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PURIFICATION OF SUGAR ESTERS

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The present invention relates to an improved process of manufacturing sugar esters and, more particularly, to an improved process of separating the sugar ester from the sugar out of which it was prepared, and also from other unreacted materials and reaction side-products, during the course of preparation of sugar ester by the reaction of sugar with a derivative of a fatty acid or other suitable acid.

Some sugar esters are of considerable interest as detergents, because they are non-ionic, non-toxic, odorless and tasteless and are particularly useful in many applications where other detergent materials are not as desirable. Such applications may include dentifrices, toilet soaps, shampoos and washing powders where their non-toxicity and non-irritation of the skin are important factors. In addition they are derived from relatively cheap raw materials, and can compete successfully with other detergent materials as general purpose detergents.

Sugar esters are also valuable emulsifiers, and their edibility and non-toxicity favor their use in the food, pharmaceutical and cosmetic industries.

One method of manufacturing the sugar esters is to react a sugar, such as sucrose, with a fatty acid ester of a volatile alcohol, in a solvent under alkaline conditions. The production of monoesters is favored by using an excess of sugar, and this form is of most interest for its detergent properties. Diesters and higher esters, which have value as emulsifiers, demulsifiers, varnish resins, etc., are favored by higher proportions of fatty acid ester with respect to sugar, in the reaction.

In the production of the monoester, the sucrose and the alcohol ester of a fatty acid (methyl stearate for example) are reacted in a mutual solvent such as dimethyl formamide, in the presence of a very alkaline catalyst such as potassium carbonate. About three moles of sucrose are employed, per mole of fatty ester, and the two substances react to form sucrose monoester (monostearate), smaller amounts of diester and higher esters of sucrose, and methanol, the latter being distilled off to maintain a minimum concentration in the reaction mixture.

The crude product is dried by distilling off the reaction solvent, and contains about equal amounts of the sucrose monoester and unreacted sugar, and it also contains appreciable percentages of higher esters, potassium soap, unreacted methyl ester, and a few percent of unevaporated reaction solvent (dimethyl formamide).

The sucrose monoester must then be separated from the unreacted sugar and other contaminants, but this has been found to be a difficult problem to accomplish in an economical manner. One way this has previously been done is to dissolve the dried reaction product in three to four times its weight of water and add salt. On heating the solution to 80–90° C., the sucrose ester forms a curd which can be removed from the remaining solution of water, sugar, salt and reaction solvent. The curd is then

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dried to yield crude sucrose monoester, which may be further purified by solvent extraction methods.

The disadvantage of this separation process is that the curd occludes much of the sugar and salt solution and yields an impure product on drying. Also it is difficult and expensive to separate from the solution the sugar and dimethyl formamide in such purity and yield that they may be employed in subsequent reaction batches economically.

An obvious alternative to the above described process of separating the ester from the unreacted sugar would appear to be by conventional solvent extraction methods, using for example, a solvent in which sugar is not soluble while the sugar ester is soluble. Such solvents are numerous and include alcohols, esters, ketones, etc. However, it has been found that during the evaporation of the reaction solvent (dimethyl formamide in the above described example) the sugar crystallizes in such fine crystals that it is very difficult to filter or otherwise separate the undissolved sugar from the slurry which is formed on treating the dried reaction product with an extraction solvent. The solution of dissolved sugar-ester adheres strongly to these crystals, and makes extraction quite incomplete, even with several washings.

As the sugar ester in the dried reaction product is amorphous, extraction of sugar is not practical, and there are no known solvents which will dissolve sugar but not the monoester of sucrose.

A further problem lies in separating from the sugar-free extract, from solvent extraction of the dried reaction product, those fatty impurities such as higher fatty esters of sugar, unreacted methyl esters of fatty acids, potassium soap, all of which may be undesirable impurities in the sucrose ester product, and yet may be otherwise returned to the reaction process and converted to the desired sugar ester by reaction with more sugar.

One object of the present invention is to provide an improved method of separating a sugar ester from sugar.

Another object of the present invention is to provide an improved method of separating a sugar ester from sugar when the sugar is present in microscopically sized crystals such as normally occur in the dried reaction product, from which it is difficult to separate the ester, and to recover the sugar in a relatively pure form which may be incorporated in a subsequent reaction mixture with little or no further treatment.

A further object of the invention is to provide an improved method of separating a sugar ester from microscopically sized sugar crystals in which the sugar ester is recovered as a solution which may be evaporated to yield a product with a sufficiently small sugar content to be sold as a commercial grade without further modification.

