79(*d*, 1H)
6b	78	106–108	0.88(*t*, 3H), 1.20–1.42(*m*, 17H), 1.63–1.68(*m*, 2H), 2.05(*s*, 3H), 3.30–3.86(*m*, 8H), 4.08–4.30(*m*, 2H), 4.57(*t*, 1H), 4.66(*d*, 1H)
6c	82	110–112	0.88(*t*, 3H), 1.20–1.42(*m*, 21H), 1.52–1.62(*m*, 2H), 1.98(*s*, 3H), 3.30–3.77(*m*, 8H), 3.94–4.13(*m*, 2H), 4.52(*t*, 1H), 4.88(*d*, 1H)

[a]Infrared spectra: **4a–d**: 3600–3000, 2900, 1600, 1100 cm^{-1}. **6a–d**: 3300, 2900, 1700, 1650, 1540, 1100 cm^{-1}. Abbreviations as in Table 1.
[b]Fast-atom bombardment mass spectra: *m/z* (rel. intens.): **4a**: 384[(M + 1)$^+$, 30], 329[15], 176[70], 63[40]. **4b**: 434[(M + Na)$^+$, 69], 412[(M + 1)$^+$, 13], 154[93]. **4c**: 440[(M + 1)$^+$, 42], 370[24], 329[24], 176[83], 154[93], 136[71]. **4d**: 462[(M + Na)$^+$, 62], 440[(M + 1)$^+$, 42], 176[83], 154[93]. **5c**: 402[(M – I)$^+$, 100]. **6a**: 462[(M + Na)$^+$, 100], 440[(M + 1)$^+$, 10], 149[41]. **6b**: 490[(M + Na)$^+$, 100], 468[(M + 1)$^+$, 10]. **6c**: 518[(M + Na)$^+$, 100], 496[(M + 1)$^+$, 18].
[c]Anal.: **5c**: Calcd. for $C_{22}H_{44}NO_5I$: C, 49.90; H, 8.38; N, 2.65; I, 23.97. Found: C, 49.65; H, 8.35; N, 2.61; I, 23.90. Components **4a–d** and **6a–c** were too hygroscopic to give satisfactory results for elemental analysis.
[d]Decomposition temperature.

