United States Patent Office 3,367,782 Patented Feb. 6, 1968

3,367,782

STABILIZATION OF SALAD OILS

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No Drawing. Filed July 31, 1964, Ser. No. 386,771
7 Claims. (Cl. 99—118)

ABSTRACT OF THE DISCLOSURE

Salad oil containing, as an inhibitor of stearin deposition, 0.001–1% of 3,3,5,5-tetrakis-(hydroxy-methyl)-4-hydroxy-tetrahydropyran, esterified with C_{14}–C_{22} fatty acids, C_{28}–C_{44} dimerized fatty acids, C_{14}–C_{22} hydroxy fatty acids with 1–8 hydroxyl groups, and mixtures of such acids. The molar ratio of straight chain saturated fatty acids to other fatty acids is at least 0.25:1.

This invention relates to improved salad oils and to a method of improving salad oils. More particularly, this invention relates to the addition of fatty esters of 3,3,5,5-tetrakis(hydroxy - methyl)-4-hydroxy-tetrahydropyran to salad oils to retard the deposition of stearin crystals and other high melting solids at low temperatures.

Various vegetable oils such as cottonseed, corn, and soybean oil are frequently used as salad oils. These oils are composed principally of a mixture of glycerides of fatty acids, some of which are normally solid and some of which are normally liquid at ordinary room temperatures. Normally solid glycerides may be entrained or dissolved in the oils which are normally liquid at ordinary temperatures, but tend to separate from the oils as solids or to produce colloidal dispersions during prolonged storage of the oil, particularly at refrigeration temperatures, such as from about 40° F. to about 50° F. Tristearin is probably the most prevalent of these normally solid glycerides, but the term "stearin" when used herein also includes the other normally high melting solid substances present in the oils which tend to separate on cooling to refrigeration temperatures or during prolonged standing at ordinary room temperature.

It has become a common commercial practice to subject vegetable oil stock, which contains both the liquid oils most suitable for use as salad oils and solid fats, to "winterization" treatment, such as fractional crystallization, to achieve a separation of a portion of the normally solid constituents. In general, however, commercial winterization of vegetable oils is ineffective for achieving complete separation of stearin from the oil. A substantial proportion of stearin remains in the salad oil, and this remaining stearin frequently imparts an undesirable cloudy or grainy appearance to the oil, particularly after prolonged storage periods at low temperatures.

Accordingly, it is an object of this invention to provide a method for retarding the deposition of stearin from salad oils, and especially from winterized oils from which the stearin has been partially removed by fractional crystallization.

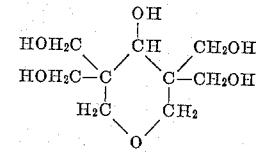
It is a further object of this invention to provide novel clear glyceride salad oils having superior resistance to deposition of stearin, particularly at low temperatures such as ordinary refrigeration temperatures of about 40° F. to about 50° F.

The above and other objects are achieved with the present invention by dissolving in a clear glyceride salad oil from about 0.001% to about 1%, by weight, of a salad oil crystallization inhibitor which consists of at least one ester of 3,3,5,5 - tetrakis(hydroxy-methyl)-4-hydroxy-tetrahydropyran. The 3,3,5,5 - tetrakis(hydroxy - methyl)-4-hydroxy-tetrahydropyran should be esterified to a degree of

at least 50% with fatty acid material selected from the group consisting of compounds containing fatty acid radicals having from about 14 to about 22 carbon atoms, dimerized fatty acid radicals having from about 28 to about 44 carbon atoms, hydroxy fatty acid radicals having from about 14 to about 22 carbon atoms and from 1 to about 8 hydroxyl groups, and mixtures thereof, the molar ratio of straight chain saturated to other fatty acid radicals in the ester being at least about 0.25:1. As used herein, the term "fatty acid material" refers to acylating agents capable of supplying the above-mentioned fatty acid radicals to the esterification reaction.

The salad oil crystallization inhibitor of this invention is prepared by esterification of 3,3,5,5-tetrakis(hydroxymethyl)-4-hydroxy-tetrahydropyran with suitable fatty acid material as herein described. The 3,3,5,5-tetrakis-(hydroxy-methyl)-4-hydroxy-tetrahydropyran, also known as anhydroenneaheptitol (AEH), is a heterocyclic polyol produced by the aldol condensation of acetone and formaldehyde. Suitable methods of preparation of the condensation product are described by Wittcoff, U.S. Patent 2,462,031, and by Robeson, U.S. Patent 2,885,408.

