The present invention relates to a process for the preparation of a monoester of glycerine with a higher fatty acid containing from 16 to 18 carbon atoms. It has previously been proposed to prepare higher fatty acid monoglyceride esters by reacting glycerine with \( \text{C}_{16-18} \) higher fatty acids or with glycerol esters of such fatty acids by a process similar to that described for the production of triacylglycerides by the reaction of glycerol with higher fatty acids. The prior art suggests the use of excess glycerine in amounts of from 5 to about 15 moles per mole of fatty acylating agent in carrying out this process in order to favor the formation of monoglyceride esters in preference to diglyceride esters. Nevertheless, in the case of acylating agents having higher fatty acids of 16 to 18 carbon atoms, the product obtained according to the prior art process is usually characterized by a glycerol monostearate content of a maximum of about 60% or less, a diester content on the order of about 35%, and a triester content of about 5%.

The present process enables the preparation of glycerol monoesters of higher fatty acids containing from 16 to 18 carbon atoms by direct reaction between glycerine and an acylating agent such as a higher fatty acid, fatty acid diglyceride, or fatty acid triglyceride, to produce a fatty acid monoglyceride of high purity, i.e., containing at least 85% monoester and not more than about 15% of diester.

In accordance with the present invention, a process for the preparation of a higher fatty acid monoglyceride comprises commingling and reacting an acylating agent containing a fatty acid radical having from 16 to 18 carbon atoms with glycerine at a temperature of at least about 270° C. to form higher fatty acid monoglyceride, said glycerine being employed in excess of the stoichiometric amount required to form glycerol monostearate of said fatty acid radical, said higher fatty acid monoglyceride being dissolved completely in said excess glycerine to form a solution therein, cooling said glycerine solution of monoglyceride to a temperature below about 100° C. within about 3 minutes to form two liquid phases, one of said phases containing principally higher fatty acid monoglyceride and glycerine and the other liquid phase consisting essentially of glycerine, separating said liquid phases, and recovering substantially pure higher fatty acid monoglyceride from said liquid phase containing higher fatty acid monoglyceride in admixture with glycerine.

In carrying out the present process it is essential to the preparation of a high purity product as hereinabove defined that the glycerine, which is employed as both a reactant and a solvent, be employed in an amount which dissolves all of the monoglyceride product formed by reaction between the glycerine and the acylating agent at the reaction temperature employed. Thus, in conjunction with prior art processes wherein first the acylating agent and then the monoglyceride product are used as solvents for the glycerine, the process of the present invention uses extraordinarily high ratios of glycerine to acylating agent, e.g., in the case of fatty triglycerides, typical proportions of reactants will be on the order of 1000 parts by weight of glycerine per part by weight of triglyceride. This corresponds to a mole ratio of total glycerine present in the system to fatty acyl groups on the order of about 3200:1, and in the case of fatty di-glycerides and fatty acids, the same molecular proportion may be employed. While it is preferred to operate at approximately this 3200:1 mole ratio, higher ratios may be employed of course, but substantially lower ratios will result in poorer yields of the desired pure monoglyceride because of the limited solubility of the fatty material in the glycerine and the need for the formation of a clear homogenous single phase solution in order to assure formation of substantially pure monoglyceride. It is unnecessary to use ratios substantially greater than about 3200:1, in addition to which such higher ratios tend to increase problems of recovery of the pure monoglyceride and separation thereof from the unreacted glycerine.

Operating temperature used in carrying out the instant process characteristically are on the order of about 270° to 295° C. and above. At temperatures substantially below about 270° C. the solubility of fatty acid monoglycerides in glycerine diminishes markedly. On the other hand, at temperatures above about 295° C., which is approximately the boiling point of glycerine at one atmosphere, pressurized equipment is required.

The present process is normally performed in the absence of atmospheric oxygen, which may conveniently be excluded by carrying out the operation under an inert atmosphere such as nitrogen, carbon dioxide or hydrogen, using a slight positive pressure to prevent entry of air into the system. A non-acid neutral or alkaline catalyst may also be employed, suitable such catalysts being inter alia, water, caustic soda, lime, alkali metal salicylates such as sodium ethoxylate, and the like. Typically these catalysts are employed in an amount ranging from about 0.001% to 0.001% by weight of the reactants.

In carrying out the present process, the fatty acylating agent is dissolved in glycerine at an elevated temperature as hereinbefore indicated. The glycerine and the acylating agent may be heated together or the glycerine may be preheated and the acylating agent added thereto. Heating is done, of course, under an inert or oxygen-free atmosphere, and the mixture of reactants is agitated in order to facilitate reaction of the acylating agent and the formation of a true solution of the monoglyceride product in the glycerine in a reasonably short time. Catalyst may be supplied by being added separately or in admixture with either of the two reactants.

