Synthesis and Interfacial Properties of Monoacyl Glyceric Acids as a New Class of Green Surfactants

Tokuma Fukuoka¹, Shintaro Ikeda², Hiroshi Habe¹, Shun Sato¹, Hideki Sakai², Masahiko Abe², Dai Kitamoto^{1*} and Keiji Sakaki¹

¹ Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST) (Tsukuba Central 5-2, 1-1-1, Higashi, Tsukuba, Ibaraki 305-8565, JAPAN)

² Faculty of Science and Technology, Tokyo University of Science (Yamazaki 2641, Noda, Chiba 278-8510, JAPAN)

Abstract: Glyceric acid (GA) is one of the most promising functional hydroxyl acids, and it is abundantly obtained from glycerol by a bioprocess using acetic acid bacteria. In this study, several monoacyl GAs were synthesized by esterification of GA and saturated fatty acyl chlorides (C12, C14, C16, and C18), forming a new class of bio-based surfactants. By the present method, a mixture of two isomers, namely 2-*O*-acyl and 3-*O*-acyl GAs, was produced, in which the 2-*O*-acyl derivatives were obtained as a major product. These isomers were isolated, and their surface-active properties were investigated for the first time. The surface tensions of 2-*O*-acyl GAs with different chain lengths were determined by the Wilhelmy method. At concentrations below 10^{-4} M, the 2-*O*-acyl GAs exhibited higher surface-active properties compared to commercially available synthetic surfactants. For example, 2-*O*-lauroyl GA reduced the surface tension of water to around 25 mN/m above the critical micelle concentration (3.0×10^{-4} M). In addition, 2-*O*-acyl derivatives showed higher surface-tension-lowering activity than 3-*O*-acyl GAs. The monoacyl GAs synthesized herein can potentially be used as "green surfactants."

Key words: glyceric acid, glycerol use, surfactant, green material, biorefinery

1 INTRODUCTION

Over the last decade, the production of biodiesel fuels based on fatty acid methyl esters from vegetable oils has dramatically increased. Glycerol is normally generated as a by-product of the transesterification of triglycerides in the biodiesel and oleochemical industry, and many projects are under way to convert the surplus glycerol into various value-added products¹⁻⁴⁾.

Recently, we developed a new and effective technique to biocatalytically produce glyceric acid (GA) from raw crude glycerol using acetic acid bacteria⁵⁻⁸⁾. GA is a promising glycerol derivative because it can be used as a kind of functional organic acid⁹⁾. In particular, D-GA has several biological actions, including diuresis¹⁰⁾, liver-stimulating and cholesterolytic activities¹¹⁾, and the acceleration of ethanol and acetaldehyde oxidation¹²⁾. However, to promote the use of GA, further functional analysis of GA and GA derivatives is necessary.

We have thus focused our attention on the multifunctionality of GA and are developing GA-based functional materials by using GA as a building block compound. For

example, we have recently reported the synthesis of branched poly(lactic acid)s containing GA and their potential use as novel bio-based modifiers for bioplastics. In addition, we have synthesized several diacyl GAs and evaluated their biological properties^{13, 14)}.

Previously, a mixture of GA esters biochemically produced by *Penicillium funiculosum* was reported to exhibit antitrypsin activity¹⁵⁾. We reported that chemically synthesized dioleoyl GAs also exhibit antitrypsin activity¹³⁾. Moreover, synthesized dilinoleoyl D-GA exhibited no significant cytotoxic effects in normal human dermal fibroblasts or microvascular endothelial cells¹⁴⁾. These results suggested that acyl GAs could potentially be used as functional lipids in pharmaceuticals and cosmetics.

