Patented Jan. 27, 1953

2,626,952

UNITED STATES PATENT OFFICE

2,626,952

DIGLYCERIDE PREPARATION

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No Drawing. Application October 26, 1949, Serial No. 123,784

8 Claims. (Cl. 260—410.7)

1

This invention relates to a process for producing diglycerides, particularly 1,3 diglycerides. A specific application of the process is the production of single-acid symmetrical diglycerides in high yield.

In U. S. Patent No. 2,442,531, there is disclosed a process for the interesterification of fats and fatty oils wherein said fats or oils are interesterified in the presence of a low temperature interesterification catalyst at a temperature sufficiently low that solid glycerides crystallize from the reaction mixture as they are formed, thereby inducing a continuation of interesterification to such an extent that the physical properties of the reacted fats or oils may be controlled to produce products within a desired range of properties such as melting point and solidifying point.

U. S. Patent 2,442,534 describes and claims a special modification of the process of Patent 2,442,531, wherein interesterification with simultaneous crystallization is practiced on the fat or oil in the presence of the catalyst and an organic compound having at least one unesterified alcoholic hydroxyl group, with the result that alcoholysis is effected and insoluble high melting mono- and/or diglycerides formed in the reaction crystallize from the reaction mix. Such mono- and/or diglycerides may be subsequently separated from the reaction mix by suitable fractionation procedures.

It is an object of the present invention to provide an improved process for the preferential formation of diglycerides of higher molecular weight fatty acids whose melting points are not substantially below 75° F., a particular object being the provision of a process for the preferential formation of 1,3 diglycerides and especially of symmetrical single-acid diglycerides of such fatty acids in substantially pure form.

The present process, which also basically involves low temperature interesterification with simultaneous crystallization, comprises (1) interesterifying, wholly in the liquid phase, higher molecular weight triglyceride (at least 10 carbon atoms in the acyl radicals) with lower molecular weight triglyceride (2 to 6 carbon atoms in the acyl radicals) to yield an interesterified mixture having random distribution of acyl radicals, (2) alcoholizing the randomized mixture with glycerol to form a single liquid phase mixture containing diglycerides of higher molecular fatty acids, (3) reducing the temperature of the system to that temperature at which higher molecular fatty acid diglycerides formed in the reaction precipitate as a solid phase, (4) reducing

2

the temperature and effecting rearrangement in the liquid phase with the aid of a low temperature interesterification catalyst while said higher fatty acid diglycerides precipitate, (5) inactivating the interesterification catalyst while maintaining precipitated higher fatty acid diglycerides as a solid phase and (6) subsequently recovering said solid fatty acid diglycerides from the system. As will be more fully apparent from specific examples given below, the diglycerides which precipitate when the system comprises only one combined fatty acid of high molecular weight are substantially wholly symmetrical diglycerides and in this connection the process has special utility.

In one of its broad aspects the process comprises interesterifying in the presence of a low temperature interesterification catalyst a liquid mixture of triglyceride of saturated fatty acid having at least 10 carbon atoms in the acyl radical and triglyceride of saturated fatty acid having 2 to 6 carbon atoms in the acyl radical, alcoholizing the interesterified mixture in the liquid phase with glycerol in amount at least stoichiometrically sufficient to form diglyceride of higher molecular combined fatty acid in the mixture, and subjecting the resulting alcoholized mixture to low temperature interesterification with simultaneous crystallization, whereby saturated higher molecular weight 1,3 diglycerides, recoverable in substantially pure form, are precipitated.

One manner in which the invention may be practiced, for example, involves effecting interesterification wholly in the liquid phase between tristearin and triacetin, thereby obtaining random distribution of fatty acid radicals, then adding glycerol to the randomized system of triglycerides in amount at least sufficient stoichiometrically to form diglycerides of the combined stearic acid in the system, and permitting interesterification and alcoholysis to take place in the presence of a low temperature interesterification catalyst, then reducing the temperature of the system whereby distearin formed in the reaction preferentially precipitates.

