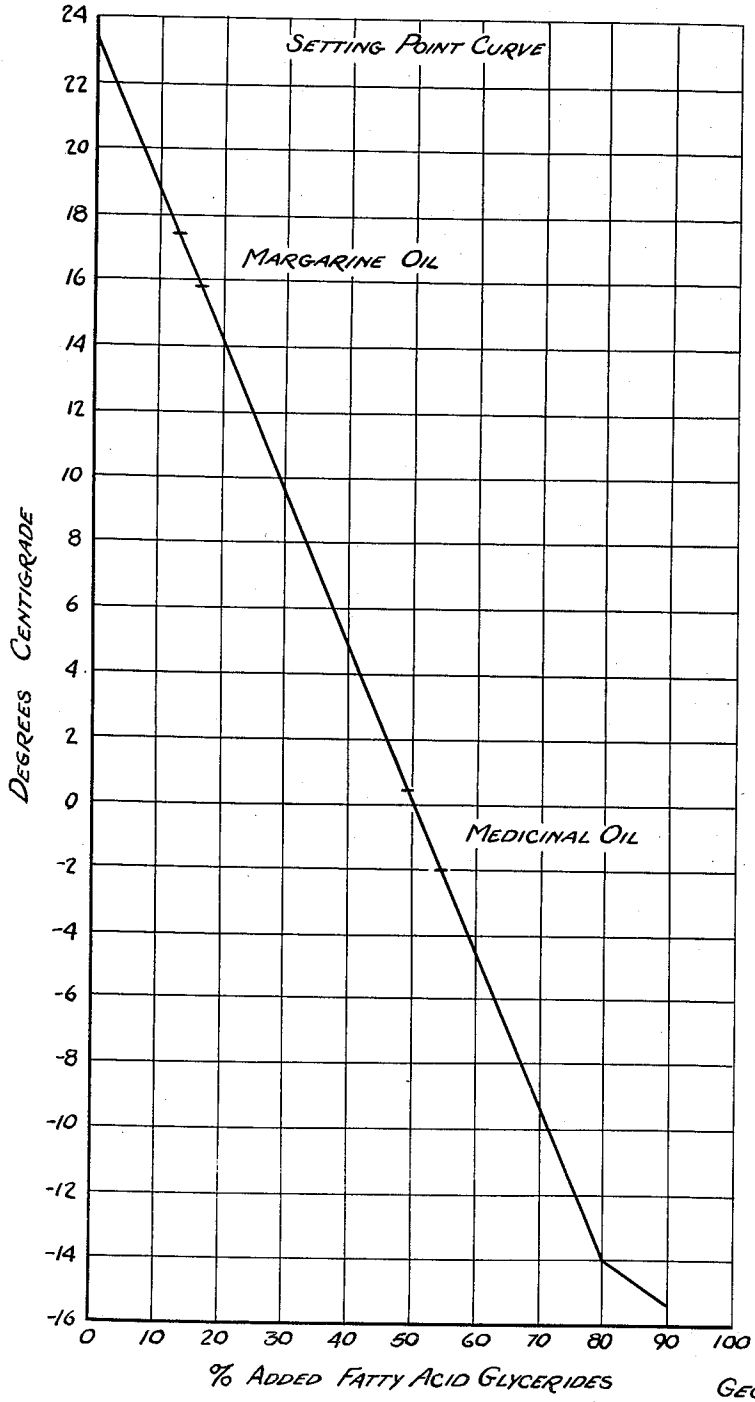
Nov. 24, 1959 G. BARSKY ET AL 2,914,546

INTERESTERIFIED MIXED GLYCERYL ESTERS

Filed May 21, 1956



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United States Patent Office 2,914,546
Patented Nov. 24, 1959

2,914,546

INTERESTERIFIED MIXED GLYCERYL ESTERS

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Application May 21, 1956, Serial No. 586,067

7 Claims. (Cl. 260—410.7)

The present invention relates to the coconut type oil and more particularly to a modified oil having improved properties for edible purposes. This application is a continuation-in-part of co-pending application Serial No. 336,882, filed February 13, 1953, for "Method of Treating Coconut Type Oils and Product Thereof," and now abandoned.

