

Rapid Synthesis of Palm-Based Monoacylglycerols

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ABSTRACT: Rapid synthesis of high-purity MAG from refined, bleached, and deodorized palm stearin (RBDPS) *via* chemical glycerolysis in the presence of pyridine was developed to obviate the conventional molecular distillation in the production of pure MAG. The optimal reaction for the sodium methoxide-catalyzed glycerolysis of RBDPS was recorded at 110°C using a 3 wt% catalyst concentration based on the weight of RBDPS, with an RBDPS/glycerol ratio of 1:2 and an RBDPS/pyridine ratio of 1:4. High yields of over 99% were achieved rapidly in 15 min, and increases in DAG and FFA were observed after a prolonged reaction time.

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KEY WORDS: Glycerolysis; monoacylglycerols; pyridine; refined, bleached, and deodorized palm stearin.

Partial glycerides are synthesized commercially on an industrial scale for application as emulsifying agents in a wide range of foods. MAG, with emulsifying properties superior to DAG, account for over 70% of the total world consumption as food emulsifiers (1). The chain length of the alkyl group in MAG in various formulations will determine the application, e.g., as emulsifiers, texturing agents, lubricants, or plasticizers in pharmaceuticals, cosmetics, or textiles (2). However, the applications of MAG are still mainly in the food industry because of their excellent self-emulsifying and surface-active properties.

MAG are usually produced commercially by the glycerolysis of natural oils and fats. The reaction involves a reversible equilibrium; thus, the reaction product will always contain a mixture of MAG, DAG, and TAG. Generally, a reaction temperature above 220°C and an inorganic catalyst are needed (3). In addition to glycerolysis starting from oils and fats, the glycerolysis of methyl esters has also been investigated by researchers. Jeromin *et al.* (4) reported the production of MAG *via* the glycerolysis of methyl esters derived from animal and vegetable fats and oils. The reaction was carried out using methyl esters at a concentration ratio of MAG and DAG that lay between 3 and 10 in the presence of an alkaline catalyst. The reaction temperatures were slightly lower than those described earlier, i.e., between 130 and 160°C, but at a vacuum of 200 to 400 mbar. Both reactions yielded technical-grade MAG consisting of a glyceride mixture containing 40–60% MAG and DAG.

Technical-grade MAG generally consists of a mixture of 40–48% MAG, 30–40% DAG, 5–10% TAG, 0.2–9% FA, and 4–8% glycerol (2). However, when used as emulsifiers, glycerides are required to contain at least 90% MAG. Hence, in the conventional production of such glycerides, it is necessary to subject the glyceride mixture to molecular distillation to enhance the content of MAG. The final yield in the conversion from TAG to MAG was reported to be about 58% (3).

The production of MAG *via* chemical synthesis can be further improved by using a suitable solvent to increase the solubility of glycerol in the oil and subsequently enhance the glycerolysis reaction. Studies using various solvents to improve the homogeneity of reactants (i.e., glycerol and fats) have also been carried out. Some effective solvents that have been reported by researchers are 1,4-dioxane, cresols, phenol, and pyridine (3). Reactions using phenol require a high temperature; in addition, phenol has been found to undergo some condensation with stearic acid and glycerol, thus giving rise to impurities that are not readily separated. For example, a high yield of MAG (83%) was obtained by Franzke *et al.* using pyridine as a solvent for the glycerolysis of sunflower seed oil in the presence of sodium bicarbonate as the catalyst (see Ref. 3). However, these solvents caused other problems because of their toxicity and odor. Yang *et al.* (5) investigated the effect of the solvent on the lipase-catalyzed glycerolysis of stearic acid. They reported that lipase-catalyzed glycerolysis yielded a relatively higher mole fraction of MAG in a polar solvent, whereas the mole fractions of DAG and TAG were greater than that of MAG in a nonpolar solvent. The highest composition of MAG was obtained when the glycerolysis was conducted in the presence of acetone. Although solvents offer the prospect of high yields of MAG at relatively low temperatures by improving the homogeneity of the reactants, glycerolysis involving a solvent has not been studied extensively because of other drawbacks such as cost and handling.

