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Glycerolysis of Linseed Oil: A Compositional Study[1]

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Abstract

Sodium hydroxide catalyzed glycerolysis of linseed oil is greatly enhanced by increase in temperature but only moderately by increase in catalyst concentration. That the active catalyst under these conditions is the glyceroxide ion and not the hydroxide ion was confirmed by performing the reaction with freshly prepared sodium glyceroxide. In all cases alcohol solubility is reached before the reaction attains equilibrium. Component glycerides analysis at these points shows that the monoglycerides content at alcohol solubility is about 35% and at equilibrium about 45%. Further, there are about twice as many 1,3-diglycerides as either 1,2-diglycerides or triglycerides. Component fatty acid analysis of these individual glycerides shows that all the fatty acids of the parent oil are present in every one of these glyceride types and in about the same proportions. Monoglycerides in the early stages of reaction are richer in saturated fatty acids indicating that the catalyst attacks the primary alcoholic ester portion of glycerides first. Similarities in the fatty acid compositions of 1- and 2-monoglycerides at these early stages indicate that the latter are formed by acyl migration from the former. Based on these observations a mechanism for glycerolysis has been proposed.

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Introduction

Glycerolysis of oils produces the valuable reactive intermediates, mono- and diglycerides which are essential in alkyd resin manufacture. Various technical aspects such as the effect of temperature, reaction time, catalysts, oil composition and ratio of oil to glycerol have been investigated in the glycerolysis of linseed oil used in the production of alkyd resins (1–6). Alcohol solubility is still the widely used control test to ascertain the end of the reaction. Attempts (5–7) have been made to correlate this solubility with the equilibrium of the glycerolysis reaction or ultimate monoglyceride content. At best these correlations are inconclusive. Information on the proportions of the component glycerides at equilibrium, or alcohol solubility, agrees on the monoglyceride content but varies on the other components (1,5). There does not appear to be any information on the distribution of component fatty acids in the mono- and diglycerides. Also, it is not known whether any one fatty acid mono- or diglyceride, or both, is formed in preference or in greater proportion over others from an oil of mixed fatty acid content such as linseed oil. The question of fatty acid reaction selectivity remains to be answered. In the present study an attempt has been made to derive some answers to these questions with the help of thin-layer and gas-liquid chromatographic techniques.

Experimental Procedures and Data

Materials

Alkali refined linseed oil was used for the glycerolysis reaction. It had A.V. −0.2, I.V. −185, N_{22}^{D} 1.4802. The fatty acid composition is shown in Table II.

Glycerol. Reagent grade was used. Periodate analysis (8) showed it to be 99.1% pure. This was further dried by heating at 190 C for 15 min under a current of dry nitrogen. It was cooled and stored under nitrogen in amber colored bottles.

NaOH in Glycerol. After drying, as above, an aliquot of the hot glycerol was cooled to 150 C and

TABLE I
Reaction Conditions and Glyceride Compositions of Samples at Alcohol Stability

Run No.	Catalyst		°C Temp.	Time to alcohol solubility min	% 1-Mono periodate method	Glyceride composition TLC-Photodensitometry				
	Type	%				1-Mono %	2-Mono[a] %	1,2 Di[b] %	1,3 Di[b] %	Tri[b] %
1	Sodium hydroxide	0.18	150	150	34.9	23.1	3.9 (3.9)	20 (16.8)	33.7 (28.2)	19.3 (16.2)
2	Sodium hydroxide	0.18	200	75	34.7	32.7	5.5 (3.9)	15.0 (14.9)	28.7 (28.5)	18.1 (18.0)
3	Sodium hydroxide	0.18	225	46	44.7	30.0	4.1 (5.0)	16.9 (12.9)	32.2 (24.6)	16.8 (12.8)
4	Sodium hydroxide	0.09	200	105	40.00	29.5	4.8 (4.4)	15.6 (13.2)	31.8 (27.0)	18.3 (15.5)
5	Sodium glyceroxide	0.11	200	50	38.8	20.9	6.5 (4.3)	15.1 (13.5)	38.8 (25.8)	19.7 (17.6)
6	Litharge (PbO)	0.20	225	40	44.3	28.3	4.6 (4.8)	19.6 (14.9)	33.0 (25.0)	14.5 (11.0)