Coconut oil is a low melting fat which is solid at moderate atmospheric temperatures and liquid at high atmospheric temperatures. It is used for edible purposes but because of certain characteristics thereof, it has not gone into extensive use in certain fields. It has a very low melting range which is generally in the neighborhood of 79° F. When solid it is quite brittle and an increase of about 2° F. in temperature causes it to become completely liquid. This temperature range between the brittle and liquid state is termed the plastic range or plastic interval. Because of this it could not used as a salad oil and which is comparable in its solidifi-temperatures and it tended to set even in standing at room temperatures. Also because of the brittleness, it could not be incorporated into various fatty compositions except in very minor amounts.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in the properties of coconut type oil, it being among the objects of the present invention to provide a modified oil which has a relatively wide range of fusibility and wherein the brittleness is substantially eliminated.

It is also among the objects of the present invention to provide a modified coconut type oil which may be used as a salad oil and which is comparable in its solidification characteristics to olive oil.

It is further among the objects of the present invention to provide a composition having an increased plastic range and which is capable of being added in relatively large amounts to such substances as margarine and mayonnaise.

In practicing the present invention there is provided a coconut type oil of which coconut, babassu, cohune, tucum and palm kernel oils are typical. This type of oil is characterized by the presence of substantial amounts of lauric acid in ester form, and is often termed "lauric acid oil." These oils are substantially saturated, containing very little unsaturated fatty acid such as oleic or linoleic. Generally they contain fatty acids having from 6 to 18 carbon atoms with substantial amounts of acids having 8, 10, 12 and 14 carbon atoms.

Such an oil is reacted under suitable conditions with the triglycerides of a mixture of fatty acids (hereinafter called added fatty acids) having 8 and 10 carbon atoms, usually containing not over about 2.5% of fatty acids having 6 and 12 carbon atoms. The amount by weight of such glycerides is usually substantially less than the amount of the oil entering into the reaction. The added fatty acid esters are reacted at elevated temperatures so as to cause rearrangement of the esters to form a larger number of mixed esters than were originally present

in the oil. It has been found that the addition of triglyceride esters of the added fatty acids contained in the coconut type oils such as caproic, caprylic and capric acids has a marked effect in obtaining the desirable properties of the oil as contemplated by the present invention. Mixtures of acids having 8 and 10 carbon atoms in the form of their glycerides may be used. Such added acids may be reacted as such with the coconut type oil provided that a sufficient amount of glycerine is introduced into the reaction to form a substantially neutral oil as an end product.

The accompanying drawing is a chart showing the various characteristics of oils modified in accordance with the present invention. As will be seen, the various proportions of added fatty acid glycerides reacted with the coconut type oils may be used for various purposes. Those oils containing between 10% and 20% of the added fatty acid glycerides are excellent margarine oils and those containing about 45% to 55% of the added fatty acid glycerides constitute excellent medicinal oils.

The added fatty acids in the above referred to glycerides have approximately the following characteristics:

F.F.A.	185±3
Unsap.	1.0 max.
Percent caproic	1–1.5
Percent caprylic	65–75
Percent capric	25–35
Percent lauric	1–2.5

The glycerine used for esterification of such a mixture of fatty acids is preferably the chemically pure glycerine currently on the market.

The following are specific examples of the operation of the present invention:

Example 1

A mixture is made of the following constituents:

200 gm. coconut oil
50 gm. capric-caprylic triglyceride
9 gm. $NaOCH_3$ (8.4%) suspension in xylene

The sodium methylate is a catalyst for the reaction, causing rearrangement of the molecules and xylene is used as the carrier.

The mixture is agitated and heated to a temperature of 55° to 57° C. for about 1½ hours, while passing nitrogen through the reaction mixture to cause the agitation and to provide a blanket of inert gas, thus avoiding darkening of the final product.

