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Preparation and Surfactant Properties of Amino Acid-based Surfactants

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Abstract: 1-O-aminoacyl-3-O-alkyl acyl glycerols were synthesized by lipases in good yields and their surfactant properties were explored.

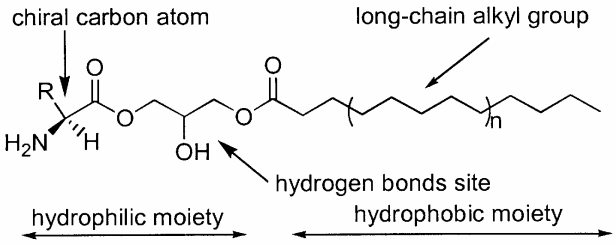
Keywords: Amino Acids, lipase, fatty acids, glycerol esters.

Recently, there has been a great deal of interest in biosurfactants, *i.e.*, surface-active compounds produced by microorganisms[1] or isolated enzymes[2]. Biosurfactants possess a number of potential advantages over their chemically manufactured counterparts, including low toxicity, biodegradability, a wide variety of possible structures and ease of synthesis from inexpensive, renewable raw materials. Consequently, biosurfactants may have important applications in numerous areas, such as foods, cosmetics, personal-care products, and pharmaceutical formulations[1], *etc*.

Amino acid-based surfactants constitute an interesting group of biosurfactants owing to their excellent surfactant properties, biocompatibility and strong antimicrobial activity[3]. Amino acid-based surfactants have been studied extensively. However, the feasibility of lipases catalyzed acylation of amino acids with a range of long-chain fatty acids (or their esters) as acyl donors was not satisfying[4], because the reaction rates were poor and the yields were low. The low conversion obtained were attributed presumably in part to the low solubility of the amino acids in the oil phase.

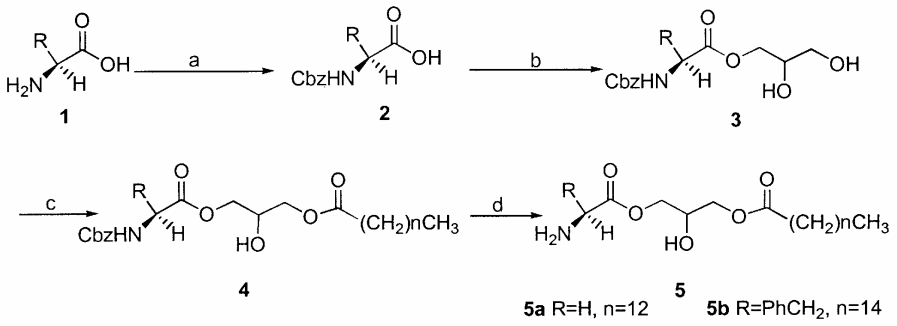
In this work, we have utilized one superior strategy to prepare amino acid-based surfactants under the catalysis of lipase. Glycerol was chosen as a linker between amino acids and fatty acids as alcohols are known to be good substrates for lipases. The compounds obtained have the following characteristic structural features: (i) they contain a long-chain alkyl group in the hydrophobic moiety; (ii) they have an amino acid moiety as the hydrophilic moiety; (iii) they contain a hydroxyl group between the hydrophobic and hydrophilic moieties, which has a hydrogen-bonding ability; (iv) they possess a chiral carbon atom in the amino acid moiety which creates a chiral aggregates-forming ability (**Scheme 1**).

Scheme 1



The procedure of preparation of 1-O-aminoacyl-3-O-alkyl acyl glycerols is shown below (**Scheme 2**).

Scheme 2



Reagents and conditions: (a) CbzCl, NaOH/$NaHCO_3$, PH=9; (b) $BF_3.Et_2O$, DMF, 60°C; (c) Novozyme 435, pentane-3-one, 70°C; (d) Pd-C, H_2, rt.

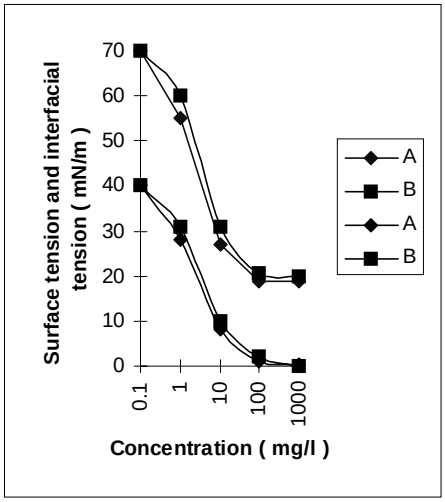
Treatment of **1** with CbzCl in aqueous sodium bicarbonate and sodium hydroxide solution gave **2** in 84% yield . Reaction of **2** with glycerol in DMF at 60°C in the presence of boron trifluoride etherate afforded **3** in 80 ~ 87% yields. Under the catalysis of lipase Novozyme 435, esterfication of **3** and fatty acids at 70°C yielded **4** in 70 ~ 80%. Deprotection of **4** by hydrogenation with palladium on carbon as catalyst achieved 5 in 95~96% yield. We have successfully produced 1-O-glcyl-3-O-tetradecanoyl glycerol with 65% yield and 1-O-L-phenylalanyl-3-O-hexadecanoyl glycerol with 45% yield[5], which proved to be a facile method for attaching lipid functionalities to amino acids.

