United States Patent Office

3,249,600
Patented May 3, 1966

3,249,600

# PROCESS FOR THE PREPARATION OF PURIFIED SUCROSE ESTERS AND PRODUCTS OBTAINED THEREBY

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No Drawing. Filed Aug. 15, 1962, Ser. No. 216,956
Claims priority, application Italy, Sept. 12, 1961, 16,468/61
10 Claims. (Cl. 260—234)

The present invention relates to a process for the separation in the pure state and the substantially quantitative recovery of sugar esters and of unreacted or partially reacted starting materials (including, along with sucrose, also lower alkyl esters of saturated and unsaturated fatty acids of 6 to 30 carbon atoms, or natural or synthetic triglycerides and partial glycerides) from mixture containing them and obtained in the transesterification or interesterification of sucrose by reaction of the latter in the presence of a basic catalyst with the lower alkanol esters of saturated and unsaturated fatty acids having from 6 to 30 carbon atoms, or with natural or synthetic glycerol triesters (triglycerides) of such high molecular weight aliphatic acids.

The invention relates in particular to the separation of the components of the reaction mixtures obtained, for example, by the transesterification processess disclosed in the United States patent to Hass et al., No. 2,893,990, dated July 7, 1959, and in the copending application of Vitangelo D'Amato, Serial No. 799,100, filed March 13, 1959, now Patent No. 3,054,789, dated September 18, 1962.

In the transeserification processes yielding the mixtures to which the present invention is applied, such mixtures containing the desired sucrose esters of high molecular weight saturated and unsaturated aliphtaic acids (hereinafter generally referred to as fatty acids), the following sources of radicals of the higher fatty acids are used: fatty acid esters of highly volatile alcohols (e.g., lower alkanols, like methyl alcohol, ethyl alcohol, etc.), the acids having from 6 to 30 carbon atoms, such as undecylenic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, behenic acid, etc., from which sugar esters of single fatty acids are obtained, and mixed naturally-occurring glycerides, such as cocoanut oil, palm oil, palmitic oil, tallow, lard, rape seed oil, and the like, either as such or hydrogenated, or mixtures thereof, from which sugar esters of different fatty acids, which we shall refer to as "mixed water-soluble sugar esters," are obtained.

The acids of fats and oils, containing from 6 to 30 carbon atoms, either saturated or insaturated, are generally preferred as raw materials. By suitably varying certain parameters and the mass ratios between the reagents, the various sugar esters are obtained.

On the other hand, the use of a higher proportion of fatty acid methyl ester in relation to sucrose leads to the production of sugar polyesters.

In particular, to effect transesterification, the sucrose is made to react with the fatty acid methyl esters, or with the mixed naturally-occurring glycerides, in dimethylformamide or dimethyl sulfoxide as reaction solvents in the presence of anhydrous potassium carbonate or other basic catalyst. The duration of the reaction is kept within the limits of 6–12 hours, with the reaction temperature ranging preferably between 90–95° C. The reaction is conducted at normal pressure when mixed naturally-occurring glycerides are used. After evaporation of the solvent there remains a residual mass which, when the methyl or other lower alkyl ester of a single acid has been used, consists of the monoester or of polyesters, and mixtures of them, of the fatty acid and sucrose, excess sucrose and the unreacted alkyl ester of the fatty acid.

When a mixture of naturally-occurring glycerides is used, the reaction mass will contain the sugar esters, excess sucrose and a fraction consisting of monoglycerides, diglycerides and unreacted triglycerides, this fraction being hereinafter sometimes referred to as "hemiglycerides." In either case, the mass contains other impurities (soaps, etc.) and variable quantities of solvent.

The general object of the invention is to afford a simple, economical method of separating and quantitatively recovering sugar esters in the pure state and to effect the recovery of the unreacted sucrose, of the unreacted methyl esters of the fatty acids, and of the hemi-glycerides (when glyceryl tri-esters are used for the transesterification) of such a grade of purity that they may be used again in the process of preparation or used as such for other purposes.

In comparison with the known methods of purifying sugar esters, the process of the present invention has important advantages, especially as regards the possibility of industrial application, and the quality of the end-product and of the products of recovery.

Of the known methods of separation, there may be mentioned the process whereby the reaction mass, after evaporation of the solvent, is treated with three or four times its own weight of water, followed by the addition of sodium chloride. The mixture is then heated to 80–90° C. The sugar ester and all the substances sparingly soluble in water separate, forming a dense, oily upper layer, while the unreacted sucrose, salt and the greater part of the residual reaction solvent pass into the lower, aqueous layer. The sugar ester is recovered from the upper, oily layer, after evaporation to dryness and purification with solvents. The disadvantage of this method is that it yields a dense oily layer, which contains not only the sugare esters but also saline solution, sucrose and methyl esters of fatty acids, and hence on drying, the products are impure.