The effect of the solvent on the glycerolysis of oils and fats was reexamined in the present study. The glycerolysis of refined, bleached, and deodorized palm stearin (RBDPS) was conducted using various reaction conditions to investigate the role of the solvent, and comparisons were made with reactions in the absence of a solvent.

EXPERIMENTAL PROCEDURES

Materials. The RBDPS was obtained from Kempas Edible Oil (M) Sdn. Bhd. (Pasir Gudang, Johor, Malaysia), whereas glycerol was purchased from Merck (Darmstadt, Germany).

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Sodium methoxide (NaOMe) and glacial acetic acid were purchased from Fluka (Buchs, Switzerland). Pyridine and *N,N*-dimethylformamide (DMF) were purchased from BDH Limited (Poole, United Kingdom), whereas dioxane was purchased from May & Baker Limited (Ikeja, Lagos, Nigeria).

Synthesis of MAG. The glycerolysis of RBDPS and glycerol was conducted under a nitrogen blanket. Twenty-five grams of RBDPS and 25 g of anhydrous glycerol (RBDPS/glycerol ratio, w/w = 1:1) were mixed with 100 mL of pyridine (RBDPS/solvent ratio, wt/vol = 1:4). The mixture was heated on a heating mantle with the thermometer set at the required temperature. A magnetic stirrer was used to agitate the mixture, and a stirring rate of 400 rpm was fixed throughout the experiment. When the reaction mixture had reached the desired reaction temperature, 0.75 g (3 wt% based on the weight of RBDPS) of the catalyst, sodium methoxide (NaOMe), was added to the mixture. Samples of the reaction mixture were withdrawn at 1, 5, 10, 15, and 30 min, and at 30-min intervals thereafter. The catalytic action of NaOMe was terminated by neutralizing it with 1.6 mL of diluted acetic acid (50%) as soon as the samples were withdrawn. The pyridine was washed off with a salt solution and the product was extracted with diethyl ether. Anhydrous sodium sulfate was added to the ethereal solution and the mixture was kept overnight to adsorb the water left in the samples. The hydrated sodium sulfate was subsequently removed from the ethereal solution using a filter paper, and the solvent was then removed using a rotary evaporator to obtain the crude product. The glycerolysis reactions were repeated by changing the following variables: catalyst concentration, RBDPS/glycerol ratio, type of solvent, RBDPS/solvent ratio, and reaction temperature.

Analysis of the reaction products. TLC was used to monitor the progress of the reactions. Silica plates (5 × 10 cm) and a solvent system of hexane/diethyl ether/acetic acid (7:3:1, by vol) were used. Iodine vapor was used as the staining reagent.

Aliquots of the reaction mixture were withdrawn during the reaction, and the final products were derivatized prior to analyses using a gas chromatograph with a flame ionization detector (Hewlett-Packard, Palo Alto, CA). Trimethylsilyl derivatives of the reaction mixture and final products were prepared by the following procedure. A 30-mg quantity of the reaction product was weighed into a 2-mL screw-capped glass vial fitted with a septum. A 0.5-mL quantity of dichloromethane was then added, rather than pyridine, as reported by Goh and Timms (6). The vial was then capped and shaken until the sample was dissolved. A 0.5-mL quantity of Sylon BTZ (Supelco, Bellefonte, PA) containing trimethylchlorosilane was then added using a clean, dry pipette. The vial was then shaken well for 1 min and left for 15 min for complete silylation.

A capillary column of 15 m × 0.32 mm i.d. was used. The temperature program was as follows: oven temperature, 100°C; initial temperature, 100°C; final temperature, 350°C; injector temperature, 254°C; detector temperature, 360°C; rate, 10°C/min; carrier gas (helium) at 2.0 mL/min. The concentration of components in the samples was calculated based on the peak area of standards and their known concentration.

RESULTS AND DISCUSSION

A high concentration of MAG was achievable in a solvent-free glycerolysis system provided a high reaction temperature was used. We noted that the reaction at 210°C yielded about 80% MAG after only 5 min, whereas no significant amount of MAG was formed after the same time at 110°C (Fig. 1). The reaction at 210°C yielded the highest MAG concentration (79.2%) after only 5 min of reaction, and the concentration decreased as the reaction proceeded. Although the concentration of MAG increased as the reaction proceeded at 110°C, only about 10% MAG was formed at the end of a 4-h reaction. Thus, we concluded that in such a solvent-free system, a high reaction temperature (200°C) and short reaction time should be used to ensure a high conversion from TAG to MAG.

