vs. (12AH + 12BH); and 3) *cis, trans* isomers of the cyclohexane ring substituents.

The second possibility, Δ10 vs. Δ12 as dieneophile can be eliminated because of the identity of the mass spectra of the two fractions and the original material, since Δ10 as dieneophile would give *no* $-(CH_2)_{10}COOCH_3$ group, while Δ12 as dieneophile would give *no* $-(CH_2)_6CH_3$ groups on the cyclohexane ring. Since both of these groups were found in the same amt in both fractions and original dimers, this explanation is untenable.

The third explanation (*cis, trans* isomers) cannot be disregarded, but appears less attractive than the first because *cis, trans* equilibration with respect to the cyclohexane ring appears possible in view of the conditions of polymerization and hydrogenation. If this occurred, one would expect that the predominant forms would be those with the least steric interference of groups, namely the all-equatorial, tetrasubstituted chair form of the cyclohexane ring (with adjacent groups *trans* to one another). Further, if the same structural feature is responsible for separation of the dehydrogenated dimer into two spots, then it cannot be *cis, trans* isomerism, since substituents on benzene cannot have *cis* or *trans* relationships.

By elimination, the first explanation, "head to head," α- or 1,2 adjacent positions of $-RCOOCH_3$ groups vs. "head to tail," β- or 1,3 positions appears to be correct for the structures of dimers in the separated spots.

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Preparation of Partial Glycerides by Direct Esterification[1]

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Abstract

A previously described procedure for the direct esterification of diglycerides without interesterification occurring has been evaluated for the preparation of mono- and diglycerides. The esterifications were accomplished with *p*-toluenesulfonic acid catalyst and with continuous removal of water of esterification by azeotropic distillation. The effect of such variables as unsaturation, chain length, mode of addition of solvent and reaction temp on the composition and yield of glycerides was observed. Chemical and chromatographic analyses were used to determine the composition of the glycerides and their component fatty acids and to detect the presence of isomeric glycerides. Simple esterification of 1-monostearin with oleic acid at 80C yielded as much as 72.3% diglycerides, and esterification of glycerol with stearic acid at 100C yielded up to 70.1% monoglycerides, each calculated on a glyceride basis. It is concluded that simple esterification predominates with some intra- and interesterification occurring.

Introduction

MONO- AND DIGLYCERIDES are usually prepared by the reaction of fat or fatty acids with glycerol in the presence of an alkaline catalyst (6,7,13). The reaction products at equilibrium are a mixture of free glycerol and mono-, di- and triglycerides, relative proportions of which can be calculated, for practical purposes, on the assumption that the esterified hydroxyl groups are distributed in a random manner among all the available hydroxyl groups (8). Even though the primary and secondary hydroxyl groups in glycerol have different activities (4,5), the calculated compositions are in reasonably good agreement with the experimental data.

The monoglyceride content of reaction products made commercially from C_{16}–C_{18} fatty acid oils without benefit of molecular distillation usually does not exceed 60% by wt, calculated on a total glyceride basis. This percentage is set by the proportion of glycerol miscible with the glycerides at the max permissible temp, ca. 250C. Even with short reaction times at these temp, some polyglycerols and other undesirable byproducts form. The max percentage of diglycerides which can be formed by the random interesterification of C_{16}–C_{18} fatty acid oils is ca. 49%, calculated on the total wt of glycerides (8).

Commercially, monoglyceride products of over 90% purity are prepared by molecular distillation. Diglyceride products can be prepared in a similar manner. Monoglyceride products of high purity also might be prepared by fractional crystallization from solvents (9).

Since the time of Berthelot (3), many investigations of the preparation of mono- and diglycerides by esterification and interesterification have been conducted. The highest yields of monoglycerides prepared by interesterification have been obtained by the use of a mutual solvent for glycerides and glycerol (16,17,24, 25). On interesterifying in a pyridine solution one part by wt of hydrogenated soybean oil with one part of glycerol, Mattil and Sims (20) obtained 78% monoglycerides, calculated on a glyceride basis. Franzke and Kretzschman (11) reported monoglyceride yields up to 90% by the catalytic glycerolysis of natural fats in pyridine solution.