It is not then possible to separate the unreacted sucrose from the sugar esters by dissolving the reaction masses in organic solvents (acetone, methylisobutylketone, etc.) which dissolve the ester of sucrose but not the sucrose, because the latter is in such a finely divided state that it is practically unfilterable, even with the help of infusorial earths (diatomite, etc.).

Another known method of separation provides for the melting of the dry reaction mixture at 100–120° C. followed by the addition of small quantities of water so as to form a gel. A boiling solvent is then added, as a result of which the sucrose esters pass into solution and the sucrose is left to crystallize. After elimination of the crystallized sucrose by filtration, the solution is cooled to room temperature, and the sugar ester precipitates in the solid mass and agglomerates, yielding a hard mass. The precipitated mass is separated from the solution and both are evaporated to dryness.

The solution after evaporation leaves a product which is ground with difficulty and incompletely.

This latter method has several disadvantages. First of all, the separation of the unreacted sucrose is incomplete, since the solvents used are partially miscible in water, and further, there are always difficulties in filtering it. The sugar esters which are separated from an almost anhydrous solvent are present as a solid paste, difficult to filter and manipulate, and in addition they contain several extraneous substances.

A syrupy paste remains in the solvent, from which it is difficult to recover the unreacted methyl esters of the fatty acids. In this process the melting temperature of the reaction mass is close to that of decomposition, as a result of which discolored products are obtained. Further, it is necessary to regulate the addition of water constantly and strictly, because if the water is insufficient, part of the sucrose remains in the melted mass obtained on evaporation of the solution, while if there is too much water, the sucrose separates as a syrup and part of it remains in the solvent layer, since the solvents used are partially water-miscible.

Finally, even when the addition of water is properly regulated, it is difficult to obtain a quantative separation of the sucrose, and the sugar esters are always impure owing to the presence of free sucrose.

According to other methods, a solution of the reaction mass is made in solvents which are not miscible or only partially miscible in water.

The sucrose is eliminated by washing with salt water and finally the solvents are evaporated to yield sugar esters. This system too has the disadvantage of yielding impure sugar esters.

More complicated processes of separation have also been suggested, involving the interruption midway of of the evaporation of dimethylformamide solvent (DMF), leaving the unreacted glycerides to stratify with subsequent separation. In the case of the production of sugar esters of single fatty acids, the distillation of DMF is stopped midway, leaving the unreacted methyl esters of the fatty acids to stratify, these being then separated, the recovery of the methyl esters being completed by extraction with hexane. In any case, contaminated products are obtained, especially in the production of mixed sugar esters.

As already indicated, sugar esters can be obtained by reaction of sucrose with lower alkyl esters (methyl, ethyl, etc.) of fatty acids, in which case sugar esters of single fatty acids are obtained; or by reaction of sucrose with mixed naturally-occurring glycerides, in which case, sugar esters of several acids are obtained. According to the process of the present invention, the reaction mass obtained after transesterification of the sucrose with alkyl esters of fatty acids, or with single or mixed glycerides (glyceryl triesters) after elimination of the reaction solvent, is dissolved in a lower alkyl acetate, such as ethyl acetate, for example, at a temperature of 60–90° C., and the solution is extracted 2–3 times with a volume of water equal to about 10–20% of the initial volume of the solvent, previously heated to the same temperature.

This extraction ensures the total recovery of the unreacted sucrose in the form of an aqueous syrup, which is separated from the supernatant organic layer at a temperature of 60–90° C., as above. If the separation is effected at this temperature, the sugar esters remain quantitatively dissolved in the organic solvent, and hence there are no losses of useful product in the aqueous phase. The organic solvent, saturated with water, is then cooled to a temperature between 0° C. and 30° C. If a fatty acid alkyl ester or a glyceride with mainly residues of fatty acids with long chains of 16 or more carbon atoms, for example, is used as starting material, it is preferable to cool 20–30° C., whereas in other cases it is advisable to cool to nearly 0° C. The result is a separation consisting of an upper layer of organic solvent in which fatty acid alkyl esters, or unreacted glycerides with partially reacted glycerides, earlier referred to as hemiglycerides, are found in the dissolved state, and a lower, aqueous layer, in which the sugar esters are found in colloidal form.

By evaporating the organic solvent phase, one obtains either fatty acid alkyl esters or hemiglycerides (depending on the starting ester of esters used), which may be recycled or reworked for other purposes. In particular, the hemiglycerides represent a new composition of substances with a wide range of applications in the field of foodstuffs and cosmetics or they can be used as emulsifiers and wetting agents. The sugar esters contained in the aqueous phase are recovered with a mixture of butanol and cyclohexane and treated in accordance with the process described in the above-mentioned patent to Vitangelo D'Amato, No. 3,054,789, supplying mono- or diesters of exceptional purity which, as they contain only negligible traces of the solvent used in the transesterification reaction, can be employed with safety even in the foodstuff and pharmaceutical industries.

