

Preparation of Sucrose Esters by Interesterification¹

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Abstract

Reactions between sucrose and esters of long chain fatty acids customarily have been conducted in a mutual solvent, such as dimethylformamide. The solvent-free interesterification of molten sucrose and fatty acid esters at temperatures between 170–187°C has now been performed with the aid of lithium, sodium and potassium soaps as catalysts and solubilizers. When the reactants were heated rapidly and then subjected to reduced pressure, the interesterifications could be brought to equilibrium in 12 min or less, including the time necessary to melt the sucrose. The several soaps and combinations of soaps employed differed markedly in their performance. No sucrose esters were obtained with lithium palmitate, while the yield with lithium oleate was among the best, but consisted of over 90% tetra- and higher esters of sucrose. Lower esters were best produced with combinations of lithium oleate with sodium or potassium oleate employed at a level of about 25% total soaps, based on the weight of sucrose. The type of fatty acid ester employed also markedly affected the yield of sucrose esters. Among the esters tested, methyl carbitol palmitate (which could be formed in situ), monopalmitin, distearin and technical grade diglycerides (48% diglycerides) prepared from completely hydrogenated cottonseed oil, interesterified readily.

Introduction

Monoester products of sucrose and fatty acids are potentially important as emulsifiers in foods and cosmetics and as household detergents (1–3). The higher esters also have potential uses, particularly those of drying oil fatty acids (4). However, the major obstacle to realizing these potentials is the lack of a suitable method of manufacture. The limited amounts of mono- and diesters of sucrose presently being marketed are manufactured by an alkali catalyzed interesterification of sucrose and methyl esters or triglycerides of the fatty acids dissolved in dimethylformamide (5,6). The process is relatively expensive and the removal of nitrogenous compounds to an acceptable level is difficult. A more recently devised process (7) consists of interesterifying sucrose and a methyl ester in a propylene glycol solution, which also contains about 50% sodium soap, based on the weight of the sucrose, and a small amount of potassium carbonate as catalyst. The propylene glycol is removed gradually by distillation under vacuum as the interesterification proceeds and the temperature is raised gradually from an original 130°C to a final level of 165–167°C.

The interesterification of molten sucrose and fatty acid esters in the absence of a solvent apparently has never been reported. The present investigation was undertaken to establish the feasibility of such an interesterification.

Materials, Procedures and Analyses

Materials

The sucrose employed in all of the interesterifications was a starch-free, powdered cane sugar of 6X fineness supplied by a local refinery. Purity was claimed to be 99.95%.

The methyl esters of palmitic and oleic acids used in the smaller scale experiments were prepared in the laboratory and were found by gas liquid chromatographic analysis to have a purity of better than 98%. Portions of these methyl esters were converted into esters of methyl carbitol, $\text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$, and methyl cellosolve, $\text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$, by interesterification and then purified.

Methyl carbitol palmitate for larger scale experiments was prepared by refluxing an excess of methyl carbitol with commercial palmitic acid (Emersol 144, Emery Industries, Cincinnati, Ohio) in the presence of a small amount of stannous chloride. The final product, after being freed of tin soaps and uncombined reactants, analyzed 98% methyl carbitol palmitate and 1% methyl carbitol stearate, the remainder being essentially methyl carbitol myristate.

The monopalmitin was a commercially available product (Myverol Type 1600, Distillation Products Industries, Rochester, New York) containing about 95% monoglycerides. The component fatty acids of the monopalmitin product were palmitic, 85%; stearic, 12%; and myristic, 3%. The distearin was a special, molecularly distilled product obtained from the supplier of the molecularly distilled monopalmitin.

Mixed glycerides of completely hydrogenated cottonseed oil were prepared in the laboratory by interesterifying 100 parts of the oil with 10.5 parts glycerol. Sodium hydroxide at the level of 0.1% was employed as catalyst. The interesterification product had approximately the following weight composition: monoglycerides, 27%; diglycerides, 48%; triglycerides, 23%; free glycerol, 2%; and sodium soaps, <1%.