The anhydrous, pure compound is a white, crystalline solid with a molecular weight of 222.1, a hydroxyl content of 38.3%, and a melting point of 156° C. It has the following structural formula:



The 3,3,5, - tetrakis(hydroxy - methyl) - 4 - hydroxy-tetrahydropyran which was used in the specific examples set forth hereinafter was obtained as a 70% solution in water. The commercial product is available as a water solution primarily for convenience of handling. Prior to the preparation of the esters used in the salad oil of this invention, the water solution of 3,3,5,5-tetrakis(hydroxymethyl)-4-hydroxy-tetrahydropyran is pre-dried under solvent reflux in order to remove the water, such as by azeotropic distillation, for example, in the presence of solvents such as benzene, toluene, or cyclohexane, by conventional methods well known to those skilled in the art.

Either complete or partial esters can be prepared from the 3,3,5,5 - tetrakis(hydroxy-methyl) - 4 - hydroxy-tetrahydropyran by conventional esterification methods well known to those skilled in the art. Both the complete and partial esters are preferably prepared by acylation with a suitable acyl chloride in the presence of solubilizers, such as dimethylformamide and pyridine, or by an alkali-catalyzed interesterification with methyl esters of suitable fatty acid material.

In the acylation method with acyl chloride, the final ester product is preferably washed in hexane and then recovered from the hexane. In the interesterification method, methanol is preferably removed from the reaction under slow distillation or by azeotroping with cyclohexane. After the solvents are removed, the mixture is preferably held at about 100° C.–125° C. under vacuum for about an hour. The product is then preferably washed in solvent such as, for example, a mixture of about four parts ethyl acetate to one part butanol. The excess methyl esters are deodorized out of the reaction mixture or extracted by ethanol from the desired ester product.

Other suitable methods of preparation of the esters used in the salad oil of this invention are described by Wittcoff, U.S. Patents 2,480,347–8 and 2,590,911.

Although specific methods for the preparation of the esters used in the salad oil of this invention are described

herein, it will be understood that the method of esterification is not part of the invention and other suitable methods of esterification will be readily apparent to those skilled in the art to which the invention appertains.

Specific examples of the saturated and unsaturated fatty acid materials which can be used to esterify the 3,3,5,5-tetrakis(hydroxy-methyl) - 4 - hydroxy-tetrahydropyran in the practice of this invention are derivatives of the higher or so-called "long-chain" fatty acids such as palmitic, oleic, and stearic acids; dimerized fatty acids such as dimerized oleic, linoleic and erucic acids; and hydroxy fatty acids such as 12-hydroxystearic, 9,10,12,13-tetrahydroxystearic, and ricinoleic acids. Mixtures of the above fatty acid materials can be used and a mixture of the acid material derived from palmitic and oleic acids is preferred. In the use of any of the above fatty acid materials for preparation of the esters used in the clear glyceride salad oil of this invention, it is essential that the molar ratio of the saturated on the one hand to the unsaturated, dimerized, or hydroxy fatty acid material on the other be at least about 0.25:1. That is, at least about one-fourth of the fatty material in the ester should be derived from saturated straight chain fatty material.

Subject to the above limitation that the 3,3,5,5-tetrakis-(hydroxy - methyl) - 4 - hydroxy - tetrahydropyran be esterified to a degree of at least 50% with one or more of the aforementioned fatty acid materials in the above proportions, the esters used in the salad oil of this invention can also contain, in part, combined short chain fatty acids, such as those having from 2 to about 6 carbon atoms, for example, acetic and propionic acids.

A wide variety of oils can be used as salad oils which can be made resistant to deposition of stearin at low temperatures and during prolonged storage at ordinary room temperatures in accordance with this invention. Included among suitable salad oils are the so-called natural salad oils such as, for example, olive oil, sunflower seed oil, safflower oil, and sesame seed oil.

Oils, for example, such as cottonseed oil and corn oil, preferably are given a preliminary "winterizing," dewaxing, or similar other treatment, such as described hereinbefore, to remove stearin to form a good base salad oil.

Other oils, such as soybean oil, may preferably be hydrogenated to improve resistance to oxidative deterioration with prolonged storage, and the higher melting glycerides formed during this hydrogenation treatment are preferably removed by winterization in order to form a suitable base salad oil.

Base salad oils also can be formed by directed, low temperature interesterification or rearrangement of animal or vegetable fatty material, followed by removal of higher melting solids formed during the reaction. See, for example, U.S. Patent 2,442,532, granted to E. W. Eckey, June 1, 1948.