After the reaction is complete, there is added 20 grams of a dilute hydrochloric acid solution in water containing 10% of said acid. This decomposes the catalyst and neutralizes the product. It is then washed with water to remove any water soluble or decomposition products which may be present, after which it is subjected to deodorization with steam at a temperature of about 175° C. with a vacuum of about 8 to 9 mm. It is then treated with activated charcoal and filtered. The product has a setting point of 15.2° C. as compared with 20.4° C. of the coconut oil used. The plastic range of the product is 5°–6° F. as compared to 2° F. of the starting material.

Example 2

The first step consists in the preparation of the triglyceride of a mixture of added fatty acids. The mixture consists essentially of 85% of caprylic acid and 15 parts of capric acid. Into a closed kettle is introduced 84.6% of the mixture of caprylic and capric acids and 15.4% of C. P. glycerine. In the glycerine there is dissolved .15% of a catalyst, which is usually zinc dust. The esterification is carried out in the usual manner,

maintaining the temperature at about 220° C. During the esterification, a vacuum of 10 to 20 inches of mercury is used in order to draw off water vapors generated in the reaction. As the esterification progresses, the vacuum is increased to about 22 to 25 inches of mercury. When the free fatty acid number drops below 10, the free fatty acids are stripped off to as low a content as practical. The resulting product is bleached and filtered and it has approximately the following analysis:

Color	70/10 max.
F.F.A.	0.2.
Sap. No	355.
I.V.	1.0.
Acetyl No	5.0.

For the preparation of the interesterified product, a mixture is made of a coconut oil having a melting point of 76° F. with an equal weight of the triglycerides of the added fatty acids. .3% of sodium methylate is used as the catalyst. The mixture was dried at 110° C. under a vacuum and cooled to 55° C. The sodium methylate was then added with agitation and the temperature was maintained at 55° to 60° C. for 1½ hours. The reacted mass was then neutralized with concentrated phosphoric acid. The product was refined, washed with caustic soda, then with water, deodorized, bleached and filtered. The finished product had the following characteristics:

Color	6.0/0.4
F.F.A.	0.04
I.V.	5.6
Specific gravity at 120° F	0.917
Refractive index at 60° C	1.4352
Setting point ° C	—2.0
Sap. No	300
Acetyl No	5.0

Example 3

In order to produce the triglycerides of the added fatty acids, the following mixture was used:

Percent caproic acid	1.02
Percent caprylic acid	66.34
Percent capric acid	30.18
Percent lauric acid	2.46

Esterification was conducted as set forth in Example 2 and the triglycerides of the added fatty acid so obtained had the following characteristics:

Color	7.2/1.0.
F.F.A	0.15.
I.V	1.0.
Sap. No	342.0.
Acetyl No	3.3.
Unsaponifiables	0.15 percent (by weight).

A mixture was made of 55% of the above described ester with 45% of coconut oil and interesterification was conducted as set forth in Example 2. The product had the following characteristics:

Color	8.2/1.9.
F.F.A	0.04.
Flavor	A.
S.P	—2.6.
I.V	5.4.
Sap. No	302.2.
Acetyl No	10.2.
Swift	150 hrs.
Peroxide No	0.1.
Kreis	Negative.

Example 4

The added fatty acid mixture had the following composition:

	Percent
Caproic acid	0.88
Caprylic acid	68.76
Capric acid	28.17
Lauric acid	2.19

It was esterified as set forth in Example 2, to form the triglycerides of the added fatty acids, which had the following characteristics:

Color	70.0/6.4 max.
F.F.A	0.8.
Sap. No	346.2.
Acetyl No	1.1.
S.P	—7.8° C.

In the interesterification, a mixture of the above triglycerides and coconut oil in the ratio of 60 to 40 was used. The interesterification was conducted as set forth in Example 2 and the product had the following characteristics:

Color	8.0/1.4.
F.F.A	0.015.
Flavor	A—.
Sap. No	306.5.
Acetyl No	7.1.
I.V	6.3.
Peroxide No	0.1.
Kreis test	Negative.
Swift test	152 hours.
Setting point	—2.5° C.

