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Methods of Preparation . . .

Fatty Acid Esters of Sucrose

Raw materials for these versatile new esters are inexpensive and plentiful. A promising process involves reaction of sucrose monoester with excess methyl ester to form a high level polyester. Addition of solvent and excess sugar gives the monoester in good yield

COMPARED with ethylene oxide or sorbitol at 15 to 20 cents per pound, sugar, at 3 to 5 cents per pound in the world market, or even the controlled market in the U. S. of 6 to 8.5 cents, is the lowest cost hydrophilic grouping available for use in the preparation of nonionic surfactants. With tallow prices stabilized at about 7 cents per pound, the combination of fats with sugar can result in low-cost nonionic surfactants, comparable in price with or lower than sodium dodecylbenzene sulfonate.

Furthermore, sugar esters of long-chain fatty acids hydrolyze in the stomach to form the normal food components, sugar and fatty acids. Thus, these nonionic surfactants can be expected to be both nontoxic and nutritional.

Very few references to sucrose esters of fatty acids appear in the literature. In 1860, Berthelot (*2*) heated sucrose and stearic acid together and failed to obtain an ester. Hess (*6*) in 1921 reacted sucrose with stearoyl chloride in quinoline to obtain the octastearoyl sucrose. Harris (*5*) refers to the stearic acid ester of sucrose obtained by heating together equimolar quantities of sucrose and steroyl chloride in pyridine. Physical properties are not reported. Lorand (*7*) used the reaction of sucrose with palmitic anhydride in the presence of monochloroacetic acid and magnesium perchlorate to obtain a product useful as a water repellent. Recently, addition of mono- or polysubstituted fatty acid esters of sucrose to lubricating oils has been the subject of a patent (*3*). However, there was no indication of a method of preparation.

Laboratory Development

There are obvious difficulties in the development of a process for the manufacture of any chemical compound that has not previously been characterized. It is necessary to prepare the compound by any means, obtain it in pure form without prior knowledge of its behavior characteristics, and then determine its properties. Finally, there is the tedious process of determining the most economical method for manufacture through laboratory, pilot plant, and industrial scale.

There are problems specific to the materials under consideration here. The solubility properties of sucrose are entirely different from those of fats or fatty acids. Sucrose is sensitive to heat and acids. There are eight hydroxyl groups in sucrose, all of which can react. In a single run, theoretically 255 different sucrose esters, including isomers, can be formed. If several fatty acid groups are present, the number of possible compounds is all the greater. It could be a Herculean task to separate the esters of even a single fatty acid into the individual pure components. Fortunately monosubstitution is primarily in the 6 position (*9*).

The preferred process developed for the preparation of fatty acid esters of sucrose involves the alcoholysis of a fatty acid ester of a volatile alcohol with sucrose. With a 3 to 1 molar ratio of sucrose to nonsugar ester, and 0.1 mole of an alkaline catalyst, about 90% of the nonsugar ester is converted to the monoester of sucrose. A similar percentage conversion to the diester of sucrose is achieved using a 1 to 2 molar ratio of sucrose to nonsugar ester.

Analysis

Good analytical methods are essential for determining the nature of a reaction, as well as for subsequent plant control. Consequently, the methods which were employed in this study are described in some detail. It should be emphasized that all analytical procedures are limited to the extent that the analyst can find only what he is looking for. The possibilities of side reactions involving sugar, the catalyst, and the solvent have not yet been fully explored. Consequently, these analyses cannot yet be regarded as definitive. The methods have been tested on synthetic mixtures with satisfactory results. This statement requires some explanation. If a product contains 3.0% methyl stearate, an error of 25% on methyl stearate is not unsatisfactory. Material balances on total sugar and solids were rarely in error by more than 2%.

