New Cleavable Surfactants Derived from Glucono-1,5-Lactone

Toshiyuki Kida, Nobuaki Morishima, Araki Masuyama and **Yohji Nakatsuji***
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka 565, Japan

New amido nonionic cleavable surfactants were synthesized in good yields by the acetalization of glucono-1,5-lactone with octanal, 2- octanone or 2-undecanone, followed by amidation with monoethanolamine, diethanolamine or morpholine. These compounds possessed good water solubilities. The compounds derived from 2-octanone showed higher critical micelle concentrations than the compounds from octanal. For the same hydrophobic chain, both the micelle-forming property and the ability to lower surface tension increased with the change in the terminal amide group in the order diethanolamide < morpholide < monoethanolamide. Interestingly, in spite of their relatively short hydrophobic chains, these compounds showed greater ability to lower surface tension than conventional nonionic surfactants, such as alcohol ethoxylates. Furthermore, their acid-decomposition properties were determined. Their decomposition rates were also compared with that of the corresponding carboxylate type of compound derived from glucono-1,5-lactone.

KEY WORDS: Acid-decomposition properties, cleavable surfactant, glucono-1,5- lactone, sugar-derived surfactant, surface-active properties.

Sugar-derived amphipathic compounds, such as sucrose fatty acid esters (1,2) and alkyl glycosides (3–8), have been widely utilized in food, cosmetics, drugs and the biochemical field. Recently they have attracted attention again because of some of their advantages over other amphiphiles. They are prepared from naturally-occurring resources and have excellent surface-active properties. Furthermore, they are safe for human use and assumed to be ecologically useful.

We have tried to develop a new sugar-derived amphiphile, which has a new function in addition to the abovementioned properties and is easily available. Recently we found that new amphiphatic carboxylates could be easily prepared by acetalization of glucono-1,5-lactone, which is an oxidation product of glucose, with a long-chain alkyl aldehyde or ketone, followed by hydrolysis under alkaline conditions (9). These compounds are stable and show surface-active properties under neutral or alkaline conditions; whereas, under acidic conditions, they decompose into nonsurface active species because their hydrophobic and hydrophilic groups are linked through an acid-sensitive acetal bond. Thus, they can be utilized as new cleavable surfactants (10–17).

In this work we synthesized new amido nonionic surfactants that possess acid-decomposition properties by acetalization of glucono-1,5-lactone with a long-chain carbonyl compound, followed by amidation with an appropriate amine. These surfactants are expected to be safer for human use than the corresponding carboxylates and are potentially useful in the biochemical field. Many amido nonionic amphiphiles derived from sugars have been reported (18–21) during recent years. However, no compounds among those have acid-decomposable properties. Here we report a synthetic method for amido nonionic cleavable surfactants, their surface-active properties and their acid-decomposition properties. The desired compounds (**2a–h**) and sodium 4,6-*O*-octylidenegluconate (**3a**) as a reference compound were synthesized according to Scheme 1.

*To whom correspondence should be addressed at Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan.

EXPERIMENTAL PROCEDURES

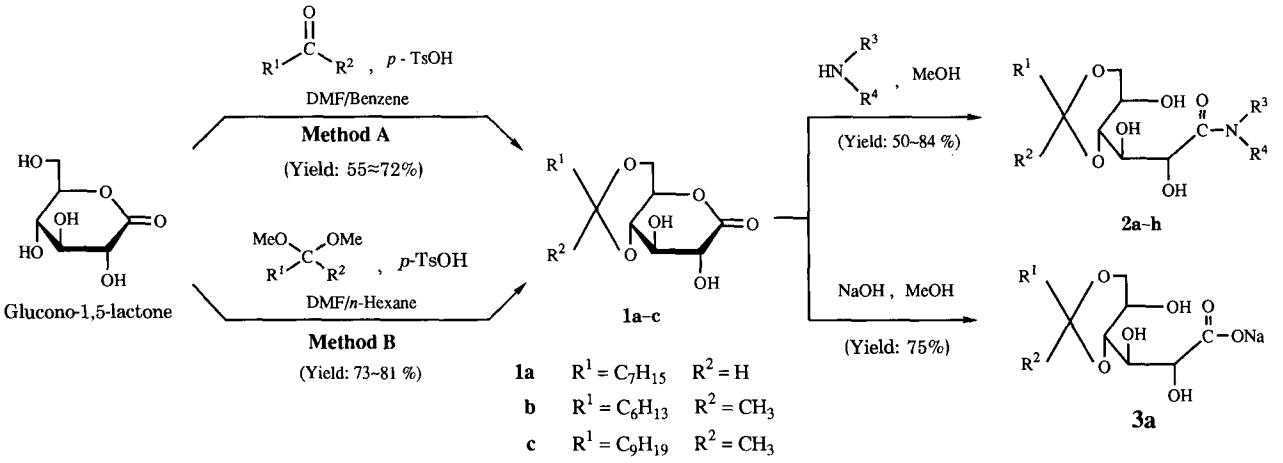
Materials. All reagents were commercially available and were used without further purification, except dimethylformamide (DMF), which was dried over molecular sieves 4A before use.