Triglycerides of fatty acids of low molecular weight other than acetic acid are operative in the practice of this invention, including triglycerides of propionic, butyric, valeric, and caproic acids, mixed triglycerides of such acids, and mixtures of such triglycerides.

The process is well adapted for use in the preparation of diglycerides of fatty acids which contain from 10 to 22 carbon atoms in the acyl radical and whose melting points are not sub-

stantially below 75° F., including saturated fatty acids such as caprylic, lauric, myristic, palmitic, margaric, stearic, arachidic, and behenic, as well as unsaturated fatty acids such as elaidic and other normally solid cis- and transisooleic acids including petroselaidic, petroselinic and vaccenic acids.

Our process will be more clearly understood from the description of the following specific examples wherein parts shown are by weight. However, it is to be understood that the scope of the invention is not limited to the specific details covered in these examples but rather is to be measured by the appended claims.

Example 1.—Tristearin obtained by recrystallization of substantially completely hydrogenated linseed oil from commercial normal hexane was used in preparing distearin as follows.

100 parts of the tristearin were melted and mixed with 50 parts of substantially dry triacetin. To this mixture was added 0.45 part of sodium methoxide as a suspension in xylene. The mixture was held at 140° F. and interesterification was permitted to take place for several hours to effect random distribution of fatty acid radicals. At the end of this period, 17.7 parts substantially dry glycerol (12.5% excess over that required for conversion of all triglycerides of the mixture to diglycerides) were added together with an additional 0.3 part of sodium methoxide catalyst. This mixture was also permitted to react wholly in the liquid phase at 140° F. for one day. The resulting mixture was then agitated at 110° F. to 115° F. for 2½ days, at 100° F. for 2½ days, at 90° F. for 2 days and at 80° F. for 2 days. Solid glycerides precipitated from the reaction mixture at 120° F. and progressive crystallization took place as the reaction temperature was reduced.

At the end of the two-day reaction period at 80° F., the sodium methoxide catalyst was inactivated by the addition of glacial acetic acid to the mixture. Then, with the temperature at about 80° F., 4 volumes of ethyl ether were added and the resulting slurry was subjected to filtration.

The residue from the filtration of the slurry, containing diglycerides, was dissolved in 10 cc. (i. e. 10 volumes) of a 50–50 normal hexane and ethyl ether mixture for each gram of residue and recrystallized therefrom at 75°–80° F. Successive crystallizations were made at 75°–80° F. from 10 volumes of normal hexane and from 10 volumes of a 50–50 mixture of normal hexane and ethyl alcohol.

The yield of recrystallized material, substantially pure distearin, amounted to 86% of theoretical. The solvent-free product had a hydroxyl value of 89 as compared with a theoretical value of 89.6. The maximum and minimum capillary melting points were 79.0° C. and 77.0° C. respectively as compared with corresponding values of 78° C. and 74° C. for symmetrical distearin as observed by Malkin, Jour. Chem. Soc. 1937, 1409. Since the corresponding melting points for unsymmetrical diglycerides are appreciably lower than those for symmetrical diglycerides it would appear that the relatively high melting characteristics of the product of this example indicates outstanding purity, especially in view of the near theoretical hydroxyl value.

In this example and in others which follow, the minimum melting point of the diglyceride was determined by placing molten diglyceride in thin-walled capillaries, thrusting these into ice water or some other cooling medium so that the fat solidifies rapidly, and then thrusting successive capillaries into liquid baths of different temperatures and noting the lowest temperature at which the material melts. The maximum melting point was determined by placing some of the solvent-free crystals in a capillary, then heating the crystals in a water bath at the rate of 0.2° C. per minute and noting the temperature at which the crystals melted completely.