The preparation of mono- and diglycerides by direct esterification has not been a preferred process because it was generally concluded that esterification was always accompanied by interesterification, which includes acidolysis, alcoholysis and ester interchange,

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and by intraesterification. The mechanisms of these reactions in the presence of acid catalysts are generally assumed to be similar; yet their rates under a given set of conditions can be quite different. Esterification can be carried out with little or no interesterification occurring (10,12). It has been shown that no reaction occurs between fat and acetic acid in the presence of *p*-toluenesulfonic acid when all reactants are anhydrous (21).

Recently, distearin was esterfiied with oleic acid to obtain a product consisting of ca. 90% oleodistearin (10). The esterification was accomplished by using *p*-toluenesulfonic acid as catalyst and continuously removing the water of esterification by azeotropic distillation with aliphatic hydrocarbons. This procedure should be suitable for large-scale production of di- and triacid triglycerides and glyceride esters of dibasic acids.

In the course of experiments in the esterification of diglycerides, data were obtained indicating that mono- and diglycerides might also be prepared in high conen by direct esterification. The present report describes some of the additional research in the preparation of mono- and diglycerides.

Experimental

Materials. The oleic acid was prepared from olive oil by methanolysis, fractional crystallization of the methyl esters from acetone, saponification under mild conditions and acidulation. Stearic acid was prepared by repeated crystallization from acetone of a commerical stearic acid, Hystrene S-97 (Humko Products, Inc.). The lauric acid employed was Eastman grade, obtained from Distillation Products Industries. By gas-liquid chromatographic analysis of each fatty acid, the following purities were found: oleic, 96.9%; stearic, 99.7%; and lauric, 97.9%.

1-Monostearin was prepared by repeated fractional crystallizations of molecularly distilled monoglycerides (Myverol 18-06, Distillation Products Industries) derived from completely hydrogenated soybean oil. The distilled monoglycerides were crystallized first from commercial hexane, three times from 70% isopropyl alcohol and then from commercial hexane. The ratio of solvent to monoglycerides was 6:1 by wt, based on the wt of monoglycerides at the start of the series of crystallizations. All crystallizations were done at 25C. The final product contained 99.0% 1-monostearin, according to periodic acid analysis and had a mp of 81.7C.

1-Mono-olein was prepared by sodium hydroxide-catalyzed glycerolysis of methyl oleate. The latter was derived from pecan oil and had a purity of 98.8%. After destruction of the catalyst and water washing, the glycerides were fractionated by molecular distillation, dissolved in acetone (1:5 by wt) and crystallized at −70C. The final product had a monoglyceride content of 98.6% by periodic acid analysis.

Mixed diglycerides of palmitic and stearic acids were obtained as molecularly distilled glycerides of completely hydrogenated lard from Distillation Products Industries. These diglycerides were freed of glycerol by water washing of a hexane solution (10). The fatty acids consisted of 3.1% myristic, 31.7% palmitic and 65.2% stearic acids.

Anhydrous glycerol was prepared by distillation of USP glycerol.

The *p*-toluenesulfonic acid and trichloroacetic acid employed as catalysts were Eastman Grade.

The commercial hexane was freed of moisture by drying over anhydrous calcium sulfate (Drierite, The W. A. Hammond Drierite Co.) and distilling. The acetonitrile (Practical Grade from Distillation Products Industries) was dried by distillation. The *p*-dioxane was freed of traces of moisture and peroxides by passage through a long column containing basic aluminum oxide, Woelm, activity grade 1.

General Esterification Procedure. All preparations were conducted in a glass fiask immersed in a hot oil bath. Either the reactants were dissolved in warm solvent and allowed to flow into the bottom of the heated reaction flask containing the catalyst, or the reactants and catalyst were placed in the flask and solvent allowed to flow into the bottom of the flask during the course of the reaction. In each case, the solvent vaporized and distilled off continuously, the rate being adjusted to help maintain the desired reaction temp. At the end of the reaction period, dry nitrogen was blown through the reaction product to remove all traces of solvent and to help cool the product quickly. Uncombined fatty acids and free glycerol were separated from the reaction product prior to making the analyses.