Analytical methods. Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer (Hitachi Co., Tokyo, Japan). ^{1}H nuclear magnetic resonance (NMR) spectra were measured in a JEOL JNM-GSX400 (400 MHz; JEOL Ltd., Tokyo, Japan) spectrometer with tetramethylsilane as an internal standard. Fast-atom bombardment (FAB)-mass spectra were recorded on a JEOL JMS-DX303 HF spectrometer. The gas–liquid chromatography (GLC) was performed with a Shimadzu GC-8APF (Shimadzu Ltd., Kyoto, Japan) equipped with 20% tricresyl phosphate on a Uniport R 60/80 packed glass column (1-m length).

Synthesis of 2,2-dimethoxyoctane. This compound was synthesized according to the previously reported method of Büchi *et al.* (25). A mixture of 2-octanone (6.41 g, 50 mmol), methyl orthoformate (26.53 g, 250 mmol) and methanol (3.2 g, 100 mmol) in the presence of *p*-toluenesulfonic acid monohydrate (0.48 g, 2.5 mmol) was refluxed for 24 h. After neutralization with Na_2CO_3 (0.53 g, 5 mmol), the methanol and the unreacted methyl orthoformate were removed *in vacuo*. The residue was extracted with H_2O (80 mL) and Et_2O (2 × 80 mL). The organic layers were combined, dried ($MgSO_4$), filtered and evaporated. The resulting oil was purified by Kugelrohr distillation under reduced pressure to give the pure product (b.p. 50°C/0.9 Torr, 90% yield). IR (neat): 2920, 1460, 1370, 1050 cm^{-1}.

Synthesis of 4,6-O-alkylideneglucono-1,5-lactone (1a–c). In this work, these compounds were prepared by the following two methods with azeotropic compounds.

Method A. A mixture of octanal, 2-octanone or 2-undecanone (20 mmol), glucono-1,5-lactone (4.28 g, 24 mmol), *p*-toluenesulfonic acid monohydrate (0.76 g, 4 mmol), DMF (30 mL) and benzene (50 mL) was placed in a round-bottom flask equipped with a Dean-Stark trap. The mixture was refluxed for 6–8 h; about 0.4 mL H_2O was collected in a Dean-Stark trap. After the solution was filtered through a short column filled with alumina (neutral) to remove *p*-toluenesulfonic acid, the solvent was evaporated *in vacuo*. The residue was extracted with brine (100 mL) and Et_2O (3 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by recrystallization from benzene/*n*-hexane for **1a** and **1b** or from *n*-hexane for **1c**. All isolated compounds (**1a–c**) were found to consist of a mixture of two diastereomers (ratio 1:1), which have different configurations at the acetal carbon atom on the 1,3-dioxane ring by ^{1}H NMR spectroscopy. These isomers were used in the subsequent reactions without further separation.



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
2a	C_7H_{15}	H	CH_2CH_2OH	H	**2f**	C_6H_{13}	CH_3		
2b	C_7H_{15}	H	CH_2CH_2OH	CH_2CH_2OH	**2g**	C_9H_{19}	CH_3	CH_2CH_2OH	H
2c	C_7H_{15}	H			**2h**	C_9H_{19}	CH_3		
2d	C_6H_{13}	CH_3	CH_2CH_2OH	H	**3a**	C_7H_{15}	H		
2e	C_6H_{13}	CH_3	CH_2CH_2OH	CH_2CH_2OH					

SCHEME 1

Method B. Instead of aldehyde (or ketone) and DMF/benzene in Method A, its dimethyl acetal derivative as a reagent and DMF/*n*-hexane as a solvent were used in this method. About 1 mL methanol was collected in a Dean-Stark trap after completion of the reaction (total reaction time, 6–10 h). The work-up procedures were carried out in the same manner as described in Method A.

The yields and analytical data of compounds **1a–c** are summarized in Table 1.

Synthesis of 4,6-O-alkylidenegluconoamide derivatives (2a–h). These compounds were synthesized by the reaction of 4,6-*O*-alkylideneglucono-1,5-lactone with monoethanolamine, diethanolamine or morpholine. The mixture of 4,6-*O*-alkylideneglucono- 1,5-lactone (2 mmol) and amine (3 mmol) was stirred in methanol (5 mL) under reflux conditions for 2 h (in the case of **2b** and **2e** for 20 h in ethanol). After evaporation of the solvent and the unreacted amine under reduced pressure, the residue was extracted with brine (20 mL) and Et_2O or ethyl acetate (3 × 25 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by recrystallization from ethyl acetate/*n*-hexane (**2a**, **2d** and **2g**) or *n*-hexane (**2h**). For **2b**, **2c**, **2e** and **2f**, purification was carried out by preparative high-performance liquid chromatography (HPLC) (column: Inertsil PREP-ODS 10 μm, 20 × 250 mm; Gasukuro Kogyo, Inc., Tokyo, Japan) with methanol as the eluent. These isolated products **2a–h** were characterized by IR and ^1H NMR spectroscopy and by elemental analyses. Yields and analytical data are summarized in Table 2.