The effect of the solvent on the glycerolysis of RBDPS reactions was studied using pyridine at 80 and 110°C. Both conditions yielded a high concentration of MAG in a rapid manner (Fig. 2). After 15 min, 72.7 and 99.1% of MAG were formed, respectively. The positive effect of pyridine on the glycerolysis of RBDPS was obvious, as 97.6% more MAG was formed at 110°C in the presence of pyridine than was obtained from the reaction at the same reaction temperature but in the absence of pyridine. Only 1.5% MAG was found in the reaction product after 15 min at 110°C in the former reaction.

The effects of three other factors, i.e., catalyst concentration, RBDPS/glycerol ratio, and RBDPS/solvent ratio were also investigated. Detailed results are presented in Figures 3–5 and Table 1. An increase in the catalyst concentration from 0.7 to 5% was found to result in a significant improvement in the formation of MAG. However, it was sufficient to use only 3% NaOMe, as no significant improvement in MAG concentration was observed at 5% NaOMe (Figs. 3, 4). In addition, use of a high concentration of catalyst resulted in greater formation of FFA (Fig. 3). The content of undesirable FFA in the reaction product in-

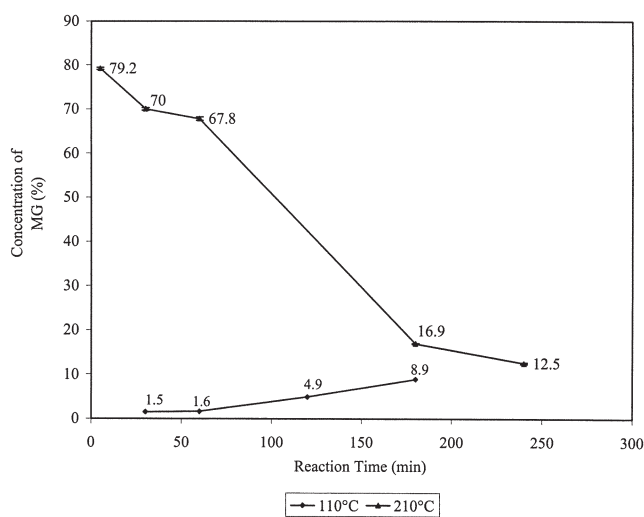


FIG. 1. Glycerolysis of refined, bleached, and deodorized palm stearin (RBDPS) in a solvent-free system. Reaction conditions: Catalyst (NaOMe) concentration (wt% based on the weight of RBDPS), 3%; RBDPS/glycerol ratio (w/w), 1:2. Error bars represent SD ($n = 3$).

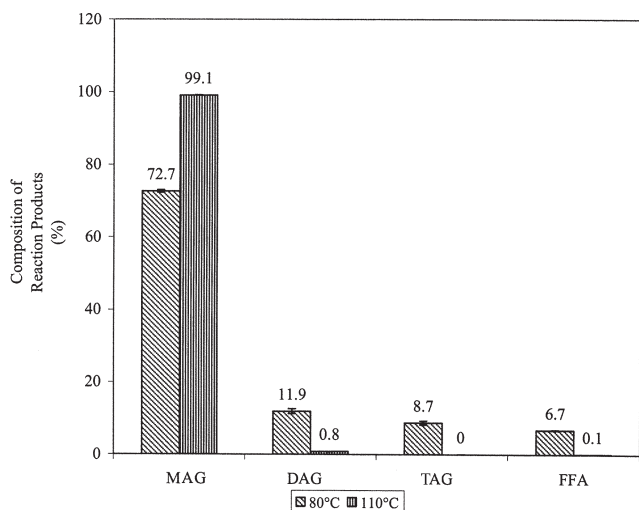


FIG. 2. Glycerolysis of RBDPS in the presence of pyridine. Reaction conditions: Catalyst (NaOMe) concentration (wt% based on the weight of RBDPS), 3%; RBDPS/glycerol ratio (w/w), 1:2; RBDPS/pyridine ratio (wt/vol), 1:4; reaction time, 15 min. Error bars represent SD ($n = 3$). For abbreviation see Figure 1.

creased as the catalyst concentration used in the reactions increased. When 10% catalyst was used, 8.4% FFA was formed after 15 min of reaction. Thus, no more than 3% NaOMe should be used, as a higher catalyst concentration will result in more than 1% FFA in the reaction product. The most desirable contents of FFA in pure and technical-grade MAG are less than 0.5% and between 0.5 and 1%, respectively.