Refining Monoglyceride-Containing Products. The removal of free fatty acids and any glycerol from the reaction products without simultaneously removing or destroying any monoglycerides presented some difficulty in preliminary investigations. In a model experiment, a synthetic mixture containing 8.00% 1-monostearin, 20.0% oleic acid and 72.00% winterized cottonseed oil was prepared. Ten g of this mixture was dissolved in petroleum ether and treated with a 14% solution of potassium hydroxide according to the Wesson loss procedure (18). No emulsions were encountered, but analysis of the separated glycerides indicated only 1.24% 1-monostearin instead of the 10.00% expected.

Eventually a satisfactory procedure was devised. In this procedure 10 g of reaction product was dissolved in 50 ml diethyl ether, 25 ml 95% ethanol was added, and the mixture was titrated to the phenolphthalein end point with a 10% solution of potassium carbonate. Then water was added to dilute the aqueous phase to 30% ethanol, and diethyl ether was added to equalize the volumes of the aqueous and nonaqueous phases. The two phases were separated, and the aqueous phase was washed with diethyl ether while the nonaqueous phase was washed with water. The washings were combined with the main solutions.

With this last-described procedure, no emulsions were encountered. Analysis of the mixture of winterized cottonseed oil, oleic acid and 1-monostearin after refining indicated that no monostearin was destroyed and all remained in the refined oil fraction.

Methods of Analysis. The fatty acids removed from the reaction products by the refining procedure were recovered quantitatively to determine the extent of the reaction. Portions of these fatty acids were converted into methyl esters by use of boron trifluoride-methanol reagent (22), and these methyl esters were subjected to gas-liquid chromatographic (GLC) analysis using a diethylene glycol succinate column.

The 1-monoglyceride content of the refined products was determined by a periodic acid oxidation method (14).

Hydroxyl values were determined by the method of West et al. (27), except that an acetic anhydride-to-pyridine ratio of 1:3 instead of 1:7 was used.

The proportions of mono-, di- and triglycerides

in the purified products were determined by chromatographic separation on a silica gel column by the procedure of Papariello et al. (23), except that a larger sample was used and minor changes in the quantity and polarity of the eluant solvents were made. Each of the glyceride classes separated by the above procedure from some of the diglyceride products were converted by interesterification to the methyl esters and analyzed by gas chromatography. Mono-, di- and triglyceride fractions separated from one of the diglyceride products were subjected to thin-layer chromatography (TLC) on silica gel impregnated with silver nitrate (2). This technique separates glyceride classes and also separates each class according to degree of unsaturation and, to some extent, according to configuration. As an aid in identification, some glycerides of known structure were also chromatographed.

When not otherwise indicated, the AOCS methods were used in the analyses (1).

Preparation of Diglycerides. In conducting the esterification experiments represented in Table I, five parts by wt of dry hexane were used for each one part of fatty reactants. In Runs 1 and 2 the monoglyceride and fatty acid were dissolved in the hexane and added dropwise to the reaction flask which contained the catalyst, *p*-toluenesulfonic acid. Just prior to starting the dropwise introduction of the fatty reactants, a small amt of pure hexane was put into the flask and heated to the boiling point. The fatty reactants were added over a period of ca. 1.5 hr, which is included in the total reaction time.

In Runs 3 through 6 the fatty reactants were all placed in the flask at the beginning, the dropwise addition of hexane was started while the contents of the flask were quickly heated to the reaction temp, and the catalyst was added.

Two runs, which are not represented in Table I, were carried out using 0.4% trichloroacetic acid as catalyst. Determination of free fatty acids and 1-monoglycerides indicated that the reactions were very incomplete, even after 6 hr at 80C.

After refining, most of the diglyceride products were separated into mono-, di- and triglyceride fractions by column chromatography. Fractions obtained from two or three of the diglyceride products were analyzed by GLC for fatty acid composition. The data for Run 3 are recorded in Table II.

The mono-, di- and triglyceride fractions obtained from the product of Run 3 were further fractionated by TLC. Development of the plate on which the monoglyceride fraction had been applied revealed a strong monostearin spot and a somewhat weaker monoolein spot. The 1- and 2-monoglycerides were not separated. It can be assumed that the mixture of monoglycerides contained ca. 10% 2-monoglycerides (19). With the diglyceride fraction there appeared a very strong 1-oleo-3-stearin spot, a strong 1,3-distearin spot, a weak 1,2-diolein spot and five other very weak spots. The latter probably were not the five other possible diglycerides. The diglyceride mixture undoubtedly contained ca. 16% 1,2-diglycerides and 84% 1,3-diglycerides (15); so it must be assumed that in this particular analysis not all of the isomers were separated. For the triglyceride fraction there were equally strong 2-oleodistearin and 1-oleodistearin spots, a weaker tristearin spot and traces of 1-stearodiolein and triolein. TLC was used only for qualitative analysis, and conclusions regarding quantities are approximate.