The lithium, sodium and potassium soaps of oleic and palmitic acids were prepared by dissolving the methyl ester of the fatty acid in methyl alcohol, adding a dilute solution of the hydroxide of the selected alkali metal and then refluxing the combined solutions. Care was taken to add 2% more methyl ester than needed to react with the hydroxide. After formation of the soap the methanol was removed by distillation and evaporation under nitrogen. This technique yielded alkali-free, anhydrous soaps.

Interesterification Procedures

In the smaller scale interesterification all of the reactants (about 10 g total) were put into a 100 ml, three-neck, round-bottom flask at room temperature. For example, in Run 2 the reactants were 5.00 g (0.0146 mole) sucrose, 5.23 g (0.0146 mole) methyl carbitol palmitate, and 1.5 g (30% based on the weight of sucrose) potassium oleate. A Teflon-coated, magnetic stirring bar was added to the flask and fittings were added which permitted flushing the flask with and keeping the reactants under nitrogen while at atmospheric pressure. The flask was im-

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mersed in a thermostatically controlled hot oil bath maintained at 185–187°C with the aid of a hot plate magnetic stirrer combination. After a few minutes in the oil bath a side arm was attached for drawing a vacuum and distilling off the alcohol or glycerol liberated by the interesterification. If removal of alcohol or glycerol was to be conducted at 170°C, the vacuum pump was started after the flask and contents were transferred to a constant temperature bath at this temperature. After a matter of minutes (usually less than 20) from the time the flask was immersed in the bath at 185–187°C, the reaction was stopped by breaking the vacuum and adding 20 ml methyl carbitol containing usually 0.67 mole citric acid per mole of soap used. Citric acid in this amount and apparently in amounts as high as 1.1 moles/mole of soap did not disproportionate the sucrose esters. After addition of the citric acid solution, the reaction product was cooled rapidly to room temperature.

The larger scale reactions, up to 200 g total reactants, were conducted in a 500 ml, three-neck, round-bottom glass reaction flask immersed in a thermostated oil bath. Only a single temperature, 187°C, was employed. Through the central neck of the flask was inserted a stainless steel, paddle-type stirrer equipped with a stuffing box. A short air condenser (23 mm diameter by 150 mm long) with a short (60 mm) vertical section consisting mostly of a half length, 24/40 standard-taper joint, was inserted in one of the side necks. To the lower end of the condenser was attached a dry ice trap which in turn could be attached to a vacuum pump. In the remaining side neck of the flask was inserted a short piece of glass tubing fitted with a 24/40 standard-taper joint at each end and a nitrogen gas inlet at the middle. The upper joint on the glass tube was used in the first stage of a reaction to attach a small polyethylene bag containing the sucrose to be used and in the second stage of the reaction to attach a small flask and provide an air-tight seal.

To conduct an interesterification in the larger scale assembly, the fatty acid ester and soap were put into the reaction flask and heated under nitrogen to 187°C. Then the finely powdered sucrose was added as desired by lifting and tapping the polyethylene bag. Finally, the empty polyethylene bag was detached, the opening was sealed, the slow flow of nitrogen was shut off, and the reactants were put under vacuum. The reaction was stopped by breaking the vacuum with nitrogen, removing the reaction flask from the hot oil bath, and quickly cooling the reaction product.

Purification and Analysis

The reaction products from the smaller scale reactions, which had been treated with citric acid to destroy the soaps, were dissolved in hot 1-butanol and washed with a 5% solution of sodium chloride in water. The products from the larger scale reactions were treated in the same manner, except that citric acid was added to the first wash water (0.67 mole citric acid per mole of soap). After water washing, the 1-butanol was removed by heating the solution under vacuum and stripping with nitrogen. The residue remaining after removal of the 1-butanol was extracted with warm chloroform, which did not take up any small amounts of salt or sucrose. The chloroform extract contained all of the sucrose esters, any unreacted fatty acid esters, and the fatty acid from the soap used as catalyst. After filtration of the hot

chloroform extract the chloroform was removed by distillation and stripping with nitrogen under vacuum.