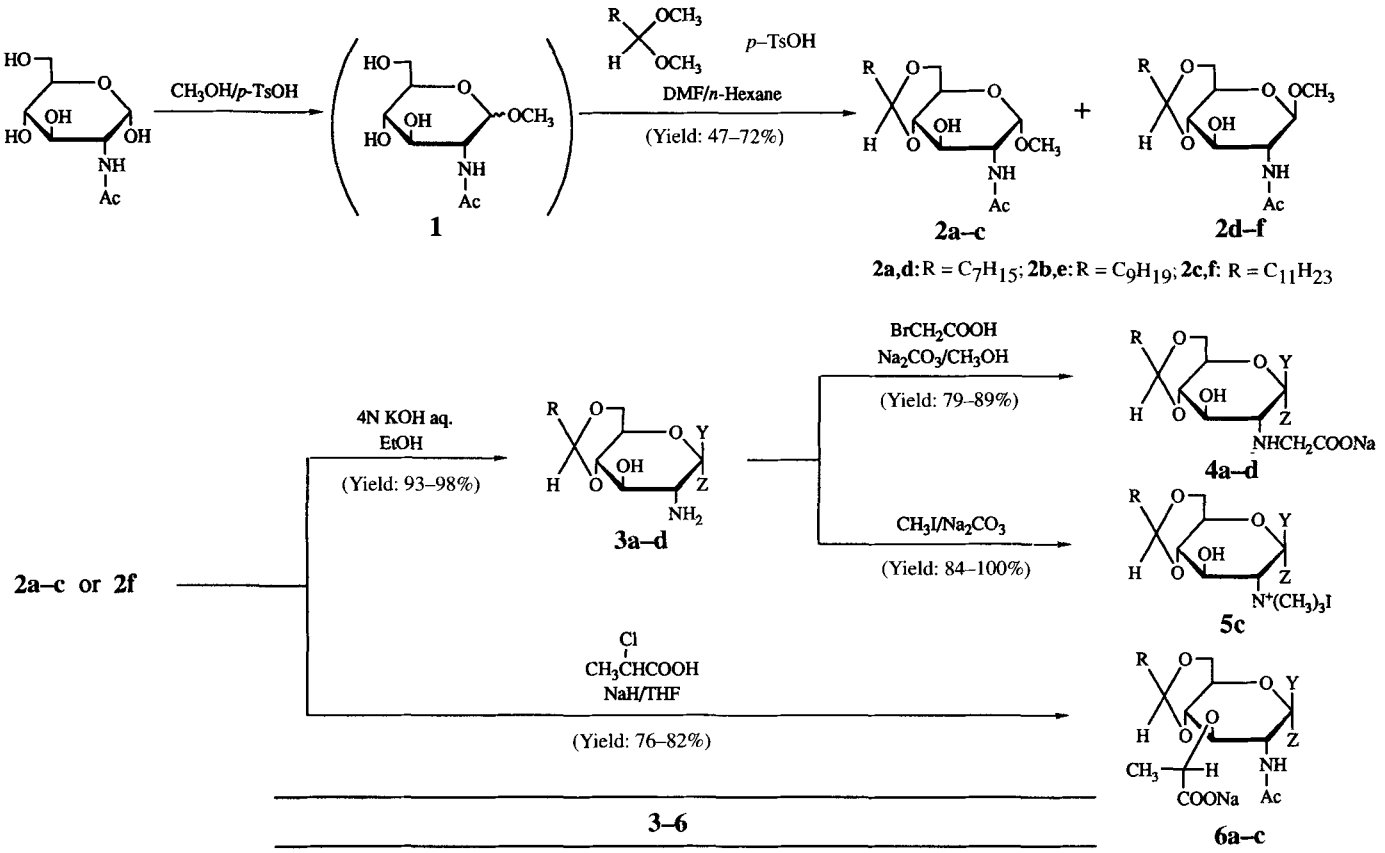
RESULTS AND DISCUSSION

Surfactants **4, 5,** and **6** were synthesized according to the route in Scheme 1.

N-Acetyl-D-glucosamine bearing an anomeric OH group is unstable under alkaline conditions; therefore, the OH group was protected by methylation first. The resulting methyl glucoside was allowed to react with an appropriate aliphatic aldehyde dimethyl acetal *in situ* to yield a mixture of methyl 2-acetamide-4,6-*O*-alkylidene-2-deoxy-α-D-glucopyranoside and the corresponding β-anomer. Under the reaction conditions in this work, the α-anomer was preferentially formed. The mixture can be easily separated by silica-gel column chromatography with methanol/chloroform (1:99) as an eluent. Compound **3**, which was obtained by deacetylation of compound **2** under alkaline conditions, reacted with bromoacetic acid to yield the surfactant **4**. On the other hand, the reaction of compound **3** with methyl iodide quantitatively produced the ammonium type of surfactant **5**. The reaction of compound **2** with 2-chloropropionic acid was carried out according to a previously reported method (20) to yield the surfactant **6**, which was designed as amphiphilic derivatives or analogues of muramic acid. Muramic acid is the main component of the bacterial cell wall. Its derivatives or analogues have attracted the attention of many researchers because of their significant biological activities (23–28).

The plots of surface tension vs. concentration for compounds **4a–d, 5c**, and **6a–c** in the presence of swamping electrolyte are shown in Figure 1. The T_{Kp}^*, the CMC, the γ_{CMC}, and the area per molecule at the liquid–gas interface (A), calculated by the Gibbs adsorption equation (21) of these surfactants, are summarized in Table 3.

Although compounds **4a** and **6a** bearing a C_7 alkyl chain as an "R" group (Fig. 1) were only slightly soluble in water at a 1 wt% concentration, compounds **4b–d** and **6b,c**, bearing longer hydrophobic chains than **4a** and **6a**, were freely soluble in water at 1 wt% concentration at any temperature. This result may be explained by considering that the length of the alkyl chain of **4a** or **6a** is too short to form stable micelles in bulk water. Concerning compounds **4** and **6**, both the micelle-forming property and the ability to lower surface tension increased with an increase in the length of their hydrophobic



3–6

a	$R = C_7H_{15}$, Y = H, Z = OCH_3	**c**	$R = C_{11}H_{23}$, Y = H, Z = OCH_3
b	$R = C_9H_{19}$, Y = H, Z = OCH_3	**d**	$R = C_{11}H_{23}$, Y = H, Z = H

