

wet strengths of the bonds are significantly increased. This possibility of modifying the glue bonds to increase their wet strengths, i.e., to increase the forces of adhesion by substituting other attractive forces for ionic forces, is the subject of another investigation.

Summary

The resistance of cottonseed and peanut meal and casein birch plywood glue bonds to organic and inorganic reagents for periods ranging from 1 to 14 days was determined. It was suggested that the principal attractive forces involved in the protein bonds were ionic or valence forces and that differences observed in the resistance of the glues to chemical reagents

were probably due to variations in the amino acid constitution of the proteins.

REFERENCES

1. Arthur, J. C. Jr., U. S. Patent 2,531,383, November 28, 1950.
2. Arthur, J. C. Jr., and Karon, M. L., *J. Am. Oil Chem. Soc.* **25**, 99-102 (1948).
3. A.S.T.M., *A.S.T.M. Standards on Adhesives*, American Society for Testing Materials, Philadelphia, January, 1950.
4. Burnett, R. S., and Parker, E. D., *Trans. Am. Soc. Mech. Eng.* **68**, 751-756 (1946).
5. Cheng, F. W., and Arthur, J. C. Jr., *J. Am. Oil Chem. Soc.* **26**, 147-150 (1949).
6. Hogan, J. T., and Arthur, J. C. Jr., *J. Am. Oil Chem. Soc.* **28**, 20-23 (1951).
7. Hogan, J. T., and Arthur, J. C. Jr., *J. Am. Oil Chem. Soc.*, **28**, 272-274 (1951).
8. Hogan, J. T., and Arthur, J. C. Jr., *J. Am. Oil Chem. Soc.* (in press.)

[Received July 9, 1951]

Fatty Acid Amides. IV.¹ Reaction of Fats With Ammonia and Amines²

EDWARD T. ROE, JEANNE M. STUTZMAN, JOHN T. SCANLAN, and DANIEL SWERN, Eastern Regional Research Laboratory,³ Philadelphia, Pennsylvania

FATTY acid amides have a well-established industrial position, and their use is widespread and increasing (7, 11). In the commercial preparation of fatty acid amides, fatty acids, rather than fats, are treated with ammonia or amines. The main reason for this is probably the availability of inexpensive, purified fatty acids, notably from vegetable oil foots and inedible animal fats. A large increase in the demand for amides, coupled with the need for utilizing fatty acids in other applications, would probably require that fats themselves be employed as starting materials. The direct conversion of fats to amides and glycerol by reaction with ammonia or amines appears to be an attractive reaction because of its apparent simplicity and the ready availability and low cost of the starting materials. Numerous studies of this reaction have been published in the patent literature, but only a few reports have appeared in technical journals describing systematic investigations (1, 7, 8, 11).

Study of the published reports reveals considerable difference of opinion regarding the best techniques for quantitative conversions of fats to amides and glycerol. The points in question are the time and temperature of reaction, the desirability of operating under anhydrous or aqueous conditions, the need for catalysts, such as ammonium chloride and other salts, and the quantity of ammonia or amines required. Furthermore the basis for assuming that high yields have been obtained is not clear from much of the published work and, in some cases, is open to serious question. In most patents the assertion that quantitative yields are obtained is usually unsubstantiated by actual experimental data.

As part of a systematic investigation of the preparation and characteristics of nitrogen-containing fatty materials in progress in our laboratory (12, 13, 14, 15, 17), it was considered desirable to study the direct conversion of some selected fats to amides and glycerol to define conditions for obtaining quantitative yields

of products. A major portion of the present investigation was devoted to a study of the direct conversion of beef fat (in this study, oleo oil) to amides and glycerol since the most plentiful inexpensive domestic industrial fats are of animal origin. To demonstrate the generality of this work and to extend its utility, olive, castor, and tobacco seed oils were included. The direct preparation of N-(*n*-dodecyl)- and N-(2-hydroxyethyl)- as well as unsubstituted amides was also studied.

