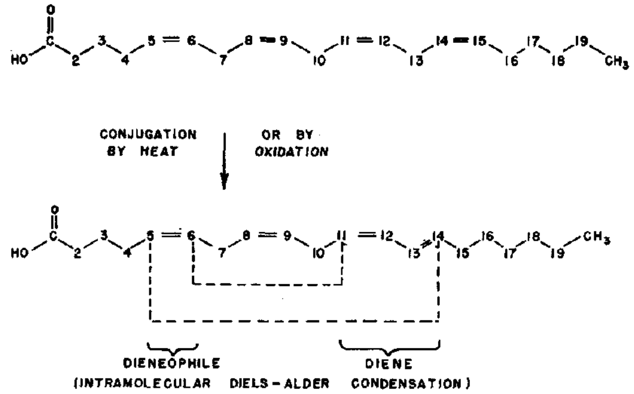
FIG. 8

POSSIBLE CYCLIZATION OF ARACHIDONIC ACID



SUGGESTED STRUCTURE OF CYCLIZED ARACHIDONIC ACID

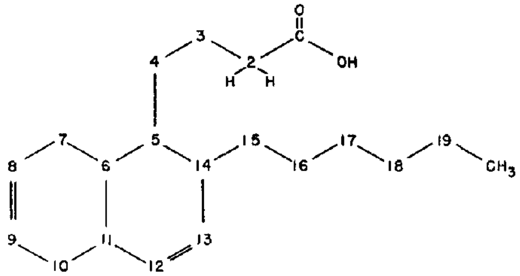


FIG. 9

W. T. Tolberg for the spectrophotometric studies they performed.

Summary

1. Methyl eleostearate has been thermally cyclized in good yields, and a concentrate of the cyclic product has been prepared.
2. Using small amounts, a technique has been devised for a) aromatization of the resultant cyclohexadiene, b) oxidation to orthophthalic acid, and c) characterization of the acid as the anhydride and the imide.
3. The significance of cyclic fatty acids in industrial processes is discussed.

Zusammenfassung

1. Ringbildung von methyleleostearat auf thermischem wege ergab gute resultate, und ein konzentrat des ring-produktes wurde prepariert.
2. Eine neue technik fuer die benutzung von kleineren mengen ermoeglichte: a) aromatisation des entstandenen cyclohexadien, b) oxdierung zu orthophthalischer säure, und c) charakterisierung der säure ais anhydrin und imid.
3. Die bedeutung von fettsäure-ringen in industriellen verfahren wird besprochen.

Resumé

1. Le méthyleleostéarate a été cyclisé thermiquement avec bon rendement et un concentré du produit cyclique a été préparé.
2. Au moyen d'une nouvelle technique, utilisant des quantités minimes de matériel, il a été possible a) d'aromatiser les cyclohexadiènes obtenus, b) d'oxyder l'acid orthophthalique, et c) d'établir la constitution de l'acide comme anhydride ou imide.
3. L'importance pour l'industrie des acides gras cycliques est discutée.