Another group of oils suitable for salad oils includes those in which one or more "short-chain" or lower fatty acids having from 2 to about 6 carbon atoms, such as acetic and propionic acids, replace, in part, the long-chain or higher fatty acids present in natural triglyceride oils.

Other base salad oils will suggest themselves to those skilled in the art, and these will be acceptable for practicing the present invention provided they have a suitable chill test as hereinafter defined. These base salad oils are generally obtained from animal, vegetable or marine fats and oils and can be used individually or as mixtures of oils. As used herein, the term "base salad oil" is intended to include any salad oil which will not immediately form solids when cooled to 30° F.

The procedure for measuring the resistance of salad oils to clouding and the crystallization inhibiting activity of the esters in the salad oils as used hereinafter involves preheating the sample to a temperature of about 140° F., then cooling in air to about 30° F., and holding at that temperature until solids form in the sample. As used herein, the term "chill test" is intended to define the total length of time elapsed during the cooling and until such solids form. Although the 30° F. temperature used in the standard chill test is lower than the normal refrigeration temperatures of about 40° F. to about 50° F., the use of the 30° F. temperature is common and accepted practice for obtaining results more quickly and under conditions more rigorous than normal. The correlation between the results at 30° F. and the higher normal refrigeration temperatures is very good.

The ester and the base salad oil can be mixed together in any convenient manner. For example, ester in liquid form can be mixed with the oil. If the ester is in solid form, it can be dissolved in the oil, although it may be desirable to heat the oil or the mixture of the oil and ester to facilitate solution. The resulting mixture of the crystallization inhibitor and the base salad oil is a physical mixture; there has been no observed chemical reaction between the ester and the oil. In order to insure clarity of the salad oil of this invention, the mixture of crystallization inhibitor and base salad oil should be kept free of moisture, alkaline agents, or any substances which might initiate either the formation of an opaque colloid or the precipitation of crystalline solids.

The following examples will serve to further illustrate the invention, although the invention is not limited by these examples. After reading the specification and claims appended hereto, the skilled artisan will be able to devise may other examples which illustrate this invention. In these examples, several types of "complete" esters are prepared. In Example 1, a pentapalmitate is prepared. In Example 2, a complete ester is prepared in which the fatty material of the ester consists of palmitic and oleic acids in a molar ratio of about 1:1. In Examples 3 and 4, complete esters are prepared in which the fatty material of the esters consists of palmitic and oleic acids in molar ratios of about 3:1. In Example 5, a complete ester is formed in which the fatty material consists of palmitic and 12-hydroxystearic acids in a molar ratio of about 3:2.

In Examples 1 and 2, the esters are prepared by acylation with the appropriate acyl chloride in the presence of dimethylformamide and pyridine. In Examples 3 and 4, the esters are formed by an alkali-catalyzed interesterification with the appropriate methyl and ethyl esters. In Example 5, the ester is formed by direct esterification with the appropriate acid and acyl chloride. Other conventional esterification methods well known to those skilled in the art can be substituted for the methods illustrated in these examples with substantially equivalent results.

Example 1

Twenty-seven grams of a 70% solution of 3,3,5,5-tetrakis(hydroxy-methyl) - 4 - hydroxy - tetrahydropyran in water is refluxed with stirring in 100 cc. benzene until 7½ cc. of water is removed in a trap. The mixture is then refluxed with 100 grams of palmitoyl chloride in the presence of 50 cc. pyridine. The reaction proceeds rapidly and is allowed to stand at ordinary room temperature (ca. 70° F.) for 12 hours without the addition or removal of external heat. The product is water washed in hexane solution and recovered, and then extracted with ethanol and recovered.

Example 2

Twenty-six and one-half grams of a 70% solution of 3,3,5,5 - tetrakis(hydroxy - methyl) - 4 - hydroxy - tetrahydropyran in water is refluxed with 100 cc. cyclohexane until 5 cc. of water is removed. Then 50 cc. of dimethylformamide is added and distillation is continued until another 6½ cc. of water is removed. To the mixture is added 37.4 grams of palmitoyl chloride, 41.0 grams of oleoyl chloride, and 50 cc. of pyridine, the amounts of both acyl chlorides being equivalent to a 20% excess. The reaction proceeds for a 5-hour period at a temperature of about

35°–60° C. The product is washed in hexane and recovered.