A further object of the invention is to provide an improved method of separating sugar ester from microscopically small sugar crystals in which the sugar ester is recovered as a solution from which, with or without other treating processes to remove certain impurities, the sugar ester may be obtained in purified form by chilling the solution to precipitate the sugar ester, leaving contaminants of a fatty nature dissolved in the cold liquor from which they may be recovered by evaporation of the extraction solvent.

A further object of the invention is to provide an improved method of separating sugar ester from a mixture of sugar and sugar-ester, with or without other reaction materials or products present, when the mixture is in the form of a fused or solidified amorphous mass such as the dried reaction product which results from a reaction between equimolar proportions of sugar and methyl fatty ester, or which results from evaporation of the reaction solvent from a reaction mixture at a sufficiently high

temperature that the non-volatile components are fused with little or no crystallization of the sugar, or which results when a portion of the unreacted sugar has been previously removed from the reaction product, and to recover the unreacted sugar in sufficient purity to permit its use in a subsequent reaction mixture, and/or to recover the sugar ester as a solution which may be evaporated to yield a product sufficiently free from sugar to be sold as a commercial grade, and/or to recover the sugar ester as a solution which may be treated to cause separation of purified sugar ester leaving a solution of the fatty impurities for separate recovery.

A further object of the invention is to provide an improved method of separating sugar ester from sugar whether the mixture is in the form of a fused or solid amorphous mass or the sugar is in the form of microscopic crystals, in the presence of small percentages of reaction solvent, which enables almost complete recovery of the adhered reaction solvent.

The economic importance of the last named object is more apparent when it is realized that the value of the solvent which may be thus recovered may be of the same order as that of the sugar ester itself.

The improved process of the present invention is applicable in general to the separation of sugar esters from sugars. It is of more particular value where both substances are present as an intimate mixture and where at least the sugar is in the form of fine micro-crystals incapable of being efficiently and economically separated by ordinary solvent extraction procedures from the ester. The term "sugars" is meant to include any of the saccharides which may be esterified by the above described process, and the term "sugar-ester" is meant to include the ester reaction products of these sugars with aliphatic saturated or unsaturated fatty acids, or fatty acid derivatives, having 10 to 20 carbon atoms per acid radical portion of the molecule, and also ester reaction products of the sugars with other carboxylic acids, or other acid derivatives capable of yielding suitable esters.

Although generally applicable as pointed out above, for economic reasons, the invention is of particular interest in the manufacture of sugar esters from sucrose and one of the higher fatty acids such as palmitic, where large excess of sugar must be employed in order to favor the formation of monoesters.

The underlying principle of the invention is the conversion of the mixture of sugar and sugar ester into a form in which the sugar is temporarily non-crystalline (amorphous) followed by the simultaneous precipitation of the sugar in an agglomerated crystalline form and solution of the sugar ester and other solubles when this amorphous mass is treated with a suitable extraction solvent. The application of this principle will be apparent in the following examples:

Example 1

A sugar ester is prepared by reacting one mole (270 g.) of methyl palmitate with three moles (1027 g.) of sucrose all dissolved in about 3500 ml. of dimethyl formamide as reacting solvent, and in the presence of about 20 g. of potassium carbonate as catalyst. The large excess of sugar is employed in order to drive the reaction toward a high yield of monoester. The reaction is carried out under about 100 mm. Hg absolute pressure, whereat the mixture boils at about 95° C., and the vapor is continually distilled to remove the methanol as it is evolved by the reaction.

The reaction is complete in about 12 hours, and the reaction solvent is evaporated as far as possible by heating the reaction mixture under vacuum at about 100° to 120° C. and 10 mm. Hg, leaving a residue which cools to form a pasty solid. The residue consists of a mass of microscopic sugar crystals in a matrix of sugar ester and other non-volatiles, and may contain about 5% of dimethyl formamide which failed to be evaporated. The

solvent content may be reduced by further heating or by other means, but this is very slow, and it is not necessary to reduce the solvent content further in utilizing the present method. The residue weighs about 1340 g. This dried reaction product contains not only the sugar ester which is being sought but also comprises more than 50% unreacted sugar, and also may contain unreacted methyl ester, higher esters of sugar, potassium soap and spent catalyst.