An additional line of work investigated, after conditions had been developed for quantitative conversion of fats to amides and glycerol, was the fractionation of amides by crystallization techniques in an attempt to prepare purified fatty acid amides. These could presumably then be readily converted to fatty acids by hydrolysis or employed in applications where their specialized properties made them valuable. The reasons for employing amides for the preparation of purified fatty acids, particularly the unsaturated ones, were that they are among the highest melting fatty acid derivatives, and their solubility in organic solvents is usually so low that they can be conveniently crystallized at or above 0°C. In general, crystallization for purification of unsaturated acids requires temperatures in the range of -40° to -80°C. (7, 11), and it would be a considerable advantage to be able to conduct the purifications at higher temperatures. With the exception of ricinoleamide from castor oil, oleamide from olive oil, and perhaps N-(2-hydroxyethyl) oleamide from oleo oil, amides of high purity (above 90%) were not obtained, presumably because the solubility of all the components of the mixtures were considerably reduced and, more important, the differences in solubility of the various amide types (based on degree of unsaturation) were probably too small for efficient fractionation. Some degree of fractionation was achieved however in all cases.

Experimental

All reactions with amines were conducted in an atmosphere of nitrogen; those with ammonia in an ammonia atmosphere.

¹ The previous paper in this series is reference 14.

² Presented at the Fall Meeting of the American Oil Chemists' Society, Chicago, Ill., Oct. 8-10, 1951.

³ One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE I
 Reaction of Methyl Oleate With Ammonia

28% Aqueous Ammonia					
Expt. No.	Temp., °C.	Time, Hours	Quantity of NH ₃	Yield of Oleamide Isolated %	Special Conditions and Remarks
1.....	25	25 ^a	0	Oleic acid added in an amount equal to 2% by weight of methyl oleate.
2.....	25	25 ^a	0	Methanol present in an amount equal to that of methyl oleate.
3.....	100	6 ^a	0.7-2.5	Conducted both in absence and presence of 2% of oleic acid.
4.....	150	1 ^a	1	
5.....	150	3 ^a	25	
6.....	150	6 ^a	45	
7.....	150	6 ^a	50	2% of oleic acid present.
8.....	150	6 ^a	32	135 g. of ammonium chloride present per 100 g. of methyl oleate. Reaction product darkly colored.
9.....	175	6 ^a	50	Conducted both in absence and presence of 2% of oleic acid.
Anhydrous Liquid Ammonia					
10.....	25	6 ^b	Trace	
11.....	100	7 ^c	7.8-9.2	
12.....	135	6 ^c	40	
13.....	135	12 ^c	62	
14.....	165	6-12 ^c	86-90	The shorter time gave the slightly lower yield.
15.....	175	3 ^c	78	
16.....	175	6-12 ^c	85-89	
17.....	175	6 ^d	86	
18.....	200	6-12 ^c	79-83	Reaction product darkly colored.
19.....	200	12 ^d	75	Reaction product darkly colored.

^a 900% excess.
^b 3 ml. NH₃ : 2 ml. methyl oleate (approx. 22 moles NH₃ per mole methyl oleate)
^c 1 ml. NH₃ : 1 ml. methyl oleate (approx. 15 moles NH₃ per mole methyl oleate)
^d 1 ml. NH₃ : 2 ml. methyl oleate (approx. 7.5 moles NH₃ per mole methyl oleate)

Starting Materials. Beef fat (edible "oleo oil"): acid number, 0.8; saponification number, 195; iodine number, 43.7-39.7 (changed during storage and handling; polyunsaturated acids, 3.3% (2).

Olive oil (edible grade): acid number, 1.5; saponification number, 193; iodine number, 80.9.

Castor oil (U.S.P. grade): acid number, 2.1; saponification number, 183; iodine number, 86.1; hydroxyl, 4.79%.

Tobacco seed oil was prepared by extracting the ground tobacco seed with petroleum naphtha (hexane fraction) in a Soxhlet extractor. The solvent-free oil had the following characteristics: saponification number, 195; iodine number, 132.0.

Methyl oleate, iodine number, 83.5, methyl oleate content, 97.5%, was prepared by the esterification of purified oleic acid obtained from olive oil by multiple low-temperature fractional crystallization and distillation (3, 16).

n-Dodecylamine and monoethanolamine were obtained by fractional distillation of the purest commercial grades through efficient columns. They had the correct physical and chemical characteristics. Anhydrous liquid ammonia was the purest commercial grade. It was purchased in cylinders and was used without further purification. The 28% aqueous ammonia was the A.C.S. grade.