REFERENCES

1. Rossman, Fettchem Umschau, *40*, 117 (1933).
2. Crampton, Farmer, and Berryhill, J. Nutr., *43*, 431 (1951).
3. Crampton, Common, Farmer, Berryhill, and Wiseblatt, J. Nutr., *43*, 533 (1951).
4. *Ibid.*, *44*, 177 (1951).
5. Crampton, Common, Farmer, Wells, and Crawford, J. Nutr., *49*, 333 (1953).
6. Paschke and Wheeler, J. Am. Oil Chemists' Soc., *26*, 278 (1949).
7. Paschke, Tolberg, and Wheeler, J. Am. Oil Chemists' Soc., *30*, 97 (1953).
8. O'Connor, Heinzelman, McKinney, and Pock, J. Am. Oil Chemists' Soc., *24*, 212 (1947).
9. Paschke and Wheeler, J. Am. Oil Chemists' Soc., *32*, 473-478 (1955).
10. Anon., Progress Thru Research, *8* (No. 4), 13 (1954); Chemical Processing, *17*, 116 (1954).
11. Paschke, Kerns, and Wheeler, J. Am. Oil Chemists' Soc., *31*, 5 (1954).
12. Abu-Nasr, Potts, and Holman, J. Am. Oil Chemists' Soc., *31*, 16 (1954).
13. Zechmeister, Chem. Rev., *34*, 270 (1944).
14. Chis Chin, J. Chem. Soc., Japan, *53*, 281 (1950).
15. *Ibid.*, *53*, 332 (1950).
16. Slansky, Paint Manuf., *24*, 121 (1954).
17. Lea, Chemistry and Industry, *1953*, 1304.
18. Privett and Lundberg, J. Am. Oil Chemists' Soc., *28*, 313 (1951).
19. Mod, Skau, and Planck, J. Am. Oil Chemists Soc., *30*, 368 (1953).

[Received March 7, 1955]

Glycerolysis of Peanut and Mustard Oils

T. N. MEHTA, C. V. N. RAO, V. LAXMIKANTHAN, and S. N. SHAH, Laxminarayan Institute of Technology, Nagpur University, Nagpur, M. P., India

COMMERCIAL monoglycerides are used in shortening to improve their cake-making properties and as emulsifiers in a variety of other products. Monoglyceride mixtures are also prepared as a first step in the manufacture of oil-modified alkyd resins and in the preparation of certain detergents. Many methods for their manufacture are known, but only two are of industrial importance. In the first method the fatty acids are esterified with excess of glycerol either alone or in the presence of mutual solvent with or without an esterifying catalyst. The second method consists of heating the fatty oils with an excess of glycerine either alone or in the presence of an ester interchange catalyst. The second method, referred to as glycerolysis, is a special case of alcoholysis which results in the formation of a mixture of mono-, di-, and triglyceride (1).

The formation of monoglycerides depends on various factors, such as the reaction temperature and time, the amount and the nature of the catalysts used, as well as the composition and proportion of fatty acids or oils and glycerols. Tsuchya and Akiyama (2) carried out the experiments with hardened fish oil to determine the effect of time, temperature, and amount of glycerol upon the course of reaction. They showed that, at a temperature of 270–280°C. and with 25–

100% of glycrol, equilibrium monoglyceride content was obtained within half an hour. The presence of diglyceride in the product was indicated by the acetyl values higher than those accounted for by the monoglycerides. Hilditch and Rigg (3) have pointed out that the extent to which the reaction between fat and glycerol can be carried out depends on the miscibility of glycerol in the fat phase.

Blagonravova (4) has studied the glycerolysis of linseed oil at temperatures in the order of 200° and 250°C. The results show that the increase in temperature is beneficial in obtaining complete hydrolysis while longer reaction time indicates dehydration due to the formation of polyglycerol derivatives resulting in the presence of an alkaline catalyst. Ross, Bell, Arrowsmith, and Gebhart (5) have shown that pure anhydrous glycerol does not react appreciably below decomposition temperatures, but water or an alkaline material, such as soap, will catalyze the reaction. According to Savary (6), catalyst forms metallic soap with the fat. The soap thus formed increases the solubility of glycerol in the fat phase promoting the reaction.

Experiments were carried out by Feuge and Bailey (7) for finding out the miscibility of glycerol at temperatures ranging from 175° to 250°C. There appears to be a linear relationship between the temperature and the logarithm of the amount of glycerol miscible. Maximum percentage of glycerol miscible in the fat at temperatures ranging from 175° to 250°C. varies from 15% to 40% anhydrous glycerol on the basis of fat.

Kawai (8) has studied the glycerolysis of coconut oil, soybean oil, Chinese tea seed oil, Japan wax, etc., and come to the conclusion that glycerolysis is selective. The low molecular weight and highly unsaturated acids are more easily split off to give monoglycerides. Runk (9) has reported 60% formation of linseed oil monoglycerides at 235°C., using lime (CaO) and litharge (PbO) as catalysts.