The dried reaction product is then treated in accordance with the present invention in order to separate the ester and sugar. It is heated to a temperature below that which causes discoloration of the sugar or sugar ester, such as 100° to 120° C., and a minimum quantity of water is added which is sufficient to dissolve the dried reaction product and to convert it to a viscous solution or gel at this temperature. If an excess of water is employed, it may be evaporated after the solution or gel is formed, to that point where the sugar starts to crystallize. In treating the 1340 g. portion of dried reaction product, about 130 ml. of water is sufficient.

A solvent is now added to the hot solution or gel, such solvent being so selected that it preferentially dissolves the sugar ester. In the present example, about 1000 ml. of isopropyl alcohol is poured on top of the hot solution or gel, and the mixture is agitated gently. As the sugar ester is extracted by the solvent, the sugar is precipitated as a crust on the top of the solution or gel, and gradually accumulates as loose crystalline agglomerates. After a few minutes this precipitated sugar settles to the bottom of the vessel, leaving a clear solution of sugar ester and other solubles dissolved in the alcohol.

The precipitated sugar is then separated from the clear solution by decantation, filtration, centrifuging or other means. If desired, the precipitate may be washed with additional hot solvent to remove adhering sugar ester solution. The solution plus the washings are then evaporated and finally dried under vacuum to remove as much solvent as possible. During this evaporation, the residual amount of dimethyl formamide which was extracted into the alcohol solution is also evaporated and recovered by condensing the solvents. This evaporation is carried out at 100° to 120° and at the highest vacuum at which the solvent can be condensed, this being about 40 mm. Hg while the isopropyl alcohol is evaporated, and being increased to 10 mm. Hg when last traces of dimethyl formamide is evaporated.

The dried residue from this evaporation is then cooled and broken into chips or is pulverized. It comprises sucrose palmitate containing a few percent of sugar, and such other fatty impurities as may have dissolved in the solvent, such as higher esters of sucrose and potassium soap. Extraction of the sugar ester from the sugar is at least 85% complete, depending upon the extent of washing of the sugar precipitate.

The precipitated sugar is dried by heating under vacuum, and any solvent is recovered. Alternatively the moist sugar may be incorporated in a subsequent batch together with dimethyl formamide, the entire batch being dried by distillation of the water and alcohol content before any catalyst is added.

The solvent mixture of isopropyl alcohol and dimethyl formamide which is evaporated from the sugar ester product may be dehydrated and distilled to yield separated isopropyl alcohol and dimethyl formamide fractions which can then be used over again in the complete manufacturing process.

Example 2

Sucrose palmitate was formed through the reaction of three moles (1027 g.) of sucrose with one mole (272 g.) of methyl palmitate in the presence of 3500 ml. of dimethyl formamide and 15 g. of potassium carbonate. The reaction was carried out at about 95° C. and 100 mm. Hg pressure, methanol being distilled during the course of the reaction, which required 12 hours.

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A portion of the reaction batch was evaporated in special equipment which permitted rapid scraping of the inner surface of the evaporating vessel, while the vessel was heated by vapor at 120° C. and evaporation was carried out at about 20 mm. Hg absolute pressure. This treatment reduced the dimethyl formamide content to a very low figure and yielded a hard brittle dried reaction product, which weighed 145 g.

This material was fused and dissolved at 110 to 120° C. in about 17 ml. of water, creating a gel which was cloudy with air bubbles. About 100 ml. of methyl isobutyl ketone was added to the gel and the mixture was heated to the boil with gentle agitation. The sugar was precipitated as a crystalline mass, slightly moistened with syrup at elevated temperature. The mixture was cooled to about 60° C. and the sugar became loose and granular. The mixture was filtered and the sugar was washed with 25 ml. of warm methyl isobutyl ketone which was composited with the filtrate.

The liquid was then cooled in tap water to about 25° C. at which point sugar ester was precipitated as a white solid which agglomerated to a stiff mass on standing. Cooling was continued to 12° C., leaving agglomerated sugar ester within a clear solution. The agglomerated sugar ester was separated from the clear liquor, and both parts were evaporated to dryness at 100° C. and 10 mm. Hg final absolute pressure.

The sugar ester (sucrose palmitate) was recovered as a brittle amorphous mass which was readily grindable to a white powder. This weighed 53 g.

The clear cold liquor was evaporated to yield 22 g. of amorphous solid which was somewhat tacky and grindable only with difficulty and incompletely.

The precipitated sugar was dried and weighed 75 g.