After the reactants have been commingled at the desired reaction temperature, reaction normally occurs substantially immediately to bring about the formation of a single phase system constituting a solution of fatty acid monoglyceride in glycerine. Suitably however, the reaction mixture may be agitated at 270° C. or higher for a period of about 1 to 10 minutes or longer to insure complete reaction, after which the solution obtained is rapidly cooled to a temperature not greater than about 100° C. Rapid cooling is employed in order to prevent reversion of the monoglyceride to higher esters during the formation of a separate glycerine-poor liquid phase which occurs upon cooling of the heated single phase solution. (Although the rate of reversion of the monoglyceride ester to an equilibrium mixture of mono-, di- and tri-esters is rapid at temperatures above about 155° C., it is substantially diminished by about 140° C. at 100° C. and below, if the rate of reversion is extremely slow and the monoglyceride may, for practical purposes, be considered stable at such low temperatures.) Thus it has been found desirable to cool the solution within a period not appreciably greater than about 3 minutes.

In the present process, rapid cooling of the heated monoglyceride reaction product to a temperature below
3. 100° C. brings about formation of a two-phase system which readily separates into a lower or glycerine layer and an upper liquid layer which contains substantially pure higher fatty acid monoglyceride emulsified with, and containing dissolved therein, excess glycerine. These layers are easily separated by decantation or centrifuging and the fatty acid monoglyceride in the upper layer may thereafter be recovered by separation from the glycerine therein by various methods including washing with aqueous solutions of inorganic salts such as 5% sodium sulphate, vacuum distillation, or vacuum-steam distillation. If desired, any alkaline catalyst present in the fatty acid monoglyceride may be decollated by neutralization with phosphoric acid or with acid phosphates such as sodium diacid phosphate.

Fatty acylating agents employed in carrying out the present process include fatty acids, fatty acid diesters of glycerine and fatty acid triesters of glycerine in which acylating agents the fatty acid component contains from 18 to 18 carbon atoms. Examples of such acylating agents are palmitic, stearic and oleic acids per se, glyceryl distearate, glyceryl dipalmitate, glyceryl dioleate, and triesters including naturally occurring as well as modified fats such as tallow, corn oil, soy bean oil, cotton seed oil, and their hydrogenated products, and mixtures thereof. The process of the present invention is specifically applicable to the preparation of mono-fatty acid esters of glycerine wherein the fatty acid contains 16 to 18 carbon atoms. This is because in the case of the preparation of monoesters of lower fatty acids in accordance with previously proposed procedures, glycerine is sufficiently soluble in the monoglycerides thereof to permit the realization of reasonably high purity monoglycerides using a 5 to 15 mole excess of a glycerine. A similar consideration of increased solubility applies in the case of the preparation of esters of propylene glycol, and it appears that the monoesters of glycerine with higher fatty acid esters of at least 16 carbon atoms are unique in their low solvent power for glycerine.

The following examples are given to additionally illustrate the nature of the invention and it will be understood that the invention is not limited thereto. Thus, although batch processes are illustrated, the present process may be conveniently carried out on a continuous basis, utilizing concurrent flow of glycerine, acylating agent, and catalyst through a heated contacting column. All parts and proportions in the following examples are by weight unless specifically indicated to be otherwise.

Example 1

One part of glyceryl monostearate which contains about 50% of glyceryl monostearate, 35% glyceryl distearate, 5% of glyceryl tristearate, and 10% free glycerine is mixed with 1000 parts of glycerine heated to about 280° C. The mixed esters dissolve almost instantly to form a clear solution. The solution is agitated at 280° C. under a nitrogen atmosphere, and the glycerol polymers react with the glycerine in which they are dissolved to form a single phase, clear glycerine solution of glycerol monostearate, a reaction which occurs substantially immediately upon mixing. After agitation and heating of the solution is continued for about 4 minutes, after which the solution is cooled to 100° C. within a period of about 2 minutes. The cooled product contains two distinct liquid phases, which are separated by centrifuging, and the lighter phase which consists of glycerol monostearate with glycerine dissolved therein is emulsified therewith is subjected to vacuum distillation at 1 mm. of mercury and 100-140° C. to remove the glycerine therefrom. This distilled glycerine is recombinated with the previously separated lower glycerine phase for reuse in the reaction.

The glycerine-free glycerol monostearate product so obtained contains about 90% glyceryl monostearate and about 10% glyceryl distearate.

In this reaction, moisture dissolved in the glycerine employed as the reactant acts as a catalyst, sufficient moisture for this purpose being retained in the glycerine even at the reaction temperature employed.