Example 3

Twenty grams of a 70% solution of 3,3,5,5-tetrakis (hydroxy-methyl)-4-hydroxy-tetrahydropyran in water is refluxed in 100 cc. of toluene to remove 5.8 cc. of water. Then 50 cc. of dimethylformamide is added to solubilize the mixture. Twenty-six grams of ethyl oleate and 70 grams of methyl palmitate are added, and to this mixture is added 0.5 gram of metallic NaK catalyst. The mixture is maintained at 110°–125° C. for about one hour to distill off toluene and alcohols formed during the reaction. To the reaction product is added 50 cc. cyclohexane to promote further removal of alcohols by distillation at about 100° C. The product is then washed with water in hexane and recovered. The recovered product is heated to 200° C. under 1–2 mm. pressure with nitrogen agitation to distill off excess methyl esters and is then further purified by extraction with ethanol.

Example 4

Example 3 is substantially repeated except that: the initial drying of the 70% solution of 3,3,5,5-tetrakis(hydroxy-methyl)-4-hydroxy-tetrahydropyran in water is conducted in cyclohexane instead of toluene; 5 cc. of "Triton B" (40% benzyl trimethyl ammonium hydroxide in methanol) is used as catalyst instead of 0.5 gram of metallic NaK; 100 cc. instead of 50 cc. of dimethylformamide is used as a solubilizer; and solvent distillation is conducted at 95°–110° C. for a period of 4 hours with final heating at 210° C. under 1–2 mm. pressure with nitrogen agitation to distill off excess methyl esters.

Example 5

Thirty-one grams of a 70% solution of 3,3,5,5-tetrakis (hydroxy-methyl)-4-hydroxy-tetrahydropyran in water is refluxed in toluene until 8.7 cc. of water is removed. Fifty-six grams of 12-hydroxystearic acid is then refluxed with the dried material in the presence of 0.5 gram of p-toluene sulfonic acid catalyst at 115°–150° C. and in the presence of 100 cc. dimethylformamide solvent with removal of H_2O of reaction in a trap. After reaction for 2½ hours, another 0.5 gram of catalyst is added and refluxing with further removal of H_2O at reaction continues for another half hour. Then 90 grams of palmitic acid is added to the reaction along with another 0.5 gram of catalyst and distillation proceeds at 150° C. to remove the toluene. Another portion of 0.5 gram of catalyst is added and distillation is continued for another 3 hours. To the reaction mixture, cooled and maintained at approximately 25° C. is then added 50 cc. of pyridine and a total of 150 grams of palmitoyl chloride, the latter being added in small portions until no further temperature rise due to reaction is observed. The product is water washed in hexane. The product is heated to 225° C. under 1–2 mm. pressure with nitrogen agitation to distill off excess fatty acids. The final product is obtained by twice extracting with ethanol at 21° C. to eliminate ethanol-soluble components, then heating on the steam bath at 1–2 minutes to remove ethanol.

The analytical values which were obtained for the final product in the above specific examples is set forth in the following table:

TABLE I

Example No.	Acid Value	Saponification Value	Hydroxyl Value	Percent Total Fatty Acid	Iodine Value
1	0.9	185	11	87.9	(1)
2	0.7	184	23	83.2	36.2
3	0.3	176	33	83.3	21.7
4	0.1	202	60	80.2	19.2
5	9.4	199	10.5	91.3	(1)

[1] Not ascertained.

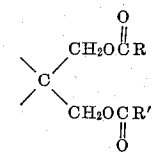
The crystallization inhibition properties of the above esters are set forth in Table II below. In each case, the ester is dissolved in a base salad oil consisting of 90% winterized cottonseed oil (refined and bleached liquid oil) and 10% cottonseed oil (refined and bleached liquid oil) and held at 30° F. until solids appear in the salad oil. By way of comparison, the base salad oil without the crystal inhibitor, which is used fo rstandard control purposes, had a chill test of 12 hours.

TABLE II

Example No.	Concentration of Ester in Weight Percent	Chill Test (hours)
1	0.1	100
1	0.3	210
2	0.1	ca. 100
2	0.3	ca. 250
3	0.001	19
3	0.01	52
3	0.1	528
3	0.3	ca. 1,440
4	0.001	19
4	0.01	52
4	0.1	365
4	0.3	528
5	0.001	19
5	0.01	52
5	0.1	365
5	0.3	528

When 55 grams of stearoyl chloride is substituted for the 100 grams of palmitoyl chloride in Example 1 and when an equivalent amount of dimerized oleic acid is substituted for 12-hydroxystearic acid in Example 5, esters are produced which markedly improve the chill test of salad oils when used in the range of 0.01% to 1% concentration. When refined, bleached, and partially hydrogenated soybean oil having an iodine value of about 107 is substituted for the mixture of cottonseed and winterized cottonseed oil in the above examples, improvements in chill test of substantially the same order are observed.