Synthesis of sodium 4,6-O-octylidenegluconate (3a). 4,6-*O*-Octylideneglucono-1,5-lactone (2.88 g, 10 mmol) was added into a sodium hydroxide (0.48 g, 12 mmol)/methanol (40 mL) solution. The mixture was refluxed for 3 h. After evaporation of the methanol under reduced pressure, the residue was purified by recrystallization from ethanol/water (9:1) to give pure **3a** (2.40 g, 73% yield). Decomposition temperature: 213–215°C; IR (neat): 3220, 2940, 1600, 1120 cm^{-1}; FAB-mass [*m/e*, relative intensity]: 351[$(M + Na)^+$, 41], 329[$(M + 1)^+$, 37], 115[100]; ^1H NMR [in D_2O, sodium 2,2-dimethyl-2-silapentane-5-sulfonate as an internal standard]; δ 0.85 (*t*, 3H), 1.27–1.38 (*m*, 10H), 1.62–1.71 (*m*, 2H), 3.81–4.06 (*m*, 4H), 4.10 (*d*, J = 4.4 Hz, 1H), 4.20–4.24 (*m*, 1H), 4.96 (*t*, J = 4.9 Hz, 0.5H) and 5.06 (*t*, J = 4.9 Hz, 0.5H).

Surface-active properties. The cloud point (T_{cp}) and Krafft point (T_{Kp}) were determined by the naked eye with a 1 wt% (or 0.1 wt%) aqueous solution. The surface tensions of the surfactant solutions were measured at 20°C with a Wilhelmy tensiometer (Shimadzu ST-1; Shimadzu Ltd.). The critical micelle concentration (CMC) was determined from the break point of each surface tension vs. concentration (on log-scale) curve. Surface-active properties of compounds **2a–h** were measured under neutral conditions (≈ pH 6), while those for compound **3a** were measured at pH 11 (adjusted by 1 × 10^{-3} N NaOH aqueous).

Decomposition properties. Acid-decomposition properties of the surfactants were evaluated by determining the quantity of liberated octanal (from **2a** and **3a**) or 2-octanone (from **2d**) with GLC under acidic conditions

TABLE 1

Yields and Analytical Data of Compounds 1a, 1b and 1c[a,b,c]

Compound	Yield (%)		^{1}H NMR (acetone-d_6) δ, *J* (Hz)	Analysis found (calcd.)
	Method A	Method B		
1a	72	81	0.88 (*t*, 3H), 1.29–1.40 (*m*, 10H), 1.57–1.67 (*m*, 2H), 3.86 (*dd*, *J* = 6.3 and 7.3, 0.5H), 3.91–3.99 (*m*, 1H), 4.14–4.17 (*m*, 1.5H), 4.35 (*m*, 0.5H), 4.40–4.45 (*m*, 1.5H), 4.59 (*dd*, *J* = 3.4 and 4.4, 0.5H), 4.74 (*dd*, *J* = 3.4 and 4.4, 0.5H), 4.85 (-OH, 0.5H), 4.86 (*t*, *J* = 4.4, 0.5H), 4.96 (-OH, 0.5H), 5.01 (*t*, *J* = 3, 0.5H), 5.42 (-OH, 1H)	C: 58.62 (58.32) H: 8.47 (8.39)
1b	55	73	0.88 (*t*, 3H), 1.27–1.44 (*m*, 11H), 1.59–1.68 (*m*, 2H), 3.90 (*dd*, *J* = 5.9 and 8.8, 0.5H, H-6a), 3.93 (*dd*, *J* = 6.6 and 8.8, 0.5H, H-6a), 4.09–4.15 (*m*, 2H, H-6e and H-2), 4.35–4.39 (*m*, 1H, H-3), 4.43 (*dd*, *J* = 6.6 and 12.5, 0.5H, H-5), 4.48 (*dd*, *J* = 5.9 and 12.5, 0.5H, H-5), 4.63 (*dd*, *J* = 4.4 and 6.6, 0.5H, H-4), 4.66 (*dd*, *J* = 4.4 and 5.9, 0.5H, H-4), 4.85 (-OH), 5.42 (-OH)	C: 58.06 (58.32) H: 8.43 (8.39)
1c	55	—[d]	0.88 (*t*, 3H), 1.27–1.44 (*m*, 17H), 1.59–1.68 (*m*, 2H), 3.90 (*dd*, *J* = 5.9 and 8.3, 0.5H, H-6a), 3.93 (*dd*, *J* = 6.4 and 8.3, 0.5H, H-6a), 4.09–4.15 (*m*, 2H, H-6e and H-2), 4.34–4.38 (*m*, 1H, H-3), 4.43 (*dd*, *J* = 6.3 and 12.2, 0.5H, H-5), 4.48 (*dd*, *J* = 6.4 and 12.2, 0.5H, H-5), 4.63 (*dd*, *J* = 3.9 and 6.4, 0.5H, H-4), 4.66 (*dd*, *J* = 4.4, 5.9, 0.5H, H-4), 4.87 (-OH, *d*, *J* = 2.0, 0.5H), 4.88 (-OH, *d*, *J* = 2.0, 0.5H), 5.44 (-OH, *d*, *J* = 4.4, 0.5H), 5.45 (-OH, *d*, *J* = 4.4, 0.5H)	C: 61.70 (61.80) H: 9.26 (9.15)

