Patented Oct. 21, 1952

2,615,160

UNITED STATES PATENT OFFICE

2,615,160

MIXED TRIGLYCERIDES

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No Drawing. Application May 28, 1949, Serial No. 96,143

19 Claims. (Cl. 260—410.8)

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This invention relates to mixtures of high molecular diacetyl triglycerides in a waxy translucent form and to ways of making them.

In copending application Serial No. 96,150 of Frank L. Jackson, bearing even date herewith, synthetically prepared high molecular triglycerides are described, having in their molecular structure two acetyl groups attached to adjacent carbon atoms of the glyceryl radical and one high molecular acyl group (i. e. containing 12 to 22 carbon atoms) attached to the third glyceryl carbon. These unsymmetrical diacetyl triglycerides are capable of solidifying in waxy translucent form, in which form they possess novel and useful properties which distinguish them from previously known fats. These diacetyl compounds possess limited stability in the waxy translucent form, sufficient to make them serviceable for some purposes but limiting their serviceability for others, since they eventually lose their waxy, translucent properties. Furthermore, although Jackson has proposed methods of preparing diacetyl fats capable of assuming the waxy translucent form, no methods prior to my invention have been entirely satisfactory for commercial practice. For example, chemical synthesis involving reaction of acetyl chloride with an unsymmetrical high molecular monoglyceride is undesirably costly.

It is an object of this invention to provide fats which may be solidified in waxy translucent form. Another object is to provide such triglycerides which are either wholly stable in waxy translucent form or are stable in that form for long periods of time. Another object is to provide such triglycerides in the alpha-3 or the subalpha-3 polymorphic forms, to be described hereinafter. Another object is to provide mixtures of such triglycerides, said mixtures containing a plurality of combined high molecular acyl groups. Another object is to provide mixtures of symmetrical and unsymmetrical high molecular diacetyl triglycerides. Another object is to provide such mixtures which are substantially free from monoglycerides, diglycerides, glycerol, fatty acids, triacetin, or triglycerides containing no acetyl groups. Another object is to provide a novel kind of edible fat. Another object is to provide an inexpensive and commercially practicable process whereby mixtures of symmetrical and unsymmetrical high molecular diacetyl triglycerides may be prepared, unsymmetrical triglycerides being in predominant amount in said mixtures and said mixtures being substantially free from monoglycerides, diglycerides, glycerol, fatty acids, triacetin or triglycerides containing no acetyl groups. Other objects will appear hereinafter.

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I have found that mixtures of diacetyl triglycerides the non-acetyl acyl radicals of which are of high molecular weight (i. e. those of fatty acids of 12 to 22 carbon atoms) are capable of crystallizing in waxy translucent form, and that when at least ten per cent by weight of the diacetyl triglycerides in such mixtures are different in composition or structure from the remainder of the diacetyl triglycerides, this waxy translucent form is of great thermodynamic stability, being capable of existing for long periods of time or indefinitely without transforming into the opaque solid form in which conventional fats exist at temperatures below their melting point. I have furthermore discovered an inexpensive and commercially practicable process whereby such mixtures of diacetyl triglycerides may be prepared in a purity which makes them suitable for cooking and other purposes.

In a favored variant of my process of preparing such mixtures of diacetyl triglycerides, the first step is to rearrange molecularly the acyl groups in a mixture of triacetin and a conventional fat. For this purpose the mixture is contacted with a rearrangement catalyst. Many such catalysts are known and may be used, such for example as water alone at high temperature and pressure, or the soaps of alkali metals, zinc, aluminum, tin or magnesium. However, I prefer low temperature rearrangement catalysts, by which I mean catalysts which are effective below 120° C., such as alkali metals or compounds whose cation is an alkali metal or a tetrasubstituted ammonium radical and whose anion is the result of removal of acidic hydrogen from any substance less acidic than phenol. Thus finely divided metallic sodium or potassium in xylene, or anhydrous suspension of potassium hydroxide in undecane may be used, or alkali metal hydrides. Also suitable for this purpose are various alkoxides such as sodium, potassium and lithium methoxides, ethoxides, propoxides and butoxides, as are also the corresponding alkoxides made from alcoholic compounds in general such as lauryl alcohol, ethylene glycol, glycerol, oleic acid monoglyceride and many others. Also suitable are alkoxides in which the cation is the tetrasubstituted ammonium radical such as tetramethyl ammonium methoxide and lauryl benzyl dimethyl ammonium methoxide, and alkali-metal-organic compounds containing the alkali metal atom directly bound to a carbon atom as in triphenyl methyl sodium or to a nitrogen atom as in potassium pyrrole. Sodium alkoxides of monohydric alcohols of less than 5 carbon atoms (for example, sodium methoxide and sodium ethoxide) are especially satisfactory catalysts. The amount

of such low-temperature catalyst required increases with the moisture content of the fat. In the case of sodium methoxide or ethoxide the amount commonly ranges from about 0.05 per cent to about 0.5 per cent, based on the weight of the fat, about 0.3 per cent being an average figure according to my experience. Such catalysts are usually suspended in xylene or other low-boiling hydrocarbon which is miscible with fats, the amount of suspending liquid being non-critical.

The low temperature catalyst is added to the dried fat (usually refined and bleached previously) or to the dry triacetin or to the mixture of the two. Rearrangement is allowed to proceed at a temperature so high that at least a substantial part of the fat is liquid, since solid fat does not readily undergo rearrangement with triacetin. As the reaction proceeds, the acetyl-containing fats which are formed tend to dissolve any remaining solid fats and thus enable them to take part in the reaction. However, in order to attain more rapid rearrangement, the mixture is commonly heated to above the complete melting point of the fat or until the mixture is completely liquid, although temperatures above 120° C. are avoided lest the activity of the catalyst be impaired. Under these preferred conditions, more than one half hour is rarely required for substantially complete rearrangement of acyl groups, although longer periods are not harmful. Furthermore, while a substantial degree of rearrangement should be effected, it is not imperative that the reaction go to final completion.