In addition, acyl GAs are amphiphilic and can thus constitute a new class of bio-based surfactants. The design of bio-environmentally compatible surfactants based on natural renewable resources has become increasingly important; surfactants that are "greener," milder, and more efficient are now demanded for a wide variety of applications. Acyl GAs have great potential for use as "green sur-

*Correspondence to: Dai Kitamoto, Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST) (Tsukuba Central 5-2, 1-1-1, Higashi, Tsukuba, Ibaraki 305-8565, JAPAN)
E-mail: dai-kitamoto@aist.go.jp

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factants” because they are readily synthesizable into simple structures from cost-effective precursors that are derived from waste products. However, the diacyl GAs synthesized in our previous study showed poor water solubility and evaluating their surface actions was difficult. In this study, we set out to selectively synthesize monoacyl GAs and evaluate their interfacial properties since these are more hydrophilic than the diacyl derivatives.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

GA was obtained from the fermentation of glycerol using the acetic acid bacterium, *Gluconobacter frateurii* NBRC103465. The standard procedure for the production of GA has previously been reported⁷⁾. The obtained GA was mainly composed of D-GA (73% ee). Other reagents and solvents were commercially available and used as received.

2.2 Synthesis of monoacyl GAs

The following standard procedure for the synthesis of monolauroyl GA (C12GA) was adopted. A mixture of GA (3.0 g, *ca.* 28 mmol), triethylamine (10 mL, *ca.* 72 mmol), and *N,N*-dimethyl-4-aminopyridine (0.25 g, *ca.* 2 mmol) was dissolved in acetone (100 mL). Lauroyl chloride (2.4 g, *ca.* 11 mmol) was added to the reaction mixture in small steps, and the mixture was stirred at room temperature for 1 h. Next, the reaction mixture was evaporated, and then 100 mL of ethyl acetate, 20 mL of 7% aqueous HCl, and 80 mL of water were added to the reaction mixture. The ethyl acetate phase was extracted, washed twice with brine, dried over MgSO₄, and then evaporated. The resulting white solid was purified by silica gel (Wako-Gel C-200) column chromatography using elution with chloroform, chloroform:acetone (80:20, vol/vol), and acetone. The fractions containing the target compound were collected and evaporated. Approximately 2.16 g of white solid was obtained (yield: *ca.* 68%).

Similarly, monomyristoyl GA (C14GA), monopalmitoyl GA (C16GA), and monostearoyl GA (C18GA) were obtained at a yield of about 70% each.

2.3 Separation of 2-*O*-acyl and 3-*O*-acyl GAs

The following standard procedure for the separation of 2-*O*-lauroyl GA (2C12GA) and 3-*O*-lauroyl GA (3C12GA) was adopted. The obtained C12GA mixture described above was subjected to precise silica gel column chromatography using elution with chloroform:acetone (80:20, vol/vol). The fractions were analyzed by high-performance thin-layer chromatography (HPTLC) on silica plates (silica gel 60F₂₅₄, Merck) with chloroform:methanol (90:10, vol/vol). The upper spot was identified as 2C12GA and the lower spot as 3C12GA. The purity of the separated lauroyl GA was con-

firmed by ¹H nuclear magnetic resonance (NMR) analysis.

2-*O*-lauroyl GA (2C12GA): ¹H NMR (CDCl₃, 600 MHz): δ 5.19 (t, 1H, *J* = 3.8 Hz, H-2), 4.08 (dd, 1H, *J* = 4.4, 12.5 Hz, H-3b), 4.01 (dd, 1H, *J* = 3.3, 12.1 Hz, H-3a), 2.44 (m, 2H, H-2'), 1.66 (m, 2H, H-3'), 1.20–1.40 (br, 16H, -CH₂-), 0.88 (t, 3H, *J* = 7.0, -CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 173.1 and 172.6 (C=O x2), 72.6 (C-2), 62.1 (C-3), 33.8 (C-2'), 24.7 (C-3'), 31.9, 29.0–29.7, and 22.7 (-CH₂-), 14.1 (-CH₃).