The purified reaction products were analyzed by a thin layer chromatographic technique which will be described in another communication (T. J. Weiss et al., manuscript in preparation). Briefly, a measured amount of chloroform solution containing a known proportion of purified reaction product was spotted on a silicic acid plate, and the spots were developed with a solution consisting of 10 vol toluene, 5 vol ethyl acetate, and 5 vol of 95% ethanol. The plates were dried and sprayed with a solution of 1 g urea in 4.5 ml of 85% phosphoric acid which had been dissolved in 48 ml of 1-butanol saturated with water. Heating these treated plates at 110°C for 0.5 hr produced a series of brown spots indicating both the type of sucrose ester (mono-, di-, etc.) and the amount of each. The amounts were measured quantitatively with the aid of a recording densitometer. Sucrose esters prepared and characterized by established laboratory techniques were used for control purposes.

Selection of Reaction Conditions

Melting of Sucrose

The solvent-free interesterification of sucrose requires, of course, that the sucrose be in the molten state. Pure sucrose melts at about 185°C and will remain clear and fluid at this temperature for several minutes before beginning to degrade to a black, tarry mass. This brief period of stability should be sufficient when an interesterification rate is attainable which will produce a sizable proportion of sucrose esters during this time. As such a reaction proceeds, dilution of the residual sucrose should enhance its resistance to deterioration.

Sucrose possesses other utilizable characteristics. Once melted it will not recrystallize readily as the temperature is decreased. High quality, commercial sucrose quickly melted at about 185°C and cooled to 164°C was found not to recrystallize in the course of 1 hr. This observed behavior probably was caused by a combination of the natural tendency of molten sucrose to supercool and the formation of a small proportion of impurities which depressed the melting point. The deliberate addition of minute amounts of impurities, including water, glycerol and glucose was investigated, and the conclusion was reached that such impurities would be useful additions if it became desirable to depress the melting point of sucrose.

Solubilizers

Fatty acid esters, including monoglycerides and the sucrose octaesters of acetic and isobutyric acids, were found to be highly insoluble in molten sucrose. Limited amounts of monoglycerides or the mono- and diesters of sucrose were not suitable emulsifiers for sucrose and fatty acid esters under the conditions usually employed for interesterifying glycerides. Attempts to interesterify sucrose-containing mixtures under such conditions always resulted in a two-phase system, one phase consisting of degraded sucrose and the other of fatty acid esters.

The problem of intimate mixing of the reactants was solved by applying the principle of solubilization enunciated by Palit (8,9). He stated that an immiscible mixture of two solvents, G, and H, where G represents any glycol or dihydroxylic solvent, particularly with two hydroxyl groups in contiguous

positions, and H represents any hydrocarbon or a solvent which can dissolve hydrocarbons, can be brought into a homogeneous solution by the addition of an amount of soap which is soluble in neither G or H. He attributed this solubilization to hydrogen bonding and the formation of a ring structure.

Preliminary experiments in the interesterification of sucrose and fatty acid esters revealed that solubilization was enhanced when H consisted of partial esters of glycerol or esters of methyl carbitol, or methyl cellosolve.

Catalysts

In establishing suitable interesterification conditions, the discovery was made that a small amount of free alkali in the soaps used as catalysts caused rapid darkening of the melted sucrose. This increased rate of darkening occurred even in the presence of fatty acid esters. Apparently, any free alkali present in the fatty components transferred readily to the sucrose and reacted with it. When precautions were taken to employ alkali-free soaps, darkening occurred at a greatly decreased rate. None of the soaps of the short chain fatty acids, such as acetic, butyric, and caproic, were good catalysts.