Example 2.—Tripalmitin was prepared by esterification of substantially pure palmitic acid with glycerol. The crude tripalmitin was refined, deodorized, and purified by recrystallization. The procedure for making dipalmitin was the same as that shown in Example 1 except that tripalmitin was substituted for tristearin and 18.2 parts of dry glycerol (10% excess over that theoretically necessary for conversion of all triglyceride to diglyceride) were employed. Also the following slightly different interesterification-crystallization schedule was used: 120° F. for 3 days, 100° F. for 3 days, 90° F. for 2 days and 80° F. for 3 days.

The final reaction mixture, after acidification, was recrystallized from solvent 3 times, each from 8 volumes of a 50–50 hexane and ethyl alcohol solvent mixture at 50° F. to give an 86% yield of dipalmitin having a hydroxyl value of 99 and a saponification value of 197.9 as compared with theoretical values of 99 and 197.2 respectively. Maximum and minimum melting points were 74.2° C. and 71.8° C. respectively as compared with corresponding values of 72.5° C. and 68° C. for symmetrical dipalmitin as observed by Malkin (ibid.). Obviously the product of this example was very pure. Accordingly to Daubert and King, Jour. Amer. Chem. Soc. 61, 3328 the melting point for unsymmetrical dipalmitin is 64° C.

Example 3.—Trimyristin was prepared by the esterification of glycerin with myristic acid obtained by frictional distillation of a mixture of fatty acids. The crude trimyristin was refined, deodorized and recrystallized from a 50–50 benzene and ethyl alcohol solvent mixture. The procedure employed in converting the trimyristin to dimyristin was substantially the same as that shown in Eaxample 2, 175 parts trimyristin, 52.5 parts triacetin, and 24.6 parts glycerol (10% excess over that theoretically necessary for conversion of all triglyceride to diglyceride) being employed. About 0.3% sodium methoxide, as a suspension in xylene, was used during the initial interesterification, and an additional 0.2% was added just prior to the interesterification-crystallization step.

After inactivation of catalyst, the reaction mixture was crystallized from six volumes of a 1:1 ethyl alcohol and ethyl ether mxture at 30° F. A 91% yield of dimyristin having a maximum melting point of 66.6° C. was obtained by this one crystallization. After two additional like crystallizations a dimyristin yield of 81% was noted. This product had a hydroxyl value of 107 and a saponification value of 221.4 as compared with theoretical values of 109.3 and 218.5 respectively. Maximum and minimum melting points were 66.8° C. and 64.4° C. respectively as compared with corresponding values of 65.5° C. and 60° C. for symmetrical dimyristin as observed by Malkin (ibid.). Daubert and King (ibid.) indicate that the melting point for unsymmetrical dimyristin is 59° C.

Example 4.—Dilaurin was prepared from tri-

laurin by substantially the same procedure as that shown in Examples 2 and 3, 150 parts trilaurin, 30 parts triacetin, and 18.9 parts (10% excess over that theoretically necessary for conversion of all triglyceride to diglyceride) glycerol being used. The dilaurin was recovered in three crystallizations, each from 4 volumes of a 1:1 mixture of ethyl ether and ethyl alcohol at 30° F. The product had a hydroxyl value of 119 and a saponification value of 246.5 as compared with theoretical values of 123 and 246 respectively. Maximum and minimum melting points were 57.8° C. and 54.5° C. respectively as compared with corresponding values of 56.5° C. and 49.5° C. for symmetrical dilaurin as observed by Malkin (ibid.).

Tripropionin can be substituted for the triacetin used in the above example without significant change in the result.

Example 5.—A sample of tristearin prepared from substantially completely hydrogenated linseed oil by recrystallization from hexane solution was used in the process of this example.

To 100 parts of the tristearin were added 40 parts of substantially dry tributyrin and 0.42 part of sodium methoxide as a suspension in xylene. The mixture, wholly in the liquid phase, was permitted to interesterify at 140° F. To the interesterified mixture were then added 12.4 parts of glycerol (10% excess over that theoretically required for conversion of all triglyceride to diglyceride) and an additional 0.42 part of sodium methoxide. Alcoholysis was permitted to take place at 140° F. until the mixture was homogeneous.