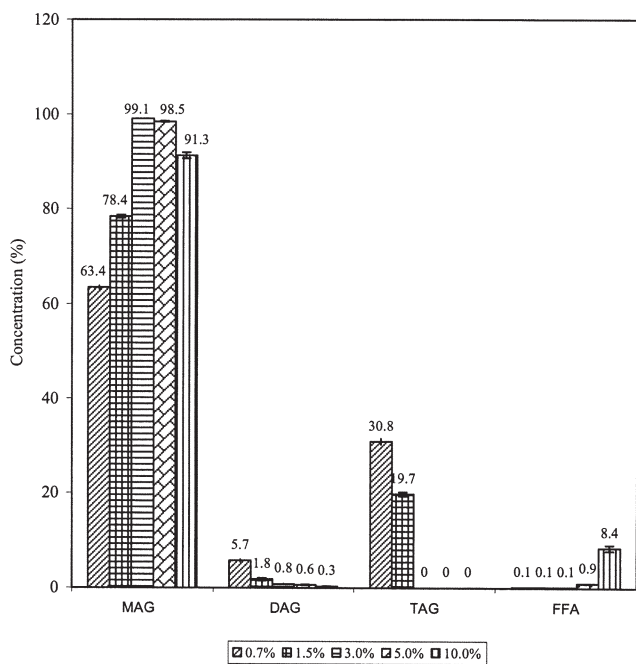


FIG. 3. Effect of catalyst concentration on the glycerolysis of RBDPS. Reaction conditions: Catalyst, sodium methoxide (NaOMe); RBDPS/glycerol ratio (w/w), 1:2; RBDPS/pyridine ratio (wt/vol), 1:4; reaction temperature, 110°C; reaction time, 15 min. Error bars represent SD ($n = 3$). For abbreviation see Figure 1.

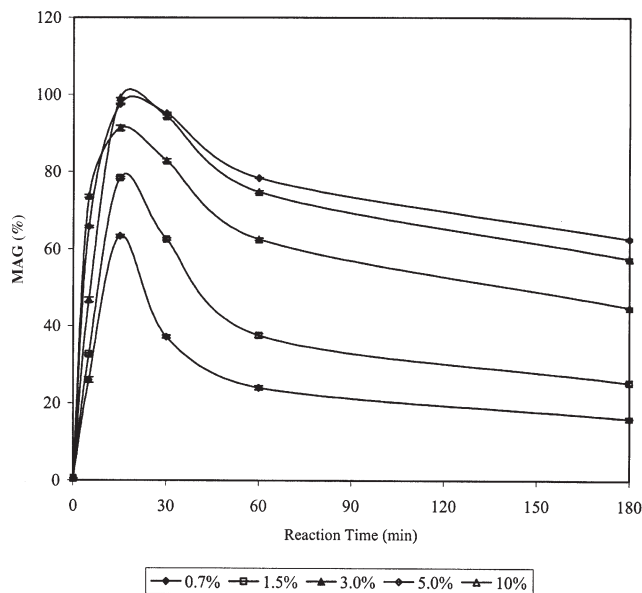


FIG. 4. Effect of catalyst concentration on MAG formation. Reaction conditions: RBDPS/glycerol ratio (wt/vol), 1:2; RBDPS/pyridine ratio (wt/vol), 1:4; reaction temperature, 110°C. Error bars represent SD ($n = 3$). For abbreviation see Figure 1.