Example II

One part of tallow is mixed with 1000 parts of glycerine which has been heated to 280° C. under a nitrogen atmosphere. 0.001 part of caustic soda is added as a catalyst. The tallow, which dissolves almost immediately in the glycerine, reacts to form a clear, single phase solution of tallow fatty acid monoglyceride in glycerine, which after heating at 280° C. for about 10 minutes, is cooled to 95° C. with a trace of glycerol, forming, a system of two liquid phases is formed. The system is centrifuged and the phases separated. The lighter phase, which comprises monoglyceride having glycerine emulsified and dissolved therein, is subjected to vacuum distillation at 140° C. and 1 mm. of mercury and the glycerine is removed. On removal of glycerine from the lighter layer, the product which is obtained contains 90% glycerol monostearer of tallow fatty acids and 10% of the glycerol diester of tallow fatty acids.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

What is claimed is:

1. A process for the preparation of a higher fatty acid monoglyceride whereupon comprises commingling an acylating agent containing a fatty acid radical having from about 16 to 18 carbon atoms with glycerine at a temperature of at least about 270° C., said glycerine being present in excess of the amount required both to form stoichiometrically the glycerol monostearer of the said fatty acid radical and to dissolve completely a stoichiometric amount of said glycerol monostearer, and reacting said acylating agent and said glycerine to form a solution of higher fatty acid monoglyceride in glycerine cooled said glycerine solution of monoglyceride to a temperature below about 100° C. in within about 3 minutes to form two liquid phases, one of said phases containing principally higher fatty acid monoglyceride and glycerine and the other liquid phase consisting essentially of glycerine, separating said liquid phases, and recovering substantially pure higher fatty acid monoglyceride from said liquid phase containing higher fatty acid monoglyceride in admixture with glycerine.

2. A process for the preparation of a higher fatty acid monoglyceride as set forth in claim 1 wherein said acylating agent is a fatty triglyceride.

3. A process for the preparation of a higher fatty acid monoglyceride as set forth in claim 1 wherein said acylating agent is a fatty diglyceride.

4. A process for the preparation of higher fatty acid monoglyceride as set forth in claim 1 wherein said glycerine is commingled with said acylating agent and the resulting mixture is maintained at at least about 270° C. for a period of about 10 minutes.

5. A process for the preparation of a higher fatty acid monoglyceride which comprises commingling and reacting an acylating agent containing a fatty acid radical having from about 16 to 18 carbon atoms with glycerine at a temperature of at least about 270° C., the molar ratio of fatty acid group and said acylating agent to total glycerol present being about 1:3200, to form a solution of fatty acid monoglyceride in glycerine, cooling said glycerine solution of monoglyceride to a temperature below about 100° C. within about 3 minutes to form two liquid phases, one of said phases containing principally higher fatty acid monoglyceride and glycerine and the other liquid phase consisting essentially of glycerine, separating said liquid phases, and recovering substantially pure
higher fatty acid monoglyceride from said liquid phase containing higher fatty acid monoglyceride in admixture with glycerine.

6. A process for the preparation of a higher fatty acid monoglyceride which comprises commingling an acylating agent containing a fatty acid radical having from 16 to 18 carbon atoms with glycerine at a temperature from about 270° to 295° C., said glycerine being present in excess of the amount required both to form stoichiometrically the glyceryl monoester of the said fatty acid radical and to dissolve completely said stoichiometric amount of said glyceryl monoester, and reacting said acylating agent and said glycerine to form a solution of higher fatty acid monoglyceride in glycerine, cooling said glycerine solution of said monoglyceride to a temperature below about 100° C., within about 3 minutes to form two liquid phases, one of said phases containing principally said higher fatty acid monoglyceride and glycerine and the other liquid phase consisting essentially of glycerine, separating said liquid phases, and removing said glycerine from said monoglyceride-containing phase to produce substantially pure higher fatty acid monoglyceride.

7. A process for the preparation of a higher fatty acid monoglyceride which comprises commingling a triglyceride with a higher fatty acid having from about 16 to 18 carbon atoms with glycerine at a temperature from about 270° to 295° C. under an inert atmosphere, said glycerine being present in excess of the amount required both to form stoichiometrically the glyceryl monoester of said fatty acid and to dissolve completely said stoichiometric amount of said glyceryl monoester, and reacting said fatty acid and said glycerine to form a clear, single phase solution of higher fatty acid monoglyceride in glycerine, cooling said solution of said monoglyceride in glycerine to a temperature below about 100° C. within about 3 minutes to form a lighter liquid phase and a heavier liquid phase, said lighter liquid phase containing principally higher fatty acid monoglyceride and dissolved and emulsified glycerine and said heavier liquid phase consisting essentially of glycerine, separating said liquid phases, and vacuum distilling said dissolved and emulsified glycerine out of said lighter liquid phase to produce a residue of substantially pure higher fatty acid monoglyceride.

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