Procedures. Upon the completion of a reaction run, sufficient sample is withdrawn to give 10 to 15 grams of dry solids. This sample is dried to constant weight in an Abderhalden drying apparatus over sulfuric acid at 100° C. and about 1 mm. of mercury pressure. Approximately 5 grams of the dried sample is added to a beaker containing 50 ml. of 10% aqueous sodium chloride and 50 ml. of 1-butanol. The mixture is heated gently while stirring until the sample is completely dissolved. After the two phases separate, the water layer is washed three times with 25-ml. portions of 1-butanol. The butanol washings are combined with the butanol layer and washed twice with 25-ml. portions of fresh 10% aqueous sodium chloride solution. These washings are added to the water layer. Anhydrous sodium sulfate is added to the 1-butanol fraction to clarify it. This fraction is then filtered. The filter cake is washed with fresh 1-butanol and the washings are combined with the filtrate. Unreacted sugar is in the water layer, and sucrose fatty acid ester and soap are in the butanol layer. The butanol and water layers are then measured in a polarimeter to determine the optical rotations of the solutions. An aliquot of the butanol layer is added to an equal volume of carbon dioxide–free distilled water and the mixture is titrated to a methyl orange end point with 0.1N hydrochloric acid to determine soap. Another aliquot of the butanol layer is taken to dryness to determine solids.

If the methyl ester of a fatty acid was employed in the alcoholysis reaction, unreacted methyl ester is determined by saponifying the dry product, distilling off the methanol, and determining it colorimetrically with chromotropic acid (*8*).

Approximately 5 grams of dried sample is accurately weighed and transferred to a 1-liter flask containing boiling stones and 25 grams of potassium hydroxide dissolved in 300 ml. of distilled water. The flask is connected to a condenser, through an adapter, then to a 250-ml. volumetric flask immersed in an ice water bath. The solution is heated and allowed to boil for 2$^1/_2$ hours to effect saponification of unreacted methyl ester and distillation of methanol. The volumetric flask is then warmed to 20° C. and made up to volume with distilled water.

A portion of this solution containing 0.02 to 0.4 mg. of methanol, usually about 0.5 ml. of the solution, is oxidized by adding 2 ml. of 3% potassium permanganate solution in 15% phosphoric acid. The mixture is kept at room temperature for about 4 minutes with occasional swirling. Excess permanganate is reduced by adding solid sodium bisulfite. Then 0.6 ml. of 10% aqueous chromotropic acid is added, followed by the slow addition, with agitation, of 10 ml. of concentrated sulfuric acid. The mixture is swirled, chilled, and diluted to 50 ml. The absorbance of the solution is measured at 570 mμ, a reagent blank is subtracted, and the amount of methanol is determined from a standard curve.

Calculations. To illustrate the calculation of results from the analytical data, assume that methyl stearate was made to react with sucrose to form sucrose monostearate, with potassium carbonate as catalyst.

$$\%\text{ methyl stearate} = \frac{\text{weight of methanol} \times 9.3}{\text{sample weight}} \times 100$$

$$\%\text{ sucrose} = \frac{\alpha_\omega \times \text{volume of water layer}}{66l \times \text{sample weight}} \times 100$$

Polarimetry measurements were made at 20° C. using a sodium vapor lamp. For sucrose, $[\alpha]^{20^\circ}_{\text{D}} = 66$, l is the length of the tube in decimeters, and α_ω is the optical rotation of the water layer.

$$\%\text{ potassium stearate} = \frac{\text{volume of acid} \times \text{normality} \times 32.1 \times \text{total volume, butanol layer}}{\text{sample weight} \times \text{volume of butanol aliquot}}$$

The percentages of sucrose monostearate and sucrose distearate are calculated as follows:

$$[\alpha]_S = \frac{\alpha_b \times \text{volume of butanol layer}}{l \times C}$$

where $[\alpha]_S$ is the specific rotation of the sucrose esters, α_b is the optical rotation of the butanol layer, and C = weight of solids in butanol layer − weight of sample × (% unreacted methyl stearate + % potassium stearate as previously determined).

The specific rotation of sucrose monostearate, as determined on material recrystallized several times from acetone, is 39.1. The specific rotation of sucrose distearate was determined using material which analyzed distearate, as an average. This value of 25.6 is probably less accurate than the value for the monostearate.