The percentage of MAG obtained was not proportionate to the RBDPS/glycerol ratio used (Fig. 5). Among the ratios investigated in the present study, the optimal RBDPS/glycerol ratio was found to be 2, where 99.1% MAG was obtained in 15 min. The effect of the RBDPS/pyridine ratio is depicted in

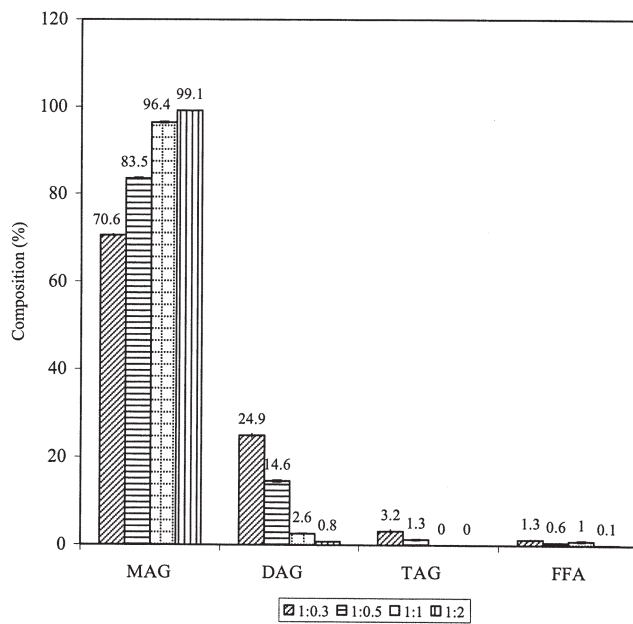


FIG. 5. Effect of oil/glycerol ratio on the glycerolysis of RBDPS. Reaction conditions: Catalyst (NaOMe) concentration (wt% based on the weight of RBDPS), 3%; RBDPS/pyridine ratio (wt/vol), 1:4; reaction temperature, 110°C; reaction time, 15 min. Error bars represent SD ($n = 3$). For abbreviation see Figure 1.

TABLE 1
Effect of Oil/Solvent Ratio on the Glycerolysis of Refined, Bleached, Deodorized Palm Stearin (RBDPS)^a

Oil/solvent ratio	Composition of reaction products (%)			
	MAG	DAG	TAG	FFA
1:1	1.2 ± 0.26	5.3 ± 0.2	93.4 ± 0.36	0.1 ± 0.01
1:4	99.1 ± 0.02	0.8 ± 0.02	0	0.1 ± 0.01

^aReaction conditions: Catalyst (NaOMe) concentration (wt% based on the weight of RBDPS), 3%; RBDPS/glycerol ratio (wt/vol), 1:4; reaction temperature, 110°C; reaction time, 15 min; solvent, pyridine. Error represents SD ($n = 3$).

TABLE 2
Effect of Different Types of Solvent on Glycerolysis of RBDPS^a

Solvent	Composition of reaction products (%)			
	MAG	DAG	TAG	FFA
DMF	11.5 ± 0.42	3.9 ± 0.10	84.0 ± 0.36	0.6 ± 0.04
Dioxane	19.8 ± 0.61	12.3 ± 0.40	67.8 ± 0.30	0.1 ± 0.01
Pyridine	94.3 ± 0.36	4.8 ± 0.06	0	0.9 ± 0.01
Solvent free	1.6 ± 0.46	4.6 ± 0.05	90.2 ± 0.53	3.6 ± 0.06

^aReaction conditions: Catalyst (NaOMe) concentration (wt% based on the weight of RBDPS), 3%; RBDPS/glycerol ratio (wt/vol), 1:2; RBDPS/solvent ratio (wt/vol), 1:4; reaction temperature, 110°C; reaction time, 30 min. Errors represent SD ($n = 3$). DMF, *N,N*-dimethylformamide; for other abbreviation see Table 1.

Table 2. Based on the composition of reaction products after 15 min, a ratio of 1:4 gave a higher conversion than when a ratio of 1:1 was used. In summary, the optimal reaction conditions for the NaOMe-catalyzed glycerolysis of RBDPS in the presence of pyridine were a temperature of 110°C when using a 3% catalyst concentration, an RBDPS/glycerol ratio of 1:2, and an RBDPS/pyridine ratio of 1:4.