SCHEME 1

chain. Compound **4** showed a higher ability to lower surface tension than the corresponding compound **6** with the same alkyl group "R." There is a correlation between γ_{CMC} and "*A*" for **4** and **6**, indicating that the closer the packing of the molecules at the surface, the lower the value of γ_{CMC}. Comparison of compound **4c** with **4d** indicates that **4c**, possessing an α-OCH_3 group at the anomeric position, has a slightly higher micelle-forming ability than **4d** possessing a ß-OCH_3 group; however, little difference was observed in the γ_{CMC} and *A* values between these compounds. These results are consistent

TABLE 3
Surface Active Properties of Compounds 4a–d[a], 5c[b], and 6a–c[a]

Compound	R[c]	Y[c]	Z[c]	T_{Kp}[d] (°C)	10^4 CMC[d] (mol/L)	γ_{CMC}[a] (mN/m)	10^2A (nm^2)
4a	C_7H_{15}	H	OMe	<0[e]	19	29	51
4b	C_9H_{19}	H	OMe	<0	5.8	28	50
4c	$C_{11}H_{23}$	H	OMe	<0	0.22	27	50
4d	$C_{11}H_{23}$	OMe	H	<0	0.45	28	51
5c	$C_{11}H_{23}$	H	OMe	<0	0.32	32	50
6a	C_7H_{15}	H	OMe	<0[e]	20	39	67
6b	C_9H_{19}	H	OMe	<0	3.6	33	66
6c	$C_{11}H_{23}$	H	OMe	<0	0.86	31	66

[a]At 20°C, pH 11, 0.1M NaCl.
[b]At 20°C, pH 6.0, 0.1M NaI.
[c]R, Y, and Z are substituents in each compound.
[d]Krafft point; measured at 1 wt% concentration. CMC, critical micelle concentration; γ_{CMC}, the ability to lower surface tension. *A*, liquid–gas interface.
[e]For **4a** and **6a**, the T_{Kp} was measured at 0.1 wt% concentration, because both **4a** and **6a** were only slightly soluble in alkaline solution at 1 wt% concentration.

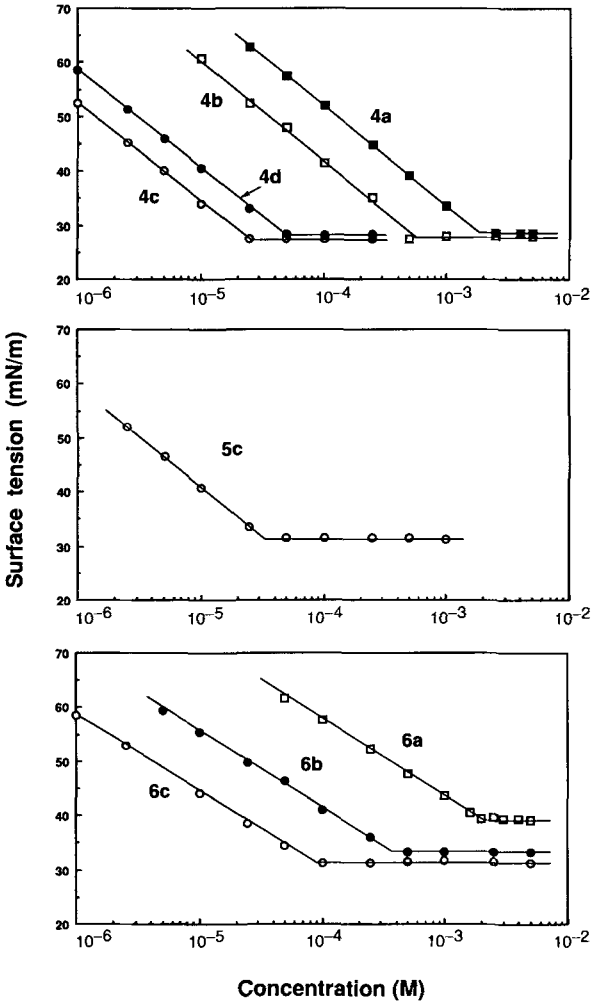


FIG. 1. Surface tension vs. concentration plots of compounds **4a–d, 5c,** and **6a–c** at 20°C. **4a–d, 6a–c**: At pH 11 in the presence of 0.1 M NaCl. **5c**: At pH 6 in the presence of 0.1 M NaI.

with the tendency reported for CMC and γ_{CMC} values of alkyl α- and β-glucosides (29). The ammonium type of compound **5c** showed higher CMC and γ_{CMC} values than the carboxylate type of compound **4c** bearing the same hydrophobic chain and the same configuration at the anomeric center. The foaming ability and foam stability of compounds **4, 5,** and **6** are summarized in Table 4.