The rearranged mixture is of complex constitution, the relative proportions of the constituents depending upon the proportions of triacetin and of fat initially used. It will comprise triacetin, high molecular triglycerides, monoacyl diacetins and diacyl monoacetins, and each of these except triacetin is capable of variation, depending on the particular glyceryl carbon atoms to which the various acyl groups are attached. For rearrangement to a diacetyl triglyceride, which is the objective in my process, two moles of triacetin are theoretically required per mole of high molecular triglyceride. In practice, the optimum proportion may differ widely from this theoretical figure and will of course vary from time to time as market costs of triacetin and fat vary. In general, for combined cost economy and high yield of diacetyl triglycerides, I usually prefer to employ the triacetin and high molecular triglyceride in a molar ratio of about 0.75:1 to about 3:1.

Rearrangement is next discontinued and its resumption in subsequent steps prevented. This may be accomplished by removing the catalyst as for example by washing with water, or by inactivating it as for example by treating it with enough acid to react fully therewith. Phosphoric and acetic acids, because of their high solubility in fats, are especially suitable for this purpose. After acidification, water-soluble salts and free acid may be removed by water-washing, or if desired any free acid may first be neutralized with alkali. In some cases, an alkali refining step is introduced after acidifying the rearranged fat mixture. Such procedures involve separation of aqueous layers, in which the greater part of any unreacted triacetin is dissolved and removed.

In order to obtain mixtures containing high molecular diacetyl triglycerides suitable for cooking purposes and of such composition as to crystallize readily in waxy translucent form, the rearranged mixture requires purification. Triacetin is especially objectionable because it lowers the temperature at which the product smokes when used for cooking purposes; it also softens the product and expands the temperature range over which it melts. I therefore remove by distillation substantially all unreacted triacetin or other low-boiling constituents which may remain in the rearranged mixture after inactivating the catalyst and washing, as previously described. In order to avoid high temperatures which might cause decomposition, I carry out this distillation under reduced pressure, preferably while passing a stream of inert gas, such for example as nitrogen or steam, through the molten fat. Under a pressure of 2 or 3 mm. of mercury, triacetin steam-distills readily before a temperature of 140° C. is reached.

I next isolate a distillation fraction consisting predominantly of high molecular diacetyl triglycerides. In order to do this, the temperature of the steam distillation or other distillation is raised and/or the pressure is reduced until diacetyl triglycerides distill, but conditions drastic enough to cause distillation of substantial amounts of triglycerides containing less than 2 acetyl groups are avoided as much as possible. The exact temperature of distillation, at a given pressure, varies with the particular fat used in the rearrangement and with the speed of distillation which is desired. Thus in the case of unhydrogenated cottonseed oil, distillation has been practiced at about 205° to 250° C. at a pressure of about 2 mm. mercury, while in the case of unhydrogenated rapeseed oil, temperatures of about 220° to 270° C. have been required. One skilled in the art is of course guided by the shape of the distillation curve (temperature vs. amount distilled) in deciding which distilled fractions to collect.

The residue after distilling off the diacetyl triglycerides is largely a mixture of monoacetyl triglycerides and of unreacted high molecular triglycerides, and this mixture may if desired be reworked in my process.

The distilled fraction consisting predominantly of diacetyl triglycerides is collected separately. It is difficult to determine with certainty its molecular composition and structure, for example the relative proportions of diacetyl triglycerides which exist in the symmetrical and in the unsymmetrical form. However, the rearrangement is purely random and is governed by the laws of chance, so that about two thirds of the diacetyl triglycerides are 1-acyl-2,3-diacetin and about one third is 2-acyl-1,3-diacetin. If the distillation cuts are not sharp, minor amounts of monoacetyl triglycerides and perhaps traces of triacetin and of acetyl-free triglycerides may also be present; thus commonly from about one third to about one half by weight of the product consists of monacetyl triglycerides and symmetrical diacetyl triglycerides, although the product is predominantly unsymmetrical diacetyl triglycerides.

On cooling, the fraction which consists predominantly of unsymmetrical diacetyl triglycerides crystallizes into a waxy form which is plastic, yielding, pliable, impressionable, non-brittle, non-friable, to a limited degree elastic, capable of being cut, scratched or deformed without fracturing, but lacking in stickiness or tackiness, these being properties referred to herein by the term "waxy." This waxy form

is also characterized by its translucency. In thin layers of only 1 or 2 millimeters it appears wholly clear and transparent; in thicker layers (5–10 mm. for example) it transmits a large proportion of incident light, although some of this transmitted light is diffused so that objects viewed through the fat layer suffer blurring of outline. In bulk, the fat has a colorless, waxlike appearance. Furthermore, the products of this process are commonly less greasy and melt over a narrower range of temperature than do conventional fats.

Another outstanding and distinguishing characteristic of the products of my invention is their great stability in the waxy translucent form when held at temperatures slightly below their melting point. The pure unsymmetrical diacetyl triglycerides described by Jackson have only a limited lifetime in waxy translucent form; on standing at temperatures slightly below their melting point for a matter of a few weeks they begin to convert into the opaque solid form of conventional fat. In contrast, the mixtures of diacetyl triglycerides which constitute my products have greatly improved stability as will be more specifically shown hereinafter; for example, the product of Example 1 below showed no evidence of losing waxiness or translucency even after storage for 20 months at room temperature.

The following examples, in which all parts are by weight, illustrate ways in which I practice the invention, but it will be understood that these examples are illustrative only and that the invention is not limited by the details thereof but only by the appended claims.

Example 1.—100 parts of refined, bleached and dried cottonseed oil were mixed at room temperature with 50 parts of dry triacetin and with 0.3 part of sodium methylate catalyst suspended in xylene. Random rearrangement of acyl radicals was allowed to proceed in the mixture for one-half hour, after which time an excess of glacial acetic acid was mixed therein in order to inactivate the catalyst. The acidified mixture was water-washed until free from acid, the greater part of the unreacted triacetin also being thereby removed. It was then steam distilled under a pressure of 2 to 3 mm. of mercury, low-boiling constituents including any remaining unreacted triacetin being thereby removed. The temperature of distillation was then raised to 205–250° C. in order to remove high molecular diacetyl triglycerides. This distillate was collected separately and amounted to 32% by weight of the original mixture of cottonseed oil and triacetin. The saponification and iodine values of the distillate were 381.0 and 65.5 respectively, which may be compared with calculated values of 382.5 and 57.7 respectively for mono-oleyl diacetin. The distillate, which thus appears to be essentially monoacyl diacetin, was next hydrogenated to an iodine value of 0.8.