### *Example 1*

One thousand twenty six grams (3 moles) of sucrose are dissolved at 60–70° C. in 6560 grams of dimethylformamide (DMF). To the solution are added 214 grams (1 mole) of methyl laurate and 6.5 grams of finely ground anhydrous potassium carbonate as catalyst. The reaction mixture is kept in an atmosphere of nitrogen at a temperature of 90–95° C. and under a pressure of 60–65 mm. Hg for 9 hours. After this, the greater part of the DMF is evaporated under vacuum. 500 grams of the reaction mass (containing 62.84% free sucrose, 74.35% total sucrose and 3.0% DMF) are dissolved by refluxing or by shaking in 1000 ml. of ethyl acetate. The unreacted sucrose remains in finely divided form in suspension. To the resulting solution 180 ml. of $H_2O$, pre-heated to 80° C., are added. The sucrose immediately passes into solution. The solution is shaken for a few minutes at 70° C. and is then left to stratify into two phases at the same temperature. The separation of the phases is rapid and clearly defined. The lower, aqueous phase is drawn off. The upper, solvent phase, still at a temperature of 70° C., is extracted twice with 90 ml. of $H_2O$ preheated to 80° C. The concentrated aqueous solutions yield about 330 grams of sucrose. The solvent phase, water-saturated, is left to cool to room temperature (20–25° C.); there is separation into two layers. The lower, aqueous layer contains the monolaurate in the fluid, oily state, that is, colloidally dissolved in water. The aqueous phase separates (aqueous phase I). The organic phase is extracted twice with water at a temperature of 5–10° C. The aqueous layers (aqueous phase II and III) are drawn off and added to aqueous phase I. The organic phase is evaporated to dryness and the residue (about 35 grams) represents the unreacted methyl monolaurate contaminated with about 8% of sugar esters. The three colloidal aqueous solutions (aqueous phases I, II and III) combined, containing the sucrose monolaurate, are taken up with 100 ml. of cyclohexane and 50 ml. of butanol.

The sucrose monolaurate passes into the upper, solvent phase. In order to eliminate the DMF almost totally, a series of salt washings is carried out on the organic phase (cyclohexane-butanol). The first washing is done with 100 ml. of 20% NaCl solution. Another six washings are effected with 250 ml. at a time of 5% NaCl solution and the final washing with water. The solvent phase (butanol-cyclohexane) is decolorized with animal charcoal and evaporated to dryness. The residual sucrose monolaurate weighs 125 grams and contains 0.0040% DMF. It is a brittle white solid, easily reduced to powder by grinding. It dissolves in water, yielding a clear, transparent colloidal solution.

### *Example 2*

One thousand twenty six (3 moles) of sucrose are dissolved at 60–70° C. in 6560 grams of DMF. To the solution are added 270 grams (1 mole) of methyl palmitate and 8 grams of anhydrous potassium carbonate. The mixture is made to react under the conditions described in Example 1. After elimination of the DMF, part of the reaction mass (500 grams) is dissolved by refluxing or by shaking in 1000 ml. of ethyl acetate. Only the excess sucrose fails to go into solution, but it remains so minutely divided that it is difficult to filter. To this solution 180 ml. of water, pre-heated to 80° C., are added. The sucrose passes into solution at once. The solution is shaken for several minutes at 70° C. and is then left so that the two phases may separate. The separation of the phases is rapid and clearly defined. The lower, aqueous phase is drawn off. Another three washings are effected under the same conditions. The combined aqueous phases after concentration yield 300 grams of sucrose. The water-saturated solvent phase is left to cool to room temperature (20–25° C.), and the lower, aqueous phase, containing sucrose monopalmitate, separates. A further two washings are carried out with water and then the solvent phase is evaporated to dryness and the residue (17 grams) represents the unreacted methyl palmitate, contaminated with 7.73% of sugar esters and 0.078% of DMF.

The residue, after distillation under vacuum, yields pure methyl palmitate ready for recycling. The aqueous phase (including the washings), containing sucrose monopalmitate, are combined and taken up with 150 ml. of cyclohexane and 60 ml. of butanol. The monopalmitate of sucrose passes into the upper, organic phase (butanol-cyclohexane). Saline washings are then carried out at a temperature of 40° C. in order almost totally to eliminate the DMF. The solvent phase is decolorized with animal charcoal and evaporated to dryness. The residue, pure sucrose monopalmitate (107 grams), contains 0.0025% of DMF. It is a brittle white solid, easily reduced to powder by grinding. It dissolves in water, yielding clear, transparent colloidal solutions. Behavior on melting: the product softens and melts completely at 102–103° C.