Chinoy and Kamath (10), while working on the glycerolysis of sesame oil, have concluded that a minimum quantity of 25% excess of glycerine is essential to obtain complete glycerolysis. Further, the presence of fatty acids or water reduces the time required to reach equilibrium when only equivalent quantities of the reactants are employed. In the case of fats rich in stearic acid they found that the rate of glycerolysis at 200°C. is low, and higher at 250°C. but resulted in the formation of a certain amount of polyglycerol derivatives.

The object of the present investigation is: a) to study the rate of formation of monoglycerides at different temperatures, using calcium oxide as the ester-interchange catalyst; b) to establish the optimum conditions for the yield of maximum monoglyceride; and c) to observe the effect of the constituent fatty acids present in peanut and mustard oils on the rate and course of their glycerolysis.

Experimental

Materials used are:
- raw peanut oil (S.V. 196, I.V. 91.3)
- raw mustard oil (S.V. 173, I.V. 99)
- C. P. glycerine (E. Merck, 98%)
- commercial glycerine (93%)
- lime (CaO), reagent grade, calcined for six hours at 600°C.

The formulation used was as follows:
- raw peanut oil in runs I, II, III, and IV, 500 g.
- raw mustard oil in runs V and VI, 500 g.
- glycerol, 34% by wt. (E. Merck's) in runs III and IV, 170 g.
- commercial glycerol, 38% by wt., in runs I, II, V, and VI, 190 g.
- catalyst CaO (0.15% metal on wt. of glycerol).

Glycerolysis was carried out in a three-necked flask fitted with a stirrer, a thermometer, and 1-m.-long air condenser. The contents of the flask were heated in a metal bath in which the reaction temperature was controlled between ± 2°C. During the course of the reaction, carbon dioxide was passed over the mixture to maintain an inert atmosphere. The reaction temperature was obtained in about 20 min. The first sample was taken out at that temperature before addition of the catalyst. Then the reaction was continued. In runs I and II (Table I) samples were taken at intervals of every 15 min. and were analyzed for monoglyceride content by the periodic acid oxidation method (11) and for hydroxyl value by the pyridine acetic anhydride method (12). The monoglyceride content was calculated according to the following equation:

TABLE I
Peanut Oil with Glycerol (93%)

Sample No.	Time (min.)	% α-Monoglyceride	
		Run I at 225°C.	Run II at 250°C.
1	0	.5374	2.146
2	15	25.35	47.56
3	30	33.7	50.05
4	45	35.77	47.8
5	60	34.43	42.75
6	75	34.38	37.45
7	90	34.36	....
8	105	34.15	....
9	120	31.61	....
10	135	29.46	....

$$\alpha\text{-monoglyceride } \% = \frac{(B-S) \times N \times X}{W}$$

B is titration of blank containing 50 ml. of chloroform
S is titration of sample
N is normality of sodium thio-sulphate solution
W is weight of sample represented by aliquot pipetted for test
X is 17.37 average mol. wt. of monoglyceride of peanut oil divided by 20, and 19.3 mol. wt. of monoglyceride of mustard oil divided by 20

From the hydroxyl values the respective diglyceride contents are calculated by using the following equation:

$$\text{Diglyceride } \% = \frac{100\,H - 322.9\,M}{93.03} \text{ in the case of}$$

peanut oil

$$\text{Diglyceride } \% = \frac{100\,H - 290.6\,M}{84.35} \text{ in the case of}$$

mustard oil

Where H is the hydroxyl value of the washed sample M is the monoglyceride %

322.9 =(OH) value of peanut oil monoglyceride
290.6 =(OH) value of mustard oil monoglyceride
93.03=(OH) value of peanut oil diglyceride

All the values are calculated on the basis of the average molecular weights of mono- and diglycerides. 84.35 = (OH) value of mustard oil diglyceride. The triglyceride % is obtained from the difference.