Compounds **4b, 4c,** and **4d** showed good foaming ability and excellent foam stability. Little difference was observed in foaming properties between the α-anomer **4c** and the β-anomer **4d**, in contrast to the data on the α- and β-anomer of alkyl glycosides (29). Compounds **6** showed lower foam stability than compounds **4**, which is to be expected based on the increase in the area per molecule at the surface of **6** in comparison with **4**. The ammonium type of compound **5c** also showed lower foam stability.

Under acidic conditions, compounds **4, 5,** and **6** would be expected to decompose into nonsurface-active species because their hydrophobic and hydrophilic groups are linked through an acid-sensitive acetal bond. Scheme 2 shows the expected hydrolytic cleavage routes for compounds **4, 5c,** and **6c**.

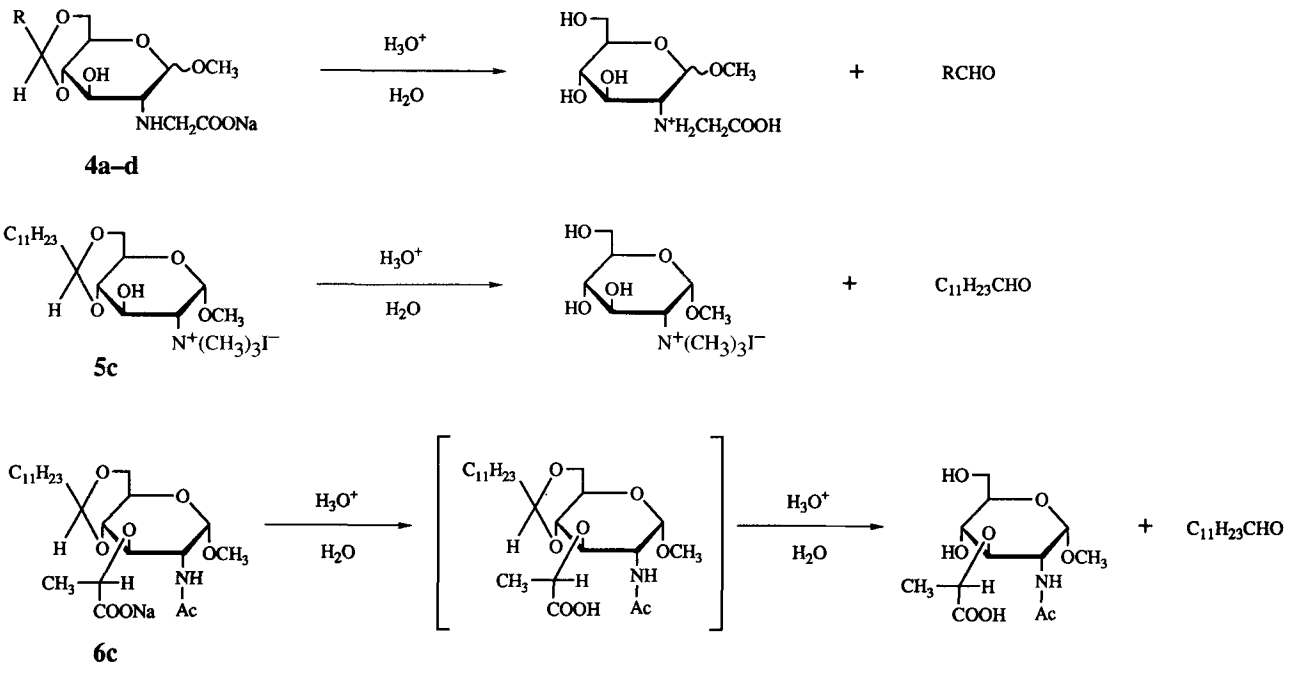
The evaluation of the acid-decomposition properties of these compounds was carried out by determining the quantity of aldehyde generated during their hydrolyses by using the GLC technique. Each surfactant concentration in the aqueous phase was adjusted to 25 mmol/L (above each CMC). The decomposition profiles of compounds **4a–d, 5c,** and **6c** in 2% aqueous HCl are illustrated in Figure 2.