[a] Values in parentheses calculated from the respective periodate 1-mono values assuming an equilibrium ratio of 90:10 for 1-mono- to 2-monoglycerides.
[b] Residual percentage after deducting the total monoglycerides distributed according to respective TLC per cent and these values are shown in parentheses.

pellets of sodium hydroxide were added to give a 1% solution. To effect solution, the temperature was raised to 190 C and held for 15 min. The solution was cooled and upon analysis it was found to contain 0.9% sodium hydroxide. This solution was also stored under dry nitrogen and used in subsequent reactions.

Sodium Glyceroxide-Xylene. Sodium glyceroxide was prepared from a well stirred dispersion of freshly cut, molten sodium in refluxing xylene. Glycerol, 1 mole and 5% excess, was added dropwise to the xylene dispersion over a period of 2 hr to 1 mole of sodium. After the addition of the last drop, the slurry was refluxed with stirring for another half hour. On cooling, the slurry was stored under dry nitrogen. Titration of an aliquot with standard acid, showed it to contain 0.26 g sodium glyceroxide per 1 ml of slurry. Requisite volumes of this slurry were used for the glycerolysis reaction.

Glycerolysis Procedures. A 1 liter three-neck flask was fitted with a stirrer, inlet tube for dry nitrogen, an outlet and a thermometer. It was charged with 400 g of linseed oil and 100 g of dry glycerol. The flask was heated with a heating mantle and when the required temperatures were reached (see Table I), the catalyst was added. The reaction was performed under gentle bubbling of nitrogen. Samples were withdrawn by interrupting the nitrogen flow and applying suction. The catalyst was killed immediately by the addition of an excess of acetic acid. The course of reaction was followed by testing for alcohol solubility (see below) and a periodate determination for 1-monoglyceride. Reactions were conducted at temperatures 150 to 225 C; the results are shown in Figure 1 and Table I. In runs 1–3 (Table I) 100 g of sodium hydroxide-glycerol solution were used and with Run 4, 50 g of this solution and 50 g of dry glycerol were used. In run 6, 0.20% of the best grade litharge was used.

Evaluation of Products

Alcohol Solubility. A 3 ml sample was added to a 10 ml graduated cylinder, diluted with 7 ml of methanol, and shaken vigorously. The appearance of the contents was noted. When a clear solution resulted it was inferred that the end of the reaction had been reached.

1-Monoglyceride. This was determined by the standard AOCS periodate method (8).

Thin-Layer Chromatography. The procedure followed was basically the same as that of Thomas et al. (9), in which a slurry of Silica Gel H in 0.4 M boric acid solution was used to coat the plates to a thickness of 0.3 mm. Proportions: 50 ml solution and 75 g Silica Gel H. After air-drying, the plates were heated for 1 hr in an oven at 105–110 C, cooled and stored in a desiccator. Before use, the plates were activated by heating at 105–110 C for ½ hr.

Variations of the solvent system consisting of chloroform-acetone-alcohol were tried. In the presence of methanol, the di-glyceride spots moved closer to those of the triglycerides. Both ethanol and isopropanol gave a good separation of all components. Different proportions of chloroform-acetone-ethanol such as 91:8:1, 90:8:2, 90:7:3, 90:9.5:0.5 and 75:25:2 were explored. Good separations and clearly distinguishable spots were obtained with the first two solvent systems. The first one was chosen for this work. Thus 5 μliters of a 10% chloroform solution of the samples were spotted and developed with the above solvent system. A typical chromatogram is reproduced in Figure 2. For quantitative work, each sample was spotted three times. The plates were heated in an oven for 15 min to drive off the solvent and sprayed with a fine mist of 50% sulfuric acid. Charring was accomplished by heating in an oven at 185 C for 5 min. The plates were run through a Photovolt Densitometer, Model 350 equipped with a Varicord Recorder with a response setting of 5. The slit width was approximately 1.5 mm. Peak areas were determined by triangulation. Results are recorded in Table I.