3-*O*-lauroyl GA (3C12GA): ¹H NMR (CDCl₃, 600 MHz): δ 4.48 (m, 1H, H-3b), 4.47 (s, 1H, H-2), 4.36 (dd, 1H, *J* = 5.5, 12.8 Hz, H-3a), 2.35 (t, 2H, *J* = 7.5 Hz, H-2'), 1.61 (m, 2H, H-3'), 1.20–1.40 (br, 16H, -CH₂-), 0.88 (t, 3H, *J* = 7.0, -CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 174.3 and 173.3 (C=O x2), 69.4 (C-2), 65.2 (C-3), 34.0 (C-2'), 24.8 (C-3'), 31.9, 29.0–29.7, and 22.7 (-CH₂-), 14.1 (-CH₃).

2.4 Measurements

Structural analysis of the obtained fatty acyl GAs dissolved in deuterated chloroform (CDCl₃) was performed by ¹H and ¹³C NMR using a JEOL JNM-LA600 (600 MHz).

The surface tension of the purified acyl GA was determined using a Krüss K100C Wilhelmy auto surface tensiometer with a platinum plate at 25°C. Continuous measurements were carried out until the change in the surface tension became less than 0.01 mN/m per 90 s.

The emulsifying activity of the obtained monoacyl GA was determined using a modified colorimetric method as previously reported¹⁶⁾: 100 μL of soybean oil, which was used as the hydrophobic phase, was added to a test tube of 4 mL of distilled water containing the purified acyl GA (1 mg). The test tubes were then vortexed thoroughly for exactly 1 min and allowed to stand at room temperature. After 3 h, the lower 1 mL of the mixture was transferred to a cuvette, and its turbidity was measured at 620 nm. The emulsifying activity was expressed as the optical density; a solution containing no surfactant was used as a control. Sodium dodecyl sulfate (SDS) and monolaurin were also used as references. All measurements reported herein are mean values from at least three separate experiments.

3 RESULTS AND DISCUSSION

3.1 Synthesis and purification of monoacyl GAs

Very recently, we synthesized diacyl GAs via the esterification of GA under the condition of excess acyl chloride. In the present study, to preferentially synthesize monoacyl GAs, we performed the esterification of GA using lauroyl (C12), myristoyl (C14), palmitoyl (C16), and stearoyl (C18) chloride under the GA-rich condition (Fig. 1). After a 1 h reaction time, as determined by thin layer chromatography, the hydrophilic monoacyl GA was obtained as a major com-

Fig. 1 Synthesis of monoacyl glyceric acids.

ponent in the reaction mixture, and the spots derived from a free fatty acid and diacyl GA were observed at the same time. We were unable to reduce the incidence of these by-products by changing the reaction conditions, but these more hydrophobic compounds could be removed by silica gel column chromatography by elution with chloroform.

As an example of the obtained monoacyl GA, a ^1H NMR spectrum of the easily separated monolauroyl GA is shown in Fig. 2. The spectrum confirmed that the product is a mixture of 2-*O*-lauroyl GA (2C12GA) and 3-*O*-lauroyl GA (3C12GA). Two clearly distinguishable peaks were detected between the peaks derived from 2C12GA (peak **a**: H-2 at 5.19 ppm, **b**: H-3 at 3.99–4.09 ppm, and **c**: H-2' at 2.44 ppm) and 3C12GA (**a'**: H-2 at 4.47 ppm, **b'**: H-3 at 4.35–4.49 ppm, and **c'**: H-2' at 2.35 ppm). The relative proportions of 2C12GA and 3C12GA were estimated to be 81% and 19%, respectively, as based on the area ratio of these peaks on the ^1H NMR chart.

These isomers could be precisely separated by column chromatography using elution with chloroform:acetone (80:20, vol/vol). By HPTLC using elution with chloroform:methanol (90:10, vol/vol), the purified 2C12GA showed a higher R_f value compared to 3C12GA (Fig. 3). ^1H NMR spectra of the purified isomers are shown in Fig. 3, and the chemical shifts of these compounds are summarized in Section 2.3.

