The Preparation and Purification of Monoglycerides. II. Direct Esterification of Fatty Acids With Glycerol

R. BASU ROY CHOUDHURY, Iowa Engineering Experiment Station, Iowa State University of Science and Technology, Ames, Iowa

Abstract

Studies have been made on the direct esterification reaction with various saturated and unsaturated fatty acids using more than theoretical concentration of glycerol (for maximum monoglyceride production) at 180C reaction temperature and in presence and absence of alkaline catalyst. The results show that the maximum monoglyceride formed is in the range of 55–60% of the fatty product at equilibrium stage of the reaction. The alkaline catalyst substantially increases the initial rate of reaction without appreciably lowering the time required for reaching the equilibrium concentration of monoglyceride in the resulting reaction mixture. Catalyst helps in depressing diglyceride formation.

Introduction

MONOGLYCERIDES are important commercial products. The two important processess used in industry for preparing monoglycerides are the glycerolysis of oils and the direct esterification of fatty acids and glycerol. In a recent paper from this laboratory (1) studies on glycerolysis of oils have been reported. The present paper deals with studies on the direct esterification of fatty acids and glycerol.

The direct esterification of fatty acids with glycerol has served as a convenient method for the preparation of monoglycerides.[1] Feuge, Kraemer, and Bailey (2) have made a careful laboratory investigation of esterification of glycerol with an equivalent quantity of mixed peanut oil fatty acids, and have tested a large number of metal compounds for catalytic activity. Feuge and Bailey (3) showed that the proportions of glycerol, mono-, di-, and triglycerides can be calculated statistically if one makes the following two assumptions: a) that there is a random distribution of acyl groups on the hydroxyls of glycerol, and b) that there is equal probability that the primary and secondary hydroxyl groups will be esterified. According to Feuge and Bailey, the predicted and experimentally estimated compositions were in reasonably good agreement.

The reaction conditions for the formation of monoglycerides by the direct esterification technique, using a greater glycerol concentration than theoretical, has not been systematically worked out. This reaction requires several conditions to insure the maximum possible yield of monoglyceride. As in the direct procedure, the glycerol molecules need an increased amount of activation energy. The reaction should be run between 175 and 250C. Various workers have carried out the esterification at temperatures of 200C and at 230C. One difficulty at these temperatures is the formation of polyglycerols and glycides which affect both the yield of monoglyceride and the resultant products of esterification.

The miscibility of glycerol in the fatty acid phase is also important in the esterification process. An increased miscibility of glycerol always insures an increased monoglyceride formation. The presence of catalyst undoubtedly increases the miscibility but its final removal from the reaction medium, the expenditure of the fatty acid (with alkali catalyst), and the effect of alkali soap on the formed monoglyceride restrict the use of the catalyst to the minimum concentration (usually 0.1% on the basis of the fatty acid). How far the reaction rate and the equilibrium concentration differ, in the presence and the absence of the catalyst for fatty acids of different molecular weight and unsaturation, has not been systematically investigated.

The purpose of the present investigation was:

1. To study the rate of formation of mono-, di-, and triglycerides in an esterification of fatty acid and glycerol, using more glycerol than that theoretically needed for maximum monoglyceride.
2. To study the esterification process in presence and in absence of sodium hydroxide catalyst to elucidate the role of the catalyst.
3. To study the effect of molecular weight of a fatty acid and the nature of unsaturation on the final concentration of monoglyceride at equilibrium stage.
4. To study the mechanism of the esterification reaction in presence of excess glycerol.

Experimental

The saturated fatty acids were British Drug House laboratory reagents purified by successive crystallization from ethyl alcohol. Oleic acid used was freed from palmitic acid by crystallization from acetone at −20C and further purified by methyl ester fractionation. Linoleic acid was obtained from the mixed fatty acids of poppy seed oil by fractionation from acetone at −60C.

The direct esterifications were carried out in a 3 necked round-bottomed flask immersed in a constant temperature bath at 180C. The flask was provided with a high speed glass stirrer passing through a stuffing box in the central neck. Nitrogen was allowed to enter the reaction vessel in measured amounts. A slight suction was maintained to carry away the water formed in the reaction but not to carry away the glycerol.