Preparative TLC. Standard 20 × 20 cm plates coated to 0.5 mm thickness of boric acid impregnated Silica Gel H were used. Sample concentrations were 5 μliters of 10% chloroform. Solutions of samples were spotted 15 times and developed with the solvent system of chloroform-acetone-ethanol (91:8:1). After developing, the solvents were driven off by heating in an oven. The plate was then placed in a tank filled with iodine vapors just long enough to visualize the spots. The plate was removed from the iodine vapors and the spots were marked. In the case of alcohol solubility or equilibrium samples, the portions corresponding to individual component glycerides were scraped off. The scrapings of the mono- and diglycerides spots were extracted with methanol containing 2% sulfuric acid. The extracts (10 ml total volume) were centrifuged. The methanol layer was separated and refluxed on a steam bath for 1 hr for conversion to methyl esters. After cooling and dilution with 20 ml of water, the esters were extracted with ether, washed with water until free from sulfuric acid and dried over anhydrous sodium sulfate. The solution was concentrated to a 0.5 μ ml volume by driving off the ether with a stream of nitrogen at 45 C. Then 2–5 μliters of this solution were in-

jected into the gas chromatograph for component ester analysis.

The scrapings of triglyceride spots were washed with methanol and centrifuged. To the separated methanol layer, sodium hydroxide (0.2 g) was added and the solution was refluxed for 1 hr. Enough sulfuric acid, 0.5 ml to neutralize the sodium hydroxide and to catalyze the esterification was added. After heating the mixture to gentle reflux, it was left at room temperature over night (16 hr) for esterification. The esters were recovered and analyzed as before. The results are recorded in Table II.

In order to determine the point of attack of glycerolysis, spots of 1- and 2-monoglycerides from samples of early stages were removed and methyl esters were prepared as described above. Fatty acid composition was determined by GLC and recorded in Table III.

Gas-Liquid Chromatography. A Barber-Coleman Model 5000 gas chromatograph equipped with a flame ionization detector was used. A 6 ft glass column of ¼ in. OD packed with 12% diethylene glycol succinate Polyester on Anakrom was used with nitrogen as the carrier gas. Isothermal runs were performed at a column temperature of 190 C. Next 2–5 μliters of the ether solutions of the respective methyl esters were injected onto the column with the carrier gas flow on the meter set at 45. The linolenate peak (last one) emerged in 10 min. Peak areas were determined by triangulation.

Results and Discussion

The 1-monoglyceride formation proceeds at a slow rate at 150 C; Figure 1 shows the rates of formation of monoglyceride. When the temperature was increased to 200 C, curve II, the reaction was markedly accelerated and equilibrium was attained in 2 hr. In both runs, the alcohol solubility point is reached at a 1-monoglyceride level of 35% which is about 10% lower than the equilibrium concentration. An increase in temperature to 225 C had a remarkable effect on the rate, and equilibrium was attained in less than 1 hr; beyond this point the reaction was reversed due to loss of glycerol by distillation at this temperature. The nitrogen flow aided glycerol removal. Thus, 200 C seems to be an optimum temperature for this reaction and (Table I) run 3 represents conditions similar to that used by the industry for the manufacture of edible monoglycerides. A decrease in the catalyst concentration by one half, curve IV, did not increase the time required to reach equilibrium, which was attained at about the same time, 2 hr, as shown by curve II. This unexpected similarity of reaction rates suggests that the real catalyst is not sodium hydroxide, rather it may be the reaction product with glycerol, namely sodium glyceroxide, which is perhaps produced in small amounts under these conditions. Confirmation of this point was obtained by preparing sodium glyceroxide and using it for the reaction as shown in curve V. With this catalyst, the reaction at 200 C proceeded at