In accordance with the special drying technique employed, the dimethyl formamide content was reduced to a very low figure, leaving a mixture of microcrystalline sugar and sugar ester which was hard. This low content of dimethyl formamide, probably about 2 or 3%, made it possible to precipitate the purified sugar ester from the original extract solution merely by cooling it. Had this degree of reduction not been achieved, it would have been necessary to remove the extraction solvent and separate its dimethyl formamide content before precipitation of the sugar ester could be induced.

A series of tests demonstrated that dimethyl formamide in excess of 13% based on the weight of sucrose palmitate, virtually inhibited the precipitation of the sugar ester by cooling of a solution of sucrose palmitate in twice its weight of methyl isobutyl ketone. This amount of contaminant reduced the precipitation temperature from 33° to 11° C., at which temperature the crystal growth was very slow and incomplete.

Example 3

Sucrose myristate was formed through the reaction of one mole (343 g.) of sucrose with one mole of methyl myristate (242 g.) in the presence of 1250 ml. of dimethyl formamide and 10 g. of potassium carbonate as catalyst. The reaction was carried out at 95° C. and 100 mm. Hg pressure, methanol being distilled during the course of the reaction.

The reaction batch was evaporated by heating the flask in an oil bath at 130° C. nearly all of the dimethyl formamide being recovered. The final pressure was 10 mm. Hg. This yielded a clear fused product which hardened into an amorphous waxy mass.

A 240 g. portion of this mass was fused by heating in an oil bath at 160°, the mass fusing at about 120°. The mass was treated with 250 ml. of hot methyl isobutyl ketone, the mixture being held at the boil. The sugar was precipitated as rather fine white crystals which settled to the bottom of the flask leaving a layer of clear solution. This mixture was filtered while hot and the sugar precipitate was washed with 50 ml. of additional hot

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solvent and filtered, the washings being combined with the first filtrate.

This clear solution was cooled with scraping until at 12° C. the sugar ester started to crystallize. Cooling continued to minus 3° C. when a mush had formed, which was immediately filtered leaving crystalline sugar ester and a clear solution of other substances.

The sugar ester was dried and fused at 100° C. and about 20 mm. Hg, yielding 100 g. of pale clear resin which on cooling could be broken and ground.

The cold solution was evaporated to yield 50 grams of an oily material, which was dispersible in water.

The sugar residue was dried and weighed 80 grams.

In Example 1 and Example 2 an amorphous form of sugar was created prior to solvent extraction, by means of adding a small quantity of water to the mixture of sugar and sugar-ester, while in Example 3 this amorphous state was achieved by fusion of the dried reaction product. (It was established previously that the reaction product from equimolar sucrose and methyl fatty ester would fuse below the decomposition temperature.) The water employed in Example 1 and Example 2, apparently served no purpose other than to create a mass which would fuse below the decomposition temperature. In all other respects the water is undesirable because it moistens the precipitated sugar, even to the extent of creating a syrup if too much is used. In all of these examples the sugar was regenerated in agglomerated or massive crystalline form by treating the fused or amorphous mixture of sugar and sugar ester with a solvent in which sugar is substantially insoluble. It is in this principle of simultaneous solution of sugar ester and precipitation of crystalline sugar that the invention differs from the usual methods of solvent extraction which had been attempted without success in the separation of sugar from sugar ester when the sugar is in microcrystalline form.

In Example 2 and Example 3, it is demonstrated that certain solvents such as methyl isobutyl ketone may be employed in the practice of the invention, which will yield an extract solution which may be chilled to precipitate purified sugar ester leaving the fatty impurities in solution. It is also demonstrated that this step can only be carried out if the dimethyl formamide has been reduced to a low concentration in the dried reaction product, or from the starting mixture of sugar, sugar ester and impurities, prior to the extraction treatment.

The sugar esters to which the extraction process of the present invention is applicable include those which result from the esterification of any suitable sugars, such as sucrose, with a fatty acid or fatty acid derivative where the fatty acid radical has from 10 to 20 carbon atoms. Examples of suitable acids are palmitic, lauric, oleic or stearic. The process is also applicable to esters which are reaction products of sugars and acids other than the long chain fatty acids.

It is of course not necessary that the mixture of sugar ester and sugar be obtained by a process as described in the above examples. Where the ester and sugar mixture has been obtained in any other way that has resulted in an intimate mixture which may be a solidified "glass" of sugar and sugar ester, or a mixture containing sugar in microscopic crystal size (of the order of one micron), and with or without contamination by reaction solvents and minor amounts of other substances, the improved extraction method of the invention is also applicable.