On cooling to about 20° C., the product solidified to a waxy translucent form having a comparatively sharp melting point, incipient at 29.4° C. and complete at 31.3° C., and a saponification value of 375. In comparison, the waxy translucent form of unsymmetrical stearyl diacetin melts sharply at 34.1° C. and has a saponification value of 381. The product of Example 1 has been held for 20 months at room temperature (about 25°–30° C.) without perceptible change in waxiness or translucency and I believe it to be permanently stable under these conditions, whereas 1-stearyl-2,3-diacetin under like storage conditions begins to convert from the waxy translucent form into a non-waxy opaque form in a matter of 3 to 4 weeks. X-ray examination of this cottonseed oil product will be discussed in a later paragraph.

Example 2.—100 parts of refined and bleached soybean oil were hydrogenated to practical completion. The dried fat was then melted and mixed with 35 parts of dry triacetin and the acyl groups of the mixture were molecularly rearranged under the catalytic influence of 0.5 part of sodium methylate as in Example 1. The catalyst was inactivated with acetic acid and the acidified mixture was alkali-refined with 14° Bé. lye. Residual unreacted triacetin was removed by steam distilling as in Example 1. The mixture remaining had a complete melting point of 52.7° C. Diacetyl triglycerides were next steam distilled at 210–230° C. under about 2 mm. of mercury. The yield of distillate was 31% by weight of the original mixture of oil and triacetin.

On cooling, the distillate solidified to a waxy translucent non-greasy form having a comparatively sharp melting point between 32.0° and 32.8° C. It was stored for one year at room temperature without any apparent change in waxiness or translucency. X-ray examination of this product will be discussed in a later paragraph.

Example 3.—Refined and bleached coconut oil was mixed with half its weight of dry triacetin and the mixture was molecularly rearranged as in Example 1. After inactivating the catalyst by acidification and water-washing, remaining triacetin was removed by steam distillation at 2 mm. mercury, leaving a product with a saponification value of 376. By more drastic steam distillation a second fraction, amounting to 40% by by weight of the original coconut oil and triacetin, was isolated. This fraction was then hydrogenated to an iodine value of 0.1. Its saponification value was 459.7, to be compared with a calculated value of 458 for the diacetin triglyceride of hydrogenated coconut oil fatty acids.

By cooling this product to about —20° C., a waxy translucent solid was obtained which melted over the range from about —19° C. to about 2° C. It was stored for 3 months at about —18° C. to —20° C. without any apparent change in waxiness or translucency. X-ray examination of the product will be discussed in a later paragraph.

Example 4.—100 parts of refined, bleached and dried rapeseed oil (saponification value 176.9; iodine value 105.3) was mixed with 35 parts of dry triacetin and subjected to molecular rearrangement at room temperature with 0.3 part of sodium methylate catalyst in xylene. After 1 hour, glacial acetic acid was added to destroy the catalyst, and the excess acid was removed by water washing. Unreacted triacetin and other low-boiling constituents were removed by steam distillation at 2–3 mm. mercury. The resulting triacetin-free rearranged oil had a saponification value of 272.1, an iodine value of 86.8, incipient melting point —25° C., and complete melting point —5° C.

Distillation was continued, raising the temperature to 220° to 270° C. in order to separate diacetyl triglycerides from monoacetyl triglycerides and from original unreacted oil. The yield of diacetyl triglycerides was 31%, based upon the original oil-triacetin weight. The saponification

value was 368.6 and iodine value was 71.2, as compared with calculated values at 364 and 72 respectively for the diacetyl compounds. The complete melting point was —7.5° C.

This material was next hydrogenated to an iodine value of 3.0 On cooling the melt a waxy, translucent solid was obtained melting incipiently at 31° and completely at 38.3° C. It was stored for 7 months at room temperature without any apparent change in waxiness or translucency. X-ray examination of the product will be discussed in a later paragraph.

The solidified products of my invention, including the specific products of Examples 1 to 4, are in marked contrast to conventional high molecular fats. The complex mixtures of mixed triglycerides which constitute animal and vegetable oils and fats of nature (herein generically referred to as "fats") as well as their hydrogenation products commonly undergo gradual solidification on cooling and assume the soft, greasy, largely opaque form to which we are accustomed. The rigidity of these so-called "solid" fats is commonly due to an interlocking network of crystals; their softness and greasiness and their transmission of a small amount of light is due to their content of liquid oil which remains enmeshed between the crystals. Only on further cooling does the material become wholly solid and liquid-free, and when this is the case it becomes opaque, hard, brittle and non-greasy. The presence in animal and vegetable fats of such a variety of mixed triglycerides, having a wide range of melting points, results in gradual softening and gradual increase in greasiness when such wholly solid fats are warmed.

The breadth of their melting range and the consequent softness and greasiness of conventional fats are objectionable for a number of applications, while for other uses the hardness and brittleness at the lower temperatures are objectionable. My products, on the other hand, are especially suitable for many uses by virtue of their waxy softness, even at temperatures at which they are wholly solid and liquid-free, and because of their narrow melting point range they become greasy on warming only when their complete melting point is approached. They are free from objectionable color, odor or flavor, and as judged by growth response and by fat utilization and digestion in nutritional studies with test animals they are nutritionally similar to conventional edible fats, hence they are especially suitable for edible purposes. When chewed in the mouth they are somewhat like a gum, and their final melting is accompanied by a cooling sensation. Those which melt above room temperature but below body temperature are especially suitable for use in candy, as chocolate coatings, in icings and frostings, as spray oils for crackers, as edible "beeswax" in synthetic honey, as an edible chewing gum base, as protective coatings for products such as fruits, cheese, preserves, frozen meats and the like in order to keep out oxygen, moisture, etc. They may be used in shortenings, margarins, confections, etc. They are suitable for inedible uses also, as for example in hair dressing compounds, as vaginal suppositories, as carrier for medicinals, and for a variety of related uses.