*Example 3*

One thousand twenty six grams (3 moles) of sucrose are dissolved at a temperature of 60–70° C. in 6560 grams of DMF. To the resulting solution 198 grams (1 mole) of methyl undecenoate and 6 grams of anhydrous potassium carbonate are added. The reaction mixture is kept in a nitrogen environment at a temperature of 90–95° C. and under a pressure of 60–65 mm. Hg and continuously shaken for 9 hours. The greater part of the DMF is evaporated under vacuum. 500 grams of the reaction mass (containing 55% free sucrose, 60.3% total sucrose and 25% DMF) are dissolved by refluxing and by shaking in 1000 ml. of ethyl acetate. To the resulting solution, containing unreacted sucrose in a very fine suspension, are added 180 ml. of $H_2O$ pre-heated to 80° C. It is shaken at 70° C. and left to stratify at that temperature. The upper solvent phase separates and, still at a temperature of 70° C., is once again extracted with 90 ml. of $H_2O$ pre-heated to 80°C. The water-saturated solvent phase is left to cool to room temperature (20–25° C.) and stratification occurs. The lower, aqueous phase, which contains the mono-undecenoate colloidally dissolved in water, is separated. The solvent phase is extracted twice with 100 ml. of $H_2O$ at a temperature of 5–10° C.

All the aqueous layers are combined. The solvent phase is evaporated to dryness and the residue (35 grams) represents the unreacted methyl mono-undecenoate.

This residue, after distillation under vacuum, yields pure methyl mono-undecenoate ready for recycling. The three combined colloidal aqueous solutions are taken up with 200 ml. of cyclohexane and 100 ml. of butanol, and to promote stratification, 120 ml. of 20% NaCl solution are added. In order to eliminate the DMF almost totally, a series of saline washings is carried out on the organic phase (butanol-cyclohexane). This phase is then decolorized with animal charcoal and evaporated to dryness. The residue, sucrose mono-undecenoate, weighs 9 grams. It is a brittle, faintly straw-colored solid, easily reduced to powder by grinding. It dissolves easily in water, yielding clear, transparent colloidal solutions. Behavior on melting: it begins to soften at 45° C. and melts totally at 103–104° C.

*Example 4*

One thousand twenty six grams (3 moles) of sucrose are dissolved in 6150 ml. of DMF at a temperature of

60° C. by shaking. To the solution 775 grams (1.2 moles) of cocoanut oil (with the following percentage composition of fatty acids: 45% lauric acid; 18% myristic acid; 10% palmitic acid; 8% oleic acids) are added. A small percentage of other fatty acids, saturated and unsaturated is present. The temperature is raised to 95° C. and 22.5 grams of anhydrous potassium carbonate are added. The resulting solution is kept at a temperature of 90–95° C. for 10 hours in an atmosphere of inert gases and is continuously shaken. At the end of the reaction the DMF is distilled until a thick paste is obtained. 500 grams of the reaction mass (containing 12.60% of DMF; 24.23% free sucrose and 46.88% total sucrose) are dissolved in 1000 ml. of ethyl acetate at the boiling point. To the solution, containing unreacted sucrose in suspension, kept at 75° C., 180 ml. of water, pre-heated to 80° C., are added.

The solution is shaken for a few minutes and then the two phases are left to stratify at a temperature of 70° C. The stratification of the two phases is rapid and clearly defined. The lower, aqueous phase is drawn off and a further three washings with water pre-heated to 75° C. are effected. From the aqueous extracts 113 grams of sucrose are reiovered. The water-saturated solvent phase is cooled to 0° C. and the monoesters separate in the fluid oily state, that is, colloidally dissolved in water. The separation of the two phases is clear-cut. The lower, aqueous phase containing the monoesters is separated. Two more extractions with water are carried out on the solvent phase, still at a temperature of 0° C. Finally, the solvent phase is evaporated.

The residue (80 grams) represents the fraction known as "hemiglycerides" (that is: monoglycerides, diglycerides and triglycerides contaminated with 11% of sugar esters). The combined aqueous extracts containing the monoesters are taken up with 300 ml. of butanol. To promote stratification, 50 ml. of 20% sodium chloride solution are added and the temperature is raised to 45° C. while shaking. In these conditions the separation takes place rapidly and totally. The lower, aqueous layer is drawn off and discarded. After evaporation of the solvent phase, an amorphous mass is obtained (240 grams), and this, after cooling, is easily ground, yielding a white powder. The powder, consisting of soluble monoesters of sucrose, with 40% combined sucrose, when dissolved in water gives rise to clear, stable colloidal solutions. After crystallization from ethyl acetate, the combined sucrose of the soluble monoesters rises to 44% (yield of crystallization 75%).