For the subsequent runs III, IV, V, and VI, the procedure adopted for the estimation of monoglycerides is slightly modified as follows: a representative

TABLE II
Peanut Oil with Glycerol (98%)

Sample No.	Time (min.)	% α-Monoglyceride	
		Run III at 200°C.	Run IV 225°C.
1	0	1.424	4.615
2	15	3.551	22.43
3	30	5.503	33.83
4	45	8.527	39.19
5	60	12.78	....
6	75	17.5	43.27
7	90	24.04	43.63
8	105	27.93	43.88
9	120	....	....
10	135	30.91	41.12
11	150	33.69	41.66
12	165	37.41	40.06
13	180	37.79	37.81
14	195	38.88	36.93
15	210	37.64	33.92
16	225	37.25	33.11

sample, taken out at intervals of 15 min. is dissolved separately with five times its volume of chloroform. The solution is given a careful washing four times with 25 cc. of distilled water each time as mentioned by Runk (9). This is to remove the free glycerine present in the mixture. The dry chloroform solution is then evaporated in a water oven. The glycerol-free product thus obtained is analyzed for α-monoglyceride contents as in the previous runs by the periodic acid oxidation method (11). Care is being taken that no stable emulsion is formed during the process of washing. The slight amount of emulsions formed may be broken with dilute acetic acid.

Discussion

Composition in terms of mono-, di-, and triglycerides against reaction time are shown in Tables 1 to V. During the course of reaction it is observed that the reactants become homogeneous only after the addition of the catalyst. When glycerolysis of peanut oil in the presence of litharge was also carried out the monoglyceride contents were the same as that obtained with lime. The consistency changes from liquid to semi-solid or solid with the increase of monoglyceride content, and color also improves. In all the cases there is a loss of 2 to 3% on weight of the reactants.

The results given in the various tables indicate that the increase of reaction temperature accelerates the monoglyceride formation. The yield of equilibrium monoglycerides is also higher at the higher temperature. At the lower temperature the induction period is more, and the time taken to reach equilibrium is also more. Beyond equilibrium the monoglyceride content and the hydroxyl value fall, a fact which may be due to the formation of cyclic derivatives or polyglycerols. Such abnormalities have been observed by Feuge and Bailey (7) and also by Blaganravova (4).

At 200°C. the diglyceride (Tables II and III) increases to a maximum and then falls. This indicates that the reaction proceeds in two stages, *i.e.,* first, triglycerides are converted into diglycerides, which are in turn converted to monoglycerides. At the initial stages the formation of diglycerides as well as monoglycerides proceeds side by side. The diglyceride formation may be due to the removal of one "acyl" radical from the triglycerides whereas monoglyceride formation may be re-esterification of the fatty acids knocked out of the triglyceride molecule. In the latter stages the amount of monoglyceride increases whereas that of the diglyceride falls. This may be due to the conversion of diglycerides into monoglycerides. At higher temperatures, such as 225°C. and 250°C. in Tables II, III, and V, these steps are not perceptible, but the diglyceride percentage is always on the increase side whereas the monoglyceride reaches a maximum and then falls. Mustard oil and peanut oil differ in three ways under identical conditions of glycerolysis. First, at the lower temperature (200°C.) the monoglyceride formation with mustard oil is negligible. Secondly, at the higher temperature (250°C.) the time taken to attain equilibrium in the case of mustard oil is 3 hrs. whereas in the case of peanut oil the maximum monoglyceride content is obtained within half an hour. Last, the yield of α-monoglycerides in the case of mustard oil is lower (36%) than that of peanut oil (51%) at the same temperature (250°C.). These results are shown

TABLE IV
Mustard Oil with Glycerol (93%)

Sample No.	Time (min.)	% α-Monoglyceride Run V at 200°C.
1	0	1.927
2	30	2.111
3	60	1.774
4	90	2.187
5	120	2.363
6	150	....
7	180	....
8	210	....
9	240	3.008