Many conventional fats contain such large proportions of highly unsaturated triglycerides that they oxidize and become rancid readily, yet when the unsaturation is decreased (as by hydrogenation) sufficiently to remedy this trouble, it is found that they are too hard for satisfactory use. My compounds have a great advantage here, for they may be completely hydrogenated and so rendered essentially immune to oxidation and rancidity, and they yet retain desirable waxlike softness.

It will readily be seen that compounds which when fresh possess the waxy translucent characteristics of my products but which with the passage of time lose them will have only limited usefulness, the breadth of their utility being less the shorter their lifetime in the waxy form. In this respect the compounds of my invention show marked superiority over pure individual high molecular unsymmetrical diacetyl triglycerides, which latter compounds, upon storage at temperatures near their melting point, begin within a few weeks to convert visibly into the conventional opaque form commonly assumed by solid fats.

It will aid in understanding the invention to discuss the polymorphism of conventional fats, of Jackson's synthetic fats and of the synthetic fats of this invention. It is well known that conventional fats assume various polymorphic forms when they solidify. The less stable forms are capable of transforming, without melting, into more stable forms, the transformation being influenced by the temporal and thermal history of the material. The lowest melting form has commonly been called "alpha" and the highest melting form, "beta," the former being unstable, the latter being stable. An intermediate unstable form known as "beta prime" also frequently exists. In none of their polymorphic forms do conventional fats have the waxy translucent properties possessed by the solid triglycerides of my invention.

The polymorphic forms of a given fat may in some cases be distinguished from one another by macroscopic or microscopic examination, by their melting points or by their dilatometric behavior, but X-ray diffraction affords in general the most accurate means of identification. For example, the alpha form of fats is characterized by a strong short-spacing line at about 4.1 to 4.2 Å., accompanying which a very weak line at about 2.35 to 2.45 Å. can be detected. The alpha form of conventional fats crystallizes when the fat is chilled rapidly to a temperature below the melting point of that form; this alpha form is unstable, converting without melting into a higher-melting form, slowly on standing and more rapidly when heated nearly to its melting point. Having once transformed into a higher-melting form, fats cannot again transform into the lower-melting alpha form without first passing through the molten condition.

The individual high molecular unsymmetrical diacetyl triglycerides also crystallize in the alpha form when cooled slightly below (e. g. 1 or 2° C. below) the melting point of the alpha form, and in that form they have the waxy translucency which is characteristic of the products of my invention. The waxy translucent alpha form of these unsymmetrical diacetyl triglycerides is far more stable than the alpha form of conventional fats, but when held for long periods of time at a temperature below but near its melting point it converts into the higher melting form (beta) in which it has the properties of conventional opaque fats.

If, however, the alpha form of individual high molecular unsymmetrical diacetyl triglycerides be cooled to and held at a temperature considerably

below (e. g. of the order of 20° C. below) its melting point, it undergoes a change, normally within 5 or 10 minutes time, which does not affect its waxy translucent character, but which is evidenced by the disappearance of the weak X-ray short-spacing line at about 2.4 Å. and its replacement by a moderately strong line at about 3.7 Å., accompanied by other weaker lines. This polymorphic form, referred to as "subalpha," is in reversible solid-to-solid equilibrium with the alpha form at a transition temperature, and is stable at temperatures below this transition temperature.

X-ray diffraction of solid fats also gives rise to long-spacing lines which are informative as to the length of the structural units making up the crystals. This length is essentially a function of the acyl radicals composing a unit structure, since the contribution of the glyceryl radical to the length is small. If the length of the structural unit is double the length of the acyl radical, it is said to have a double-chain-length structure, designated as "alpha-2," "beta-2," etc. This is the prevailing form among most conventional fats whether alpha, beta or beta prime, unless indeed there is a large difference in length between the different acyl chains present in the molecule. On the other hand, if the length is thrice the length of the acyl radical, the structure is said to be triple-chain-length (designated as "alpha-3," etc.), and this is the case with individual high molecular unsymmetrical diacetyl triglycerides. The relationship between long spacings and structure is discussed by Lutton, Jour. Am. Chem. Soc., 70, 248 (1948).

The polymorphism of my products is in some respects similar to that just described for the individual high molecular unsymmetrical diacetyl triglycerides and in other respects dissimilar. My products, when cooled below their melting point, solidify in the waxy translucent alpha-3 form, or in some cases directly in the waxy translucent subalpha-3 form without passing through the alpha-3 form. Those which solidify first in the alpha-3 form are transformed into subalpha-3 by sufficient cooling, and again convert into alpha-3 upon re-warming, melting finally taking place from the alpha-3 form. Those which solidify directly in the subalpha-3 form cannot be converted into alpha, i. e. upon warming they melt without previous change of phase.

Illustrative X-ray data on the products of Examples 1 to 4 are given below. The diffraction patterns were obtained by the general technique described in George L. Clark's "Applied X-rays," third (1940) edition, chapter XIII. A beam of X-rays from a copper target in a vacuum tube operating at 40–45 kilovolts (peak on rectified current) and 20 milliamperes was collimated by means of a pinhole system in order to render the rays essentially parallel. These rays were then passed through a thin layer of the triglyceride sample in a thin-walled glass capillary, and the resulting diffracted rays were recorded on a flat photographic plate located at a measured distance of either 5 or 10 centimeters beyond the sample. The duration of exposure of the plates was about one hour in the former case and about 4 hours in the latter. Between sample and plate a nickel foil was placed in order to filter out the copper K-beta wave lengths. The short and long spacings were calculated in conventional manner from the resulting diffraction rings, using Bragg's law.

Product of Example 1, derived from cottonseed oil.—The distilled fraction rich in diacetyl triglycerides was completely hydrogenated and cooled to about 20° C. The resulting waxy translucent solid was in the alpha-3 form as shown by a strong short-spacing line at 4.09 Å., a weak one at 2.42 Å., and a long spacing line at 35.3. (The long-spacing calculated for triple-chain-length stearyldiacetin by the method of Lutton, Jour. Am. Chem. Soc. 70, 248 (1948), is 35.9 Å.)