*Example 5*

The procedure described in Example 4 is repeated but with an altered cocoanut oil-sucrose molecular ratio; that is, instead of using the ratio 1:2.5, the ratio 1:1.4 is used. At the end of the reaction, the DMF is evaporated to dryness under a high vacuum. Separations of sucrose, hemiglycerides and soluble monoesters are carried out on 500 grams of reaction mass containing 1.67% DMF, 12.56% free sucrose and 40.30% total sucrose. The following are obtained: 54 grams of sucrose from the sugar solutions; a fraction of hemiglycerides equivalent ot 138 grams contaminated with 14% sugar esters, and finally, a fraction of monoesters (274 grams) having 34% combined sucrose. After cooling, this fraction solidifies, but is difficult to grind. After purification with ethyl acetate, a brittle product is obtained. This is easily reduced to powder and has a content of 37% combined sucrose.

*Example 6*

The procedure described in Example 4 is repeated but with altered cocoanut oil/sucrose molecular ratio, i.e., 1:2 instead of 1:2.5. Effecting the usual separation of the hemiglycerides and the soluble monoesters from the sugar solution on a 500-grams sample of reaction mass (containing 12.87% DMF; 21.13% free sucrose and 41.35% total sucrose), the yields are as follows: recovered sucrose 98 grams; hemiglycerides with 13% combined sucrose 108 grams; soluble monoesters of sucrose 215 grams. This product contains 38% combined sucrose and is difficult to grind.

After purification with ethyl acetate, the combined sucrose content constitutes 41% of the precipitated product (soluble monoester). Monoesters are thus obtained in the solid state. They are brittle and easily reduced to powder by grinding. Dissolved in water, the product yields clear, transparent colloidal solutions.

### *Example 7*

Whereas in Example 4 the fat/sucrose molecular ratio was 1:2.5, in this example the fat/sucrose molecular ratio is 1:3. The sugar syrup, hemiglycerides and soluble sugar esters are separated on a 500-grams sample of reaction mass (containing 14.29% DMF) 26.51% free sucrose and 46.97% total sucrose). In the sugar washings 125.92 grams of sucrose are recovered. A 58 grams fraction of hemiglycerides contaminated with 14% sugar esters is obtained. The fraction of soluble monoesters of sucrose (223 grams) has a combined sugar content of 41%. The amorphous mass, after cooling, is brittle and easily ground to a white powder. It dissolves colloidally in water, yielding a clear, transparent solution. On crystallization from ethyl acetate, the product's properties improve and it presents 46% combined sucrose.

### *Example 8*

The procedure of Example 4 is repeated with altered cocoanut oil-sucrose molecular ratio, that is, 1:5 instead of 1:2.5. At the end of the reaction, the DMF is evaporated. 500 grams of reaction mass having 41.65% free sucrose, 64.24% total sucrose and 7.56% DMF are subjected to separation by the procedure described in Example 4. 216 grams of sucrose are recovered from the sugar syrup. A hemiglyceride fraction weighing 44 grams contaminated with 18% sucrose esters is separated, and then the fraction of soluble monoesters of sucrose weighing 213 grams and having a combined sucrose content of 47.87%. After cooling, the amorphous mass is brittle and easily ground to a white powder. This dissolves colloidally in water, yielding a clear, transparent solution. On crystallization from ethyl acetate, the properties of the product improve and it contains 50% combined sucrose.

### *Example 9*

The procedure described in Example 4 is repeated with an altered cocoanut oil/sucrose molecular ratio, viz. 1:6.4 instead of 1:2.5. At the end of the reaction, the DMF is evaporated to dryness. 500 grams of reaction mass (having 48.60% free sucrose and 8.71% DMF) are subjected to separation in accordance with the method described in detail under Example 4. 247 grams of sucrose are rcovered from the sugar syrup. The hemiglyceride fraction weighs 32 grams and is contaminated with 18% sugar esters. The fraction of soluble monoesters weighs 168 grams and has a combined sucrose content of 48.3%. After cooling, the amorphous mass is brittle and easily reduced to powder by grinding. It dissolves colloidally in water, yielding a clear, transparent solution. On crystallization from ethyl acetate, the properties of the product improve, and it contains 51.6% combined sucrose.