[a]Melting point: **1a**, 93–95°C; **1b**, 71–74°C; **1c**, 88–90°C. NMR, nuclear magnetic resonance.
[b]Infrared spectra: **1a**, 3600–3200, 2950–2850, 1750, 1100 cm^{-1}; **1b**, 3550–3300, 3000–2850, 1800–1730, 1140 cm^{-1}; **1c**, 3500–3450, 3000–2850, 1780–1750, 1080 cm^{-1}.
[c]Fast-atom bombardment-mass spectra; *m/z* (relative intensity): **1a**, 289[$(M + 1)^+$, 77], 161[50], 69[100]; **1b**, 289[$(M + 1)^+$, 100], 129[97], 93[76]; **1c**, 331[$(M + 1)^+$, 13], 185[73], 93[100].
[d]Not carried out.

(pH 1 or 3, adjusted by 0.1 or 1×10^{-3} N aqueous HCl). Typical procedures for compound **2a** are as follows: Compound **2a** (34.9 mg, 0.1 mmol) was dissolved in 0.1 N hydrochloric acid (5 mL, pH 1). *n*-Hexane (5 mL) and *p*-xylene (10.6 mg, 0.1 mmol, as an internal standard) were added into this solution. The mixture was shaken at 20°C, and some of the solution was sampled from the hexane layer after a certain period. The quantity of liberated octanal into the hexane layer was determined by the GLC–calibration curve analysis.

RESULTS AND DISCUSSION

Synthesis of surfactants **2a–h** and **3a** was carried out according to the routes in Scheme 1. The intermediates, 4,6-*O*-alkylideneglucono-1,5-lactones (**1a–c**), were prepared by two different methods (A and B). Yields for both are summarized in Table 1. In Method A, glucono-1,5-lactone reacted with a long-chain alkyl aldehyde or ketone in the presence of an acid catalyst. Water generated during the acetalization was removed from the reaction systems as a benzene azeotrope. In Method B, instead of the carbonyl compounds, the corresponding dimethyl acetal derivatives were used. In this case, the acetalization proceeded at a lower temperature than that in Method A, and the resulting products, 4,6-*O*-alkylideneglucono-1,5-lactones, were obtained in higher yields as compared with the yields in Method A. The lower reaction temperature might suppress the thermal decomposition of glucono-1,5-lactone, which leads to the higher yields of the desired compounds. The reactions of 4,6-*O*-alkylideneglucono-1,5-lactone (**1**) with amines gave the corresponding 4,6-*O*- alkylidenegluconamide derivatives (**2**). The products were purified by recrystallization of preparative HPLC. The yields and analytical data of compounds **2a–h** are shown in Table 2. Additionally, hydrolysis of 4,6- *O*-octylideneglucono-1,5-lactone under alkaline conditions into sodium 4,6-*O*-octylidenegluconate **3a** was also carried out.

The plots of surface tension vs. concentration for compounds **2a–g** and **3a** are shown in Figure 1. The cloud point (T_{cp}) for nonionic compounds **2** or Krafft point (T_{Kp}) for **3a**, the CMC, and the ability to lower surface tension (γ_{CMC}) of these surfactants are summarized in Table 3. Those values for compound **2h** could not be measured because of its low solubility in water.