If the fraction of sucrose monostearate is X and sucrose distearate is $(1 - X)$, then

$$39.1X + 25.6\,(1 - X) = [\alpha]_S$$

$$X = \frac{[\alpha]_S - 25.6}{13.5}$$

$$\%\text{ sucrose monostearate} = \frac{100\,CX}{\text{sample weight}}$$

$$\%\text{ sucrose distearate} = \frac{100C(1 - X)}{\text{sample weight}}$$

First Procedure for Sucrose Monoesters

Although the first procedure shows little promise of development into an economical manufacturing process, it is given in some detail because it was used in the preparation of the esters on which the physical properties described later were determined.

Three moles of sucrose and 1 mole of the methyl ester of the appropriate fatty acid were dissolved in 4 liters of dimethylformamide. The mixture was warmed to 60° C. and 0.2 mole of sodium methoxide was added as catalyst. After 3 hours at 60° C., about two thirds of the solvent was removed by distillation from a boiling water bath at 10 to 20 mm. of mercury pressure. The concentrated solution was extracted eight times with 1-liter portions of hexane to remove unreacted methyl ester. The raffinate was then diluted with five volumes of acetone. The resulting sugar precipitate was filtered and washed with hot butanol. About 90% of the original sugar is recovered in this manner. This butanol solution was combined with the acetone solution and distilled from a boiling water bath at 10 to 20 mm. of mercury pressure. Complete drying was effected in an Abderhalden drying apparatus over sulfuric acid at 80° C. and 5 mm. of mercury pressure. The dry powder was then dissolved in acetone, using 200 ml. of acetone to 10 grams of sucrose ester. The solution was cooled to −20° C. to precipitate the product, which was recovered by cold filtration and dried in a vacuum desiccator over sulfuric acid. The yield in a series of runs averages about 25% based on the methyl ester. All starting materials employed were technical grade and were not further purified. Approximately the same yield is obtained when a glyceride ester replaces the methyl ester.

Second Procedure for Sucrose Monoesters

The preferred method for the preparation of sucrose monoesters of fatty acids involves the use of 3 moles of sucrose to 1 mole of a fatty acid ester of a volatile alcohol with about 0.1 mole of an alkaline catalyst and sufficient solvent to dissolve the reactants completely. Since the usual source of fatty acids is natural glyceride fats, the glycerol is first replaced by methanol with glycerol recovery as sweet water. This interesterification reaction is too well known to require description here (*7*). With dimethylformamide or dimethylsulfoxide as a solvent, potassium carbonate is a suitable catalyst. Unlike more alkaline catalysts, such as sodium methoxide, it can be used at temperatures sufficiently high for rapid stripping of the volatile alcohol without the occurrence of undesirable side reactions. The following procedure for the preparation of a laboratory batch of sucrose stearate was also used to prepare a 50-gallon batch by increasing the quantities of materials. In this case 0.14 mole of potassium carbonate was used per mole of methyl stearate.

Employing completely dry materials, dissolve 387 grams of sucrose in 1275 ml. of dimethylformamide by heating with vigorous agitation. Add 112.5 grams of methyl stearate and 7.5 grams of potassium carbonate. Maintain the reaction mixture at 90° to 95° C. under 80 to 100 mm. of mercury pressure. A six-plate fractionating column is suitable for stripping the methanol from the system. After 9 to 12 hours, distill off part of the dimethylformamide and dry the residue under vacuum. The course of the reaction proceeds as follows:

Material Present after Indicated Time	Percentages Based on Dry Solids			
	3 hr.	6 hr.	9 hr.	12 hr.
Sugar	62.4	59.4	54.7	53.9
Sucrose monostearate	12.5	26.2	37.3	37.9
Sucrose distearate	20.0	9.1	2.4	1.6
Methyl stearate	1.1	0.0	0.0	0.0
Potassium stearate	1.1	2.2	2.7	2.9
Potassium carbonate	1.4	1.3	1.3	1.3
	98.5	98.2	98.4	97.6