On cooling to below 0° C. this product transformed into waxy translucent subalpha-3, as shown by a strong short-spacing line at 4.13 Å., a medium strong line at 3.66 Å., and a long spacing of 35.3 Å.

Product of Example 2, derived from hydrogenated soy bean oil.—On cooling to slightly below 32° C., the fraction rich in diacetyl triglycerides solidified in the waxy translucent alpha-3 form as shown by a strong short-spacing at 4.11 Å., a very weak one at 2.35 Å., and a long-spacing of 37.2 Å. When cooled to below 0° C., the waxy translucent material had a strong short-spacing at 4.10 Å., a medium strong line at 3.66 Å., and a long-spacing of 37.2 Å., indicating the subalpha-3 form.

Product of Example 3, derived from coconut oil.—The distilled fraction rich in diacetyl triglycerides was completely hydrogenated and cooled to about —20° C., when it solidified in waxy translucent form. This form was shown to be subalpha by a strong short-spacing line at 4.13 Å. and a medium strong line at 3.74 Å. Long-spacing lines were found at 37.5 Å. and 28.5 Å., which correspond roughly with triple chain lengths of 35.9 Å. and 28.4 Å. calculated respectively for stearyldiacetin and lauryldiacetin. This product could not be crystallized in the alpha form.

Product of Example 4, derived from rapeseed oil.—The distilled fraction rich in diacetyl triglycerides was hydrogenated to substantial completion and was cooled to slightly below 31° C. The resulting waxy translucent solid showed the strong short-spacing at 4.08 Å. which is characteristic of alpha forms of fat. It had a long spacing of 36.9 Å. It was therefore concluded that it was in the alpha-3 form.

The length of the high molecular acyl chains and the degree of unsaturation in my product affect its melting point and whether it crystallizes in the subalpha-3 form only or in both alpha-3 and subalpha-3. In general, long chain and saturation go with high melting point and capacity to exist in both alpha-3 and subalpha-3 form, while short chain and unsaturation go with low melting point and capacity to exist in subalpha-3 form only. By varying the chain length and the degree of unsaturation, I am thus able to obtain waxy translucent products having any desired melting point. While products melting between body temperature and the normal room temperature of temperate zones have particularly wide variety of uses, it will be perceived that products which are liquid at such temperatures may yet be of high utility as waxy translucent solids at low temperatures, such for example as in cold storage, in winter weather or in northern latitudes. On the other hand, products of very high melting point may have especial applicability to use in tropical regions or under similar high temperature conditions.

Products which contain wide variation in high molecular acyl groups with respect to either chain

length or saturation or both, melt over a wide range of temperatures. It will be seen that in such cases, where melting of some of the constituents occurs while other constituents remain solid, the products will lose their waxiness and become greasy within this temperature range, thus leaking liquid oil before melting is complete. In order partially to avoid this condition, which is seldom desirable, I frequently prefer to have only saturated products. This can be accomplished by using fully saturated fats to begin with, such for example as tristearin or tripalmitin or completely hydrogenated animal or vegetable fats. However, instead of hydrogenating animal or vegetable fats before molecularly rearranging them with triacetin, I may introduce a hydrogenation step at any other stage in the process of preparing my products. Thus I may hydrogenate the molecularly rearranged mixture before distilling off unreacted triacetin, or after distilling off unreacted triacetin but before distilling the diacetyl triglyceride fraction, or the distilled diacetyl triglyceride fraction only may be hydrogenated.

This saturation of ethylenic double bonds by hydrogenation serves another purpose also, in that it reduces the susceptibility of the product to oxidation and rancidity. Thus my saturated products have the combined properties of low oxidation susceptibility and of softness even at low temperature. In contrast, softness at low temperatures is commonly associated with oils of high iodine value and consequent susceptibility to oxidation, while slight susceptibility to oxidation is customarily found only in oils of low iodine value and consequent great hardness and high melting point.

In order that the synthetic fat of my invention exist, depending upon temperature, in both the waxy translucent alpha-3 and subalpha-3 polymorphic forms, it is in general needful that 50 per cent or more by weight of the combined high molecular fatty acids be saturated and contain at least 16 carbon atoms. With more than about 50 per cent of combined unsaturated fatty acids and fatty acids of less than 16 carbon atoms, there are indications that only the subalpha-3 form exists. From a practical viewpoint it is of little importance whether the products are alpha-3 or subalpha-3, since most physical properties are essentially the same in both cases. For example, a pliable coating of one of my diacetyl triglyceride mixtures may exist at one temperature in one of these forms and at another temperature in the other form, and yet appear the same and perform its function equally well in both.

Especially useful properties are possessed by mixed diacetyl triglycerides derived predominantly from palmitic and stearic acids, since such triglycerides crystallize in waxy translucent form of high stability and have relatively sharp melting points, and these melting points are not far below the temperature of the human body. They hence melt readily in the mouth, and yet they do not become soft or greasy or leak liquid oil until heated nearly to their melting point.

While I have determined the fact that mixed symmetrical and unsymmetrical diacetyl triglycerides which I have described are greatly superior to individual unsymmetrical diacetyl triglycerides in stability in waxy translucent form, I have not been able to determine the cause for their improved stability. I have found, however, that although individual unsymmetrical diacetyl triglycerides have limited waxy translucent stability, the corresponding symmetrical diacetyl triglycerides have even poorer stability, and yet that on mixing these isomeric forms products are obtained which are more stable in the waxy translucent form than either of the isomers alone. This behavior is illustrated in Table 1 in which the visual appearance of samples after storing at about 25° C. is recorded, this being a temperature at which all of the samples crystallize in waxy translucent alpha-3 form.

Table 1

Percent ASA[1]	Percent SAA[2]	Days before appreciable conversion to opaque form
100	0	1
80	20	43
70	30	98
60	40	[3] >120
40	60	[3] >120
20	80	66
0	100	20

[1] ASA=symmetrical stearyldiacetin.
[2] SAA=unsymmetrical stearyldiacetin.
[3] Observation terminated after 120 days.