Low temperature interesterification was then begun at 120° F., the temperature being progressively lowered in 10° F. increments at intervals of 1 to 2 days until a final temperature of 80° F. was reached. At the end of the low temperature interesterification, the catalyst was inactivated by the addition of glacial acetic acid and the resulting product was dissolved in about 7½ volumes of a 50–50 solvent mixture of commercial normal hexane and ethyl alcohol at room temperature. The solid glycerides were recrystallized from such a solvent mixture 4 times to give a 70% yield of distearin having a complete melting point of 79.9° C. and a minimum melting point of 77.6° C.

In an auxiliary example, 50 parts of tributyrin and about 14.1 parts of glycerol were used, the other conditions of processing being substantially the same as in Example 5. The product from this auxiliary example had a complete melting point of 79.7° C. and a minimum melting point of 77.4° C. The saponification value was 177.2 and the hydroxyl value was 90 as compared with theoretical values of 179.2 and 89.6 respectively.

Substantially the same results are obtainable by substitution of tricaproin for tributyrin in this Example 5.

Example 6.—100 parts of trielaidin, 30 parts of washed, distilled triacetin, and about 0.3% (based on total triglycerides) of sodium methoxide (as a xylene suspension) were mixed and reacted at 140° F. for several hours to effect random distribution of acyl radicals. To the mixture were then added 12.0 parts of dry glycerol (a 5% excess over that required for conversion of all triglyceride to diglyceride) and alcoholysis was permitted to take place at 120° F. until the mixture became a homogeneous single phase. The reaction mix was allowed to cool to 100° F. and the temperature was then reduced at 10° increments every 1 or 2 days until the temperature had reached 60° F. The catalyst was then inactivated by the addition of glacial acetic acid at 60° F. and the resulting mixture was recrystallized five times as follows:

(1) From 2 volumes of a 1:1 mixture of ethyl ether and ethyl alcohol at 70° F.

(2) From 5 volumes of a 1:1 mixture of ethyl ether and ethyl alcohol at 75–80° F.

(3) From 2½ volumes of a 1:1 mixture of ethyl ether and ethyl alcohol at 75–80° F.

(4) From 3 volumes of a 4:1 mixture of ethyl ether and ethyl alcohol at 75–80° F.

(5) From 6 volumes of ethyl ether at 50° F.

A yield of substantially pure dielaidin amounting to about 65% was obtained. This material had a hydroxyl value of 94 and an iodine value of 80.8 as compared with theoretical values of 94.2 and 81.8 respectively.

Example 7.—Tribehenin was prepared by esterification of glycerin with behenic acid. The crude tribehenin was refined, deodorized, and purified by recrystallization.

A mixture of 60 parts purified tribehenin and 30 parts triacetin were interesterified for several hours wholly in the liquid phase with the aid of 0.3% sodium methoxide catalyst. To the interesterified mixture were added 9.7 parts glycerol (about 10% excess over that required for conversion of all triglycerides to diglycerides). Alcoholysis was permitted to take place at about 140° F. until a single liquid phase resulted, and low temperature interesterification was then begun, an additional 0.2% sodium methoxide being added to the reaction mixture. After reaction at 120° F. for 3 days, the temperature was held at 100° F. for 2 days, at 90° F. for 2 days and at 80° F. for 3 days. Progressive crystallization of solid diglycerides took place as the reaction temperature was reduced.

At the end of the reaction period the low temperature interesterification catalyst was inactivated with glacial acetic acid and the resulting mixture was recrystallized four times as follows:

(1) From 9 volumes of a 5:4 mixture of hexane and ethyl alcohol containing 5% water at 75–80° F.

(2) From 10 volumes of a 4:1 mixture of hexane and ethyl alcohol at 75–80° F.

(3) From 10 volumes of hexane at 75–80° F.