Preparation of Amides. Before investigating the reaction of fats with ammonia, a systematic study was conducted on the ammonolysis of methyl oleate. This compound was selected because the determination of yield is simpler when a single amide is produced and

the reaction conditions can be translated directly to the ammonolysis of triglycerides.

Reaction of Methyl Oleate With 28% Aqueous Ammonia. Fifty-nine grams (0.2 mole) of methyl oleate and 123 g. of 28% aqueous ammonia (2.0 moles of NH₃) were placed in a specially constructed stainless steel bomb (400 ml. capacity), which was then rotated end over end in a thermostatically controlled oil bath (9). Experiments were conducted from 25° to 175°C. for various reaction times (Table I). After the bomb had cooled, the contents were transferred to a beaker and agitated while being warmed on the steam bath to expel excess ammonia. The mixture was then made slightly acid by the addition of 6N hydrochloric acid, and the melted layer of fatty material was washed with warm water until free of acid. It was then dissolved in petroleum naphtha (hexane fraction) (3 ml. /g.), treated with activated carbon, and filtered. The filtrate was adjusted to 5 ml. of solvent per gram of solute and cooled to 0°C. to precipitate oleamide. Table I shows the results of these experiments. The yield of oleamide given is that isolated as precipitate from petroleum naphtha at 0°C. Based upon recrystallization experiments with crude and pure samples of oleamide, it is estimated that approximately 85 to 90% of the oleamide present was isolated.

Evaporation of the filtrate after separation of oleamide yielded a liquid product consisting almost entirely of free acids.

Reaction of Methyl Oleate With Liquid Ammonia. Thirty grams of methyl oleate (0.1 mole) were placed in a stainless steel bomb (400-ml. capacity) and cooled

TABLE II
 Characteristics of Mixed Amides From Fats

Amides	M. P., °C.	Iodine No.		Ester No.	Acid No.
		Calcd.	Found		
Unsubstituted amides (from oleo oil)	78-84	41.8	41.7	2.9	2.6
Unsubstituted amides (from olive oil)	73-74	84.9	83.2	3.0	1.5
Unsubstituted amides ^a (from castor oil)	62-64	90.1	85.6	4.3	1.5
Unsubstituted amides (from tobacco seed oil)	59-65	138.6	136.5	2.7	3.4
N-(<i>n</i> -Dodecyl) amides (from oleo oil)	62-68	28.4	28.1	3.2	4.1
N-(2-Hydroxyethyl) amides ^b (from oleo oil)	76-85	39.4	38.4	3.2 ^c

^a Hydroxyl, 4.69% (calcd. 5.0%).

^b Hydroxyl, 5.46% (calcd. 5.4%).

^c Saponification number.

to -45°C . Thirty ml. of liquid ammonia were drawn off into a graduated cylinder (4, 6), packed in solid carbon dioxide, and added to the cold methyl oleate. The lid (also cooled to -45°C .) was then quickly put in place and screwed down. Experiments were conducted from 25° to 200°C . for various reaction times (Table I), as described in the previous paragraph. After cooling, the excess ammonia was vented through a needle valve before the bomb was opened. The granular solid was dissolved in petroleum naphtha and then decolorized and crystallized at 0°C . using 7 ml. of solvent per gram of solute. Substantially quantitative conversion of methyl oleate to oleamide was accomplished by heating it for 6 hours at $170^{\circ} \pm 5^{\circ}\text{C}$. with one-half its volume of liquid ammonia (experiment nos. 14, 16, and 17; Table I).

Reaction of Fats With Liquid Ammonia. In the initial experiments the volume of liquid ammonia was one-half that of the fat since it had been shown with methyl oleate that quantitative conversion to amides was obtained in this way (Table I). Similar results were obtained however even when the volume of liquid ammonia was one-fourth that of the fat, and all subsequent work was conducted with this ratio.

The preparation of unsubstituted amides from oleo oil is typical of the reaction of all the triglycerides with liquid ammonia.

