Preparation of Monoglycerides by Guanidine-Catalyzed Processes

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ABSTRACT: Glycerolysis of methyl stearate and tristearin has been carried out in the presence of alkylguanidines—strong nonionic bases—as catalysts. When applied at 10 mol%, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 1,2,3-tricyclohexylguanidine, and 1,3-dicyclohexyl-2-*n*-octylguanidine give monoglycerides in more than 90% selectivity, in a maximum of 6 h reaction time. *JAOCS 75,* 755–756 (1998).

KEY WORDS: Glycerolysis, guanidines, methyl stearate, monoglycerides.

Long-chain monoglycerides are largely applied as emulsifying agents in food, cosmetics, and pharmaceuticals (1,2). Normally, they are produced through transesterification of fats and oils (or their fatty acid ester derivatives) with an excess of glycerol, at high temperatures (*ca*. 200°C), and with inorganic compounds as catalysts (3–6). However, in these glycerolysis processes, the reaction yields are typically low (*ca*. 50%), and a considerable amount of dark-colored undesirable by-products is frequently observed, as a consequence of the high temperature levels (7). The use of enzymes for synthesizing monoglycerides offers the advantage of high selectivities at milder temperatures. However, the procedures often require some tedious preparation steps (8–10). Recently, we found that guanidines (strong nonionic bases) are efficient catalysts for the transesterification of vegetable oils with short-chain monohydric alcohols, in homogeneous (11) or heterogeneous (12) phase. Even at low molar concentrations, guanidines give high yields of fatty acid alkyl esters, without forming undesirable by-products. As an extension of our work, we decided to investigate the catalytic activity of some guanidines in glycerolysis processes because, to the best of our knowledge, there are no reports related to this subject.

EXPERIMENTAL PROCEDURES

Guanidines. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, >98%; Fluka, Buchs, Switzerland) was used as purchased. 1,3-Dicyclohexyl-2-*n*-octylguanidine (DCOG) was prepared according to our previously described method (11). 1,2,3-Tricyclohexylguanidine (TCG) was prepared in the same way as DCOG.

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Glycerolysis of methyl stearate/tristearin. All reactions were carried out in a 100-mL one-necked flask with a glycerol/methyl stearate (99%; Aldrich, Milwaukee, WI) or tristearin molar ratio of 2.5:1 and, typically, 10 mol% of guanidine. The reaction mixture was maintained under vigorous stirring at 110°C and 16 mbar for 2, 4, 6, or 8 h. After returning to ambient temperature, 50 mL of cold methanol (p.a.) was added to the crude product. After 30 min of stirring, the insoluble fraction was filtered and washed two more times. The monoglycerides were isolated from the methanol-insoluble fraction (which contains a mixture of mono-, di-, and tristearate of glycerol) through extraction by repeated washings with 30 mL of hot ethanol (p.a.), and dried under vacuum until constant weight. The purity analysis and characterization of the product were performed by thin-layer chromatography and ^{1}H nuclear magnetic resonance (300 MHz, Gemini 300; Varian, Palo Alto, CA).

RESULTS AND DISCUSSION

All catalytic tests were carried out at 110°C, which is the temperature at which the reaction mixture becomes homogeneous, and which gives the best results. Table 1 summarizes the results of the glycerolysis of methyl stearate with TBD, TCG, and DCOG as catalysts. After 6 h, with 2 or 5 mol% TBD [the most active guanidine for methanolysis of vegetable oils (11)], monoglycerides were obtained in 80 and 90% selectivity, respectively. However, at these conditions, the conversions of methyl stearate were low (less than 50%). In contrast, increasing the catalyst concentration to 50 or 100 mol% resulted in high conversions of methyl stearate (about 80%) but lower selectivities for monoglycerides (62 and 49%, respectively). When using 10 mol% TBD, however, the conversion of methyl stearate and the selectivity for monoglycerides assumed equilibrated values (75 and 77%, respectively) after 6 h reaction time. At longer reaction times (8 h), the conversion of methyl stearate remained practically unchanged, but the selectivity for monoglycerides decreased. TCG or DCOG, when applied under the same conditions, were less active than TBD. The conversions of methyl stearate were in the range of 52–55%, but greater selectivities (~92%) were observed. No significant difference was observed between the behavior of TCG and DCOG, which have

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TABLE 1
Conversions of Methyl Stearate (%)/Selectivities for Monoglycerides (%) as a Function of Time, Type of Catalyst, and Catalyst Concentration[a]

Catalyst (mol%)	2 h	4 h	6 h	8 h
TBD (2)			25/80	
TBD (5)			50/90	
TBD (10)	21/95	43/83	75/77	76/60
TBD (50)			80/62	
TBD (100)			81/49	
TCG (10)			52/92	
DCOG (10)			55/92	

[a]TBD, 1,5,7-triazabicyclo[4.4.0]dec-5-ene; TCG, 1,2,3-tricyclohexylguanidine; DCOG, 1,3-dicyclohexyl-2-*n*-octylguanidine.

similar basicities (11) but distinct molecular structures. It seems, therefore, that the only factor that influences the course of these glycerolysis reactions is the base strength of the catalyst. With tristearin instead of methyl stearate, the reactions proceeded more slowly. After 8 h of reaction time at 110°C and 16 mbar with 10 mol% TBD, only 40% monoglycerides were obtained.

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