TABLE VI
Operational Data

Run No.	III	IV	VI
Temp. °C.	200°C.	225°C.	250°C.
Time in hrs. min.	4–0–0	4–0–0	4–0–0
Glycerol % on fat basis	34.0[a]	34.0[a]	38.0[b]
(OH) values of fatty portion	158.8	199.6	169.7
Monoglyceride in fatty portion %	37.54	43.88	26.07
Combined glycerol in fatty portion %	20.69	21.42	18.712
Composition of fatty portion, by wt.%[c]			
Monoglyceride	37.54	43.88	36.17
Diglyceride	40.31	62.24	59.74
Triglyceride	22.15	−6.12	4.09

[a] C. P. glycerine. [b] Commercial glycerol (93%). [c] At max. monoglyceride.

TABLE III
Peanut Oil at 200° and 250°C.

Run	Temperature	Reaction time (min.)	Hydroxyl values	% Combined-glycerol[a]		% Glycerides on fat basis		
				Original	Reacted	mono-	di-	tri-
III	200°C.	45	56.72	10.26	3.10	8.527	29.95	61.523
		90	136.40	10.26	7.45	24.04	63.22	12.74
		135	146.4	10.26	8.00	30.91	50.07	19.02
		225	158.8	10.26	8.68	37.25	41.39	21.36
IV	225°C.	15	78.52	10.26	4.29	22.43	6.546	71.024
		45	149.1	10.26	8.15	39.19	24.18	36.63
		105	199.6	10.26	10.91	43.88	62.24	− 6.12
		135	196.7	10.26	10.75	41.42	67.63	− 9.05
		195	187.7	10.26	10.26	36.93	73.64	−10.57

[a] Reacted glycerol H/1829 × 100.

TABLE V
Run VI—Mustard Oil with Glycerol (98%) Temperature 250°C.

Sample No.	Time of reaction (min.)	Hydroxyl value	% Combined-glycerol[a]		% Monoglyceride (p)	% Diglyceride (q)	% Triglyceride [100-(p+q)]
			Original	Reacted			
1	0	10.73	9.436	0.9145	0.9208	16.65	82.43
2	15	26.02	9.436	1.422	3.321	19.41	77.27
3	30	32.85	9.436	1.796	7.499	13.11	79.39
4	45	36.63	9.436	2.003	8.943	12.69	78.37
5	60	46.28	9.436	2.530	9.788	21.14	69.07
6	90	50.47	9.436	2.758	12.280	18.72	69.00
7	120	67.01	9.436	3.390	16.860	15.43	67.71
8	150	124.80	9.436	6.822	21.680	43.74	24.58
9	180	155.50	9.436	8.500	36.170	59.74	4.09
10	210	169.30	9.436	9.145	33.440	82.80	—16.24
11	240	169.70	9.436	9.276	26.07	108.50	—34.57

[a] Reacted glycerol, H/1829 × 100.

in Tables I and V. This difference in the behavior of mustard oil may be due to the presence of isothiocyanates (13), or it may be an inherent property of erucic acid oils.

Equilibrium monoglyceride contents of peanut and mustard oils are lower than those of linseed oil (58–60%), as reported by Runk. This may be due to the better solubility characteristics of the unsaturated fatty acids of linseed oil in glycerol. Further lowering of equilibrium monoglyceride content of mustard oil may be due to the presence of high molecular weight acid (erucic acid). Kawai (8) has also found that glycerolysis is selective and that fatty acids of low molecular weight and higher unsaturation are primarily re-esterified while those of high molecular weight and lower unsaturation are mostly left unchanged. Thus the nature of component acids present in the oil influences the relative amounts of mono- and diglycerides formed.

Summary

The glycerolysis of peanut and mustard oils has been carried out in the presence of catalysts such as lime and litharge. The effect of time and temperature on the rate of glycerolysis has been studied. The monoglyceride contents and hydroxyl values of the washed samples have been determined. The diglyceride and triglyceride contents of the products have been computed from the monoglyceride percentage and the hydroxyl values.