In the present study, the profile of the reaction product was also studied using a prolonged reaction (3 h) under the best conditions established (Fig. 6). It was interesting to note that the highest formation of MAG was found after a 15-min reaction. The reaction in the presence of pyridine achieved a rapid formation of MAG, resulting in 99.1% MAG in 15 min. As the reaction progressed, the percentage of DAG and TAG increased, and as a result, the percentage of MAG decreased. Thus, to produce a high yield of MAG, the reaction time should not exceed 30 min and a short reaction time (*ca.* 15 min) will suffice. Figure 6 shows that a prolonged reaction time also caused a high percentage of FFA (up to 7.4%) after 3 h of reaction.

Glycerolysis using NaOMe and pyridine has been investigated by other researchers. Täufel *et al.* (7) reported that the glycerolysis of soybean, peanut, sunflower seed, and rapeseed oils in the presence of pyridine using catalysts such as sodium methoxide, sodium ethoxide, and sodium carbonate could achieve MAG yields of up to 72% in reactions conducted between 100 and 110°C for 15 min. The glycerolysis of tung oil in the presence of 1% sodium methoxide and an excess of glycerol at 30% has been reported to yield a product containing 32.2% MAG after a 2-h reaction at 65°C (8). Significant improvement was observed when the catalyst concentration was increased to 2%, the reaction temperature was raised to 80°C, and the reaction was conducted in the presence of five parts of pyridine. Under these conditions, the crude tung oil MG were

found to contain 78.2% MAG after a 30-min reaction time (8). In the present study, a relatively higher percentage of MAG (*i.e.*, 99.1%) was obtained after reaction for 15 min at 110°C. This may be attributed to the higher catalyst concentration used (3% based on the weight of RBDPS) and the lower degree of unsaturation in RBDPS. Relatively speaking, RBDPS is much less unsaturated (Table 3) than the oils studied by Täufel *et al.* (7). Mehta and Shah (10) reported that oils with nearly the

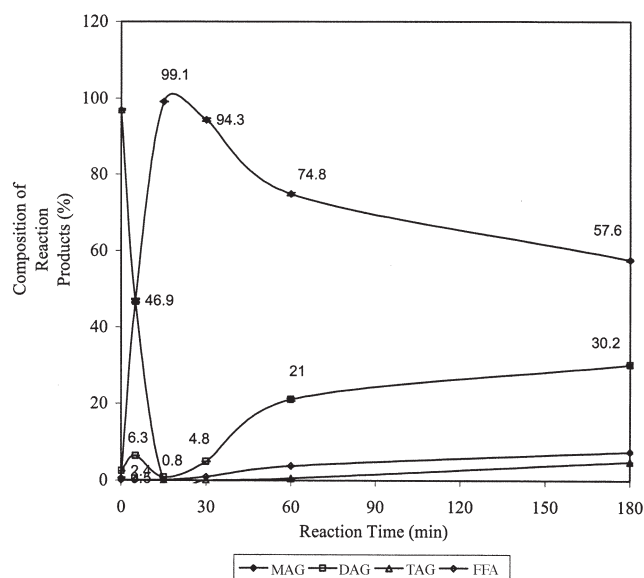


FIG. 6. Glycerolysis of RBDPS using sodium methoxide (NaOMe) as the catalyst and pyridine as the solvent. Reaction conditions: Catalyst (NaOMe) concentration (wt% based on the weight of RBDPS), 3%; RBDPS/glycerol ratio (wt/vol), 1:2; RBDPS/pyridine ratio (wt/vol), 1:4; reaction temperature, 110°C. Error bars represent SD ($n = 3$). For abbreviation see Figure 1.