In a series of compounds **4**, the order of decreasing acid-decomposition rate is: **4a** ≫ **4b** > **4c** = **4d**, which is the same order of increasing CMC in this series. There was little difference in decomposition profiles between compounds **4c** and **4d**, which have the opposite configuration at the anomeric position. The ammonium type of compound **5c** decomposed more slowly than the corresponding carboxylate **4c**. Because of the electrostatic repulsion between protons in the bulk phase and the positively charged micellar surface, it may be hard for protons to attack the acetal groups through the Stern layers of the cationic micelles (8). In the case of compound **6c**, because the water-insoluble carboxylic acid was predominantly formed under these experimental conditions, its decomposition percentage converged on only 20%.

TABLE 4
Foaming Properties of Compounds 4a–d, 5c, and 6a–c[a]

Compound	R	Y	Z	Foam volume (mL) per min			
				0	3	5	10
4a[b]	C_7H_{15}	H	OMe	270	0	—	—
4b	C_9H_{19}	H	OMe	280	280	280	280
4c	$C_{11}H_{23}$	H	OMe	280	280	280	280
4d	$C_{11}H_{23}$	OMe	H	280	280	280	280
5c[c]	$C_{11}H_{23}$	H	OMe	280	80	30	0
6a[b]	C_7H_{15}	H	OMe	270	0	—	—
6b	C_9H_{19}	H	OMe	270	20	0	—
6c	$C_{11}H_{23}$	H	OMe	270	20	0	—

[a]At 20°C, pH 11, 1 wt%. See Table 3 for R, Y, Z explanations.
[b]Measured at 0.1 wt% concentration. Both **4a** and **6a** were only slightly soluble at 1 wt% concentration.
[c]At 20°C, pH 6, 1 wt%.



SCHEME 2

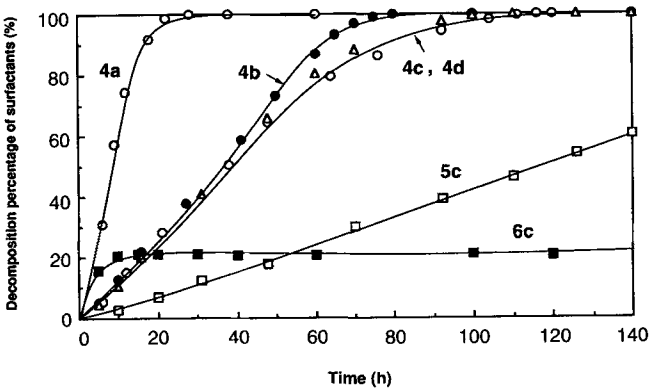


FIG. 2. Decomposition percentage of surfactant vs. time plots of compounds **4a–d, 5c,** and **6c** in 2% aq. HCl. Surfactant concentration: 25 mM.

TABLE 5
Biodegradability of Surfactants 4a, 4c, 4d, 5c, and 6c

Surfactant	BOD/TOD × 100 (%)[a] One week	Two weeks
4a	9	24
4c	31	40
4d	20	27
5c	6	−3
6c	36	52
$C_{11}H_{23}COONa$	34	43

[a]BOD, biochemical oxygen demand; TOD, theoretical oxygen demand.

The biodegradabilities (%) (BOD/TOD × 100) of compounds **4a, 4c, 4d, 5c**, and **6c** after one or two weeks are shown in Table 5, along with the data for sodium dodecanoate under the same conditions.

The biodegradabilities of the carboxylate types of surfactants **4** and **6** were much higher than that of the ammonium type of surfactant **5** bearing the same hydrophobic alkyl chain. Concerning compounds **4**, the biodegradability was affected by both the length of the alkyl chain and the anomeric configuration. It is noteworthy that compound **6c** showed higher biodegradability than sodium dodecanoate under these experimental conditions. The negative biodegradation value of the ammonium type of compound **5c** after two weeks is mainly attributed to the antimicrobial activity of this compound for microbes existing in the activated sludge.

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