The fatty acids along with 0.1% sodium hydroxide catalyst (if required) were added to the reaction flask. When the reaction temperature was attained, a weighed amount of glycerol preheated to the reaction temperature was poured into the flask. The fatty acid-glycerol used were in the molar ratios of 1:3.

The reaction was followed by taking out samples every hour and determining acid value and analyzing the fatty product. The reaction was discontinued after 6 hours when the equilibrium was reached. Further continuation resulted in unnecessary blackening of the esterified product.

The acid value of the reaction product was first determined by the official AOCS method (4). The alkali catalyst of each sample was then destroyed by the addition of phosphoric acid. The fatty product

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[1] The background of this reaction has been adequately covered in a number of review articles as well as certain reference books.

was dissolved in ether, and the ether solution washed free of uncombined glycerol by washing with 20% solution of sodium sulphate in water. The free fatty acids were removed from the ether solution by several washings with small portions of sodium bicarbonate solution and the solution was again washed with sodium sulphate solution to remove soaps. The ether solution was finally dried over anhydrous sodium sulphate, and the ether was evaporated under vacuum.

The alpha-monoglyceride content of the product was determined by the official AOCS method (5). The hydroxyl value was determined by the method of Hind et al. (6). From the monoglyceride content and the hydroxyl value, the composition of the reaction product was calculated.

TABLE I

Esterification of 1 Mole of Fatty Acid with 3 Moles of Glycerol at 180C

Time in hours	Acid value of reaction product	Composition of glycerides in neutral product		
		Mono- %	Di- %	Tri- %
Lauric Acid Without catalyst				
1	90.0	31.8	20.3	47.9
2	70.2	39.6	26.3	34.1
3	56.8	43.7	33.5	22.8
4	50.7	47.8	40.1	12.1
5	42.2	49.4	43.4	7.2
6	30.3	52.3	44.1	3.6
With 0.1% NaOH on basis of fatty acid as catalyst				
1	89.6	42.1	11.8	46.1
2	59.9	46.6	16.3	37.1
3	43.7	49.6	27.2	23.2
4	27.1	54.1	34.6	11.3
5	17.3	57.9	37.2	4.9
6	9.6	60.4	37.5	2.1
Myristic Acid Without catalyst				
1	96.1	28.8	20.4	50.8
2	88.2	34.7	27.2	38.1
3	60.0	40.4	36.3	23.3
4	45.4	45.1	39.3	15.6
5	36.5	48.8	44.7	6.5
6	27.2	50.1	47.3	2.6
With 0.1% NaOH on basis of fatty acid as catalyst				
1	95.0	40.5	12.3	47.2
2	88.5	44.8	17.2	38.0
3	40.8	47.3	28.7	24.0
4	25.6	52.4	35.8	11.8
5	15.9	57.8	36.5	5.7
6	12.3	59.2	36.9	3.9

The results of esterification of 1 mole each of lauric, myristic, palmitic, stearic, oleic, and linoleic acid with 3 moles of glycerol both in presence of 0.1% sodium hydroxide catalyst and in absence of any catalyst are shown in Tables I–III. The data indicate that in the first hour of the catalyzed reaction the rate of formation of monoglycerides is greater than in the uncatalyzed reaction. During the remainder of the reactions the rates differ little. In contrast the formation of diglyceride during the first hour is less in the catalyzed reaction. After the first hour the triglyceride content of the mixture decreases rapidly.

Apparently the esterification process proceeds in two stages. In the first stage the fatty acid molecules distribute themselves randomly among the three alcoholic linkages of the glycerol molecules resulting in a predominant formation of triglycerides. The second stage is a combined process of esterification and glycerolysis. The results indicate that the catalyst is more specific for the formation of monoglycerides especially in the initial stages of the reaction. The minor differences in the final yield of monoglycerides probably result from variations in the miscibility of the glycerol with the fatty acids or the reaction product.