The procedure may be modified in several respects and the compositions may be altered to obtain specific properties in the final products. Also, the products may be treated to modify them in order to adapt them for special purposes. For instance, the products of the present invention may be subjected to winterization to provide an oil, for use as salad oil or other purposes, which have quite low setting points. The solid residue is adapted for use for various edible purposes. The temperatures necessary for such winterization are not extremely low, so that only a moderate amount of refrigeration is utilized. The following is a specific example of such a modification.

Example 5

The product as obtained in Example 2 is subjected to reduced temperatures for an extended period of time in order to winterize the material. It is held at a temperature of about 50° to 55° F. for a period of about 48 hours. The crystallized portion is filtered off, whereby the setting point thereof is reduced to about 6° C. by the removal of about 20% of the product by filtration.

It is also possible to treat any of the other products described above in a similar manner, as for instance, the product of Example 4. It is held at a temperature of 50° F. for about four days, causing crystallization of about 25% of the constituents. This is filtered off and the resulting oil has a setting point of about 2° C. In a similar manner, the products may be cooled to lower temperatures or for longer periods of time, or both, so as to crystallize more or less of the glycerides present in order to obtain a liquid product having a predetermined setting point.

The oils modified in accordance with the present invention may be used alone as salad oils or in mayonnaise. They also may be used in admixture with other edible oils for these purposes. Products made with coconut oil treated as herein described do not show the brittleness of the unmodified coconut oil, especially at refrigerator temperatures. The properties thereof as far as plasticity is concerned, are very similar to those of butter.

Example 6

The following composition is provided:

700 g. coconut oil
700 g. SC triglyceride
50 g. $NaOCH_3$ (8.4%) suspension in xylene

The SC triglyceride is an example of the neutral glycerides of acids having the following composition:

	Parts
Caproic	0.5 to 5
Caprylic	60 to 70
Capric	25 to 35

The composition is placed in a suitable flask, provided with mechanical agitation and nitrogen gas is passed into the flask to act as a blanket and prevent access of air. The constituents of the composition are substantially free from moisture and usually are first dried under vacuum before the catalyst is added.

The mixture is heated for about 1½ hours at a temperature of 55° to 57° C. to complete the reaction. Thereafter 50 grams of an aqueous 10° solution of hydrochloric acid is added with stirring, in order to decompose the catalyst. The product is washed with water until it is substantially free from acid. It is then dried, bleached and deodorized, as is common in the art.

The setting point of the coconut oil used in the reaction is about 22° C. The setting point of the modified product is about −6° C. It is liquid under all ordinary conditions of temperature, even down to the freezing point of water.

The product has good keeping qualities as it does not tend to become rancid or to oxidize on standing at room temperatures. It has a pleasant taste and an agreeable aroma. In various operations, both in the manufacture of products therefrom and in the use in the kitchen, it is easier to handle such as in measuring or weighing, and in transferring from one receptacle to another.

While the invention has been described in connection with several specific examples illustrating the use of triglycerides of added fatty acids, preferably of those having 8 and 10 carbon atoms in certain proportions, the ratios of these acids may be varied and they may contain minor amounts of other acids, such as caproic and lauric. Such acids are found in coconut oil and the addition of such acids in the form of their glycerides to modify said oil does not introduce any foreign constituent. The product is fully edible and digestible and the properties thereof are equivalent to the best olive oil for food purposes.

The above examples illustrate only some of the compositions which may be made by following the procedures such as set forth herein. As shown in the accompanying drawing, still other products may be obtained by varying the proportions of the coconut type oil and the added fatty acid triglycerides. The margarine base oil shown on the drawing has the following characteristics:

M.P., w	° F.	77–78
I.F.	° F.	61–62
M.P., cc.	° F.	78–79
Set. pt.	° C.	16–17
Sap. No.		260–270

When compounded with suitable gelling and thickening agents, the finished margarine will show excellent spreading characteristics at all refrigerator temperatures and show good body at the elevated temperatures encountered in the kitchen.

The medicinal oil shown on the drawing has the following characteristics:

Set. pt.	° C.	0 to −2
Sap. No.		296–305
Sp. gr. at 120° F.		0.9170

The added fatty acids used in making the compositions shown in the drawing consisted of about 85% of caprylic acid and about 15% of capric acid.