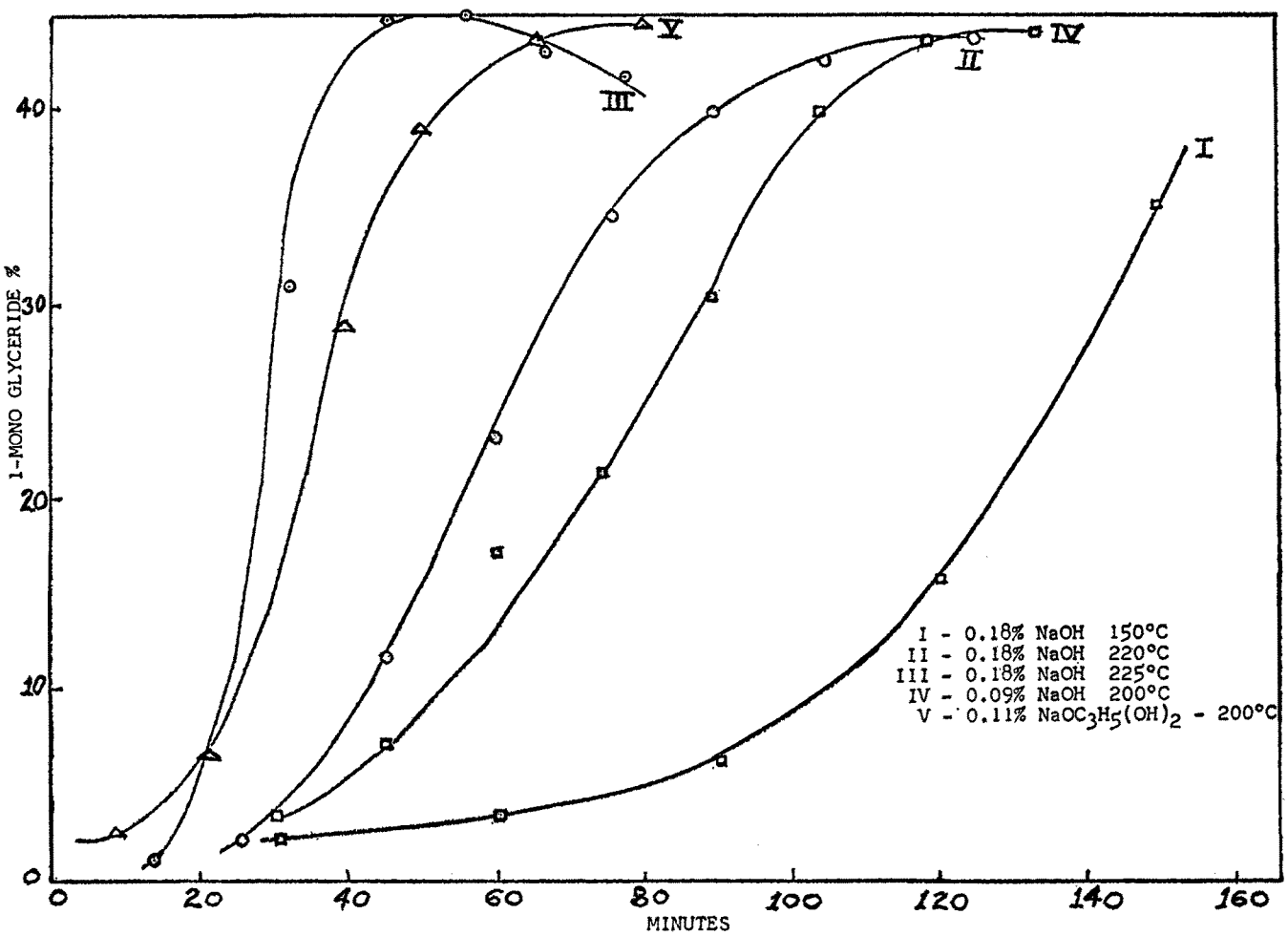

FIG. 1. Rates of glycerolysis of linseed oil at different temperatures.