### *Example 10*

One thousand ninety four grams (3.2 moles) of sucrose are dissolved in 7000 grams of DMF at a temperature of 60–70° C. To the solution are added 349 grams (0.5 mole) of palm oil with the following approximate percentage acid compositions: 49% lauric acid, 15% myristic acid, 8% palmitic acid, 2% stearic acid, 17% oleic acid, 5% caprylic acid, 3% caprinic acid and small amounts of other, saturated and unsaturated, fatty acids; and 10 grams of finely ground anhydrous potassium carbonate. The resulting solution is kept in an atmosphere of nitrogen at a temperature of 90–95° C. and shaken for 10 hours. At the end of the reaction, the DMF is distilled off until a thick paste is obtained. 500 grams of reaction mass (containing 3% DMF, 56.63% free sucrose and 67.90% total sucrose) are dissolved by refluxing in 1000 ml. of ethyl acetate. The unreacted sucrose remains in suspension.

To the solution, which is kept at a temperature of 75° C., 180 ml. of water, pre-heated to 80° C., are added. The solution is shaken for several minutes and left to stratify at a temperature of 70° C. Separation into two phases is rapid and clear-cut. The sugar, aqueous phase, is drawn off. After a further two washings with 90 ml. of $H_2O$, heated to 80° C. and under the same conditions as the first, almost all the sucrose is recovered. In both cases the separation into two phases is rapid and clear-cut. From the combined aqueous phases, 280 grams of sucrose are obtained. 90 ml. of $H_2O$ are added to the upper solvent phase and the whole is cooled to 0° C. while shaking. It is left for 30 minutes to stratify. The lower layer, consisting of monoesters of sucrose colloidally dissolved in water, is drawn off. The treatment with water is carried out twice more in the same way, 90 ml. of $H_2O$ being added to secure total recovery of the monoesters. The organic solution (ethyl acetate) is evaporated to dryness under vacuum. 52 grams of hemiglycerides contaminated with 16% of sugar ester are obtained. The three colloidal solutions containing the sugar esters are combined and taken up with 88 ml. of butanol and 200 ml. of cyclohexane. To facilitate the separation of the phases, 120 ml. of 20% NaCl solution are added and the whole is heated to 40–45° C. while shaking. The sugar esters pass quantitatively into the upper solvent phase, which is then washed six times with a 5% NaCl solution and finally with water. The mixture of the solvents is decolorized with decolorizing charcoal and evaporated to dryness. The residue of 131 grams represents the monoesters of sucrose of the acids contained in the palm oil with a content of 47% combined sucrose and 0.0055% DMF. It is a brittle, amorphous solid, easily reduced to powder. It dissolves in water, yielding clear, transparent colloidal solutions.

### *Example 11*

Nine hundred fifty eight (2.8 moles) of sucrose are dissolved at a temperature of 60–70° C. in 6130 grams of DMF while shaking. To the solution are added 1526 grams (2 moles) of ox tallow (with the following approximate percentage composition of fatty acids: 32.5% palm-oil, 14.5% stearic acid, 48.3% oleic acid, 2.0% myristic acid, 2.7% palmitoleic acid and small percentages of other fatty acids) and 36.5 grams of potassium carbonate. The temperature is raised to 95° C. The resulting solution is kept in a nitrogen environment at a temperature of 90–95° C. and under normal pressure for 10 hours while shaking. At the end of the reaction, the DMF is evaporated until a thick paste is obtained. 500 grams of reaction mass containing 12.8% free sucrose and 0.42% DMF are dissolved in 1000 ml. of ethyl acetate by refluxing and shaking. To the solution containing the unreacted sucrose in very fine suspension, 200 ml. of water, preheated to 80° C., are added. The solution is shaken for a few minutes and then, still at 70° C., is left to stratify into two phases. The aqueous phase separates. To the upper solvent phase 300 ml. of water are added and the whole cooled to 28–30° C. The lower, aqueous phase is drawn off. Another two extractions with 100 ml. of water at a time are carried out on the solvent phase at a temperature of 25° C. The organic layer (ethyl acetate) is evaporated to dryness; 185 grams of hemiglycerides containing 11% sugar esters are obtained. The combined colloidal aqueous solutions are taken up with 400 ml. of cyclohexene and 250 ml.

of butanol. To facilitate the separation into two phases, 200 ml. of 20% NaCl solution are added and the temperature is raised to 40° C. Under these conditions, separation into two phases is rapid and clear-cut.

To remove the DMF almost completely, a further six washings are carried out with 250 ml. of 5% NaCl solution at a time, and a final one with 250 ml. of water. Finally, the mixture of solvents is decolorized with charcoal and evaporated to dryness. The residue consists of 235 grams of sugar esters with 33.57% combined sucrose, with a solid, waxy appearance, and is difficult to grind. It dissolves in water yielding turbid solutions.