Three hundred and fifty ml. (314 g., 0.364 mole) of oleo oil (iodine number 39.7) were placed in a stainless steel bomb (700-ml. capacity), and the lid,

which was provided with a needle valve, was put in place and securely tightened. The bomb was cooled to -50°C . and evacuated by means of a mechanical pump. Ninety ml. of liquid ammonia were drawn off into a graduated separatory funnel packed in solid carbon dioxide, and the ammonia was then introduced into the bomb through the needle valve. The bomb was then heated to $170^{\circ} \pm 5^{\circ}\text{C}$. for six hours with rocking (calculated pressure, approximately 2,500 lb./sq. in.), after which it was cooled to room temperature. The excess ammonia was allowed to escape through the needle valve, and the yellow solid remaining in the bomb was transferred to a beaker and washed free of glycerol with several hot water washes. On cooling, the oily layer formed a hard cake which was broken up and dried, yielding 294 g. (98%) of mixed amides, characteristics of which are given in Table II.

By the same procedure unsubstituted amides of olive oil, tobacco seed oil, and castor oil were also prepared in substantially quantitative yield (Table II).

Glycerol was readily recovered in high yield from the aqueous washes by evaporation of the water and vacuum distillation of the crude glycerol concentrates.

N-(*n*-Dodecyl) Amides of Oleo Oil. A mixture of 43 g. (0.05 mole) of oleo oil (iodine number 43.7) and 30 g. (0.156 mole) of *n*-dodecylamine was heated for three hours at 230°C . When the mixture had cooled below 100°C ., 1N hydrochloric acid was added with stirring. The layers were allowed to separate, and the aqueous layer was removed after the amides had solidified. The amide cake was remelted and washed several times with hot water until free of acid, yielding 65.6 g. (98%) of mixed dodecyl amides; m.p. 62° to 68°C . (Table II). Glycerol was readily isolated by distillation of the combined aqueous layers.

In a larger run consisting of 500 g. of oleo oil and 325 g. of *n*-dodecylamine, an approximately 90% conversion to amides, m.p. 62° to 68°C ., was obtained. This material was employed in the fractionation reported in Table III.

N-(2-Hydroxyethyl) Amides of Oleo Oil. A mixture of 500 g. (0.58 mole) of oleo oil (iodine number 43.7) and 159 g. (2.1 moles) of monoethanolamine was refluxed for 15 minutes. The cooled reaction mixture was dissolved in warm petroleum naphtha (10 ml./g.) and washed several times with warm 10% sodium sulfate solution to remove the excess monoethanolamine and

 TABLE III
 Fractional Crystallization of Mixed Amides From Fats

Mixed Amides	Crystallized Amides																	
	M.p. Iodine		Solvent ^a	Fraction I				Fraction II				Fraction III				Filtrate		
	°C.	no.		Crystn. Temp. °C.	Yield %	M.p. °C.	Iodine no.	Crystn. Temp. °C.	Yield %	M.p. °C.	Iodine no.	Crystn. Temp. °C.	Yield %	M.p. °C.	Iodine no.	Yield %	M.p. °C.	Iodine no.
Unsubstituted amides																		
Oleo oil ^b	78-84	41.7	A, 5/1	25	46.8	95-97	13.4	-20	37.0	67-72	69.6	11.2	39-40	67.1
Olive oil ^b	73-74	83.2	A, 8/1	24	8.8	87-88	34.2	0	74.9	74-75	82.9	-30	8.0	69-73	98.6	4.7	39-53	157.9
Castor oil ^c	62-64	85.6	A, 5/1	0	69.0	65-66	86.3	-20	13.3	62-63	91.2	-40	4.4	59-60	99.5	5.7	39-43	107.5
Tobacco seed oil.....	59-65	136.5	A, 5/1	15	8.0	85-90	43.3	5	11.0	67-71	116.2	-40	70.0	52-63	150.7	11.0	solid	119.2
N-(<i>n</i> -dodecyl) amides																		
Oleo oil ^d	62-68	28.4	E, 25/1	24	45.2	78-79	6.1	-20	37.7	45-55	46.6	16.3	semi-solid	39.2
N-(2-hydroxyethyl) amides																		
Oleo oil ^e	76-85	38.4	A, 15/1	0	54.8	86-92	9.2	-20	27.2	57-59	71.0	15.5	32-36	73.0

^a A = acetone, E = 95% ethanol. The numbers indicate solvent ratio in ml./g.

^b Calcd. for oleamide: iodine number 90.2.

^c Calcd. for ricinoleamide: iodine no. 85.3; % OH 5.72. The % OH of the mixed amides was 4.69; Fraction I, 5.39; Fraction II, 4.82; Fraction III, 4.39; and Filtrate, 4.32.