TABLE I

Preparation of Diglycerides by Esterification of Monoglycerides and Fatty Acids[a]

Run no.	Reactants	Mole ratio, monoglyceride to fatty acid	Cat. concn, %	Reaction temp, C	Fatty acids esterified, wt %	Composition of uncombined fatty acids, wt %							Acid-free product				
						Capric	Lauric	Myristic	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic	1-Monoglycerides, wt %	Hydroxyl value[b]	Iodine value[c]	Glyceride composition, wt %	
																	Mono-	Di-	Tri-
1	monostearin, oleic acid	1:1	0.4	80	81.7	....	.....	....	1.5	0.3	5.5	89.9	2.8	15.9	119.2	30.0	18.6	69.2	12.2
2	monostearin, oleic acid	1:2	0.4	80	48.6	....	.....	....	1.3	0.2	3.4	93.0	1.1	12.2	98.6	39.3	13.2	65.2	21.6
3	monostearin, oleic acid	1:1	0.4	80	86.4	....	.....	....	1.0	0.2	6.5	91.2	1.1	14.9	102.5	37.6	13.9	72.3	13.7
4	monostearin, oleic acid	1:1	0.2	100	79.4	....	.....	....	1.1	0.4	4.0	93.3	1.2	15.2	124.6	32.4	.....	.....	.....
5	mono-olein, stearic acid	1:1	0.4	80	84.0	....	.....	0.1	0.3	....	87.0	12.6	....	16.9	92.4	43.3	16.5	63.1	20.4
6	monostearin, lauric acid	1:1	0.4	80	93.2	0.6	91.2	0.3	0.3	....	7.6	.....	....	13.0	99.0	0	13.2	66.6	20.2

[a] Reaction time, 2 hr.
[b] Hydroxyl value of 1-oleo-3-stearin, 90.0; value of 1-lauro-3-stearin, 103.7.
[c] Iodine value of 1-oleo-3-stearin, 40.7.

TABLE II

Fatty Acid Composition of Glycerides from Run 3

Fraction	Fatty acid composition, wt %				
	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic
Monoglyceride	2.5	0.2	53.4	43.0	0.9
Diglyceride	2.3	0.3	51.2	45.5	0.7
Triglyceride	3.2	0.1	48.2	47.5	1.0

To establish the extent of interesterification occurring during the esterification reaction, equimolar quantities of 1-mono-olein and diglycerides of hydrogenated lard were placed in the reaction flask, heated to 120C and 0.4% *p*-toluenesulfonic acid was added. The reaction was continued for 2 hr while hexane vapors were passed continuously through the mixture. Only a trace of free acids and glycerol in the product were observed. A product produced by random interesterification should have the following composition by wt: 28.9% monoglycerides, 50.2% diglycerides, 18.4% triglycerides and 2.5% glycerol. The product was separated into mono-, di- and triglyceride fractions by column chromatography and each fraction wsa analyzed by GLC for fatty acid composition. Data for this run are recorded in Table III.

Preparation of Monoglycerides. Commercial hexane was used to remove the water of esterification in one experiment to determine whether or not glycerol and a fatty acid could be esterified to yield a relatively large proportion of monoglycerides. The glycerol and oleic acid in a mole ratio of 1:1 were placed in the reaction flask, heated to 80C and 0.4% *p*-toluenesulfonic acid, calculated on the wt of oleic acid, was added. The reaction was continued for 2 hr while hexane vapors were passed continuously through the mixture. Only a small proportion of glycerides formed, and their content of 1-mono-olein was 5.7%.

Richardson (24) claimed to have prepared monoglycerides in a concn of 90% (glycerol-free basis) by esterifying commercial stearic acid and glycerol in a dioxane solution containing a catalytic amt of sulfuric acid. The reaction was carried out over a period of 3 hr and at 107C. The water of esterification was removed by passing the refluxing dioxane over a drying agent. The results could not be duplicated by Mattil and Sims (20).