*Example 12*

One thousand ninety-four grams (3.2 moles) of sucrose are dissolved in 7000 grams of DMF. To the solution are added 436 grams (0.5 mole) of hydrogenated rape seed oil (with an approximate composition of fatty acids as follows: 50% behenic acid, 45% stearic acid, 1% palmitic acid, 1% myristic acid, 1% lignoceric acid and small amounts of other fatty acids) and 12 grams of potassium carbonate, with shaking. The temperature is raised to 95° C. and nitrogen is bubbled into the simmering mass. Duration of the reaction is about 10 hours. At the end of the reaction, the DMF is distilled off but not to dryness. 500 grams of reaction mass (containing 38.96% free sucrose and 17.2% DMF) are dissolved by refluxing sucrose in suspension, 180 ml. of $H_2O$, preheated to 80° C., are added. The solution is shaken for several minutes and then, still at 70° C., it is left to stratify into two phases. The lower aqueous sugar phase is drawn off. Still at a temperature of 70° C. another two washings are effected with water preheated to 80° C. In all, 195 grams of sucrose are recovered. To the water-saturated solvent phase 100 ml. of $H_2O$ are added and the temperature is lowered to 30–35° C. Separation of the phases takes place. The lower, aqueous phase is drawn off.

Still at a temperature of 25–30° C., another two extractions with water are carried out. The upper solvent phase (ethyl acetate) is evaporated to dryness and 40 grams of hemiglycerides, contaminated with 16% sugar esters, are obtained. The three combined colloidal aqueous phases are taken up with 150 ml. of butanol and 300 ml. of cyclohexane. To the mixture 120 of 20% NaCl solution are added. To eliminate the DMF almost completely, another six washings with 5% NaCl solution, 250 ml. at a time, are carried out and then a final washing with 250 ml. of $H_2O$. The mixture of solvents is then decolorized with animal charcoal and evaporated to dryness. The residue (150 grams), consisting of mixed monoesters of sucrose with a content of 44.7% combined sucrose, is a brittle, amorphous mass easily reduced to powder. It dissolves in hot water, yielding clear, transparent solutions.

*Example 13*

One thousand twenty-six (3 moles) grams of sucrose are dissolved in 6570 grams of DMF. To the solution 1452 grams (6 moles) of methyl myristate and 29 grams of potassium carbonate are added while shaking. The temperature is raised to 90° C. The resulting solution is kept in an atmosphere of nitrogen at a temperature of 90° C. and under a pressure of 60–70 mm. for 9 hours with shaking. At the end of the reaction, the DMF is evaporated until a thick paste is obtained. 500 grams of reaction mass, containing 18.10% free sucrose and 2.11% DMF, are dissolved in 1000 ml. of ethyl acetate. To the solution, containing unreacted sucrose in very fine suspension, 200 ml. of water, preheated to 80° C., are added. The solution is shaken for a few minutes and with the temperature still at 70° C. is left to stratify into two phases.

The aqueous phase separates. Still at a temperature of 70° C., another two washings are carried out with water preheated to 80° C. 90 grams of sucrose altogether are recovered from the aqueous phases. The water saturated solvent phase is cooled to 25–30° C. Separation into two liquid phases occurs. The lower, aqueous phase containing sucrose dimyristate is drawn off. Still at a temperature of 25–30° C., another extraction with water is carried out and the lower, aqueous phase separates. The upper, solvent phase (ethyl acetate) is evaporated to dryness. 192 grams of unreacted methyl myristate with a small percentage of sucrose esters, as impurity, are obtained. The two combined aqueous phases are taken up with 150 ml. of butanol and 300 ml. of cyclohexane. To the resulting mixture 100 ml. of 20% NaCl solution are added. To eliminate the DMF almost completely, another six washings with 5% NaCl solution, 250 ml. at a time, are carried out and a final washing with 250 ml. of water. The mixture of solvents is decolorized with animal charcoal and evaporated to dryness. The residue (198 grams), consisting of sucrose dimyristate, is a white amorphous mass. The product, after cooling, is reduced to powder by grinding. Sucrose dimyristate has no clearly defined melting point. It begins to soften at 30° C. It dissolves in water, yielding turbid, gelatinous solutions, like all sucrose diesters.

As shown by the above example, the product of the interesterification of sucrose with either a lower alkyl ester of an aliphatic (saturated or unsaturated fatty) acid of 6 to 30 carbon atoms, or a natural or synthetic glycerel tri-ester (triglyceride) in an organic reaction solvent, such as DMF, is first heated to evaporate the solvent, and is then dissolved in a hot lower alkyl ester of a lower alkanoic acid, such solution being then extracted with hot water. Although ethyl acetate is the preferred solvent for the recation product, other liquid lower alkyl esters of lower alkanoic acids, like methyl and ethyl propionate and butyrate, will be found with certain transesterification reaction products to be efficient solvents.