Although it is not desired to be bound by theory, it is believed that the crystallization inhibition properties of the 3,3,5,5-tetrakis(hydroxy-methyl)-4-hydroxy-tetrahydropyran esters in salad oils is attributable, in part, to the unique heterocyclic ring configuration and to the branched carbon chain structural group



in which R and R' are radicals derived from suitable fatty material hereinbefore defined. It is noted that the ring configuration in the esters used in the salad oils of this invention, by requiring a compact geometry, must bring all molecular parts close together, and this apparently contributes to interference with deposition of substrate molecules in the salad oil. It is also noted in the ring configuration in the esters used in the salad oil of this invention that glycol configuration is completely absent. The ability to obtain excellent crystallization inhibition with esters which have no glycol configuration is unexpected since a glycol structural arrangement usually is associated with those esters which have previously been disclosed to have high crystallization inhibition potency as noted, for example, with many of the compounds, such as the esters of sorbitol, mannitol, and erythritol, described in U. S. Patent 2,266,591, granted to Eckey and Lutton, Dec. 16, 1941.

It is also noted that maximum inhibiting power with the esters of this invention is achieved with an intermediate adsorbability (or insolubility) of the 3,3,5,5-tetrakis(hydroxymethyl) - 4 - hydroxy - tetrahydropyran esters. Thus, for example, the 3:1 mixed palmitoyl-oleate

ester is preferred to either the straight palmitate ester, which is relatively insoluble, or the 1:1 mixed palmitoyl-oleate ester, which is relatively soluble and not as adsorbable as the preferred ester.

If too large an amount of inhibitor is present in the salad oils of this invention, it will be precipitated out of the oil as the sample is cooled, and possibly even promote crystallization of high melting solids in the oil. Moreover, amounts of ester in excess of about 1%, by weight, are usually unnecessary as affording no significant added crystallization inhibition improvement to the oil. Too small an amount of inhibitor such as less than about 0.001%, by weight, will be relatively ineffective. It is preferred to use from about 0.05% to about 0.5%. It is also preferred to use a substantially complete ester of 3,3,5,5 - tetrakis(hydroxy - methyl) - 4 - hydroxy - tetrahydropyran, the fatty acids of which are palmitic and oleic in proportions of about 3:1, respectively.

What is claimed is:

1. A clear glyceride salad oil having improved resistance to deposition of stearin at refrigeration temperatures of about 40° F. to about 50° F. comprising a base salad oil having dissolved therein from about 0.001% to about 1%, by weight, of at least one ester of 3,3,5,5-tetrakis(hydroxymethyl) - 4 - hydroxy - tetrahydropyran, substantially completely esterified with fatty acid material selected from the group consisting of compounds containing long-chain fatty acid radicals having from about 14 to 22 carbon atoms, dimerized long-chain fatty acid radicals having from about 28 to about 44 carbon atoms, hydroxy fatty acid radicals having from about 14 to about 22 carbon atoms and from 1 to about 8 hydroxyl groups, and mixtures thereof, the molar ratio of straight chain saturated to other fatty acid radicals in the ester being at least about 0.25:1.

2. The clear glyceride salad oil of claim 1 in which the fatty acid material of the ester is a mixture of palmitic and oleic acids.

3. A clear glyceride salad oil having improved resistance to deposition of stearin at refrigeration temperatures of about 40° F. to about 50° F. comprising a base salad oil having dissolved therein from about 0.001% to about 1%, by weight, of at least one ester of 3,3,5,5-tetrakis(hydroxymethyl) - 4 - hydroxy - tetrahydropyran, substantially completely esterified with a mixture of palmitic and oleic acids in a ratio of about 3:1, respectively.

4. The clear glyceride salad oil of claim 1 in which the base salad oil is derived from winterized cottonseed oil.

5. The clear glyceride salad oil of claim 1 in which the base salad oil is derived from partially hydrogenated soybean oil.

6. The clear glyceride salad oil of claim 1 in which the ester is present in an amount of from about 0.05% to about 0.5% by weight.

7. A clear glyceride salad oil having improved resistance to deposition of stearin at refrigeration temperatures of about 40° F. to about 50° F. comprising a base salad oil having dissolved therein from about 0.05% to about 0.5%, by weight, of an ester of 3,3,5,5-tetrakis (hydroxy - methyl) - 4 - hydroxy - tetrahydropyran, substantially completely esterified with a mixture of palmitic and oleic acids in a ratio of about 3:1, respectively.

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