The cloud points of nonionic compounds **2a–g** were more than 82°C at 1 wt% concentration, and those results clearly show that they have good water solubilities. The Krafft point for **3a** was less than 0°C at 0.1 wt% concentration (pH 11). The ketone-derived compounds **2d–f** showed higher CMC values than the aldehyde-derived compounds **2a–c** containing the same number of carbon atoms in the alkylidene part. This is consistent with the general tendency that the CMC value of a surfactant bearing a branched hydrophobic chain is higher than that of a surfactant having the corresponding straight-chain (26). The micelle-forming ability of the ketone-derived compound increased with an increase in the alkyl chainlength (**2d** and **2g**). Concerning the nonionic compounds that possess the same hydrophobic chain (for example, **2a**, **2b** and **2c**), both the micelle-forming property and the ability to lower surface tension increased in the order of diethanolamide < morpholide < monoethanolamide. The γ_{CMC} values of nonionic compounds **2a**, **2b** and **2c** were smaller

TABLE 2

Yields and Analytical Data of Compounds 2a-h[a,b,c]

Compound	Yield (%)	^{1}H NMR[d] δ, J (Hz)	Analysis found (calcd.)[e]
2a	60	0.88 (*t*, 3H), 1.29-1.38 (*m*, 10H), 1.53-1.56 (*m*, 2H), 3.35 (*t*, J = 6, 2H), 3.61 (*m*, 2H), 3.37 (*m*, 0.5H), 3.85 (*m*, 1.5H), 3.98 (*m*, 2H), 4.08 (*m*, 1H), 4.21 (*dd*, J = 4.4, 5.9, 1H), 4.83 (*t*, J = 4.9, 0.5H), 4.93 (*t*, J = 4.9, 0.5H)	C: 54.66 (55.00) H: 8.98 (8.94) N: 3.99 (4.01)
2b	50	0.88 (*t*, 3H), 1.29-1.38 (*m*, 10H), 1.53-1.58 (*m*, 2H), 3.36-3.43 (*m*, 1H), 3.60-3.65 (*m*, 1H), 3.72-3.87 (*m*, 8H), 3.96-4.10 (*m*, 3H and 3OH), 4.31-4.39 (2OH), 4.74-4.77 (*m*, 1H), 4.83 (*t*, J = 4.9, 0.5H), 4.93 (*t*, J = 4.9, 0.5H)	C: 53.99 (53.72) H: 9.12 (9.02) N: 3.34 (3.48)
2c	73	0.88 (*t*, 3H), 1.30-1.39 (*m*, 10H), 1.54-1.62 (*m*, 2H), 3.61-3.64 (*m*, 8H), 3.77-3.84 (*m*, 1H), 3.86-3.88 (*m*, 2H), 3.99-4.11 (*m*, 2H), 4.66 (*t*, 1H), 4.83 (*t*, J = 4.9, 0.5H), 4.94 (*t*, J = 4.9, 0.5H)	C: 57.36 (57.58) H: 8.91 (8.86) N: 3.56 (3.73)
2d	78	0.88 (*t*, 3H), 1.24-1.36 (*m*, 11H), 1.55-1.62 (*m*, 2H), 3.32-3.40 (*m*, 2H), 3.62 (*t*, J = 5.4, 2H), 3.76-3.82 (*m*, 1H), 3.89-3.99 (*m*, 2H), 4.03-4.07 (*m*, 1H), 4.10-4.19 (*m*, 1H), 4.22 (*t*, J = 4.4, 1H)	C: 54.73 (55.00) H: 8.92 (8.94) N: 4.05 (4.01)
2e	55	0.88 (*t*, 3H), 1.29-1.37 (*m*, 11H), 1.58-1.63 (*m*, 2H), 3.37-3.41 (*m*, 1H), 3.59-3.77 (*m*, 8H), 3.88-4.15 (*m*, 4H and 2OH), 4.30-4.38 (2OH), 4.72-4.76 (*m*, 1H)	C: 55.34 (54.95) H: 9.14 (8.96) N: 3.17 (3.56)
2f	73	0.88 (*t*, 3H), 1.25-1.36 (*m*, 11H), 1.55-1.63 (*m*, 2H), 3.60-3.70 (*m*, 9H), 3.87 (*t*, J = 3, 1H), 3.89-3.95 (*m*, 1H), 4.03-4.07 (*m*, 1H), 4.08-4.16 (*m*, 1H), 4.65 (*t*, J = 4, 1H)	C: 57.44 (57.58) H: 8.99 (8.86) N: 3.49 (3.73)
2g	84	0.88 (*t*, 3H), 1.24-1.38 (*m*, 17H), 1.55-1.62 (*m*, 2H), 3.33-3.38 (*m*, 2H), 3.60-3.64 (*m*, 2H), 3.76-3.83 (*m*, 1H), 3.89-3.99 (*m*, 2H and OH), 4.02-4.07 (*m*, 1H), 4.09-4.19 (*m*, 1H and OH), 4.20-4.24 (*m*, 1H), 4.80 (OH), 7.48 (NH)	C: 58.14 (58.29) H: 9.52 (9.53) N: 3.46 (3.58)
2h	70	0.88 (*t*, 3H), 1.26-1.30 (*m*, 14H), 1.33 (*s*, 3H), 1.56-1.62 (*m*, 2H), 3.10-3.30 (-OH, *br*), 3.55-3.72 (*m*, 9H), 3.89 (*m*, 1H), 3.97 (*dd*, J = 6 and 8, 1H), 4.06 (*m*, 1H), 4.12 (*m*, 1H), 4.15-4.25 (-OH, *br*), 4.61 (*d*, J = 2.4, 1H)	C: 60.30 (60.41) H: 9.45 (9.41) N: 3.37 (3.35)