In a modification of the Richardson technique, glycerol and oleic acid were mixed in a mole ratio of 1:1, 0.4% *p*-toluenesulfonic acid was added and then *p*-dioxane (bp 101.3C) was added in a wt ratio of 3:1. The resulting homogenous solution was allowed to react for 3.5 hr at 80C while hexane vapors were passed continuously through the solution. Only a small proportion of glycerides formed, and their content of 1-mono-olein again was only a few per cent.

Acetonitrile finally was selected for use as a solvent in the preparation of monoglycerides. It boils at 81.5C and forms an azeotrope with water. The latter boils at 76.0C. At the reaction temp employed it dissolves glycerol, fatty acids and *p*-toluenesulfonic acid. Acetonitrile hydrolyzes in the presence of dilute strong acids and water to form acetic acid, which should not be too objectionable if hydrolysis occurred to some extent in the reactions under discussion. All of the monoglyceride products represented in Table IV were prepared with the aid of acetonitrile. In Runs 7 through 9 approx six parts by wt of acetonitrile/ one part of fatty acid to be esterified was passed through the reactants during the course of the reaction. In Runs 10 through 13 this ratio was increased to 12:1.

TABLE III

Composition of Glycerides

Fraction	Glyceride composition, wt %	Fatty acid composition, wt %				
		Myristic	Palmitic	Palmitoleic	Stearic	Oleic
Monoglyceride	20.4	0.9	18.8	0.7	42.2	37.4
Diglyceride	72.5	1.0	19.0	0.4	42.4	37.2
Triglyceride	7.1	1.2	20.3	0.4	41.6	36.5

Discussion

Diglyceride Preparations. The choice of reaction temp, type of catalyst and catalyst concn was made on the basis of data obtained in an earlier investigation (10) and in other preliminary experiments. An acid catalyst like *p*-toluenesulfonic acid was found best for esterification when interesterification is not desired and other side reactions are to be reduced to a min. *p*-Toluenesulfonic acid was found to be preferable to stannous chloride and other metal salts, which can function as acid catalysts, and to strong mineral acids.

It also was found that the esterification of a monoglyceride with an excess of fatty acid proceeded rapidly in the early stages and then slowed rather abruptly. At 200C the greatest rate of change occurred at ca. 80% completion of the reaction, but at 100C this change occurred at ca. 60%. The content of monoglyceride decreased rapidly during the early stage of the reaction. It was concluded that a low reaction temp should be used if the objective of the esterification is the preparation of diglycerides.

In preliminary esterification runs of the type represented in Table I, it was found that at 80C and with 0.1% catalyst the reaction was only ca. 10% complete in 3 hr. At 55C and with 0.4% catalyst the reaction was ca. 35% complete in 3 hr.

The compositions of the free fatty acids in the reaction products represented in Table I indicate that very little acidolysis occurred during the esterification. Usually less than 10% of the small proportions of free fatty acids remaining when the reactions were stopped consisted of acids which originally were present as monoglycerides. This same low degree of acidolysis was found in similar esterifications of diglycerides with fatty acids (9).

Previously, it was reported that monoglycerides disproportionated in the presence of *p*-toluenesulfonic acid and that free glycerol formed; however, this reaction was believed not to be as rapid as esterification when free fatty acids were present in sufficient quantity (10). This belief is supported by the data in Table II. When the esterification of 1-monostearin with oleic acid was discontinued in Run 3, approx 53% of the residual monoglycerides consisted of monostearin. Virtually all of the 43% of mono-olein which was found undoubtedly resulted from the esterification of glycerol produced by the disproportionation of monostearin. Because this percentage was found after the esterification was 86.4% complete, it must be concluded that much less that half of the diglycerides which were formed resulted from reaction between two molecules of monostearin.

