

A Novel Technique for the Preparation of Secondary Fatty Amides.

III. Alkanolamides, Diamides and Aralkylamides

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A low-temperature synthesis of fatty alkanolamides, fatty diamides and fatty aralkylamides directly from triglycerides and primary amines provides essentially quantitative yields of the various products. The reactions run to completion in 3–12 h at temperatures of 50–60°C, approximately 100°C lower than employed in present conventional practice. The amines are used in excess and serve as solvent, reagent and, perhaps, as catalyst. The amides were characterized by melting point and spectroscopic (infrared and nuclear magnetic resonance) methods. If the mixed amides produced from the various natural triglyceride mixtures of fats and oils are acceptable products, this synthetic method provides these products in satisfactory quality while conserving energy and avoiding the intermediate production of free fatty acids or their esters.

KEY WORDS: Alkanolamides, amidation, aralkylamides, diamides, methyl tallowate, palmitic acid, tallow, tripalmitin.

Previously we determined that secondary fatty amides may be prepared in high yield and purity by reaction of fatty triglycerides, such as tallow or vegetable oils, with primary amines at room temperature (20°C), although it was beneficial to run the reactions at 50–60°C (1). The amine was used in 10:1 molar excess and served as reagent, as solvent for the fat and the fatty amide that formed, and possibly as a basic catalyst for the reaction. The excess amine prevented the reaction mixture from solidifying and permitted the reaction to go to completion. The by-product glycerol was readily separated from the reaction product. This study extends this concept to the preparation of other high-volume and industrially important secondary fatty amides, e.g., fatty alkanolamides, fatty diamides and the fatty aralkylamides.

Fatty alkanolamides (107 million kg produced in 1989) (2) have a broad spectrum of uses, such as detergents, shampoos, lubricants, cosmetics, foam control agents and water repellents (3). These are produced industrially from fatty acids or fatty acid methyl esters and alkanolamines, such as ethanolamine, by heating at 140–160°C for 6–12 h in an agitated vessel with a means of removing excess amine, water or alcohol (4). Fatty diamides (34 million kg produced in 1989) (2) also have a multitude of uses, such as lubricants, antistatic agents, release agents, corrosion inhibitors and water repellents (3). These are produced industrially by reaction of 2 moles of fatty acid with 1 mole ethylenediamine at 180–185°C for 6 h under nitrogen with continuous removal of water (3). A second type of diamide is prepared from the reaction of fatty acids and diethylenetriamine. These basic diamides have a wide variety of applications, such as detergent additives, fungicides, rust inhibitors, and corrosion inhibitors (3). Fatty acids and diethylenetriamine are heated at 140–150°C for 11 h (4) to produce these diamides. Subsequent heating of the products to 200°C results

in the formation of imidazolines, which have antibacterial properties (5). Fatty anilides, which are used as herbicides, fungicides, insecticides, defoliants and bacteriostats (6,7), are another important class of fatty nitrogen derivatives (8). Anilides are obtained by heating the fatty acids with aniline for 2–3 h at 150–170°C (5).

Because the production of all of these fatty amides requires large amounts of energy, it was of interest to develop an alternative, lower-energy process. Our objective, therefore, was to determine if the procedure developed for synthesizing the unsubstituted secondary fatty amides mentioned above (1) was applicable to these substituted secondary fatty amides. Because tallow melts at 42°C, a temperature range of 50–60°C was selected.

EXPERIMENTAL PROCEDURES

Materials. The amines (ethanolamine, diethanolamine, ethylenediamine, diethylenetriamine, 3,3'-imino-bis-propylamine, aniline and benzylamine) and palmitic acid were purchased from Aldrich Chemical Co. (Milwaukee, WI). Bleached tallow was supplied by Chemol Inc., (Greensboro, NC). Tripalmitin was furnished by Eastman Kodak Co. (Rochester, NY). Methyl tallowate (TE 1618) was supplied by Procter and Gamble, Industrial Chemical Division (Cincinnati, OH). All reagents were used as received without further purification.