REFERENCES

1. Markley, "Fatty Acids," Interscience Publishers Inc., New York, p. 303 (1947).
2. Tsuchya and Akiyama, J. Soc. Chem. Ind., Japan, *36*, suppl. binding, 233 (1933).
3. Hilditch, T. P., and Rigg, J. Chem. Soc., 1774 (1935).
4. Blaganravova, Antipova, Savvina, and Svetlichnaya, J. Applied Chem. (U.S.S.R.), *14*, 192 (1941); Chem. Abst. *36*, 1590 (1942).
5. Ross, Bell, Arrowsmith, and Gebhart, Oil and Soap, *23*, 257 (1946).
6. Savary, Compt. rend., *226*, 1284 (1948).
7. Feuge and Bailey, Oil and Soap, *23*, 259 (1946).
8. Kawai, J. Soc. Chem. Ind., Japan, *44*, 705 (1941); Chem. Abst. *42*, 2118 (1948).
9. Runk, Ind. Eng. Chem., *44*, 1124 (1952).
10. Chinoy and Kamath, Paintindia, *3*, No. 5, 27 (1953); *3*, No. 6, 27 (1953).
11. Pohle, W. D., and Mehlenbacher, V. C., J. Am. Oil Chemists' Soc., *27*, 54 (1950).
12. Pohle, W. D., and Mehlenbacher, V. C., Oil and Soap, *23*, 48 (1946).
13. Pal and Mukherji, Indian Soap Journal, *13*, 291 (1948).

[Received July 12, 1954]

The Fractionation of Marine-Oil Fatty Acids with Urea[1]

CLAUDE DOMART,[2] D. T. MIYAUCHI, and W. N. SUMERWELL, Fishery Technological Laboratory,[3] Seattle, Washington

Oils obtained from marine animals such as the menhaden, herring, and seal are characterized by their substantial content of long-chain fatty acids having 20 to 24 carbon atoms and 3 to 6 double bonds. On the other hand, such oils also contain abundant amounts of the shorter chain, more saturated fatty acids. The heterogeneous make-up of marine oils is exemplified by the analysis of North Atlantic menhaden oil reported by Armstrong and Allen (1). They found 23.5% of saturated fatty acids varying from 14 to 18 carbons in chain length. The unsaturated constituents were composed of 15.5% C_{16} acids having one double bond, 30% C_{18} acids having an average of two double bonds, and 31% C_{20} and C_{22} acids, each series having an average of five double bonds per molecule.

This broad mixture of saturated and unsaturated fatty acids in marine oils makes necessary a preliminary separation before the oils can be used for some purposes, particularly those requiring oils with good drying properties. Fractional crystallization at low temperatures and fractionation with propane by the Solexol process are examples of methods used to remove the more saturated components from oils.

The demonstration by Bengen (2, 3) that urea forms crystalline complexes with saturated fatty acids, monoenoic fatty acids, and less readily with more highly unsaturated fatty acids opened the way for the development of a simple and rapid means of concentrating the more unsaturated fatty acids occurring in marine oils. In 1950 papers by Schlenk and Holman (4) and Newey *et al.* (5) called attention to the possibilities of the urea method for segregating the more highly unsaturated fatty acids or their esters from a number of commercial oils including linseed oil, soybean oil, corn oil, and olive oil. Newey and his co-workers also applied urea crystallization to long-chain fatty alcohols prepared from linseed oil and to nitriles prepared from soybean-oil fatty acids. A recent review by Schlenk (6) thoroughly discusses the urea inclusion compounds of fatty acids.

---

[1] Presented at the Regional American Chemical Society Meeting, Richland, Wash., June 11–12, 1954.

[2] Smith-Mundt Fellow at the University of Washington, 1952–1953.

[3] One of the laboratories of the Branch of Commercial Fisheries, Fish and Wildlife Service, U. S. Department of the Interior.