(4) From 13 volumes of benzene at 75–80° F.

An 80% yield of dibehenin having a maximum melting point of 87.6° C., a minimum melting point of 86.7° C., a hydroxyl value of 77.1 and a saponification value of 154.0 was obtained. The theoretical hydroxyl value and saponification value of dibehenin are 76.2 and 152.4 respectively.

In an auxiliary example 45 parts of triacetin were used in place of the 30 parts of the above example with substantially equal success.

Example 8.—Trimargarin was prepared from margaric acid and glycerin. To 62.3 parts of purified trimargarin were added 31.1 parts of triacetin and 0.28 part sodium methoxide. Interesterification wholly in the liquid phase (140° F.) was permitted to take place for several hours. To the randomized mixture were added 10.9 parts of glycerol (about 10% excess over the theoretical amount necessary for conversion of all triglyceride into diglyceride). This mixture was reacted for one day at 120° F. to give a single homogeneous phase. After the further addition of 0.19 part sodium methoxide catalyst, low temperature interesterification was conducted for one day at 100° F., for 3 days at 90° F., and 3 days at 80° F.

As the temperature was reduced crystallization of diglycerides took place simultaneously with interesterification.

At the end of the above described reaction period, the mixture was acidulated with glacial acetic acid to inactivate the catalyst, and the resulting mixture was recrystallized five times as follows:

(1) From 4 volumes of a 1:1 mixture of hexane and ethyl alcohol containing 5% water at 75–80° F. (From this single recrystallization a 91% yield of a product having a minimum melting point of 73.9° C. was obtained.)

(2) From 5 volumes of a 3:2 mixture of hexane and ethyl alcohol containing 5% water at 75–80° F.

(3) From 4 volumes of 1:1 mixture of benzene and ethyl alcohol at 75–80° F.

(4) From 9 volumes of benzene at 50° F.

(5) From 150 volumes of petroleum ether at 75–80° F.

An 87% yield of dimargarin having a maximum melting point of 76.3° C. and a minimum melting point of 74.4° C. was obtained. The saponification value and hydroxyl value were 188.6 and 94 as compared with theoretical values of 188 and 94 respectively.

Example 9.—In this example less than the theoretical amount of glycerin required to form diglycerides of all triglycerides in the reaction mixture was used.

50 parts trimyristin, 20 parts triacetin, and 0.3% of sodium methoxide (suspension in xylene) were mixed and reacted at 140° F. to effect interesterification wholly in the liquid phase to a randomized mixture. 3.7 parts of dry glycerol were then added and alcoholysis was effected at 140° F. until a single phase liquid mixture resulted. An additional 0.2% of the sodium methoxide was added and the low temperature interesterification step was permitted to take place at 120° F. for 1 day, at 100° F. for 2 days, at 90° F. for 1½ days, at 80° F. for 2½ days and at 70° F. for 2 days.

After inactivation of the catalyst at 70° F. the mixture was dissolved in 8 volumes of a 50–50 mixture of commercial normal hexane and ethyl alcohol. Dimyristin was crystallized from such a solvent mixture five times. A 53% yield of dimyristin having a maximum melting point of 65.8° C. and a minimum melting point of 63.9° C. was obtained.

The above examples have dealt with the preparation of single acid diglycerides primarily for the purpose of showing that high yields of substantially pure diglycerides are obtainable by the practice of the present invention. If substantially pure diglyceride of a single fatty acid is desired, then it is preferable to use as a starting material a high molecular triglyceride which includes but one high melting combined fatty acid, notably because of the difficulty in segregating mixed high melting diglycerides from desired pure single-acid diglyceride. As indicated in the examples such pure single-acid diglycerides are for the most part symmetrical in nature.

Obviously the process may also be employed to preferentially produce "mixed" diglycerides, i. e. diglycerides constituted of two combined fatty acids of high molecular weight. In such practice, the reaction mix prior to low temperature interesterification should contain the desired mixture of high molecular fatty acids in combined form. The process is then conducted as previously described to effect simultaneous interesterification and precipitation of the mixed diglycerides in the presence of low molecular glycerides.