TABLE II
Fatty Acid Composition of Individual Glycerides of Samples at Alcohol Solubility

Run No.	Glyceride type	Methyl esters composition %				
		Palmitate	Stearate	Oleate	Linoleate	Linolenate
4	1-Monoglycerides	7.3	3.1	10.0	13.4	57.2
	2-Monoglycerides	5.3	1.2	16.7	15.0	61.8
	1,2-Diglycerides	8.2	3.7	24.6	16.9	46.6
	1,3-Diglycerides	7.9	2.9	23.5	14.7	51.0
	Triglycerides	7.5	3.6	22.4	15.4	51.1
5	1-Monoglycerides	7.2	2.8	22.8	14.4	52.8
	2-Monoglycerides	5.7	2.5	21.9	15.3	54.6
	1,2-Diglycerides	7.9	2.8	22.6	14.1	52.6
	1,3-Diglycerides	7.4	3.1	21.3	12.1	56.2
	Triglycerides	7.8	2.6	21.5	15.7	52.4
6	1-Monoglycerides	12.3	4.9	32.1	13.7	37.0
	2-Monoglycerides	7.4	2.0	30.6	22.3	37.7
	1,2-Diglycerides	11.3	4.6	31.0	13.7	30.4
	1,3-Diglycerides	9.1	4.0	28.4	16.4	42.1
	Triglycerides	9.2	3.3	22.1	16.8	48.5
	Linseed oil	6.8	3.1	21.0	16.0	53.1

a faster rate and closely resembled the run with sodium hydroxide at 225 C. Equilibrium was attained in 1 hr with half the catalyst concentration. This superiority again suggests the fact that the glyceroxide anion is the base. Calcium glyceroxide (10) seems to have been used for glycerolysis, but has not received much attention. Litharge is one of the preferred catalysts used by the paint industry; Run 6, Table I, resembles commercial manufacture. The litharge took about 20 min at 225 C to dissolve completely in the reaction mixture, and alcohol solubility and equilibrium were reached in 40 min. In this case, the alcohol solubility indicates the attainment of equilibrium.

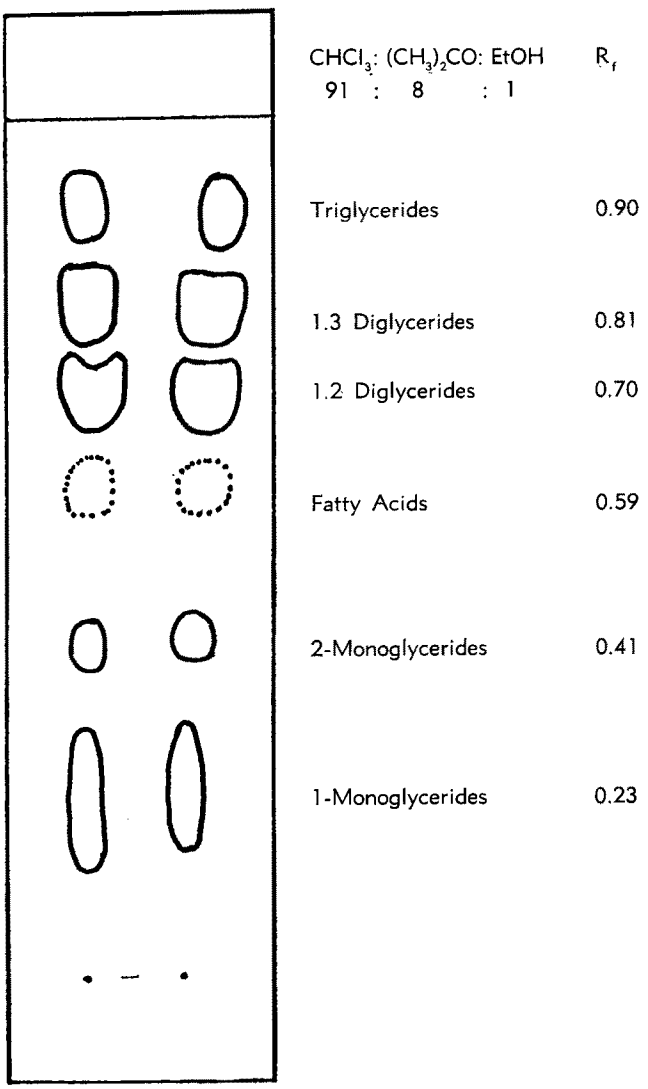

FIG. 2. TLC of a glycerolysis product.