The fatty acid composition of the diglyceride fraction from Run 3 indicates that a large proportion of the diglycerides could have consisted of oleostearin. Analysis by TLC confirms that much of the fraction consisted of oleostearin, a very strong spot being obtained at the position corresponding to that of 1-oleo-3-stearin. However, a strong spot corresponding to 1,3-distearin also was obtained. A weak spot cor-

TABLE IV

Preparation of Monoglycerides by Esterification of Glycerol and Fatty Acids[a]

Run no.	Reactants	Mole ratio, glycerol to fatty acid	Reaction temp, C	Reaction time, hr	Fatty acids esterified, wt %	Acid-free product			
						1-Monoglycerides, wt %	Glyceride composition, wt %		
							Mono-	Di-	Tri-
7	glycerol, stearic acid	1:1	80	2	.....	51.2	.....	.....	....
8	glycerol, stearic acid	1.5:1	80	2	61.5	50.3	.....	.....	....
9	glycerol, stearic acid	1.5:1	100	2	.....	63.0	70.1	27.9	2.0
10	glycerol, stearic acid	1.5:1	80	4	66.6	54.6	.....	.....	....
11	glycerol, stearic acid	1.5:1	100	6	82.2	60.0	64.9	33.8	1.3
12	glycerol, oleic acid	1.5:1	100	6	33.6	57.2	65.6	33.2	1.1
13	glycerol, lauric acid	1.5:1	100	6	81.4	67.7	70.8	29.0	0.2

[a] Catalyst concentration, 0.4%.

responding to diolein further confirms that most of the oleic acid was present as oleostearin.

The fatty acids from the triglyceride fraction of Run 3 contained 48.2% stearic acid and 47.5% oleic acid. If the triglycerides had been formed mainly by the simple esterification of monostearin with oleic acid, then the content of oleic acid would have been twice that of stearic acid. The relatively high content of stearic acid could have been the result of reaction between two molecules of monostearin to form distearin, which subsequently was esterified with oleic acid to oleodistearin. This possibility is supported by the fact that analysis by TLC gave two strong spots corresponding to those of 1-oleodistearin and 2-oleodistearin.

The diglyceride contents found in the purified reaction products represented in Table I ranged between 63.1 and 72.3%. If extensive random interesterification had occurred in these reaction, the contents of diglycerides in the oleic-stearic acid products could not have exceeded ca. 49%. Obviously, the esterification procedure which was employed is to be preferred to a random interesterification procedure if diglycerides are to be prepared.

The extent of interesterification occurring is indicated by data recorded in Table III. Undoubtedly the 7.1% triglycerides result from interesterification of mono-olein and the saturated diglycerides. The fatty acid compositions of the glyceride fractions are nearly identical indicating much interchange between the mono- and diglycerides.

Monoglyceride Preparations. The monoglyceride products prepared by the esterification of glycerol (Table IV) are reasonably similar with regard to contents of 1-monoglycerides, which range from 50.3–67.7%. Yet, the glycerol-fatty acid ratios and the temp and reaction times are different. The percentage of free fatty acids esterified varied from 33.6–82.2.

While the composition in terms of mono-, di- and triglycerides resembles that of C_{18} fatty acid triglycerides interesterified at 250C with 40% glycerol by wt (8), the products at the end of the reaction times given were not interesterified in a random manner. This is quite evident on considering the data for Run 12. This esterification, as well as the others reported in Table IV, was conducted in a homogeneous solution. Therefore, all of the hydroxyl groups in the free glycerol were available for participation in the glycerolysis reaction by which monoglycerides usually are prepared. At the end of the reaction period only 33.6% of the fatty acids had esterified; therefore, the equivalents ratio of esterified fatty acids to hydroxyl groups was never greater than 1:13.5. Assuming the esterified hydroxyl groups were randomly distributed, the mole ratio of mono- to diglycerides can be calculated to be 19.0:1.5, which equals a wt ratio of 7.3:1. The wt ratio atcually found was 2:1.

It is believed that most of the diglycerides were formed by the disproportionation of monoglycerides, and that this reaction slowed markedly as the concn of diglycerides increased. Therefore, all of the products seem to have a fairly similar composition.

One or two other facts about the runs represented in Table IV should be noted. A comparison of Runs 11 and 12 reveals that under similar conditions the oleic and stearic acid did not esterify to the same extent. This is in agreement with a report (26) that the esterification rate of oleic acid is less than half that of stearic acid. On the other hand, a comparison of Runs 11 and 13 reveals that the esterification rates of lauric and stearic acid are similar, which again is in agreement with previously published data (26).

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