Instrumentation. Instruments used in this investigation were: Fisher-Johns melting point apparatus (Fisher Scientific Co., Pittsburgh, PA), Perkin-Elmer infrared spectrophotometer (Model 1610; Perkin-Elmer Corp., Norwalk, CT), JEOL nuclear magnetic resonance spectrometer (Model GX-400; JEOL USA, Inc., Peabody, MA).

Method of preparation. *N*-(2-hydroxyethyl)tallowamide. Tallow (25 g, 0.03 mol) and ethanolamine (18.3 g, 0.3 mol) were weighed into a 100-mL, round-bottom flask and reacted with agitation at 50–60°C for 8 h. The reaction product was dissolved in 300 mL hexane, and placed in a separatory funnel to isolate the lower layer, a mixture of glycerol and excess ethanolamine, from the fatty amide. The alkanolamide, obtained from the hexane layer by crystallization at 10°C, was recrystallized from acetone to give a white powder, *N*-(2-hydroxyethyl) tallowamide (22 g, 88% yield). Similarly, tripalmitin (25 g, 0.031 mol) was reacted with ethanolamine (18.9 g, 0.31 mol) to produce *N*-(2-hydroxyethyl) palmitamide (24.1 g, 95.4% yield). Identification of the fatty amide was confirmed by melting point, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy by comparison to standards prepared from tripalmitin according to previously published methods (4,5, 8–11) (Table 1). ¹³C NMR spectroscopy was used to compare the chemical structures of the substituted palmitamides with those prepared by standard procedures. The palmitamides contained peaks at 43.6, 36.8, 31.9, 29.7, 29.5, 25.8, 22.7 and 14.1 ppm, characteristic of the palmitic backbone, and 159.4 ppm, characteristic of the amide group. The individual substituted palmitamides displayed the following characteristic peaks: *N*-(2-hydroxyethyl) palmitamide, 62.6 ppm (CH₂OH); *N,N'*-ethylene-bis-

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TABLE 1

Preparation of Substituted Fatty Amides

Reaction	Fatty amide product	Yield (%)	Melting point (°C)		Literature reference
			Found	Lit.	
A. Alkanolamides					
1. TA ^a + HOCH ₂ CH ₂ NH ₂ →	<i>N</i> -(2-Hydroxyethyl)tallowamide	88	93.5–94.0		
2. TP ^b + HOCH ₂ CH ₂ NH ₂ →	<i>N</i> -(2-Hydroxyethyl)palmitamide	95	98.0–98.5	99	9
3. TA + (HOCH ₂ CH ₂) ₂ NH→	No amide formation	—			
B. Diamides					
1. TA + NH ₂ CH ₂ CH ₂ NH ₂ →	<i>N,N'</i> -Ethylene- <i>bis</i> -(tallowamide)	92	93.0–93.5		
2. TP + NH ₂ CH ₂ CH ₂ NH ₂ →	<i>N,N'</i> -Ethylene- <i>bis</i> -(palmitamide)	85	96.5–97.0	99.5	4
3. MeTA ^c + NH ₂ CH ₂ CH ₂ NH ₂ →	<i>N,N'</i> -Ethylene- <i>bis</i> -(tallowamide)	88	93.0–93.5		
4. TA + (NH ₂ CH ₂ CH ₂) ₂ NH→	Di-(tallowamidoethyl)amine	83	55–60		
5. TP + (NH ₂ CH ₂ CH ₂) ₂ NH→	Di-(palmitamidoethyl)amine	93	108–108.5	116	5
6. MeTA + (NH ₂ CH ₂ CH ₂) ₂ NH→	Di-(tallowamidoethyl)amine	90	55–60		
7. C ₁₅ H ₃₁ COOH + (NH ₂ CH ₂ CH ₂) ₂ NH→	No amide formation	—			
8. TA + (NH ₂ CH ₂ CH ₂ CH ₂) ₂ NH→	Di-(tallowamidopropyl)amine	88	57.0–58.0		
9. TP + (NH ₂ CH ₂ CH ₂ CH ₂) ₂ NH→	Di-(palmitamidopropyl)amine	86	110–112	114	10
C. Arylamides					
1. TA + C ₆ H ₅ NH ₂ →	Tallowanilide	8.2	55–57		
2. TP + C ₆ H ₅ NH ₂ →	Palmitanilide	7.5	92–93	90	8
3. TA + C ₆ H ₅ CH ₂ NH ₂ →	<i>N</i> -Benzyltallowamide	90	86–87		
4. TP + C ₆ H ₅ CH ₂ NH ₂ →	<i>N</i> -Benzylpalmitamide	94	93–94	95.1	11