The essential features of the present invention involve effecting interesterification, wholly in the liquid phase, between the triglyceride of high molecular weight and the triglyceride of low molecular weight and alcoholizing the randomized mixture with glycerol to form a single liquid phase containing desired diglycerides, prior to effecting low temperature interesterification during which high molecular weight diglycerides formed in the reaction preferentially precipitate as a solid phase. The amount of low molecular weight glyceride that must be used in order that the benefits of the present invention may be achieved is not sharply critical. We have found, for example, that amounts in the neighborhood of 20 per cent of low molecular weight triglyceride, based on the higher molecular triglyceride, will effectively participate in the formation and preferential precipitation of high molecular diglyceride during the reaction. Amounts in excess of 20 per cent may of course be employed, and we have found that 35 to 50 per cent is to be preferred. Larger amounts, such as 75 per cent, of course may be employed, but such amounts represent an unnecessary excess.

The quantity of glycerol to be used in the practice of the invention must be sufficient for the formation of the diglyceride of the higher molecular fatty acid in the reaction mixture. When theoretical quantities of glycerol are employed, optimum yields are not obtained. Higher yields are obtained when a 5 per cent to 50 per cent excess over the amount theoretically necessary for conversion of all combined fatty acid (both high and low molecular weight) of the system to diglyceride is employed. It is preferable, however, that the amount of glycerol used be less than that amount which will convert all of the fatty acids to monoglycerides. One of the surprising results of the present process is that although monoglyceride of the higher molecular fatty acids may be present in the reaction mixture in substantial amount, and although monoglycerides are generally higher melting than corresponding diglycerides, 1,3 diglycerides preferentially precipitate in high purity presumably because the crystallization rate of such diglycerides in the reaction system employed is higher.

With regard to temperatures used in the practice of the invention, it is to be borne in mind that the process initially requires effecting interesterification and alcoholysis in a single liquid phase system wherein random distribution of fatty acid radicals is effected. Temperatures sufficient to effect complete liquefaction should therefore be used in the initial stages of the process. However, after equilibrium has been established and such is readily effected in a short time (30–60 minutes) with highly active low temperature interesterification catalysts such as sodium methoxide, then the temperature is reduced to effect crystallization of higher melting diglycerides from the reaction mixture. The temperature schedule employed during this phase of the process is not critical. However, it is preferable from the standpoint of yield to conduct the process so that a gradual reduction in temperature occurs as the crystallization of diglyceride proceeds. The temperature schedule during this later stage of the process can also be controlled so that the precipitation of the diglycerides approaches or reaches completion at a series of successively lower temperatures, as fully disclosed in the examples. In this connection, it is to be understood that the invention

is not limited to the times or temperatures specifically shown herein. These are variable, obviously within limits, and may be increased or decreased in practicing the process to suit existing conditions. For example, if the sensible heat of the mixture and heat of crystallization can be extracted rapidly without substantial supercooling then the desired diglyceride can be formed in a matter of hours instead of days. In one instance, a mixture containing symmetrical dibehenin in good yield was prepared, although low temperature interesterification was effected in about two hours.

Although it is preferable to agitate the reaction mixture during the low temperature interesterification, such a procedure is not essential. Results have shown that it is possible to obtain the advantages of the present invention without the use of agitation. However, in the early stages of low temperature interesterification and when the process is conducted on large batches of materials, agitation is especially advantageous and its use is then preferred.