The alkoxides and free alkalies frequently employed as interesterification catalysts proved to be entirely unsatisfactory in the preparation of sucrose esters at high temperatures. Undoubtedly, these compounds were converted into soaps before the reaction temperature was reached (10). Also, their use resulted in a very rapid darkening and deterioration of the sucrose.

Results and Discussion

Data obtained from a number of the smaller scale interesterifications are recorded in Table I. The reactants in none of these interesterifications formed a clear solution, but those which contained mono-palmitin approached this state. All formed homogeneous emulsions. As a rule the emulsions formed with lithium and sodium soaps were whiter, more opaque, and stiffer than those formed with potassium soaps. As each reaction proceeded, the reactants became darker in color, and the rate of darkening increased as the alcohol portion of the fatty acid esters

employed was removed by distillation under vacuum. A small proportion of free alcohol appeared to have a protective effect. However, the final reaction products appeared, as a rule, to be no darker in color than sucrose esters made on a semicommercial scale by the dimethylformamide process.

The phase relationships in any given interesterification are quite complicated; and, as is evident on comparing data for Runs 4 to 6, increasing the proportion of soap under a given set of conditions may markedly decrease the yield of sucrose esters.

When a single soap was used as both catalyst and solubilizer, the yield of sucrose esters obtained with different soaps varied greatly. Lithium palmitate produced no sucrose esters, while lithium oleate produced more than any other soap (Run 2). However, 91.9% of the sucrose esters produced with lithium oleate were tetra- and higher esters.

Sodium and potassium soaps generally were similar in performance. In each case the oleate performed decidedly better than did the palmitate. The performance of the sodium and potassium oleates and palmitates could be enhanced by adding a small amount of lithium oleate. Probably the sodium and potassium soaps performed better as solubilizers than did the lithium oleate, while the latter performed best as a catalyst, which might have been anticipated (11).

While Table I does not contain data showing the effect of large variations in the ratio of sucrose to fatty acid esters and the effect of reaction time, these variables were evaluated. Increasing the ratio of sucrose to fatty acid esters increased, as expected, the proportion of sucrose monoesters, calculated on a total sucrose ester basis. Short reaction times produced a high proportion of sucrose monoesters, while very short reaction times produced practically only monoesters.

Methyl palmitate (Run 13) proved to be a relatively unsatisfactory intermediate for the preparation of sucrose esters by the interesterification conditions employed. Performance undoubtedly could have been improved over that indicated in Run 13 by using a combination of soaps and possibly a different proportion. The performance of methyl palmitate was made equal to that of methyl carbitol palmitate by adding

TABLE I
Proportion of Sucrose Esters Formed Under Different Conditions of Interesterification^a