I have further found that while 1-stearyl-2,3-diacetin and 1-palmityl-2,3-diacetin, each taken alone, have limited stability in the waxy translucent form, yet mixtures of these have vastly increased stability in that form. This is illustrated in Table 2, wherein the visual appearance of samples is recorded after storing at 21° C. for six months, this being a temperature at which all of the samples crystallize in waxy translucent alpha-3 form.

Table 2

Percent SAA[1]	Percent PAA[2]	Appearance
100	0	Opaque.
75	25	Waxy and translucent.
50	50	Do.
25	75	Do.
0	100	Opaque.

[1] SAA=1-stearyldiacetin, alpha-3 melting point 34.1° C.
[2] PAA=1-palmityldiacetin, alpha-3 melting point 22.4° C.

X-ray examination of the samples of Table 2 showed that the mixtures were entirely in the alpha form when the experiments were terminated at the end of six months, whereas during the first month's storage SAA underwent a 40% conversion into beta form and PAA underwent a 5 to 10% conversion into a beta prime or related form.

Noticeably improved stability in the waxy translucent form is in general found in mixtures of high molecular diacetyl triglycerides in which at least 10% by weight of the high molecular acyl groups are different from the remainder of the said acyl groups, and especially when this percentage figure exceeds 20%. Likewise, noticeably improved stability in the waxy translucent form is in general found in mixtures of high molecular symmetrical and unsymmetrical diacetyl triglycerides in which at least 10% by weight of said triglycerides differ from the remaining triglycerides in structure or composition or both, and especially when this percentage figure exceeds 20%.

Structurally, my invention covers mixtures

containing (a) from 10% to 90% by weight of triglycerides of the formula

$$\begin{array}{l} RCO\cdot OCH_2 \\ | \\ CH_3CO\cdot OCH \\ | \\ CH_3CO\cdot OCH_2 \end{array}$$

and inversely from 90% to 10% by weight of triglycerides of the formula

$$\begin{array}{l} R'CO\cdot OCH_2 \\ | \\ CH_3CO\cdot OCH \\ | \\ CH_3CO\cdot OCH_2 \end{array}$$

wherein RCO· represents acyl radicals of the group consisting of either saturated or unsaturated high molecular fatty acids and R'CO· represents any other acyl radicals from the same group, (b) corresponding mixtures containing the symmetrical isomers of the above compounds, and (c) mixtures containing from 10% to 90% by weight of triglycerides of the formula

$$\begin{array}{l} CH_3CO\cdot OCH_2 \\ | \\ RCO\cdot OCH \\ | \\ CH_3CO\cdot OCH_2 \end{array}$$

and inversely from 90% to 10% by weight of triglycerides of the formula

$$\begin{array}{l} RCO\cdot OCH_2 \\ | \\ CH_3CO\cdot OCH \\ | \\ CH_3CO\cdot OCH_2 \end{array}$$

wherein RCO· has the same meaning as above, whether these acyl radicals be the same or different.

Complete thermodynamic stability in waxy translucent form at temperatures below the melting point appears to be possessed by fatty mixtures which consist essentially of high molecular diacetyl triglycerides from ½ to ⅔ by weight whereof being unsymmetrical diacetyl triglycerides the high molecular acyl groups of which are those of substantially saturated fatty acids of 16 to 22 carbon atoms, at least ⅕ by weight of these high molecular acyl groups differing from the remainder of said groups and at least ⅕ of said triglycerides being isomers of the remaining portion of said triglycerides. An example of such a fatty mixture is a mixture of diacetyl triglycerides in which the non-acetyl acyls are palmityl and stearyl in equimolar amounts and in which ⅓ of the diacetyl triglycerides are symmetrical and ⅔ of them are unsymmetrical.

Mixtures of high molecular diacetyl triglycerides which upon cooling solidify in waxy translucent form of improved stability may be prepared in a variety of ways. One of these ways involves interesterification or random molecular rearrangement of esters, in which process there is interchange of acyl groups between acetic esters and esters of high molecular fatty acids. Molecular rearrangement of triacetin and conventional fats has been described hereinbefore. It is obvious that instead of using triacetin in this process, other non-glyceride esters of acetic acid may be used as acetylating agents, such for example as methyl acetate. Conversely, instead of triglycerides of high molecular fatty acids, other non-glyceride esters of these fatty acids, such for example as methyl palmitate, may be interesterified with (i. e. acetylated by) triacetin. In using esters (whether of acetic acid or of high molecular fatty acids) of alcohols other than glycerin, those should be selected which have boiling points which differ substantially from those of the high molecular diacetyl triglycerides, in order that any excess of these non-glyceride esters which remains in the reaction mixture may be readily separated therefrom by fractional distillation or otherwise. In the case of non-glyceride acetic esters, there is the further limitation that these be esters of alcohols which, when reesterified with the high molecular fatty acids in question form therewith esters which differ substantially in boiling point from the diacetyl triglycerides. Thus if non-glyceride esters are present in the rearrangement reaction mixture, they should be only those which have boiling points enough higher than or enough lower than the diacetyl triglycerides to permit separation therefrom by fractional distillation.

Interesterification processes whereby high molecular diacetyl triglycerides are formed are also practicable, using incomplete or partial esters. For example, coconut oil monoglyceride or diglyceride or mixtures thereof can be catalytically rearranged with triacetin to give a mixture comprising diacetyl triglycerides of coconut oil fatty acids, and conversely, coconut oil can be rearranged with mono- or diacetin or mixtures thereof to give like products.

Interesterification acetylations lead to mixtures comprising diacetyl triglyceride isomers, whether the original esters consisted of mixtures of isomers or whether only one isomeric form was originally present.