The examples indicate the advantageous use of solvents in the separation of diglyceride from the final reaction mixture. In some instances the reaction mixture, after inactivation of catalyst, may be first slurried in a solvent such as ethyl ether or commercial hexane, the undissolved solid diglycerides in relatively impure form being separated by filtration and subsequently purified by crystallization from solvents or mixtures of polar and non-polar solvents such as benzene and alcohol, hexane and ethyl ether, hexane and ethyl alcohol, and the like. If it is desired to eliminate the slurrying step then the reaction mixture, with catalyst inactivated, may be dissolved in solvents and the desired diglyceride then recovered by fractional crystallization. If non-polar solvents, such as petroleum ether and benzene, or mixtures thereof are used, glycerin and low molecular weight acid glycerides may separate as the lower layer in a two-phase liquid system, the upper layer containing the diglyceride which may be separated by fractional crystallization. If polar solvents, such as ethyl alcohol or mixtures thereof with non-polar solvents such as hexane, benzene, ether and acetone are used, a one-phase system can be formed from which the diglycerides and impurities can be separated by fractional crystallization. It is to be especially noted from examples above that the products produced by only one crystallization are relatively high in purity but several successive recrystallizations can be employed from different solvent mixtures if desired.

In the above disclosure we have shown the use of a low temperature interesterification catalyst (sodium methoxide) as the catalyst for randomization (interesterification wholly in the liquid phase), alcoholysis and low temperature interesterification and such catalysts are preferred, but effective practice of the invention does not depend solely upon the use of this particular compound. In the early stages of the reaction where, for example, tristearin and triacetin are interesterified wholly in the liquid phase, any suitable interesterification catalyst may be employed, and these include substances such as zinc chloride, sodium hydroxide and barium acetate, for example.

In the low temperature interesterification-crystallization phase of the invention, however, it is essential that a low temperature interesterification catalyst be employed. Sodium methoxide is a preferred compound adapted to this purpose, but other materials, such as the reaction product of an alkali metal with mono-, di- or triglyceride may be used. Similarly, the reaction product of an alkali metal with a great number of compounds may be used. Thus, for example, potassium or sodium in combination with practically any material less acidic than phenol can form the catalyst when added to the glyceride. Sodium phenoxide appears to be on the borderline between what may be referred to in the present sense as "active" and "inactive" materials, because only slight activity of this material in low temperature interesterification is noted when liberal quantities are added to the glyceride mixture. Moreover, methoxides of alkali metals other than sodium, such as lithium and especially potassium, are also active in forming catalytic materials with the glycerides. Calcium methoxide and methoxides in which the cation is the tetrasubstituted ammonium radical, such as tetramethyl ammonium methoxide and lauryl benzyl ammonium methoxide also show activity in the reaction of the present invention.

In addition to the methoxides, the corresponding ethoxides, propoxides, butoxides and alkoxides made from alcoholic compounds in general, such as lauryl alcohol, ethylene glycol, mono- and diglycerides of the diglyceride mixture, and others may be employed. Triphenyl methyl sodium and potassium pyrrole are also active as are suspensions of finely divided metallic potassium or sodium or anhydrous suspensions of potassium hydride and sodium hydride or any material which is capable of forming an alkoxide with an alcoholic compound.

For more details regarding low temperature interesterification catalysts and their use reference is made to the two issued U. S. patents above referred to.

Having thus described our invention, what we claim and desire to secure by Letters Patent is:

1. A process of preparing 1,3-diglyceride of a single fatty acid, which comprises forming a liquid single-phase system of a triglyceride of a normally higher molecular weight fatty acid having from 10 to 22 carbon atoms and melting point above 75° F. and from about 20 per cent to about 75 per cent thereof by weight of triglyceride of lower molecular weight fatty acid having from 2 to 6 carbon atoms; catalytically effecting interesterification wholly in the liquid phase; adding to the interesterified mixture substantially anhydrous glycerol in amount at least equal to the amount stoichiometrically necessary to convert the high molecular weight triglyceride to diglyceride, and catalytically alcoholizing the mixture to form a single liquid phase; reducing the temperature of the system to that temperature at which 1,3-diglyceride of the normally solid higher molecular weight fatty acid formed in the reaction precipitates as a solid phase, continuing interesterification in the liquid phase of the system in the presence of a low temperature interesterification catalyst while said higher fatty acid diglyceride precipitates, inactivating the low temperature interesterification catalyst while maintaining precipitated fatty acid diglyceride as a solid phase; and separating fatty acid diglyceride from the system.