Run No.	Ester used	Catalyst		Sucrose esters in fatty fract., wt. %	Composition of sucrose esters, wt. %			
		Type	Amt., sucrose basis, wt. %		Mono-	Di-	Tri-	Higher
1	Methyl carbitol palmitate	No catalyst	0.0	0.0	0.0	0.0	0.0
2	Methyl carbitol palmitate	Li oleate	30	43.9	1.5	4.0	2.6	91.9
3	Methyl carbitol palmitate	Li palmitate	30	0.0	0.0	0.0	0.0	0.0
4	Methyl carbitol palmitate ^b	Na oleate	30	24.9	42.3	50.0	4.6	3.0
5	Methyl carbitol palmitate ^b	Na oleate	20	41.6	30.8	48.6	10.6	10.0
6	Methyl carbitol palmitate ^b	Na oleate	10	18.3	29.3	50.8	14.0	6.0
7	Methyl carbitol palmitate	Na palmitate	30	11.5	51.6	33.8	14.6	0.0
8	Methyl carbitol palmitate	K oleate	30	24.7	59.4	29.7	7.4	3.5
9	Methyl carbitol palmitate	K palmitate	30	11.8	30.6	36.1	33.3	0.0
10	Methyl carbitol palmitate ^b	Na oleate + Li oleate	30 + 5	48.7	35.3	38.1	18.0	8.6
11	Methyl carbitol palmitate	K palmitate + Li oleate	30 + 2.5	17.0	38.9	32.9	27.3	0.8
12	Methyl carbitol palmitate	K palmitate + Li oleate	30 + 5	19.0	39.2	30.5	26.9	3.4
13	Methyl palmitate	Na oleate	30	7.5	67.4	28.8	3.5	0.0
14	Triglycerides ^c	Na oleate	30	3.0	100.0	0.0	0.0	0.0
15	Monopalmitin	K oleate	20	29.2	45.9	34.6	13.6	5.9
16	Monopalmitin	K oleate + Li oleate	20 + 5	35.3	40.9	34.6	15.5	9.0
17	Monopalmitin	Na oleate + Li oleate	20 + 5	55.6	38.5	38.5	13.1	9.6
18	Diglycerides ^d	K oleate + Li oleate	20 + 5	37.0	40.9	40.2	8.5	10.4
19	Mixed glycerides ^e	K oleate + Li oleate	20 + 5	40.4	36.1	44.8	13.9	5.1
20	Methyl cellosolve palmitate	K oleate + Li oleate	20 + 5	25.9	42.2	41.4	12.7	4.0

^a Flask containing reactants immersed in 185 C bath for 7 min while reactants under 1 atm. nitrogen, then flask transferred to 170 C bath and reaction continued under vacuum for 10 min. One equivalent of fatty acid groups per mole of sucrose, unless noted otherwise.

^b Mole ratio of methyl carbitol palmitate to sucrose, 0.8:1.0.

^c Completely hydrogenated cottonseed oil.

^d Molecularly distilled diglycerides of completely hydrogenated soybean oil.

^e Mixture of monopalmitin, distearin and tripalmitin in mole ratio 3:2:1.

TABLE II
 Interesterification of Sucrose and Methyl Carbitol Palmitate at 185 C^a

Run No.	Time under vacuum, min	Sucrose esters in fatty fract., wt. %	Composition of sucrose esters, wt. %			
			Mono-	Di-	Tri-	Higher
21	0	34.0	29.0	51.0	20.0	0.0
22	2	39.0	33.2	44.5	22.3	0.0
23	5	67.0	35.7	47.5	16.8	0.0
24	10	63.0	33.3	51.1	15.6	0.0

^a Flask containing reactants immersed in 185 C bath for 7 min and then vacuum was applied. Mole ratio of sucrose to methyl carbitol palmitate was 1:1. Catalyst was sodium oleate, 30% based on weight of sucrose.

a small amount of methyl carbitol (2 moles/mole methyl palmitate), which resulted in methyl carbitol palmitate being formed in situ.

Triglycerides, like methyl palmitate, performed poorly as intermediates, but the performance could be improved greatly by adding mono- and diglycerides. Mono- or diglycerides used alone produced good yields of sucrose esters.

Starting an interesterification at 185 C and then reducing the temperature to 170 C, or perhaps even lower, retards the degradation of sucrose and permits the use of longer reaction times. Another solution to this problem is to conduct the entire reaction at 185 C, which increases the reaction rate and reduces the amount of time required. This latter approach was evaluated in the series of interesterifications represented in Table II.

Simply immersing the flask and reactants in an oil bath at 185 C and stirring the reactants under an atmosphere of nitrogen as the flask was heated for 7 min (which includes the time required to heat the flask from room temperature and melt the reactants) resulted in a product containing 30.0% sucrose esters, based on the weight of the fatty fraction. Identical conditions, except that after 7 min of heating a vacuum (pressure, 1–3 mm mercury) was put over the reactants for 5 min (Run 23), yielded a fatty fraction containing 67% sucrose esters which amounts to a conversion of 79.4% of the original methyl carbitol palmitate into sucrose esters. Based on the yield calculated for Run 24, the interesterification had come essentially to equilibrium after 5 min under vacuum, and there was no advantage in extending the reaction time.