Non-interesterification acetylations of high molecular monoglycerides are practicable wherein the monoglycerides, either melted or dissolved in a solvent, are for example heated with acetic anhydride in the presence of sodium acetate, or with acetic acid in the presence of a desiccating agent and a catalyst, or with acetyl chloride in the presence of sodium carbonate, pyridine or other tertiary amine as an acid acceptor, or by other means. Such acetylations result in mixed isomers (such as 1-stearyl-2,3-diacetin and 2-stearyl-1,3-diacetin) when the original monoglycerides were likewise mixed isomers. Monoglycerides may be selected, however, which are of only one isomeric form but which are derived from a plurality of high molecular fatty acids, in which case the acetylated product will comprise a mixture of diacetyl triglycerides of only one isomeric form, such as a mixture of 1-stearyl-2,3-diacetin and 1-palmityl-2,3-diacetin. More commonly the monoglycerides comprise both mixed isomers and mixed fatty acids, so that the diacetyl triglycerides obtained are highly complex mixtures, various individuals of which vary from one another both isomerically and with respect to the high molecular acyl group.

It is obvious that the individual monoglycerides may be acetylated separately and the acetylated products be thereafter mixed with one another, and that the individual monoglycerides may be isomeric esters of the same fatty acid or one isomeric form of esters of a plurality of fatty acids.

The monoglycerides to which reference has been made may be prepared in various ways. A convenient method is to rearrange molecularly a mixture of glycerin and a fatty acid ester, such for example as an edible fat triglyceride or diglyceride (or alternatively the fatty acids themselves), in random manner under the influence of a low-temperature rearrangement catalyst. Conditions may be substantially those described in Example 1. See article by Feuge and Bailey in "Oil and Soap," vol. 23, page 359, for an exposition of the relationship between initial and final

proportions of constituents in random rearrangement of glycerin-fat mixtures.

The resulting rearranged mixture comprises rearranged triglycerides, free glycerin, and mono- and diglycerides, and can be acetylated in any conventional manner. The acetylated mixture will thus comprise rearranged high molecular triglycerides, triacetin (from glycerin), diacetyl triglycerides (from monoglycerides), monoacetyl triglycerides (from diglycerides), and commonly acetic acid as well (from excess acetylating agent). Low boiling impurities, i. e. those boiling below diacetyl triglycerides, such as acetic acid and triacetin, are first removed, as previously described, by steam distillation or otherwise. A fraction consisting predominantly of mixed isomers of diacetyl triglycerides is next distilled, the distillation being discontinued before substantial amounts of high boiling components, such as monoacetyl triglycerides and non-acetyl triglycerides, are distilled. The resulting fraction may then be chilled to form a waxy translucent solid. It will be understood, however, that my invention also contemplates separations by means other than distillation, as for example crystallization processes or fractional separations by solvents, and my invention is thus not restricted to any one physical means of separating and isolating the diacetyl triglycerides.

When I use the term "acetylating" herein and in the appended claims I mean thereby any process which introduces acetyl groups into a chemical compound to form acetic acid esters, rearrangement of high molecular triglycerides with triacetin and reaction of acetyl chloride or acetic anhydride with monoglycerides being among the examples of acetylation which I have given.

In the foregoing discussion of the various ways of making the products claimed herein the word "may" is used to indicate that one has a choice between two or more entirely practicable alternatives; it denotes ability, not mere possibility. All of the foregoing methods result in satisfactory preparation of the novel products of the invention.

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

1. A fatty composition consisting essentially of diacetyl triglycerides, the non-acetyl, acyl radicals of which are those of a fatty acid of 12 to 22 carbon atoms, each 100 parts of the said mixture containing from about 10 to about 90 parts by weight of diacetyl triglycerides selected from the group consisting of symmetrical and unsymmetrical diacetyl triglycerides and inversely from about 90 to about 10 parts by weight of triglycerides selected from the group consisting of, (*a*) diacetyl triglycerides differing from the aforementioned diacetyl triglycerides only in isomeric form, (*b*) diacetyl triglycerides differing only in chain length of the high molecular fatty acid acyl radical from the said aforementioned diacetyl triglycerides, and (*c*) mixtures of (*a*) and (*b*), the total mixture of triglycerides being substantially free of triacetin and of triglycerides solely of high molecular fatty acids and being in waxy translucent form of great stability.

2. A mixture of diacetyl triglycerides the non-acetyl radicals of which are those of fatty acids of 12 to 22 carbon atoms, at least 10 per cent by weight of the diacetyl triglycerides being different isomerically from the remainder of the diacetyl triglycerides, and the said mixture being substantially free from triacetin and acetyl-free triglycerides and in waxy translucent form of great stability.

3. A mixture of high molecular diacetyl triglycerides in which at least 10 per cent by weight of the combined high molecular acyl groups differ from the remainder of the combined high molecular acyl groups, the said mixture being substantially free from triacetin and acetyl-free triglycerides and in waxy translucent form of great stability.

4. A triglyceride mixture consisting predominantly of unsymmetrical diacetyl triglycerides containing high molecular combined fatty acids, at least one-third by weight of said mixture consisting of other triglycerides containing both acetyl and high molecular fatty acid groups, the said mixture being substantially free of triacetin and of triglycerides solely of high molecular fatty acids, and being in a waxy, translucent polymorphic form of great stability.

5. The triglyceride mixture of claim 4 predominantly in a waxy translucent, subalpha-3 polymorphic form.

6. A fatty mixture consisting predominantly of high molecular 1-acyl-2,3-diacetyl triglycerides at least one-half of the high molecular acyl groups of which are those of saturated fatty acids of at least 16 carbon atoms and at least one-third of said mixture consisting of other triglycerides containing both acetyl and high molecular fatty acyl groups, the said mixture being substantially free of triacetin and of triglycerides solely of high molecular fatty acids and being in a highly stable waxy translucent alpha-3 polymorphic form.

7. A fatty mixture consisting predominantly of high molecular 1-acyl-2,3-diacetyl triglycerides the high molecular acyl groups of which are those of palmitic and stearic acids, from one-third to one-half of said fatty mixture consisting of other triglycerides containing both acetyl and high molecular fatty acyl groups, said mixture being substantially free of triacetin and of triglycerides solely of high molecular fatty acids and being in a highly stable waxy translucent solid form which melts sharply below body temperature.