The glyceride composition shown in Table I, with the exception of Run 2, shows no agreement on the value of 1-monoglyceride content between the periodate and TLC methods. This discrepancy arises because the 1-monoglyceride has moved to an Rf value of 0.23 while at least an Rf value of 0.3 is needed for a linear relationship between amount of sample and peak area (9,11). Further, the intensity of the charred spots is dependent on the structure and, to correct for this, the peak areas for mono- and diglycerides must be multiplied by an empirical proportionality constant (1,12) derived by analyzing standard glycerides under the same conditions. This was not done in this study.

To make the results more quantitative, in this work, the following calculations were performed. (a) From the periodate 1-monoglyceride values, the corresponding 2-monoglyceride contents were calculated on the basis that these two glycerides always exist in an equilibrium amount of 90% of the former to 10% of the latter (13); and (b) for the other glycerides although they are eluted at Rf values suitable for quantification, the peak area values are influenced by the errors of the 1-monoglyceride values. However, the relative proportions of these glycerides would not be affected and thus these peak area values can be used to distribute the residuals percentages after deducting the total monoglycerides (1-mono- + 2-mono-). The amounts calculated on these lines are shown in parentheses in Table I and these are used in the following discussion.

The 1-monoglycerides varied from 35% to 45% in the different products but the diglycerides and triglycerides do not show such wide variations. The 1,3-diglycerides are found in greater amounts than either 1,2-diglycerides or triglycerides both of which seem to be present in about equal amounts.

The ratio of 1,3-di- to 1,2-diglycerides falls within the narrow range of 1.6–1.9 to 1 in spite of the variations in temperatures and catalysts. This indicates that a common catalyst is apparently operative. These isomers seem to be formed in equilibrium amounts. Expressed in percentages, this equilibrium occurs at a 1,3-diglyceride level of 62–66% and at 38–34% of 1,2-diglyceride from which a 2:1 ratio of 1,3-diglycerides to 1,2-diglycerides is a fair approximation. For the same equilibrium others (13,14) have reported 58–84% for 1,3-diglycerides and 42–

TABLE III
Fatty Acids Composition of 1- and 2-Monoglycerides of Intermediary Samples

Run No.	Glycerides analyzed	Reaction time min	% 1-Mono periodate method	Methyl esters composition %				
				Palmitate	Stearate	Oleate	Linoleate	Linolenate
	1-Monoglycerides	30	3.2	11.1	3.3	21.3	17.3	47
	2-Monoglycerides			18.5	5.3	25.9	14.7	35.5
	1-Monoglycerides	45	8.8	7.4	3.0	19.9	13.4	56.2
	2-Monoglycerides			4.9	1.9	12.3	17.8	63.1
	1-Monoglycerides	75	21.3	6.7	2.8	18.9	13.0	58.6
	2-Monoglycerides			3.9	1.1	14.2	16.3	64.5
4	1-Monoglycerides	120	44.0	7.0	3.1	23.7	13.4	52.8
	2-Monoglycerides			3.2	1.0	20.2	18.1	57.5
	1-Monoglycerides	8	2.6	12.7	3.8	22.1	13.5	47.8
	2-Monoglycerides			20.5	7.9	17.0	20.1	34.5
5	1-Monoglycerides	22	6.4	8.5	3.1	18.6	11.0	58.8
	2-Monoglycerides			11.7	3.3	19.8	19.8	45.4
	1-Monoglycerides	40	28.6	9.1	3.5	21.8	12.3	53.3
	2-Monoglycerides			7.6	2.9	22.2	16.1	51.2

16% for 1,2-diglycerides. Curiously the triglycerides also bear the same ratio to the 1,3-diglycerides, but the significance of this is not clear.