Heating all of the reactants quickly from room temperature to the reaction temperature was a convenience when the small-scale exploratory interesterifications represented in Tables I and II were conducted. Obviously, for larger-scale reactions the fatty acid esters and soaps, which are relatively resistant to thermal degradation, would be combined and heated to the reaction temperature, and then the sucrose would be added. The sucrose is the only component critically sensitive to degradation when held for an extended time at the reaction temperature. One series of experiments conducted in this mode is represented in Table III.

In Runs 25–27 the total time from the moment the addition of sucrose was completed to the moment the reaction was stopped was 8 min. As is evident, good yields of sucrose esters were obtained. This mode of operation was tested with total quantities of reactants up to 200 g and similar results were obtained. In these reactions the soaps were not destroyed before the temperature was lowered. The solubility of the reaction products apparently did not change significantly before the temperature was lowered to a level at which the soaps no longer were effective interesterification catalysts and could promote the disproportionation of the sucrose esters.

In Run 27, the technical diglycerides, which contained 48% diglycerides, 27% monoglycerides, and 23% triglycerides and which were prepared from completely hydrogenated cottonseed oil by a very simple procedure, yielded sucrose esters about as readily as did the molecularly distilled monoglycerides. Thus, the conversion of ordinary triglycerides to glyceride mixtures suitable for interesterification with sucrose should be relatively inexpensive. Run 27 was repeated after removing from the technical diglycerides the approximately 2% free glycerol and 0.8% sodium soaps present. The proportion and composition of the resulting sucrose esters remained practically unchanged.

In Run 28 a relatively large mole ratio of monopalmitin to sucrose was used, and the reactants formed a clear solution. As anticipated, the percentage of sucrose monopalmitate in the reaction product was relatively low. More important, in this interesterification free sucrose disappeared rapidly, and the reaction products were quite resistant to heat-induced deterioration. During the 15 min under vacuum the color of the reaction product changed very slowly. This suggests a mode of operation for preparing edible sucrose ester products for use as food emulsifiers.

The process would consist of heating the selected fat with the necessary soap and a small proportion of glycerol to obtain a mixture of mono-, di-, and triglycerides and then adding a portion of the predetermined amount of sucrose to prepare a sizable proportion of sucrose esters. Then the remainder of the sucrose would be added, and the reaction would be continued for a short time. No vacuum would be

 TABLE III
 Interesterification of Sucrose at 187 C After Preheating Other Reactants^a

Run No.	Ester used	Fatty acid equiv. per mole sucrose	Time, min			Sucrose esters in fatty fract., wt. %	Composition of sucrose esters, wt. %			
			Addn. of sucrose	Mixing at 1 atm.	Under vacuum		Mono-	Di-	Tri-	Higher
25	Methyl carbitol palmitate	0.8	3	3	5	30.0	53.0	34.3	10.2	2.6
26	Monopalmitin	0.8	3	3	5	52.5	38.2	42.8	13.4	5.5
27	Tech. diglycerides ^b	0.8	3	3	5	46.6	44.0	39.8	7.1	9.1
28	Monopalmitin	4.0	1.2	0.8	15	41.2	24.4	31.8	16.7	27.1

^a Catalysts and solubilizers were 20% K oleate and 5% Li oleate, based on weight of sucrose. Total weight of reactants was approximately 100 g in each run.

^b Prepared by interesterifying completely hydrogenated cottonseed oil with 10.5% glycerol.

applied to remove glycerol, and the mono- and diglycerides in the reaction product would not be removed in the subsequent purification. The final product would be a mixture whose surface active components would be monoglycerides and sucrose monoesters.

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