^aTallow, bleached.^bTripalmitin.^cMethyl tallowate.

(palmitamide), 41.95 ppm; *N,N'*-di-(palmitamidoethyl)amine, 52.3 ppm; *N,N'*-di-(palmitamidopropyl)amine, 37.6 ppm; and *N*-benzylpalmitamide, 128.7, 127.8 and 127.5 ppm (aromatic peaks). The ¹³C NMR spectra of substituted palmitamides were identical to those synthesized by standard techniques.

The adaptability of the procedure to fatty amidations with other substituted amines was demonstrated by using tallow or tripalmitin (0.031 mol) and the following series of substituted amines (0.31 mol)—ethylenediamine, diethylenetriamine, 3,3'-imino-*bis*-propylamine, aniline, and benzylamine.

The structural effect of various fatty substrates on amidation at 50–60°C was determined in a series of reac-

tions in which diethylenetriamine (0.31 mol) was reacted, respectively, with tallow, methyl tallowate and palmitic acid (0.031 mol) by the procedure given above.

Product formation and reactant disappearance were monitored by IR spectroscopy. Small samples (1–2 drops) were removed hourly from the reaction mixtures, and IR absorption spectra were measured. The relative intensities of the ester peak at 1735 cm⁻¹ and the amide peak at 1648 cm⁻¹ were determined. As the reactions progressed beyond 75%, the amide peak intensity became unreliable as an indicator of reaction progress. On the other hand, a continued decrease of the ester peak was observed and, thus, this IR band was used as an indicator of extent of reaction (see Fig. 1).

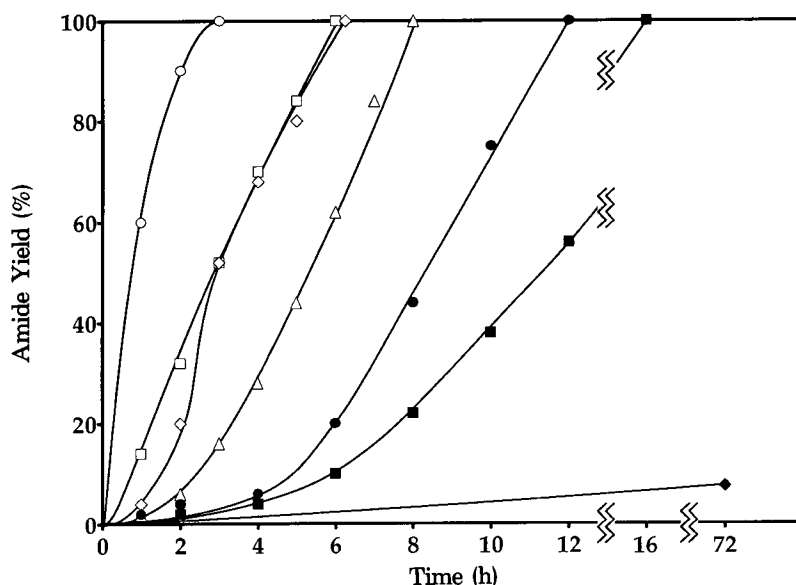


FIG. 1. Formation of substituted fatty amides at 50–60°C. ○, tallow + ethylenediamine; □, tallow + diethylenetriamine; ◇, tallow + 3,3'-imino-*bis*-propylamine; △, tallow + ethanolamine; ●, methyl tallowate + diethylenetriamine; ■, tallow + benzylamine; and ◆, tallow + aniline.