TABLE 3
FA Composition of Oils^a

FA	Palm stearin	Peanut oil	Rapeseed oil	Soybean oil	Sunflower oil
6:0	ND	ND	ND	ND	ND
8:0	ND	ND	0.1	ND	ND
10:0	ND	ND	ND	ND	ND
12:0	0.1–0.4	0–0.1	ND	0.0–0.1	0.0–0.1
14:0	1.1–1.8	0–0.1	0.2	0.0–0.2	0.0–0.2
16:0	48.4–73.8	8.3–14.0	1.5–6.0	8.0–13.3	5.6–7.6
16:1	0.05–0.2	0–0.2	0.0–3.0	0.0–0.2	0.0–0.3
17:0	ND	ND	ND	ND	ND
17:1	ND	ND	ND	ND	ND
18:0	3.9–5.6	1.9–4.4	0.5–3.1	2.4–5.4	2.7–6.5
18:1	15.6–36.0	36.4–67.1	8–60	17.7–26.1	14.0–39.4
18:2	3.2–9.8	14.0–43.0	11–23	49.8–57.1	48.3–74.0
18:3	0.1–0.6	0–0.1	5–13	5.5–9.5	0.0–0.2
20:0	0.3–0.6	1.1–1.7	0.0–3.0	0.1–0.6	0.2–0.4
20:1	ND	0.7–1.7	3–15	0.0–0.3	0.0–0.2
20:2	ND	ND	0.0–1.0	0.0–0.1	ND
22:0	ND	2.1–4.4	0.0–2.0	0.3–0.7	0.5–1.3
22:1	ND	0–0.3	5–60	0.0–0.3	0.0–0.2
22:2	ND	ND	0.0–2.0	ND	0.0–0.3
24:0	ND	1.1–2.2	0.0–2.0	0.0–0.4	0.0–0.3
24:1	ND	0–0.3	0.0–20	ND	ND

^aSource: Gunstone *et al.* (9). ND, not detected.

same M.W. but with lower iodine values (or having lower unsaturations) reacted more rapidly than those having higher iodine values.

Optimal conditions for the production of MAG in the presence of pyridine were established. MAG >99%, which is equivalent to the specification of distilled MAG, was obtained. The established method obviated the need for a molecular distillation step, as in the conventional glycerolysis process, and required a relatively shorter reaction time. MAG produced *via* the current process is more suitable for use in the nonfood sector, as pyridine is a nonfood-grade solvent.

Two other solvents, namely, dioxane and DMF, were chosen to study the effect of the solvent on the glycerolysis of RBDPS further. Under the optimal conditions established, both reactions failed to yield a high concentration of MAG (Table 2). After 30 min, only 19.8 and 11.5% MAG were formed when using dioxane and DMF, respectively, whereas 94.3% MAG was formed in the presence of pyridine. We postulated that NaOMe was more readily dissociated in pyridine, followed by dioxane and DMF, as the formation of MAG is dependent on the availability of CH₃O⁻.

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REFERENCES

- Young, F.V.K., C. Poot, N. Krog, L.A. O'Neil, and N.G.L. Davidson, Processing of Fats and Oils, in *The Lipid Handbook*, edited by F.D. Gunstone, J.L. Harwood, and F.B. Padley, Chapman & Hall, New York, 1986, pp. 226.
- Meffert, A., Technical Uses of Fatty Acid Esters, *J. Am. Oil Chem. Soc.* 61:255–258 (1984).
- Sonntag, N.O.V., Glycerolysis of Fats and Methyl Esters—Status, Review, and Critique, *Ibid.* 59:795A–802A (1982).
- Jeromin, L., G. Wozny, and P. Li, Process for the Production of Monoglyceride Based on the Glycerolysis of Methyl Ester, U.S. Patent 6,127,561 (2000).
- Yang, Y.C., S.R. Vali, and Y.H. Ju, A Process for Synthesizing High Purity Monoglyceride, *J. Chin. Inst. Chem. Eng.* 34:617–623 (2003).
- Goh, E.M., and R.E. Timms, Determination of Mono- and Diglycerides in Palm Oil, Olein and Stearin, *J. Am. Oil Chem. Soc.* 62:730–734 (1985).
- Täufel, K., C. Franzke, and I. Schlicker, The Catalytic Glycerolysis of Natural Fats in Pyridine Solution, *Fette, Seifen, Anstrichm.* 64:513–517 (1962).
- McKinney, R.S., and L.A. Goldblatt, Preparation and Some Properties of Tung Oil Monoglycerides, *Ibid.* 34:585–587 (1957).
- Gunstone, F.D., J.L. Harwood, and F. Padley (eds.), *The Lipid Handbook*, 2nd edn., Chapman & Hall, London, 1994.
- Mehta, T.N., and S.N. Shah, Glycerolysis of Coconut, Sesame, and Linseed Oils. Fractionation of the Products with Alcohol and Urea. *Ibid.* 34:587–591 (1957).

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