[a]Melting point: **2a**, 101-104°C; **2b**, viscous liquid; **2c**, waxy; **2d**, 60-63°C; **2e**, viscous liquid; **2f**, viscous liquid; **2g**, 62-65°C; **2h**, 86-89°C.
[b]Infrared spectra; **2a, 2d, 2g:** 3450-3300, 2950, 2880, 1680-1620, 1100-1060 cm^{-1}; **2b, 2e:** 3500-3200, 2950, 2880, 1640-1600, 1120, 1040 cm^{-1}; **2c, 2f, 2h:** 3500-3300, 2950, 2850, 1680-1600, 1130 cm^{-1}.
[c]Fast-atom bombardment-mass spectra; *m/z* (relative intensity); **2a:** 350[$(M + 1)^+$, 100], 220[58], 93[56], 62[95]; **2b:** 394[$(M + 1)^+$, 100], 266[47], 106[94]; **2c:** 376[$(M + 1)^+$, 100], 248[58], 114[61], 88[70]; **2d:** 350[$(M + 1)^+$, 95], 222[100], 62[45]; **2e:** 394[$(M + 1)^+$, 86], 266[100], 106[82]; **2f:** 376[$(M + 1)^+$, 60], 248[100], 114[63], 88[57]; **2g:** 392[$(M + 1)^+$, 83], 222[100], 93[48], 62[57]; **2h:** 418[$(M + 1)^+$, 53], 248[62], 185[100], 93[100].
[d]Acetone-d_6 for **2a-g** and $CDCl_3$ for **2h** as a solvent. NMR, nuclear magnetic resonance.
[e]A calculated value for **2b** is based on the assumption that it contains 0.5 mole of water.

TABLE 3

Surface-Active Properties of Compounds 2a-g[a] and 3a[b]

Compound	R^1	R^2	T_{cp}[c] (or T_{Kp}[d]) (°C)	CMC[e] (mM)	γCMC (mN/m)	10^2 A (nm^2)
2a	C_7H_{15}	H	>90	1.8	26	50
2b	C_7H_{15}	H	>90	3.2	30	51
2c	C_7H_{15}	H	82	3.0	29	51
2d	C_6H_{13}	CH_3	>90	16	29	56
2e	C_6H_{13}	CH_3	>90	29	33	55
2f	C_6H_{13}	CH_3	>90	23	31	56
2g	C_9H_{19}	CH_3	>90	0.57	28	38
2h[f]	C_9H_{19}	CH_3	—	—	—	—
3a	C_7H_{15}	H	<0[d]	3.0	35	94

[a]At 20°C, pH 6.
[b]At 20°C, pH 11.
[c]Measured at 1 wt% concentration. T_{cp}, cloud point.
[d]For **3a**, the Krafft point (T_{Kp}) was measured at 0.1 wt% concentration. **3a** was slightly soluble in alkaline solution at 1 wt% concentration.
[e]CMC, critical micelle concentration.
[f]**2h** was slightly soluble in water at any temperature even at 0.1 wt% concentration.

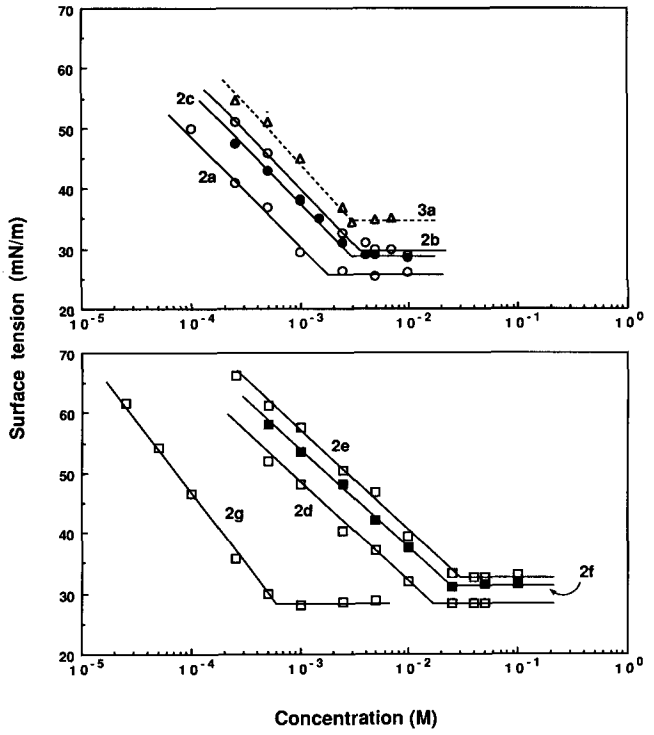


FIG. 1. Surface tension vs. concentration plots of compounds 2a–f [in aqueous solution (≈ pH 6)] and 3a (in pH 11 solution) at 20°C.