^d The acid number of the mixed amides was 6.0; Fraction I, 1.0; Fraction II, 1.7; Filtrate, 30.0.

^e Calcd. for N-(2-hydroxyethyl) oleamide: iodine number 78.0.

the glycerol formed. The solvent was evaporated, yielding 525 g. (95%) of N-(2-hydroxyethyl) amides, m.p. 76.3° to 85.1°C. (Table II).

Fractional Crystallization of Amides. Table III summarizes the results obtained in the crystallization of the amides prepared from the various fats. Crystallization temperatures above 0°C. were maintained for two hours; 0°C. or below, overnight.

Hydrolysis of Amides to Free Acids. One mole of amide fraction, obtained by crystallization as just described, was refluxed with 1 l. of constant boiling (approximately 20%) aqueous hydrochloric acid. Analytical samples were removed at intervals, dissolved in petroleum naphtha, and washed with warm water until free of hydrochloric acid. Iodine and acid numbers were then determined on the dried samples.

An oleamide-rich fraction (iodine number 85.5; acid number, 1.4) required only two hours refluxing to yield free acids with an iodine number of 78.4 (calcd. 85.2) and an acid number of 192. Longer hydrolysis, up to 24 hours, did not increase the acid number.

An N-(2-hydroxyethyl) oleamide-rich fraction (iodine number, 62.0; acid number, 0.8) was also completely hydrolyzed in two hours, yielding free acids with an iodine number of 70.3 (calcd. 71.5) and an acid number of 191.

On the other hand, an N-(*n*-dodecyl) oleamide-rich fraction (iodine number, 44.9; acid number, 1.4) required 24 hours to obtain an acid number as high as 183.2. The iodine number of the free acids was 28.5 (calcd. 56.4). Their chlorine content was 6.35%, indicating substantial addition of hydrochloric acid to the double bond.

Hydrolysis of the amides with aqueous sulfuric acid or alcoholic potassium hydroxide proceeded too slowly for practical use. With the former considerable increase in color was noted.

Discussion

Table I shows that the maximum yield of oleamide isolated from the reaction of methyl oleate with excess 28% aqueous ammonia was about 50% (6 hours reaction at 150° to 175°C., experiment nos. 6, 7, and 9). This yield appeared to be a limiting value probably because of the competition between the hydrolytic and ammonolytic reactions. Evidence for this conclusion is the fact that evaporation of solvent from the acidified filtrate after separation of oleamide yielded a liquid product consisting almost entirely of free acids.

Emulsions were frequently encountered in working up the products from experiments in which water was present apparently because of the formation of ammonium soaps. In the early experiments (nos. 1, 3, 7, and 9, Table I) a small amount of oleic acid was added to the methyl oleate to obtain ammonium oleate immediately, which would presumably favor contact between the ester and the aqueous system, thus speeding up the reaction. This was soon abandoned because it had no beneficial effect and soaps were being formed anyway. Addition of ammonium chloride did not favor amide formation (experiment no. 8) and resulted in a dark reaction product. Oleamide was not formed or was obtained only in traces at or below 100°C. (experiment nos. 1, 2, and 3).

With anhydrous ammonia, quantitative conversion of methyl oleate to oleamide was obtained (6 to 12 hours at 165° to 175°C., experiment nos. 14, 16, and 17, Table I). Above 175°C. (experiment nos. 18 and

19), the yield was lower and the reaction product was darkly colored. Oleo oil, olive oil, castor oil and tobacco seed oil were also converted to amides and glycerol in substantially quantitative yields in the same way (Table II). The ester numbers of the crude mixed amides from the fats were about 3 to 4. These values are not significant because even with rigorously purified amides, such as oleamide, ester numbers in this range are usually obtained when the compounds are refluxed with 0.2N alcoholic potassium hydroxide for 30 minutes.

It can be concluded from these studies that anhydrous liquid ammonia is preferable to 28% aqueous ammonia for the conversion of fatty esters to amides, a reaction temperature of 170° ± 5°C. for 6 hours is sufficient, ammonium chloride is not required and is actually deleterious and, in the case of glycerides, glycerol is readily recovered in high yield.