The improvement in the extraction process of the present invention is in converting the sugar content of the mixture into an amorphous state, such as a fused mass or a fused mass containing a small amount of water, or a solidified glass, before adding the extraction solvent for separating the ester from the unreacted sugar. The proportion of water to be incorporated with the ester-sugar in order to create a fused mass varies with the fusion temperature and also the proportion of the ingredients,

none being required when for example the mixture results from the reaction of equimolar portions of sugar and methyl fatty ester. In the usual case of three moles of sugar reacting with one mole of methyl fatty ester, the addition of about 10% of water, based upon the weight of the dried mass, is sufficient. Any other suitable material which would cause fusion at a safe temperature might also be employed, instead of water. If too little is used, undissolved sugar micro-crystals may remain in the fused mass of solution, and if too much water is used, sugar syrup tends to be separated out when the extraction solvent is added, and a transfer of water to the solvent phase may cause solution of some sugar in the solvent phase, reducing the efficiency of the separation.

The preferred procedure is to add just enough water to the mixture of sugar ester and sugar that it will fuse at a temperature below that where discoloration of the mixture commences, which is between 110 and 120° C., approximately. The extraction solvent is to be added to the fused mass is any liquid which will readily dissolve the sugar ester being separated and which will not dissolve any appreciable proportion of sugar. The solvent should not react to any appreciable extent with any of the materials present during extraction. It should be sufficiently volatile to be evaporated from the dissolved sugar ester and residual sugar without decomposing either of the solids and leaving a solvent-free residue. Where the mixture of ester and sugar has been obtained by a process that results in some of the reaction solvent being absorbed therewith even after drying, the extraction solvent must be one which can be separated from the reaction solvent by distillation or other means.

A number of different types of organic liquids are suitable extraction solvents in this process. Among these are lower aliphatic alcohols such as propyl, isopropyl, normal or secondary butyl. Ketones such as methyl ethyl ketone or methyl isobutyl ketone are also suitable. Various esters such as isopropyl acetate can also be used, as can also such mixtures as lacquer solvent, or hydrocarbons and alcohols.

It is preferred to use a considerable excess of solvent over that which is just sufficient to dissolve the ester, particularly where it is intended to precipitate purified sugar ester by chilling the extraction solvent.

The process of the invention can be used even when the mixture of fine crystals of sugar and ester contains much more sugar than ester. The process was carried out with mixtures in which the ester to sugar ratio was 2:1, 1:1 and 1:2 and the separation was effected equally well.

When the sugar settles out of the extract solution as has been described above, it is in the form of agglomerated masses about 100 or more microns in size, although these agglomerates can be seen with the aid of a microscope to be constituted of much smaller crystallites.

There has thus been described an improved method of extracting a sugar ester from sugar where the sugar is originally present as crystals which are microscopic in size and where the sugar ester is so tightly adsorbed upon the sugar that ordinary solvent extraction procedures are not effective. The process is effective in the commercial production of sugar esters in general and is operative in the presence of minor amounts of various contaminants usually present in processes of this general type. This method makes possible a simple process by which purified sugar ester may be precipitated from an extract solution, while sugar which was not dissolved and fatty impurities which are not precipitated may be recovered and returned to the reaction process to yield additional sugar ester product.

I claim:

1. A method of separating a sucrose monoester of a fatty acid having 10 to 20 carbon atoms per molecule, from sucrose, where said ester is adsorbed upon micro-crystals of the sucrose, comprising adding sufficient water to the mixture of ester and sucrose to form a viscous solution substantially free of sucrose crystals, evaporating a portion of the water leaving just sufficient to maintain the mixture as a stiff gel with substantially no sucrose crystals present, and then extracting said ester from the gel with a liquid which is a good solvent for said ester and is substantially a non-solvent for said sucrose.

2. The method of preparing a sugar monoester in purified form from a mixture of sugar, sugar monoesters and fatty impurities comprising reducing the mixture to a form in which the sugar is substantially in a non-crystalline state, adding a heated solvent which precipitates the sugar content while dissolving the sugar monoester and said fatty impurities, separating the precipitated sugar from the hot solution, cooling the solution to cause precipitation of the desired sugar monoester, and then separating the precipitated sugar monoester from the cooled solution containing the said fatty impurities.

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