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The esterification of glycerine with lauric acid catalyzed by multi-valent metal salts. Selective formation of mono- and dilaurins

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Abstract

Multi-valent metal salts, such as zirconium, ferric, and aluminum salt hydrates gave high catalytic activity for the esterification of glycerine (GL) with lauric acid (LA) without the solvent. Among them, $ZrOCl_2 \cdot 8H_2O$ and $AlCl_3 \cdot 6H_2O$ gave lauric acid monoglyceride (Monolaurin; ML) in high selectivity. $Fe_2(SO_4)_3 \cdot nH_2O$ and $Zr(SO_4)_2 \cdot 4H_2O$ gave lauric acid diglyceride (Dilaurin; DL) even in the excess of GL.

Keywords: Multi-valent metal salt; Esterification; Glycerine; Lauric acid; Monolaurin; Dilaurin

1. Introduction

The selective esterification of glycerine (GL) with long chain aliphatic acids has been of interest in the manufacture of functional materials for medicines, cosmetics, surfactants, etc. [1,2]. These esters have been manufactured by the esterification of GL with fatty acid or by transesterification of fatty acid triglyceride by GL. For the esterification, the strong acid such as sulfuric acid or a strong base such as cesium and sodium hydroxide has been conventionally used as the catalysts. However, there are some drawbacks from the environmental aspects, such as corrosiveness, hazards of waste catalysts, etc. [3]. The development of alternative catalysts for the esterification, which have high activity, high productivity, and easy recovery without severe environmental pollution, is the emerging topics concerning the aspect of the green-chemical processes.

Recently, the esterification of GL with fatty acid has been examined by the heterogenized sulfonic acids over MCM-41 [4–9], ion-exchanged resins [10], zeolitic molecular sieves [11], and bases [12]. Although they are active for the esterification to form the fatty acid monoglyceride and diglyceride, the preparation of the catalysts is tedious and has a long way to go for the obtainment of the catalysts.

Yamamoto and his co-workers found that zirconium chloride is active for the esterification of acids with equal amount of alcohols [13]. We also described the effective esterification of long-chain fatty acids with fatty alcohols by using multi-valent salt hydrates as the catalysts [14–16]. Some multi-valent metal salts of chloride, sulfate, nitrate, and acetate of zirconium, aluminum, and iron were highly effective in these esterifications [14].

In this paper, we describe the esterification of GL with lauric acid (LA) by using some multi-valent metal salts as the catalysts, and selective formation of lauric acid monoglyceride (Monolaurin; ML) and lauric acid diglyceride (Dilaurin; DL) (see Scheme 1).

2. Experimental

Multi-valent metal salts, GL and LA were obtained commercially and used without purification. Typical procedures of the esterification of GL with LA were as follows: GL 1.151 g (12.5 mmol), LA 0.501 g (2.5 mmol), and a metal salt (0.125 mmol) were placed in a two-necked flask (50 cm^3) under atmospheric pressure, heated and stirred

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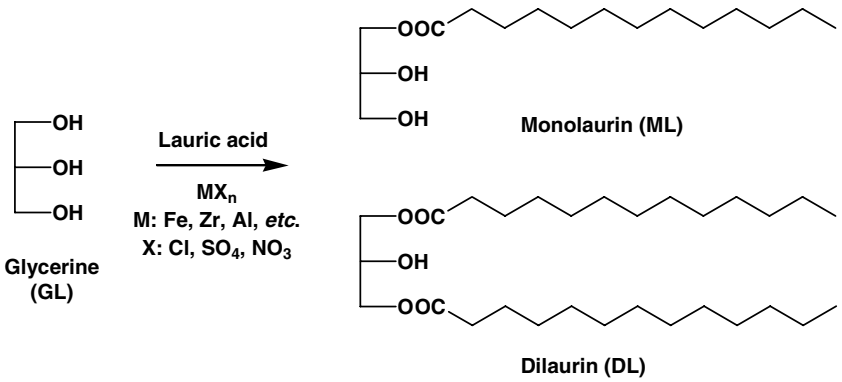

Scheme 1. The esterification of glycerine with lauric acid.

at 100 °C for 3 h in a N_2 flow of 10 cm^3/min. Reaction products were analyzed using a gas chromatography (GC-14A; Shimadzu Corporation, Kyoto, Japan). Analysis of LA was carried out by an Ultra 1 (25 m length and 0.20 mm internal diameter and a 0.32 μm thick layer; Agilent Technologies, MA, USA). Analysis of the laurates was carried out by an Ultra Alloy$^+$-65 (15 m length and 0.25 mm diameter with 0.10 μm thick layer; Frontier Laboratories, LTD., Fukushima, Japan). Phenyl benzoate was used as a standard in both analyses. The conversion was expressed based on the LA consumed. The yield for ML, DL, and lauric acid triglyceride (Trilaurin; TL) are based on LA present in them.