Material Present after Indicated Time	Percentages Based on Alcohol-Solubles			
	3 hr.	6 hr.	9 hr.	12 hr.
Sucrose monostearate	36.0	70.0	88.0	89.5
Sucrose distearate	57.7	24.3	5.6	3.8
Methyl stearate	3.15	0.0	0.0	0.0
Potassium stearate	3.15	5.7	6.4	6.7
	100.0	100.0	100.0	100.0

It appears that, first, the methyl ester reacts very rapidly to form mono- and diester in approximately equimolar proportions—the percentage figures at the end of 3 hours are equal to molar quantities of almost exactly 1 to 1. On further heating the sucrose reacts with the diester to form more monoester. That is completely consistent with other work in which polyesters up to the tetraester are heated with excess sucrose in the presence of solvent for conversion to the monoester. After 6 hours, the ratio of monoester to polysubstituted esters calculated as diester is about 2 to 1. After 12 hours, it is about 23.5 to 1. The amount of soap increases gradually. After 12 hours, almost 20% of the potassium carbonate present has been converted to soap.

In the experiment previously described, the volume to weight ratio of dimethylformamide to sucrose was 3.3 to 1. When the ratio of dimethylformamide to sucrose was reduced to 2.3 to 1, and the ratios of other materials to sucrose were not changed, these results were obtained:

Material Present After Indicated Time	Percentages Based on Dry Solids	
	7 hr.	14 hr.
Sugar	58.9	56.1
Sucrose monostearate	26.7	31.2
Sucrose distearate	8.7	7.0
Methyl stearate	0.0	0.0
Potassium stearate	2.7	2.9
Potassium carbonate	1.3	1.3
	98.3	98.5

The molar ratio of monostearate to distearate after 7 hours, 3.1 to 1, is consistent with the ratio of 2.9 to 1 obtained after 6 hours in the more dilute solution. However, after 14 hours this ratio had increased only to 4.5 to 1, compared with 23.5 to 1 for the more dilute solution.

The major effect of increasing the concentration of catalyst is the formation of more soap. Thus, when the concentration of potassium carbonate was increased sevenfold, after 12 hours approximately 50% of the methyl stearate originally present had been converted to potassium stearate.

The following process, still in the early stages, appears promising. React sucrose monoester with excess methyl ester to form a high level of polyester, of the tri- or tetraester range. This proceeds relatively rapidly and without solvent present. Then to the polyester add excess sugar and solvent to dissolve it for reaction to convert back to the monoester.

Preparation of Sucrose Diesters

Sucrose diesters of fatty acids (*4*) are prepared under essentially the same conditions as the monoesters. For the diesters, 2 moles of a fatty acid ester of a volatile alcohol are employed for each mole of sucrose, in place of the 1 to 3 molar ratio used for the monoesters.

Dissolve 150 grams of methyl stearate and 82 grams of sucrose in 1 liter of dimethylformamide. Add 15 grams of potassium carbonate and heat to 90° to 95° C. Maintain this temperature and a pressure of 80 to 100 mm. of mercury for 6 hours. A six-plate fractionating column is employed to strip off the methanol. Distill off part of the solvent and vacuum dry. Analytical data from one experiment showed that the dry product contained 5% potassium stearate, 2% methyl ester, and less than 1% unreacted sugar. The remaining material assayed as sucrose diester.

Purification of Sucrose Esters

After distillation of the solvent from the sucrose monoester run, the dry residue contains about 54% sugar, 1 to 2% potassium carbonate, and about 45% active agent. This product is suitable without purification for numerous applications, including detergency. Economic considerations will require the recovery of the sucrose for recycling in some countries. This can be accomplished by dissolving the dry residue in 3 to 4 times its weight of water, followed by the addition of 5% of sodium chloride based on the water. The mixture is heated to 80° to 90° C. and maintained at this temperature until the sugar ester has layered completely. The curd is then withdrawn and dried. This curd as filtered contains 50 to 60% solids, of which 80 to 85% is alcohol-soluble. The remainder is sugar and salt. The aqueous layer can be reused several times, after which the water is removed and the sugar and salt recycled.