TABLE II

Esterification of 1 Mole of Fatty Acid with 3 Moles of Glycerol at 180C

Time in hours	Acid value of reaction product	Composition of glycerides in neutral product		
		Mono- %	Di- %	Tri- %
Palmitic Acid Without catalyst				
1	96.5	27.9	20.1	52.0
2	90.6	33.8	26.9	39.3
3	75.8	39.2	35.8	25.0
4	51.9	44.2	39.1	16.7
5	43.8	48.0	44.2	7.8
6	29.6	49.9	46.8	3.3
With 0.1% NaOH on basis of fatty acid as catalyst				
1	97.0	39.8	12.9	47.3
2	90.0	43.9	18.1	38.0
3	50.6	46.1	29.3	24.6
4	36.5	51.1	36.5	12.4
5	27.9	56.0	37.3	6.7
6	20.3	58.8	38.4	2.8
Stearic Acid Without catalyst				
1	108.0	26.5	21.2	52.3
2	100.7	32.1	27.3	40.6
3	83.6	38.6	36.1	25.3
4	70.5	42.8	39.2	18.0
5	53.1	47.5	44.5	8.0
6	39.5	48.1	46.8	5.1
With 0.1% NaOH on basis of fatty acid as catalyst				
1	107.5	38.5	13.1	48.4
2	98.6	42.7	17.2	40.1
3	85.3	45.8	30.2	24.0
4	60.2	50.2	37.2	12.6
5	41.1	55.1	37.8	7.1
6	28.5	57.2	38.1	4.7

In the present work the presence of 2-monoglycerides in the reaction product has been neglected because it is generally assumed that the amount of 2-monoglycerides formed in the reaction is small. If the presence of 2-monoglycerides had been taken into account, it would have resulted in slightly more monoglyceride than shown by the standard method and less diglyceride than calculated.

TABLE III

Esterification of 1 Mole of Fatty Acid with 3 Moles of Glycerol at 180C

Time in hours	Acid value of reaction product	Composition of glycerides in neutral product		
		Mono- %	Di- %	Tri- %
Oleic Acid Without catalyst				
1	107.0	33.2	19.3	47.5
2	93.2	38.5	25.4	36.1
3	80.1	43.4	31.8	24.8
4	63.2	48.5	38.2	13.3
5	45.1	51.7	41.1	7.2
6	32.2	53.2	43.1	3.7
With 0.1% NaOH on basis of fatty acid as catalyst				
1	106.5	43.2	11.6	45.2
2	80.1	47.4	15.9	36.7
3	57.9	50.1	26.7	23.2
4	41.2	54.6	34.0	11.4
5	30.2	58.2	35.6	6.2
6	18.3	61.2	37.0	1.8
Linoleic Acid Without catalyst				
1	106.8	34.5	19.4	46.1
2	92.7	38.3	24.8	36.9
3	79.2	43.7	31.2	25.1
4	61.8	48.8	38.6	12.6
5	44.7	52.1	41.7	6.2
6	30.1	53.6	44.0	2.4
With 0.1% NaOH on basis of fatty acid as catalyst				
1	105.8	44.1	11.5	44.4
2	80.8	48.2	17.8	34.0
3	56.8	51.1	27.2	21.7
4	40.7	55.2	34.1	10.7
5	29.2	59.1	35.8	5.1
6	17.5	61.5	36.5	2.0

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[Received May 2, 1961]

The Preparation and Properties of Some Nitrogen-Containing Derivatives of Petroselinic Acid[1]

LIDA L. PLACEK and F. G. DOLLEAR, Southern Regional Research Laboratory,[2] New Orleans, Louisiana

Abstract

Petroselinonitrile was prepared by distilling the ammonolysis products of petroselinic acid over phosphorus pentoxide, and also from parsley seed oil without first isolating the petroselinic acid. A high-boiling antioxidant was employed during the reaction to control polymerization. The reaction by-products were segregated from the pure petroselinonitrile by urea complexing. Petroselinamide was obtained from petroselinic acid by the acidolysis of urea. Although it was not possible to reduce the petroselinonitrile by catalytic hydrogenation without affecting the ethylenic linkage or without producing a mixture of the primary, secondary, and tertiary amines, petroselinonitrile was converted to primary petroselinylamine in good yields by reduction with metallic sodium and alcohol in toluene. The hydrochloride and the acetyl derivative of the pure primary amine have also been prepared.