The hot water extract contains the unreacted sucrose, while the sucrose ester or esters remain quantitatively dissolved in the organic layer. The latter is then cooled to about room temperature or better and extracted one or more times with water of about the same temperature. The water extract now contains the sucrose ester or esters, while the organic solvent contains the unreacted starting esters and in the case of the use of glycerol triesters, also the partially reacted di- and mono-esters. Obviously other solvents can be used in place of the lower alkyl alkanoates which have at most only a slight solubility in or miscibility with water, have high solvent action on the starting esters and on the glycerol di- and mono-esters but low solvent action on sucrose esters at about room temperature and below.

We claim:

1. A process for the substantially quantitative isolation of high purity sucrose mono- and di-esters of high molecular weight aliphatic acids with the recovery of unreacted sucrose and unreacted lower alkyl or unreacted and only partially reacted glyceryl esters of said acids, from the product of the interesterification reaction of an excess of sucrose in an organic reaction solvent with a member selected from the class consisting of lower alkyl esters and fatty acid glycerides, comprising evaporating the reaction solvent, dissolving the residue in a lower alkyl acetate at about 60–90° C., extracting the solution with water at substantially the same temperature, separating the aqueous phase containing the unreacted sucrose, cooling the organic layer to 0–30° C., and extracting the same with water at substantially the same temperature and separating the aqueous phase to effect substantially quantitative isolation of the sugar ester fraction from the remaining organic fraction of the reaction product.

2. A process to claim 1, in which the reaction product subjected to extraction with alkyl acetate is derived from an interesterification reaction between sucrose and the starting ester material in which the sucrose is present in a ratio calculated to yield diesters of sucrose.

3. A process according to claim 1, in which the reaction product subjected to extraction with alkyl acetate is derived from an interesterification reaction between sucrose and the starting ester material in which the sucrose is present in a ratio calculated to yield monoesters of sucrose.

4. A process according to claim 1, in which the lower alkyl acetate is ethyl acetate.

5. A process according to claim 1, in which the starting ester material is a glycerol triester, and wherein the organic phase, following the extraction with cold water, is evaporated to yield the unreacted and partially reacted glycerides.

6. In a process for the isolation of the sucrose mono- and di- ester fraction of the product of the interesterification reaction of sucrose in an organic solvent with one or more esters of aliphatic acids having from 6 to 30 carbon atoms and an alcohol of the group consisting of lower alkanols and glycerol, which comprises evaporating the organic solvent from the reaction product, dissolving the residue in a liquid lower alkyl ester of a lower alkanoic acid at a temperature considerably above room temperature, extracting the solution with water at substantially the same elevated temperature, separating the aqueous phase containing unreacted sucrose, cooling the organic solvent phase to a temperature no higher than about 30° C., and extracting the same with water of about the same reduced temperature, whereby the formed sucrose ester fraction is separated from the organic phase.

7. Process according to claim 6, wherein the starting ester material is a lower alkanol ester of the aliphatic acid, whereby a substantially pure sucrose ester is isolated.

8. A process for the substantially quantitative isolation of the sucrose mono- and di-ester fraction of the product of the interesterification reaction of sucrose in dimethylformamide solution with a lower alkanol ester of an aliphatic acid having from 6 to 30 carbon atoms, which comprises evaporating the dimethyl formamide from the reaction product, dissolving the residue in hot ethyl acetate, extracting the hot solution with water preheated to about 80° C., allowing the phases to separate and removing the aqueous phase containing the unreacted sucrose, extracting the ethyl acetate solution while still at elevated temperature with water of about 80° C. to remove additional quantities of sucrose, cooling the ethyl acetate solution to about 20–25° C. and separating the aqueous layer that is formed, further extracting the ethyl acetate solution with water of below room temperature, combining the aqueous extracts and separating the sucrose ester therefrom.

9. A process for the isolation of the sucrose mono- and di-ester fraction of the product for the interesterification reaction of sucrose of dimethylformamide with a natural triglyceride material, which comprises evaporating the dimethylformamide from the reaction product, dissolving the residue in hot ethyl acetate, extracting the ethyl acetate solution with water preheated to about 80° C., allowing the phases to separate and removing the aqueous phase containing unreacted sucrose, cooling the ethyl acetate solution to approximately 0° C., extracting the same with water of approximately the same temperature to effect separation of the sucrose ester fraction, and separating the sucrose esters from the aqueous extract.

10. A process according to claim 6, wherein the starting ester material is a lower alkanol ester of the aliphatic acid in the molecular ratio of approximately 0.5 mol. of the sucrose to 1.0 mol. of ester, whereby a sucrose diester is obtained.

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