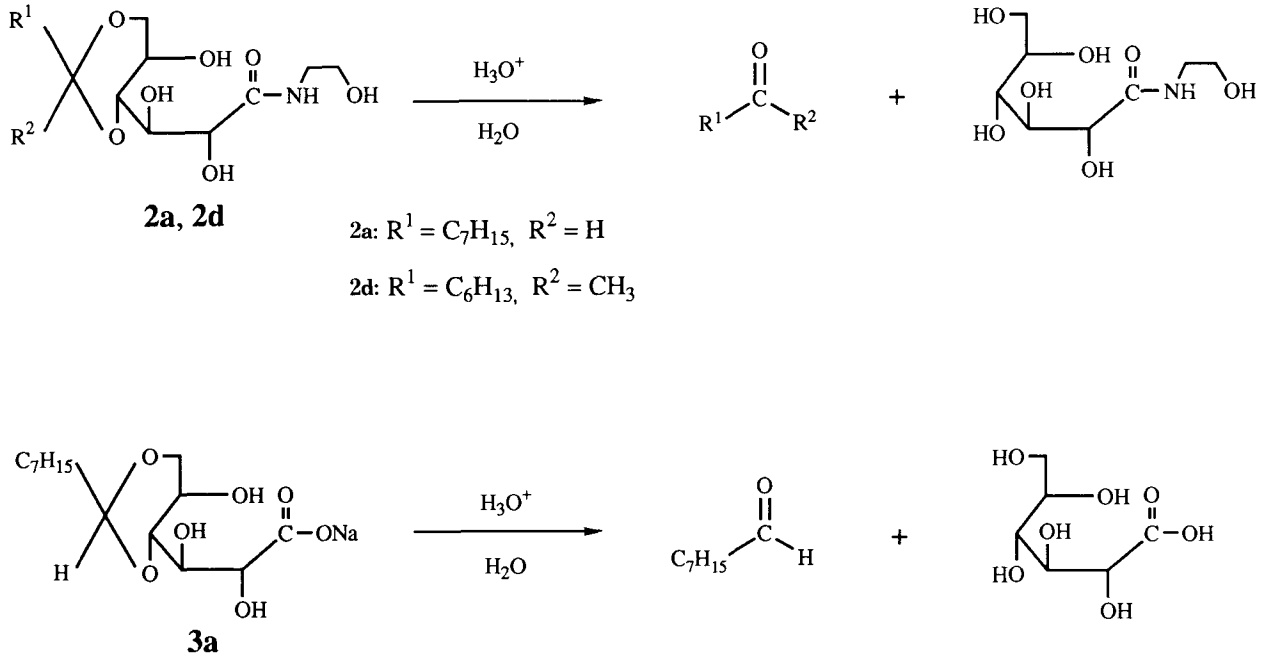
than that of carboxylate compound **3a**, which has a structure similar to that of **2a–c** except for the terminal hydrophilic moiety. It is interesting that these compounds (**2a–f**) showed greater ability to lower surface tension in spite of their relatively short hydrophobic chain when compared to conventional nonionic surfactants, such as alcohol ethoxylates (26). The area per molecule at the liquid–gas interface (A) (26) of a series of compounds 2 decreased with an increase in the number of carbon atoms in the R^1 group. On the other hand, differences in the kind of terminal amide moiety had little effect on the area per molecule at the surface of these types of compounds.

Under acidic conditions, compounds 2 and 3 would be expected to decompose into nonsurface active species, that is, gluconamide derivatives (or gluconic acid) and carbonyl compounds, because their hydrophobic and hydrophilic groups are linked through an acid-sensitive acetal bond. Therefore, these compounds can be used as cleavable surfactants, which has attracted the attention of many researchers (10–17). Scheme 2 shows the expected hydrolytic cleavage route for compounds **2a**, **2d** and **3a**.

The acid-decomposition properties of those sugar-derived compounds were evaluated by determining the quantity of aldehyde or ketone generated during their hydrolysis by the GLC technique. Figure 2 shows the decomposition profiles of compounds **2a** and **2d** at pH 1.