8. A fatty mixture in waxy translucent form which is highly stable in that form at temperatures below its melting point, and which consists essentially of high molecular diacetyl triglycerides from one half to two thirds by weight of said triglycerides being unsymmetrical diacetyl triglycerides the high molecular acyl groups of which are those of substantially saturated fatty acids of 16 to 22 carbon atoms, at least one fifth by weight of these high molecular acyl groups differing from the remainder of said groups and at least one fifth of said triglycerides being isomers of the remaining portion of said triglycerides.

9. A process of preparing a waxy translucent form of diacetyl triglycerides of high molecular fatty acids which comprises (*a*) preparing a mixture comprising a plurality of diacetyl triglycerides of high molecular fatty acids, substantially free of non-glyceride esters having essentially the same boiling point range as that of the said diacetyl triglycerides; (*b*) isolating said diacetyl triglycerides from materials which differ substantially therefrom in boiling point; and (*c*) chilling the thus purified diacetyl triglycerides to below their minimum melting point thereby solidifying them in waxy translucent form of great stability.

10. In the process of preparing high molecular

diacetyl triglycerides in waxy translucent form of great stability, the steps which comprise: (*a*) acetylating glycerides of high molecular fatty acids to form a reaction mixture a substantial proportion of which consists of a plurality of diacetyl triglycerides of high molecular fatty acids; (*b*) isolating from the reaction mixture a fraction which consists predominantly of a mixture of said diacetyl triglycerides; and (*c*) chilling said diacetyl triglyceride fraction to solidify it in waxy translucent form.

11. In the process of preparing high molecular diacetyl triglycerides in waxy translucent form of great stability, the steps which comprise acetylating a mixture of monoglycerides of high molecular fatty acids to form a reaction mixture which contains a substantial proportion of a plurality of diacetyl triglycerides of said fatty acids, isolating said diacetyl triglycerides and chilling them to solidify them in waxy translucent form.

12. In the process of preparing high molecular diacetyl triglycerides in waxy translucent form, the steps which comprise acetylating a mixture comprising glycerol and mixed monoglycerides of high molecular fatty acids, thereby to form a mixture comprising triacetin and triglycerides which contain in their molecular structure both acetyl and high molecular fatty acyl groups; removing triacetin from the product; and isolating a fraction consisting predominantly of mixed symmetrical and unsymmetrical diacetyl triglycerides and being substantially free of triglycerides containing less than two acetyl groups; and chilling said diacetyl triglycerides to below their minimum melting point thereby solidifying them in waxy translucent form of great stability.

13. In the process of preparing high molecular diacetyl triglycerides in waxy translucent form, the steps which comprise contacting a liquid mixture of triacetin and high molecular triglycerides with a rearrangement catalyst to effect molecular rearrangement of acyl groups therein; discontinuing the rearrangement reaction; removing unreacted triacetin from the product; and isolating a fraction consisting predominantly of unsymmetrical diacetyl triglycerides and being substantially free of triglycerides containing less than two acetyl groups; and chilling said diacetyl triglycerides to below their minimum melting point thereby solidifying them in waxy translucent form of great stability.

14. The process of claim 13 wherein the high molecular triglycerides which are mixed with triacetin are substantially saturated fats.

15. The process of claim 13 wherein the high molecular triglycerides which are mixed with triacetin contain unsaturated constituents and wherein at any stage in the process substantially all ethylenic double bonds which are present at that stage are saturated by catalytic hydrogenation.

16. The process of claim 13 wherein unreacted triacetin is removed from the rearranged mixture by fractional distillation under reduced pressure subsequent to discontinuing the rearrangement reaction, and wherein the fraction consisting predominantly of unsymmetrical diacetyl triglycerides is isolated by fractional distillation under reduced pressure subsequent to removal of triacetin.

17. A process of preparing high molecular diacetyl triglycerides in waxy translucent form which comprises contacting a liquid mixture of triacetin and high molecular triglycerides at a temperature below 120° C. with a catalyst which is an alkali metal alkoxide of an aliphatic monohydric alcohol having less than 5 carbon atoms to effect molecular rearrangement of acyl groups in said mixture, the molar ratio of triacetin; high molecular triglycerides being from about 0.75:1 to about 3:1; acidifying the reaction mixture to inactivate the catalyst; removing acidic material and unreacted triacetin from the mixture; isolating a fraction consisting predominantly of unsymmetrical diacetyl triglycerides and being substantially free of triglycerides containing less than two acetyl groups; and chilling said diacetyl triglycerides to below their minimum melting point thereby solidifying them in waxy translucent form of great stability.

18. In the process of preparing high molecular diacetyl triglycerides in waxy translucent form, the steps which comprise contacting a liquid mixture of triacetin and high molecular triglycerides with a low-temperature rearrangement catalyst to effect a substantial degree of molecular rearrangement of acyl groups therein; acidifying the mixture to check the rearrangement reaction; steam distilling the mixture under reduced pressure to remove therefrom materials of boiling point lower than diacetyl triglycerides of high molecular fatty acids; steam distilling the residue under more drastic conditions to remove a fraction consisting predominantly of diacetyl triglycerides of high molecular fatty acids; terminating the distillation before substantial amounts of material of higher boiling point than the said diacetyl triglycerides distill; and chilling the fraction consisting predominantly of diacetyl triglycerides to below its minimum melting point to solidify it in waxy translucent form.

19. In the process of preparing saturated high molecular diacetyl triglycerides in waxy translucent form, the steps which comprise contacting triacetin and high molecular triglycerides in molar proportions of about 0.75:1 to about 3:1 with a low temperature catalyst for molecular rearrangement of glycerides at a temperature below 120° C. but above the melting point of said mixture until substantial molecular rearrangement of acyl groups therein has taken place; adding acid to the rearranged mixture to inactivate the catalyst; fractionally distilling the rearranged mixture under reduced pressure to remove unreacted triacetin therefrom; distilling from the substantially triacetin-free product under more drastic conditions a fraction which is predominantly unsymmetrical diacetyl triglycerides and which contains only minor amounts of triglycerides having less than two acetyl groups, and at any stage in the process, catalytically hydrogenating substantially all ethylenic double bonds which are present; and chilling said diacetyl triglycerides to below their minimum melting point thereby solidifying them in waxy translucent form of great stability.

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