3. Results and discussion

Fig. 1 shows the esterification of GL with LA catalyzed by multi-valent metal chlorides at 100 °C. Among them, only $ZrOCl_2 \cdot 8H_2O$, $HfOCl_2 \cdot 8H_2O$, and $AlCl_3 \cdot 6H_2O$ gave the laurates in 50–70% yields based on LA. The selectivities for ML based on LA were 74% for $ZrOCl_2 \cdot 8H_2O$, 76% for $AlCl_3 \cdot 6H_2O$, and 80% for $HfOCl_2 \cdot 8H_2O$. In every case, TL was not observed much under our conditions. However, other chlorides are less active for the esterification. After the reaction, the salts were homogeneously dissolved or dispersed in the reaction mixtures.

Fig. 2 shows the influence of glycerine/lauric acid (GL/LA) ratio on the esterification by using $ZrOCl_2 \cdot 8H_2O$ as catalyst. The conversion of LA was increased from 2.0 to 5.0 accompanying the increase in the yield of ML; however, the increase in the conversion and yield of ML was not observed by a further increase in G/L ratio. These results suggest that G/L ratio of 5 was enough for the selective formation of ML.

Fig. 3 shows the influence of reaction period on the esterification by using $ZrOCl_2 \cdot 8H_2O$ as catalyst, where the reaction was carried out at 100 °C with GL/LA ratio of 5.0. The yields of ML and DL increased by increasing the period, and the conversion was saturated after 3 h. However, the yield of ML was unchanged with further increase in reaction period.

Fig. 4 shows the influence of the type of sulfates on the esterification. Among the metal salts, $Fe_2(SO_4)_3 \cdot nH_2O$

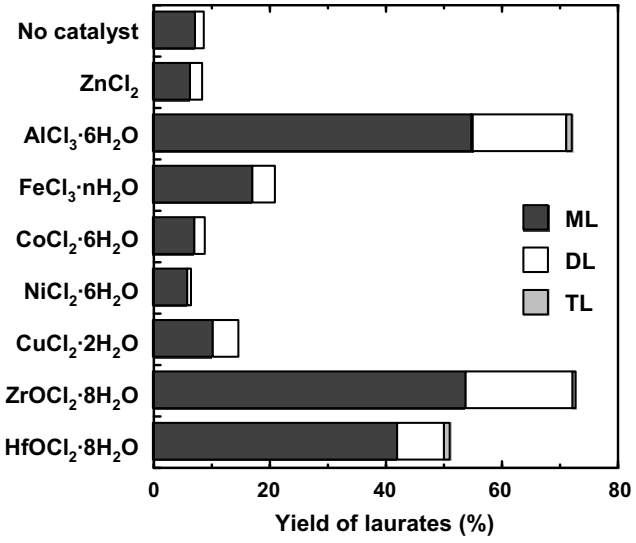

Fig. 1. The esterification of glycerine with lauric acid by multi-valent metal chlorides as catalyst. Reaction conditions: GL, 12.5 mmol; LA, 2.5 mmol; catalyst, 0.125 mmol; temperature, 100 °C; period, 3 h.

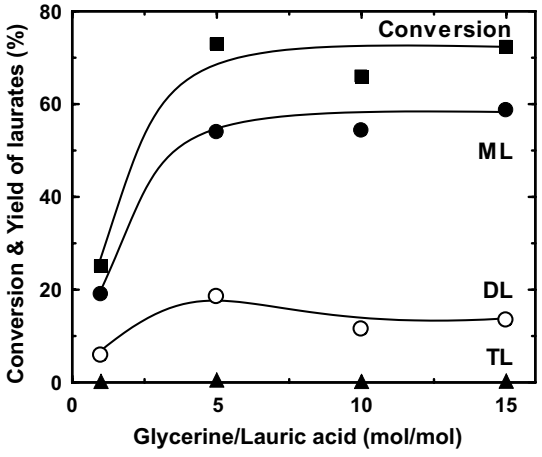

Fig. 2. The influence of glycerine/lauric acid ratio on the esterification of glycerine with lauric acid by using $ZrOCl_2 \cdot 8H_2O$ as catalyst. Reaction conditions: GL, 2.5–37.5 mmol; LA, 2.5 mmol; catalyst, $ZrOCl_2 \cdot 8\ H_2O$, 0.125 mmol; temperature, 100 °C; period, 3 h.