Complete removal of sugar and salt is accomplished by partitioning the solids obtained after distillation of the solvent between an aqueous salt solution and 1-butanol. Distillation of the butanol results in a product which is about 90% sucrose monoester. The remainder is soap and polysubstituted esters of sucrose. This product can be recrystallized from acetone to give pure sucrose monoester.

Sucrose diester obtained after simple distillation of the reaction solvent is better than 90% pure sugar ester. Further purification is not required for most commercial applications.

Discussion

The procedures which have been described for the preparation and purification of sucrose monostearate and distearate have also been applied without substantial modifications to the preparation of other fatty acid esters of sucrose. By increasing the ratio of methyl ester to sucrose in the reaction mixture, more highly substituted derivatives of sucrose are obtained.

The sucrose esters are new and complex chemical compounds. Further improvements will undoubtedly be made in the manufacturing process. For example, it can be expected that an increase in the reaction temperature will reduce both solvent requirements and the reaction time.

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Surface Activity of Monoesters . . .

Fatty Acid Esters of Sucrose

Evaluation studies indicate that these esters are emulsifying agents and good detergents. They are sufficiently stable to hydrolysis for use in cotton detergency applications. Low toxicity also points to particular usefulness in cosmetic, pharmaceutical, and food applications.

THE monoesters were prepared by the first procedure described in the preceding paper. They were purified by repeated crystallization from acetone.

Physical Properties

The specific rotation, softening point, and per cent acyl radical determined by saponification of each of the sucrose esters employed in this study are given in Table I. Comparison of the experimental saponification value with the theoretical value for the monoester indicates that all of the sucrose esters are essentially pure monoesters. Equilibrium solubility values were not determined. All these sucrose esters appear to be soluble in warm water, ethanol, methanol, and acetone. Solutions of sucrose palmitate and sucrose stearate, 20% in hot water, formed viscous solutions and gels on cooling to room temperature. Aqueous solutions of sucrose laurate are low-viscosity fluids at room temperature, even at 30% concentration. The solubility of the sucrose

Table I. Physical Properties of Sucrose Esters

			% Acyl Radical		*Surface Tension, Dynes/Cm.*[b]				*Interfacial Tension, Dynes/Cm.*[b,c]			
					Concn., %							
Surfactant	$[\alpha]^{20}_{D}$ *(Ethyl Alcohol)*	*Softening Point, ° C.*	*Theoretical*[a]	*Found*	*1.0*	*0.2*	*0.1*	*0.05*	*1.0*	*0.2*	*0.1*	*0.05*
Sucrose laurate	+42.5°	90–91	35.0	35.0	33.4	33.4	33.7	35.6	7.6	7.1	7.9	8.4
Sucrose myristate	+42.2°	67–69	38.2	39.0	33.1	33.1	34.8	34.8	7.3	6.3	7.0	7.4
Sucrose palmitate	+39.8°	60–62	41.25	40.0	33.7	33.7	33.7	35.0	6.3	5.9	6.2	6.2
Sucrose oleate	+37.6°	50–54	42.0	39.2	31.8	30.8	31.5	32.7	5.4	5.0	5.0	6.2
Sucrose stearate	+39.35°	52–53	42.3	44.1	33.5	33.1	34.0	33.7	6.2	6.6	7.7	7.2
Tall oil–polyoxyethylene condensate					40.4	41.0	41.0	42.0	6.7	7.0	7.2	7.7
Polyoxyethylene-polyoxypropylene condensate					43.0	47.0	48.0	48.0	13.0	15.2	16.1	16.5
Sodium dodecylbenzene sulfonate					31.0	30.9	29.4	29.3	2.3	2.3	2.0	2.6

[a] Based on monoester.
[b] Aqueous solutions at room temperature.
[c] Against Nujol.