The coconut oil or equivalent oil of the coconut type, may be modified with the glyceride of one of the acids having 6, 8 and 10 carbon atoms or mixtures of two of such acids or of all three acids. The amount, proportions and character of the added fatty acids used in the reaction are dependent upon the properties of the final product desired.

It has been proposed to treat fats having a relatively high iodine number of about 60 to 77 triacetin to increase the plastic range thereof, but such modified fats are often solid at room temperatures. In the present process substantially saturated oils are used, in which the iodine number is usually below 10 and practically never above 15–20, and which at room temperatures are solid but which melt at slightly higher temperatures. The coconut type oils have practically no plastic range and by the present invention the oils are so modified as to exhibit a substantial plastic range, in addition to the lowering of the setting point in a critical range of temperatures whereby even liquid oils at all room and refrigeration temperatures are obtained.

The amount of added fatty acid glyceride used in the operation varies in accordance with the desired characteristics of the final product. About 5% to 100% of said glyceride based on the weight of the oil is used, and the proportion is dependent on the number of carbon atoms in the added fatty acids, as well as the melting point and plastic range of the product. In conducting the operation various temperatures may be used up to about 200° to 220° C. or even higher. The capric-caprylic acids of Example 1 may contain small amounts of caproic and lauric acids, and the caprylic acid is usually substantially greater in amount than the capric acid. The added triglycerides may be replaced by equivalent quantities of the added fatty acids or by the mono- or diglycerides of the added fatty acids, and sufficient glycerine to form the triglycerides therefrom.

The procedure in the manufacture of the products may be varied. For instance, other catalysts than those specifically described may be used. The conditions of the reaction, such as time, temperature and proportions of reactants, may be those best suited for the particular product.

What is claimed is:

1. The interesterified mixed esters constituting reaction products of an oil of the coconut type with a mixture of capric and caprylic acid triglycerides in an amount of about 5–100 parts by weight based on 100 parts of said coconut oil, said products having a plastic interval of about 5°–15° F. and a setting point substantially below that of said coconut oil.

2. The interesterified mixed esters constituting reaction products of an oil of the coconut type with a mixture of capric and caprylic acid triglycerides in an amount of about 35–45 parts by weight based on 100 parts of said coconut oil, said products having a plastic interval of about 5°–15° F. and a setting point of about 2°–6° C.

3. The interesterified mixed esters constituting reaction products of an oil of the coconut type with a mixture of capric and caprylic acid triglycerides in an amount of about 10–100 parts by weight based on 100 parts of said coconut oil, said products having a plastic interval of about 5°–15° F. and a setting point of below 19° C.

4. The interesterified mixed esters constituting reaction products of an oil of the coconut type with a mixture of capric and caprylic acid triglycerides in an amount of about 45–55 parts by weight based on 100 parts of said coconut oil, said products having a plastic interval of about 5°–15° F. and a setting point of about 0° to −2° C.

5. The interesterified mixed esters constituting reac-

tion products of coconut type oil with the triglycerides of a mixture of lower fatty acids having about the following composition:

	Percent
Caprylic	65–75
Capric	35–25

in amount of about 5–100 parts by weight based on 100 parts of said coconut oil.

6. The interesterified mixed esters constituting reaction products of coconut type oil with the triglycerides of a mixture of lower fatty acids having about the following composition:

	Percent (by weight)
Caprylic	85
Capric	15

in amount of about 10–20 parts by weight of said triglycerides based on 100 parts of said coconut oil.

7. The interesterified mixed esters constituting reaction

products of coconut type oil with the triglycerides of a mixture of lower fatty acids having about the following composition:

	Percent (by weight)
Caprylic	85
Capric	15

in amount of about 45–55 parts by weight of said triglycerides based on 100 parts of said coconut oil.

References Cited in the file of this patent

UNITED STATES PATENTS

1,505,560	Grun	Aug. 19, 1924
1,873,513	Van Loon	Aug. 23, 1932
2,309,949	Gooding	Feb. 2, 1943
2,442,532	Eckey	June 1, 1948
2,558,547	Eckey	June 26, 1951
2,808,421	Brokaw	Oct. 1, 1957