Introduction

THE NITROGEN-CONTAINING derivatives of the high molecular weight fatty acids continue to hold interest and importance among aliphatic derivatives owing to the wide range of their physical and chemical properties which characterize the various representatives of this class. Aside from being useful chemical intermediates, their surface active and biological properties have made them a subject of commercial interest and many scientific investigations.

Much literature has been published on the preparation of the various amides, nitriles, and amines of the long chain fatty acids, and especially of stearic and oleic acids. During our investigation of the chemistry of petroselinic acid (*cis*-6-octadecenoic acid) isolated from parsley seed oil (1), it became of interest to prepare some of its nitrogen derivatives and determine their properties and potential industrial utility. Although the preparation of petroselinamide and its subsequent reduction to the petroselinylamine with lithium aluminum hydride has already been published (2), the preparation and characterization of petroselinonitrile has not been reported. The purpose of this paper is to describe the chemical modification of petroselinic acid at the carboxyl group with the view of preparing and characterizing some of its nitrogen-containing derivatives.

Experimental

Materials. The parsley seed oil was obtained by extraction of the flaked seed with hexane. When the solvent was removed, the dark green oil had an I.V. of 100.5 and a saponification number of 172.9. The fatty acid composition of parsley seed oil is approximately: 76% petroselinic, 15% oleic, 6% linoleic, and 3% saturated acids.

Pure petroselinic acid used in this experiment (mp 29.5–30.1C) was obtained from the oil by low temperature fractional crystallization of the mixed fatty acids (1). Ozonolysis of this acid and chromatography of the degradation products yielded adipic acid as a sole dibasic acid, indicating that no other unsaturated acids were present as impurities.

Preparation of Petroselinonitrile from Petroselinic Acid. A 500 ml three-necked round bottom flask was equipped with a thermometer, a gas-dispersion tube with a fritted cylinder, and 75 cm long water condenser through which steam was circulated throughout the reaction. The flask was charged with 130 g of pure petroselinic acid and 1 g of Ionol antioxidant,[3] and the mixture was heated to 150C. The temperature was maintained at 150C for three hr and then raised to and maintained at 250C for an additional 17 hr while a fast stream of anhydrous ammonia gas was passing through. The rate of the ammonia stream was such that the water formed during the reaction was continually swept out. The removal of water was facilitated by the steam-heated condenser which also melted the solid petroselinamide (mp 73C) being swept up with the hot ammonia allowing it to drip back into the reaction flask. The reaction mixture, which was first allowed to cool to room temperature, was then distilled over 6.5 g of phosphorus pentoxide at reduced pressure (120–140 mm) with anhydrous ammonia sweeping through it at a slow rate. The first fraction distilling at 69–188C was composed mostly of short chain pyrolysis products and was discarded. The major part of the second fraction (101.3 g, I.V. 94.5) which distilled at 188–242C was composed of *cis*-6-octadecenonitrile with some *trans*-6-octadecenonitrile (as shown by infrared analysis) and a small amount of saturated by-products. The entire second fraction was dissolved in 300 ml. of ether, washed with 100 ml. of 3% aqueous sodium hydroxide to remove the unreacted petroselinic acid and then with three 100 ml portions of water. The ethereal solution was dried over anhydrous sodium sulfate and on removal of the solvent there remained 100 g of crude petroselinonitrile. The product was then dissolved in 600 ml. of boiling methanol containing 100 g of urea. The urea complex which precipitated overnight at room temperature was filtered off and on decomposition with 3% aqueous hydrochloric acid yielded 12.4 g

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[1] Presented at the AOCS meeting in New Orleans, Louisiana, May 7–9, 1962.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.

[3] A Shell Chemical Corporation brand name for 2,6-di-*tert*-butyl-4-methyl phenol, bp 257–266C.