2. Process of claim 1 in which the amount of low molecular weight triglyceride is from about 35 per cent to about 50 per cent weight of the higher molecular weight triglyceride.

3. Process of claim 1 in which the separation

of the diglyceride is effected by recrystallization from a solvent.

4. Process of claim 1 in which the amount of glycerol employed is in excess of that stoichiometrically required to convert all of the fatty acids to diglycerides but less than that stoichiometrically required to convert all of the fatty acids to monoglycerides.

5. Process of claim 4 in which the excess is from about 5 per cent to about 50 per cent of the stoichiometric amount necessary to convert all of the fatty acids to diglycerides.

6. A process for producing 1,3 diglyceride of a single higher molecular weight saturated fatty acid which comprises forming, in the presence of a low temperature interesterification catalyst, a single liquid phase reaction mixture of triglyceride of saturated fatty acid having from about 10 to about 22 carbon atoms in the acyl radical and from about 20 per cent to about 75 per cent thereof by weight of triglyceride of saturated fatty acid having from 2 to 6 carbon atoms in the acyl radical and effecting randomization of fatty acid radicals in the mixture, then alcoholizing the randomized mixture in the liquid phase with glycerol in amount at least stoichiometrically sufficient to form diglycerides with all of the higher molecular weight fatty acids present, and subjecting the liquid mixture to low temperature interesterification with simultaneous crystallization, whereby 1,3 diglyceride of the saturated higher molecular fatty acid, recoverable in substantially pure form, is precipitated.

7. A process of preparing 1,3 diglyceride of a single fatty acid, which comprises forming a liquid, single-phase system of a triglyceride of a normally solid fatty acid having 10 to 22 carbon atoms and a melting point above 75° F., from about 20 per cent to about 75 per cent thereof by weight of triglyceride of a fatty acid having from 2 to 6 carbon atoms, and a low temperature interesterification catalyst; effecting interesterification; adding glycerol to the system in amount at least sufficient stoichiometrically to convert the higher molecular weight fatty acid triglyceride to diglyceride; effecting alcoholysis of said triglyceride mixture with said glycerol to form a single phase liquid system; reducing the temperature of the system to that temperature at which diglyceride of normally solid higher molecular weight fatty acid formed in the reaction precipitates as a solid phase; continuing the reaction while said higher fatty acid diglyceride precipitates; inactivating the catalyst while maintaining precipitated fatty acid diglyceride as a solid phase; and separating fatty acid diglyceride from the system.

8. A process of preparing 1,3 diglyceride of a single fatty acid, which comprises forming a liquid, single-phase system of a triglyceride of a normally solid higher molecular weight fatty acid having 10 to 22 carbon atoms and a melting point above 75° F. and from about 20 per cent to about 75 per cent thereof by weight of triglyceride of a lower molecular weight fatty acid having 2 to 6 carbon atoms; catalytically effecting rearrangement of fatty acid radicals wholly in the liquid phase; adding to the rearranged mixture substantially anhydrous glycerol in amount at least equal to the amount stoichiometrically necessary to convert the high molecular weight triglyceride to diglyceride and catalytically alcoholizing the mixture to form a single liquid phase; reducing the temperature of the reaction mix to that temperature at which higher fatty acid diglyceride formed in the reaction precipitates as a solid phase, allowing the liquid phase of the mixture to react further in the presence of a low temperature interesterification catalyst; lowering the temperature progressively to precipitate higher molecular diglyceride as formed in the reaction; inactivating the low temperature interesterification catalyst while maintaining precipitated diglyceride as a solid phase; and separating and recovering said higher fatty acid diglyceride from the system.

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REFERENCES CITED

The following references are of record in the file of this patent:

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