^{13}C NMR spectroscopy was used to confirm the chemical structure of each substituted fatty amide. The spectra were measured at 100 MHz and 35°C in CDCl_3 . All chemical shifts are reported as ppm from tetramethylsilane. The spectra of the products were compared to the spectra of amide standards, prepared by standard procedures.

RESULTS AND DISCUSSION

Synthesis. When the initial reaction of tallow with ethanolamine was carried out at 45°C and atmospheric pressure, the reaction mixture quickly solidified due to the precipitation of the high-melting *N*-(2-hydroxyethyl) tallowamide. It was therefore necessary to increase the temperature to 50–60°C to maintain homogeneity of the reaction mixture while maintaining a fat/amine molar ratio of 1:10. The reaction proceeded slowly for the first two hours and then went more rapidly (Fig. 1). The amidation was completed in 8 h, compared to 6–12 h for the industrial process. We were initially concerned about the reactivity of the amino group vs. the hydroxyl group of ethanolamine, but found no evidence of esterification of the hydroxyl group at 50–60°C. The product was readily isolated from the glycerol-excess amine mixture.

This experiment was then repeated with tripalmitin and ethanolamine to form *N*-(2-hydroxyethyl) palmitamide. The yields and melting points of these ethanolamides, together with references, are given in Table 1. No evidence of amidation was observed in a mixture of tallow and diethanolamine. We had found in our earlier studies (1) that secondary amines do not react with triglycerides under these conditions.

Fatty diamides were readily formed by the reaction of tallow or tripalmitin with diamines that contained primary amino groups, e.g., ethylene diamine, diethylenetriamine and 3,3'-imino-*bis*-propylamine. It was of interest to learn whether the reaction product would be a mono- or a diamide for the latter two.

Tallow reacted completely with ethylenediamine to form *N,N'*-ethylene-*bis*-(tallowamide) in 3 h at 50–60°C (Fig. 1) as compared to 6 h at 180–185°C being required in the present industrial procedure. We confirmed the diamide chemical structure, and that of its companion diamide, *N,N'*-ethylene-*bis*-(palmitamide), by IR, NMR and comparison to known standard compounds. The yields, melting points and spectral results indicated that diamides were the major products and there was little evidence of monoamide formation. Evidently, the monoamide is itself a ready substrate for further amidation and, therefore, does not accumulate in the reaction mixture.

We then carried out the reactions of tallow or tripalmitin with diethylenetriamine and 3,3'-imino-*bis*-(propylamine). The respective diamides were formed in high yield in 6 h (Fig. 1). Chemical structures of the products were confirmed as reported.

The chemical form of the fat moiety has a significant effect on the rate of amidation, as was seen in a comparison of the reactions of diethylenetriamine with tallow and methyl tallowate (Fig. 1). The tallow amidation was completed in 6 h, whereas the reaction involving methyl tallowate required 14 h. No amidation was observed for the reaction with palmitic acid (data not shown).

A third class of primary amines studied was amines that contained aryl groups. When tallow was reacted with aniline, only a 7% yield of tallowanilide was obtained, even after 72 h (Fig. 1). However, when tallow was reacted with benzylamine, a 90% yield of *N*-benzyltallowamide was obtained in 16 h (Fig. 1). This difference can be explained by the structure of aniline where the nonbonded pair of electrons, responsible for the nucleophilicity of amino groups, is dispersed over the aromatic ring. Aniline is 10^6 times weaker as a nucleophile than are aliphatic amines (12), resulting in small amounts of anilide being formed. In the reaction of tallow with benzylamine, however, the methylene group of the amine prevents the delocalization of the nonbonded electron pair into the aromatic ring and, hence, it reacts as an aliphatic amine.