In the case of C14, C16, and C18GA, 2-*O*-acyl derivatives were also preferentially obtained (>80%), which was estimated by NMR. The 2- and 3-*O*-acyl derivatives were purified using the same method.

A 3-*O*-acyl GA was previously isolated from plants¹⁷⁾. In addition, Ahn *et al.* reported the synthesis of 3C12GA by selective oxidation of the primary alcohol in 1-monolau-

Fig. 2 ^1H NMR spectrum of a mixture of monolauroyl glyceric acids.

Fig. 3 ^1H NMR spectra of the purified monolauroyl glyceric acids: (a) 2-*O*-lauroyl glyceric acid (2C12GA) and (b) 3-*O*-lauroyl glyceric acid (3C12GA).

rin¹⁸⁾. In contrast, herein, we preferentially prepared and characterized 2-*O*-acyl GAs for the first time. We next investigated the interfacial properties of these monoacyl GA homologs.

3.2 Surface-active properties of monoacyl GAs

We determined the surface tension of aqueous solutions of purified monoacyl GAs by the Wilhelmy method. First, we evaluated the surface activities between 2-*O*-acyl GAs with different chain lengths (C12–C18) because 2-*O*-acyl derivatives can be obtained as a major product in the present reaction. Figure 4 shows the surface (air–water) tension *versus* concentration plots for 2C12GA, 2C14GA, and 2C16GA in distilled water at 25°C. The estimated critical micelle concentrations (CMCs) and surface tensions at the CMC (γ_{CMC}) of these compounds are summarized in Table 1. The surface tension of 2C18GA was not measured because of its poor water solubility.

The CMC values for these compounds decreased with increasing chain length. This surface behavior, based on the increase in hydrophobic interactions, corresponds well with the general rules of synthetic surfactants. The surface tension of these compounds, however, had a tendency to decrease with decreasing chain length. In particular, 2C12GA reduced the surface tension to around 25 mN/m above the CMC. These results indicate that the present 2-*O*-acyl GAs show excellent interfacial activity compared to commercially available synthetic surfactants such as saturated fatty acid sodium salts (fatty acid soaps)¹⁹⁾, SDS²⁰⁾, and 1-*O*-monolauroyl glycerol (1-monolaurin)²¹⁾. CMC and γ_{CMC} values for these surfactants were as follows: C12 soap (2.0×10^{-2} M, *ca.* 36 mN/m), C14 soap (4.0×10^{-3} M, *ca.* 36 mN/m), C16 soap (1.8×10^{-4} M, *ca.* 36 mN/m), mea-

Fig. 4 Surface tension-concentration plots of the purified 2-*O*-acyl glyceric acids (C12, C14, and C16).

Table 1 Physicochemical properties of 2-*O*-acyl GAs

	CMC (M)	γ CMC (mN/m)
2C12GA	3.0×10^{-4}	25.6
2C14GA	9.3×10^{-5}	28.7
2C16GA	2.9×10^{-5}	34.1

sured in 0.01 M NaOH solution; SDS (8.1×10^{-3} M, *ca.* 38 mN/m); and 1-monolaurin (4.4×10^{-5} M, 36.2 mN/m). The remarkable surface-tension-lowering activity of these GA-based surfactants compared to commercially available materials is attributable to strong intermolecular hydrophilic interactions (*i.e.*, hydrogen bonding) between the bulky polar carboxyl and hydroxyl head groups of GA and water at the surface.

In addition, by carefully observing the surface tension curves of these 2-*O*-acyl GAs, a biphasic change of surface tension seemed to occur (Fig. 4). This behavior suggests a rather complicated molecular event in the surfactant solution; however, in this study, we could not demonstrate the morphology changes of the aggregates by dynamic light scattering and pyrene fluorescence. Further investigations are needed to clarify this surface behavior of monoacyl GAs.