All surfactants were used at concentrations above their CMC. The reactions followed pseudo-first-order kinetics up to approximately 90% decomposition. The observed rate constants for hydrolysis of compounds **2a** and **2d** were $k_{2a} = 1.3 \times 10^{-4}s^{-1}$ and $k_{2d} = 1.5 \times 10^{-3}s^{-1}$, respectively. This difference in decomposition rate is explained by considering the greater stability of the carbocation generated from compound **2d** in the hydrolysis than that of the carbocation from compound **2a**. At pH 3, the ketone-derived compound completely decomposed after three days, whereas the aldehyde derivative did not completely decompose even after three weeks. Furthermore, the decomposition property of compound **2a** was compared with that of the carboxylate **3a** bearing the same hydrophobic chain. Their decomposition profiles at pH 1 and 3 are illustrated in Figure 3.

At pH 1, there was little difference in decomposition profiles between **2a** and **3a**. On the other hand, at pH 3



SCHEME 2

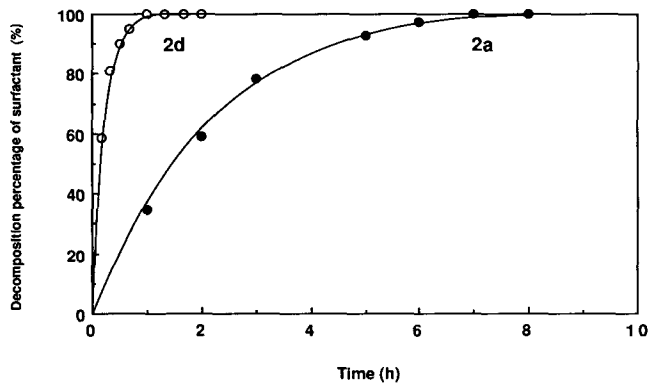


FIG. 2. Decomposition percentage of surfactant vs. time plots of compounds 2a and 2d at pH 1 (20°C). Surfactant concentration, 20 mM.

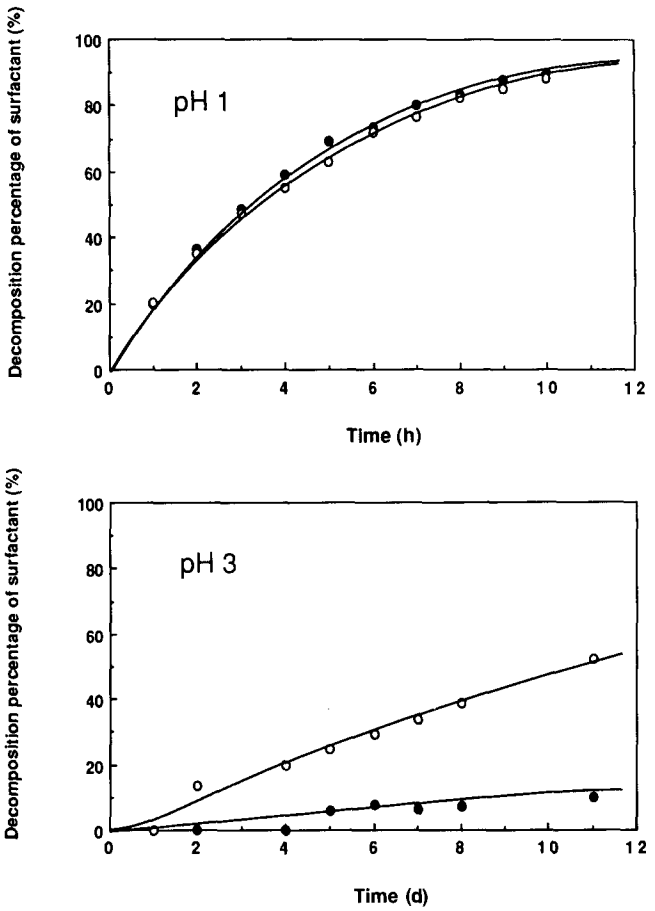


FIG. 3. Decomposition percentage of surfactant vs. time plots of compounds 2d and 3a at pH 1 (left) and pH 3 (right), at 20°C; ○, 2d; ●, 3a. Surfactant concentration, 5 mM.

(initial proton concentration), the nonionic compound decomposed more rapidly than the corresponding carboxylate compound. The pH value in the **3a** solution changed from 3 to *ca.* 4.3 after 1 h, whereas that value in **2a** solution changed little. When the solution was maintained at pH 3 by means of Clark-Lubs buffer solution (HCl-potassium hydrogen phthalate), the decomposition rate of the carboxylate compound increased up to the same level as that of the nonionic compound. These results indicate that for hydrolysis of the carboxylate compound, the protonation onto the carboxylate anion on the micellar surface occurs before the protonation at the acetal oxygen atoms, and the decomposition rate of the carboxylate compound is greatly influenced by the proton concentration in the solution. These compounds **2a–h** and **3a** are stable at ambient temperature in a desiccator at least for three months.

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