A disadvantage to the use of anhydrous liquid ammonia was the relatively high pressures involved. It may be possible however to conduct the reaction at moderate pressures by simultaneously introducing and venting ammonia. In the conversion of fats to N-(*n*-dodecyl)- and N-(2-hydroxyethyl) amides however atmospheric pressure reaction conditions were employed (Table II). Particularly significant was the quantitative conversion of oleo oil to N-(2-hydroxyethyl) amides in only 15 minutes by refluxing with ethanalamine. The conversion to N-(*n*-dodecyl) amides however required 3 hours heating at 230°C. with *n*-dodecylamine, and conversion to unsubstituted amides required 6 hours heating at 170°C. under pressure with liquid ammonia.

Crystallization of the amides from the various fats gave some interesting results although fractionation was not as clear-cut in all cases as had been hoped when this work was initiated.

In Table III are shown results of the fractional crystallization from acetone of the unsubstituted amides of oleo oil. Two main precipitate fractions were obtained at room temperature and -20°C., respectively. These can be described as predominantly saturated (iodine number 13.4) and predominantly monounsaturated (iodine number 69.6), but no separation into pure amides could be achieved under a variety of conditions, including recombination of selected fractions and recrystallization. Petroleum naphtha and 95% ethanol were also employed as solvents. Petroleum naphtha gave results similar to those with acetone with respect to crystallization temperatures and yields, but the precipitates were difficult to filter and dry. Ethanol also gave results similar to those with acetone, but lower crystallization temperatures were required. Acetone was the best all-round solvent.

Both acetone and 95% ethanol were employed with the unsubstituted amides of olive oil. Acetone was superior. As shown in Table III, after removal at room temperature of a small amount (8.8%) of amide fraction, which was predominantly saturated (iodine number 34.2), a substantial precipitate amounting to about 75% of the starting material and consisting mainly of oleamide (estimated purity 92%) was then obtained at 0°C. Thus a high recovery (93% yield based on the assumption that olive oil contains 80% oleic acid) of oleamide was readily obtained from olive oil amides by precipitation at 0°C. whereas precipitation of oleic acid from olive oil acids requires temper-

atures of about -60°C . The filtrate amides (iodine number, 157.9) were predominantly linoleamide.

In Table III are shown the results obtained in the crystallization from acetone of the unsubstituted amides of castor oil. An 86% yield (based on the assumption that castor oil contains 80% ricinoleic acid) of ricinoleamide (estimated purity, $>95\%$) (5) was obtained by a single crystallization of the amides at 0°C . Ethanol was not as satisfactory for this fractionation as was acetone.

The results obtained in the crystallization from acetone of unsubstituted amides of tobacco seed oil were not as good as had been anticipated, considering the predominance of linoleic acid (as glycerides) in this oil (Table III). It is estimated that the precipitate obtained at -40°C . (iodine number, 150.7) contained only about 70% of linoleamide. Petroleum naphtha as solvent gave even less satisfactory results.

The N-(*n*-dodecyl) amides of oleo oil were fractionated (Table III) only from 95% ethanol because of their extremely low solubility in acetone and petroleum naphtha. An approximately equal division into two fractions was obtained: one consisting predominantly of saturated dodecyl amides (iodine number 6.1) and the other (iodine number 46.6) predominantly of dodecyl oleamide.

In Table III are shown the results obtained in the fractional crystallization from acetone of the N-(2-hydroxyethyl) amides of oleo oil. Acetone was superior for one reason or another to 95% ethanol, petroleum naphtha, isopropyl alcohol, and mixtures of acetone and petroleum naphtha. In crystallizing N-(2-hydroxyethyl) amides from acetone, care should be exercised to remove free monoethanolamine completely from the amides because of its reaction with acetone. We avoided the use of hydrochloric acid to neutralize excess monoethanolamine because of the possibility of an acid-induced rearrangement of N-(2-hydroxyethyl) amides to amino esters (10).

The N-(2-hydroxyethyl) amides yielded a fraction predominantly saturated (iodine number 9.2) and a fraction (iodine number 71.0) consisting of about 90% N-(2-hydroxyethyl) oleamide.

Attempts were made to isolate fractions even richer in oleamide or substituted oleamides by recrystallization of fractions rich in these substances. These experiments were unsuccessful.

The hydrolysis of unsubstituted amides and N-(2-hydroxyethyl) amides with constant boiling aqueous hydrochloric acid was rapid and complete within two hours, and the parent fatty acids could be readily isolated. N-(*n*-Dodecyl) amides however hydrolyzed slowly (24 hours), and chlorine-containing products were obtained when the hydrolysis was carried to completion.