We then compared the surface activities of 2- and 3-*O*-acyl GAs. For example, Fig. 5 shows the surface-tension-lowering activities of 2C14GA and 3C14GA. The estimated CMC and γ CMC of 2C14GA were 9.3×10^{-5} M and 28.7 mN/m, respectively, and the respective values for

Fig. 5 Surface tension-concentration plots of the purified monomyristoyl glyceric acids.

those of 3C14GA were 7.0×10^{-5} M and 35.0 mN/m. Both C14GA isomers showed higher water solubility and surface-tension-lowering activity compared to similarly structured 1-*O*-monomyristoyl glycerol (1-monomyristin; CMC = 5.8×10^{-6} M, γ CMC = 48.0 mN/m)²¹. The increase in hydrophilicity is attributable to the presence of a carboxyl group in the hydrophilic domain. In addition, the 2-*O*-acyl derivative exhibited higher surface tension-lowering activity compared to the 3-*O*-acyl derivative. The data suggest that the 2-*O*-acyl derivative has stronger intermolecular polar head interactions compared to the 3-*O*-acyl derivative. On the other hand, based on a molecular dynamics study of monoacyl GAs (data not shown), the 2-*O*-acyl derivative has more sterically bulky hydrophilic groups on the hydrophobic acyl chain compared to the 3-*O*-acyl derivative. The differences in the molecular configuration of monoacyl GAs may also significantly contribute to their excellent surface-tension-lowering activities.

Meanwhile, we also examined the surface activities of the unpurified mixture of monoacyl GA isomers. The mixture was confirmed to exhibit surface-tension-lowering activity comparable to those of the corresponding 2-*O*-acyl GAs described above. Therefore, from a practical point of view, the mixture of the present GA-based surfactants is more easily available since it is capable of being used without separation and purification.

We next examined the emulsifying activity of monoacyl GAs by simple turbidity measurements as previously reported¹⁶). The activity of C12GA was comparatively evaluated using synthetic surfactants bearing lauric acid as a hydrophobic chain. With respect to soybean oil, the present

Fig. 6 The emulsifying activity of the monolauroyl glyceric acid and synthetic surfactants.

C12GA exhibited higher emulsion stability than that of monolaurin and SDS (Fig. 6). In a previous report, oxidized 1-monolaurin (3C12GA) exhibited higher emulsion stability than 1-monolaurin as determined by a backscattering method¹⁸⁾. The present result corresponded with that of the previous study.

In this study, we focused our attention on the properties of the acyl derivatives of GA. Other studies have suggested the use of alkoxyl glycerates as lyotropic liquid crystal (reverse hexagonal phase; H_{II})-forming materials^{22–24)}. Unlike glycerate surfactants and monoglycerides, the acyl GAs reported herein possess a combination of hydroxyl and carboxyl groups in the hydrophilic moiety. Therefore, acyl GAs are likely to act as anionic surfactants and the water solubilities and surface activities of these compounds are expected to be pH-controllable. In addition, acyl GAs are expected to not only be easier to handle in water but also exhibit specific liquid crystal formation. Further investigation into the aqueous phase behavior of acyl GAs is recommended to determine their suitability to a wide variety of applications.

4 CONCLUSION

In this study, monoacyl GAs were easily and preferentially synthesized. In the synthetic method used herein, the major products were 2-*O*-acyl GAs. The interfacial properties of the monoacyl GA isomers differed depending on the specific structure. The obtained monoacyl GAs, particularly 2-*O*-acyl derivatives, exhibited excellent surface-tension-lowering activity compared to commercially available synthetic surfactants. These results indicate that monoacyl GAs are potentially useful as bio-based high-performance “green” surfactants. Thus, the present study on the appli-

cation of GAs contributes to the development of a new technology for utilizing surplus glycerol.

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