The component fatty acids of the glycerides are shown in Table II. It appears that within experimental error the fatty acids as found in the parent oil, occur in about the same proportions in the partial glycerol esters. This is an unexpected finding and may have a bearing on the mechanism of glycerolysis. The lower amounts of linolenates and linoleates with the litharge catalyst, Run 6, Table II, are no doubt indicative of some polymerization due to this catalyst.

To gain an insight into the mode of attack on the parent oil glycerides, fatty acid compositions of 1- and 2-monoglycerides of the samples in the early stages of the reaction were determined and are shown in Table III. The first samples are richer in saturated acids. Also, lipolysis (15) of linseed oil has shown that the saturated acids occur essentially in the 1 and 3 positions. These facts indicate that the glycerolysis attack apparently begins at these positions. The 2 position in the parent oil is almost exclusively taken by unsaturated acids, but even in the early stages the 2-mono- and 1-monoglycerides are equally rich in saturated acids. It appears that 2-monoglycerides are probably formed by acyl migration from the 1-monoglycerides to satisfy forces of equilibrium. If these findings are correct, namely that glycerolysis attack is at 1 or 3 positions, or both, 2-monoglycerides are formed by acyl migration, 1,3- and 1,2-diglycerides occur in equilibrium proportions and also as it appears the diglycerides are in equilibrium with the triglycerides, the following mechanism can be visualized for the glycerolysis reaction, as shown in Figure 3. In this case the glyceroxide ion attacks and forms monoglyceride and glyceride ion by addition to the carbonyl group (16,17). Then equilibrium forces set in causing acyl migration to form the isomeric mono- and diglycerides and glycerol enters the reaction as a proton donor to regenerate the glyceroxide ion. As the reaction proceeds towards equilibrium the component fatty acids of the glycerides change. This is due to an attack by the catalyst on regenerated glycerides in order to assume an equilibrium composition which is nearly the same as the parent oil.

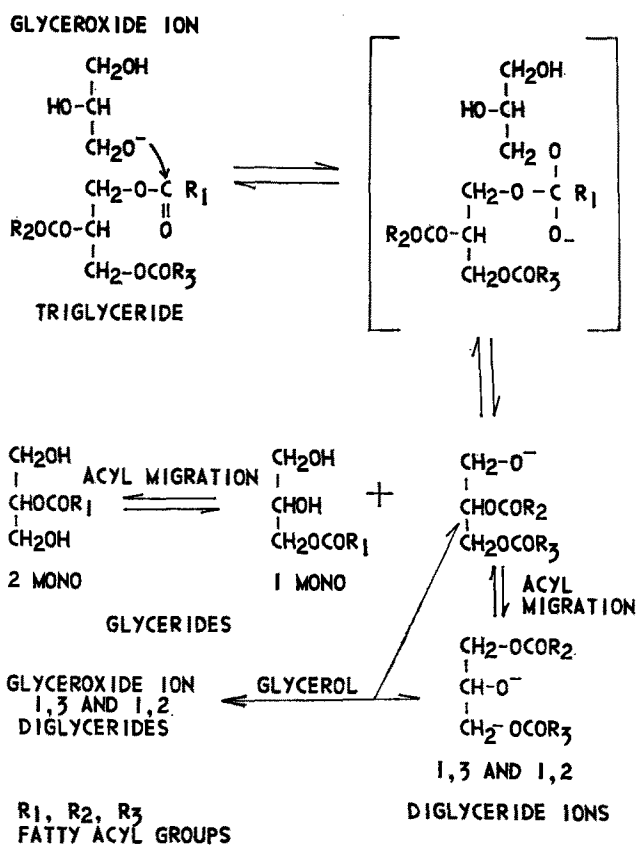

FIG. 3. Mechanism of glycerolysis.

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