Summary

Conditions have been worked out for the quantitative conversion of oleo oil, olive oil, castor oil, and tobacco seed oil to amides and glycerol by reaction with liquid ammonia under pressure. Similarly methyl ole-

ate has been converted to oleamide in excellent yield. The reaction of aqueous ammonia with methyl oleate, however, gives a maximum yield of isolated oleamide of only 50%, apparently because of competition between hydrolytic and ammonolytic reactions.

N-(2-hydroxyethyl)- and N-(*n*-dodecyl) amides have also been prepared by the reaction of oleo oil with monoethanolamine and *n*-dodecylamine, respectively, at atmospheric pressure. Particularly significant is the quantitative conversion of oleo oil to N-(2-hydroxyethyl) amides by refluxing with monoethanolamine for only 15 minutes. The conversion to N-(*n*-dodecyl) amides however required three hours heating at 230°C . with *n*-dodecylamine, and conversion to unsubstituted amides required six hours heating at 170°C . under pressure with liquid ammonia.

Crystallization of the amides obtained from the various fats yielded oleamide (purity, 92%) from olive oil, ricinoleamide (purity, $>95\%$) from castor oil, and N-(2-hydroxyethyl) oleamide (purity, 90%) from oleo oil. Little fractionation was accomplished with the amides of tobacco seed oil however. In the fractionation of the unsubstituted and N-(*n*-dodecyl) amides from oleo oil, fractions which were predominantly saturated and monounsaturated were obtained readily, but no greater purification could be effected by recrystallization.

Unsubstituted and N-(2-hydroxyethyl) amides were readily converted to the corresponding free acids by refluxing for two hours with constant boiling (approximately 20%) aqueous hydrochloric acid.

Acknowledgment

The authors are indebted to Wilfred R. Noble Jr., Thomas D. Miles, and Reba Baum for technical assistance.

REFERENCES

1. Balaty, V. F., Fellingner, L. L., and Audrieth, L. F., *Ind. Eng. Chem.*, **31**, 280 (1939).
2. Brice, B. A., Swain, M. L., Schaeffer, B. B., and Ault, W. C., *Oil and Soap*, **22**, 219 (1945); Brice, B. A., and Swain, M. L., *J. Optical Soc. Am.*, **35**, 532 (1945).
3. Brown, J. B., and Shinowara, G. Y., *J. Am. Chem. Soc.*, **59**, 6 (1937).
4. Franklin, E. C., "The Nitrogen System of Compounds" (A.C.S. Monograph No. 68), Appendix, Reinhold Publishing Corporation, New York (1935).
5. Herrera-Batteke, P., *Philippine J. Sci.*, **32**, 35 (1927).
6. Johnson, W. C., and Fernelius, W. C., *J. Chem. Education*, **6**, 441 (1929).
7. Markley, K. S., "Fatty Acids, Their Chemistry and Physical Properties," Interscience Publishers Inc., New York, 489-493 (1947).
8. Oda, R., and Wada, S., *J. Soc. Chem. Ind. Japan*, **37**, Suppl. binding, 295-6 (1934).
9. Phillips, M., *Ind. Eng. Chem.*, **17**, 721 (1925).
10. Phillips, A. P., and Baltzly, R., *J. Am. Chem. Soc.*, **69**, 200 (1947).
11. Ralston, A. W., "Fatty Acids and Their Derivatives," John Wiley and Sons Inc., New York, 584-585 (1948).
12. Roe, E. T., Scanlan, J. T., and Swern, D., *J. Am. Chem. Soc.*, **71**, 2215 (1949).
13. Roe, E. T., Scanlan, J. T., and Swern, D., *J. Am. Chem. Soc.*, **71**, 2219 (1949).
14. Roe, E. T., Stutzman, J. M., and Swern, D., *J. Am. Chem. Soc.*, **73**, 3642 (1951).
15. Roe, E. T., and Swern, D., *Anal. Chem.*, **22**, 1160 (1950).
16. Swern, D., Knight, H. B., and Findley, T. W., *Oil and Soap*, **21**, 133 (1944).
17. Swern, D., Stutzman, J. M., and Roe, E. T., *J. Am. Chem. Soc.*, **71**, 3017 (1949).

[Received July 19, 1951]