Energy calculations. To estimate the energy savings achievable with the low-temperature reaction, we used a hypothetical batch reaction of 1000 kg fat as a basis for calculation. The reactor assumed was 946 L, 1.07-m diameter and 1.07-m high. The surface area was 5.57 m². Assuming insulation with a heat transfer coefficient of 0.30 cal-cm/cm²-h°C, the energy loss was 2×10^3 cal/h for every °C above 20°C.

There are five components of the energy requirements: melting the fat, bringing the reaction up to required temperature, heat of reaction, maintaining temperature at reaction temperature and cooling to 50°C at the completion of the reaction. Equation 1 was used for calculating the energy required for melting the fat and is the same for all reactions:

$$q = 1000 \text{ kg} \times 50 \text{ cal/gm} \times 1000 \text{ gm/kg} = 5 \times 10^7 \text{ cal} \quad [1]$$

where 50 cal/gm is the latent heat of melting.

Equation 2 was used for calculating the energy required for bringing the reaction up to the required temperature (T):

$$q = 1000 \text{ kg} \times 0.5 \text{ cal/gm}^\circ\text{C} \times 1000 \text{ gm/kg} \times (T - 20)^\circ\text{C} \quad [2]$$

where 0.5 cal/gm°C is the specific heat capacity. We assumed that the heats of reaction were equal. Energy loss was calculated from Equation 3:

$$q = 2 \times 10^3 \text{ cal/h} \times (T - 20)^\circ\text{C} \times \text{reaction time (h)} \quad [3]$$

Because the low-temperature reaction is already at 50°C, there is no cooling energy required. The industrial processes require the energy calculated by Equation 4 for cooling from the reaction temperature (T) to 50°C:

$$q = 1000 \text{ kg} \times 0.5 \text{ cal/gm}^\circ\text{C} \times 1000 \text{ gm/kg} \times (T - 50)^\circ\text{C} \quad [4]$$

The total energy savings is the difference between the summation of the five calculated energy requirements for the two cases. The results of these calculations for the three types of compounds, the alkanolamide, the diamide and benzylamide, are given in Table 2, along with the savings to be realized between the standard industrial practices and the method proposed here. In addition to this energy saving, the preparation of these products directly from tallow, or other oil, without prior hydrolysis to free fatty acids or conversion to fatty acid methyl esters

TABLE 2

Energy Savings at 50°C per 1000 kg Fat

Substituted fatty amide	Method	Temperature (°C)	Time (h)	Energy consumed ^a (cal)	Energy saved (cal)
Alkanolamides	Ind ^b	160	10	17.8×10^7	11.2×10^7
	Exp ^c	50	8	6.6×10^7	
	Dif ^d				
Diamides	Ind	150	6	16.7×10^7	10.2×10^7
	Exp	50	3	6.5×10^7	
	Dif				
Aralkylamides	Ind	140	3	15.6×10^7	9.0×10^7
	Exp	50	16	6.6×10^7	
	Dif				

^aNeglecting heat of reaction.^bInd, industrial practice.^cExp, experimental procedure.^dDif, difference.

eliminates the needs for those energy-intensive steps. Thus, if the products desired are the mixed, substituted secondary fatty amides, such as the tallowamides, they can be prepared directly from the natural fats and oils in high yield by this straight-forward, low-temperature procedure.

These energy considerations are presented to show the differences in the energy requirements for the reactions only. Reduced energy in the reaction does not ensure reduced energy for the entire process or lower costs to make the finished product. The cost for making any of these products can only be calculated from complete process considerations, including separation and purification. The laboratory procedure presented here is not a process and could not compete economically with existing technology. The next logical step in this research is the development of a process, bench or pilot-plant scale, to determine overall energy requirements, technical feasibility and a reliable estimate of costs. Critical to economic feasibility will be the efficient recycling of reactants and of the solvent used to separate the product. It is premature to present a cost estimate at this stage.

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