The surfactants properties of these two compounds were also investigated. **Figure 1** shows that they caused significant lowering not only of surface tension of different aqueous solution but also of interfacial tension between aqueous solutions and n-hexadecance.

The results of the foaming ability of the products were summed in **Figure 2**. Both of them have high foaming ability. **Figure 3** indicated the results of the emulsification test of these two compounds. They had excellent emulsification power.

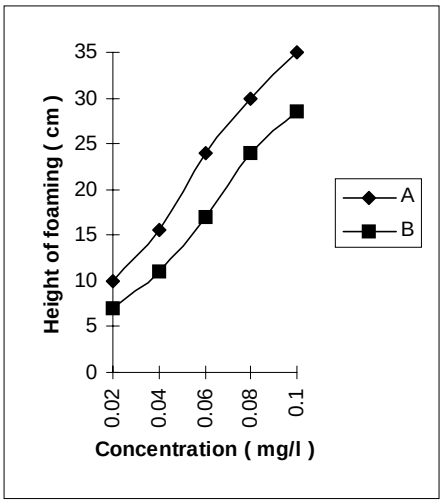
In conclusion, 1-O-aminoacyl-3-O-alkyl acyl glycerol, as a group of amino acid-based surfactants have excellent surfactant properties, which made them attractive for potential applications.

Figure 1. Surface tension and interfacial tension[a] of amino acid-based surfactants



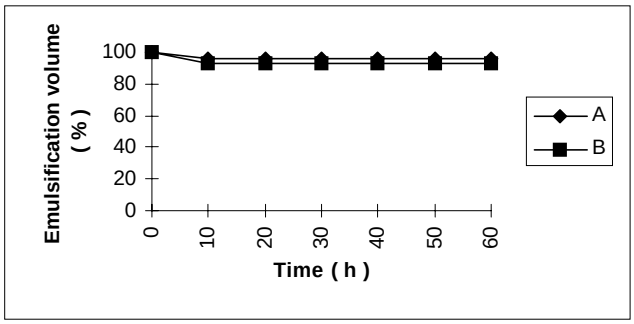
A: 1-O-glycyl-3-O-tetradecanoyl glycerol
B:1-O-L-phenylalanyl-3-O-hexadecanoyl glycerol a. The interfacial tension was determined against n-hexane in water solution of A or B at 25℃.

Figure 2. Foaming ability of amino acid-based surfactants[a]



A: 1-O-glycyl-3-O-tetradecanoyl glycerol
B: 1-O-L-phenylalanyl-3-O-hexadecanoyl glycerol
a. The foaming ability was determined by the air-current method[6] at 25℃.

Figure 3 Emulsification test on amino acid-based surfactants[a].



A: 1-O-glycyl-3-O-tetradecanoyl glycerol
B: 1-O-L-phenylalanyl-3-O-hexadecanoyl glycerol

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5. Spectrum data of **5a** and **5b**:
   5a: mP: 59-61℃, IR ($cm^{-1)}$: 3300, 2918, 1731, 1471, FAB-MS: 360 (M+H) ^{1}HNMR (300MHz, $CDCl_3$): 0.90 (t, 3H, J = 6.42, teteradecanoyl-H_{14}), 1.30 (m, 20H, teteradecanoyl-$H_{4\sim13}$), 1.61 (m, 2H, teteradecanoyl-$H_{3)}$, 2.37 (t, 2H, J = 7.24Hz, teteradecanoyl-H_2), 3.60~3.75 (m,2H), 3.95 (m, 1H, glycerol-H_2), 4.20 (m, 4H, glycerol-H_1+H_3)
   5b: mP: 64-65℃, [α]$^{20}_D$ = +5.45 (C = 0.7, CH_3OH), EI-MS(m/z): 476 (0.09 M-H), 239 (7.43), 149 (58.74), 91 (23.67), ^{1}HNMR (300MHz, $CDCl_3$):0.90 (t, 3H, J = 6.31Hz, hexadecanoyl-$H_{16)}$, 1.25 (m, 24H, hexadecanoyl-$H_{4\sim15}$), 1.65 (m, 2H, hexadecanoyl-H_3), 2.35 (t, 2H, J = 7.49Hz, hexadecanoyl-H_2), 2.65 (m, 2H, Phe-CH_2), 3.55~4.20 (m, 6H), 7.25 (m, 5H, Phe-Arom-H)
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