Purification of Sucrose Esters by Selective Adsorption[1]

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ABSTRACT

Long chain fatty acid esters of sucrose from the solvent-free, soap-catalyzed interesterification of molten sucrose and glycerides were acidulated to destroy the soaps, washed to remove unreacted sucrose, and freed of unreacted glycerides and free fatty acids by a procedure adaptable to large scale use. Separation of the glycerides and free fatty acids from the sucrose esters was accomplished by passing the product through selected adsorbents, up to a 1:2 ratio of product to adsorbent, and eluting with selected solvents. Effectiveness of the separations was monitored by thin layer chromatography. Neutral bleaching clay would be the adsorbent of choice for a large scale purification scheme employing benzene as the eluent for the removal of glycerides and free fatty acids followed with ethanol for removal of the sucrose esters.

INTRODUCTION

Sucrose esters of fatty acids have a number of potential uses, such as emulsifiers in foods, specialty components in cosmetics, biodegradable household detergents, and preservatives for fresh vegetables (1-7). Until recently, sucrose esters were prepared commercially by interesterifying sucrose with methyl esters or triglycerides of fatty acids dissolved in dimethylformamide (8,9). But this method yielded products containing residual nitrogenous compounds above the acceptable level for human consumption. Among alternative methods for the large scale preparation of sucrose esters, three (10-12) use sizable proportions of soaps as catalyst and solubilizer. Although for some uses the removal of soaps and other by-products may not be necessary, other uses do require relatively pure sucrose esters. Methods of removing soaps and glycerides from sucrose ester products prepared by the soap-catalyzed interesterification of partial glycerides and molten sucrose (10) were investigated. The results of one phase of this investigation are reported in this communication.

EXPERIMENTAL PROCEDURES

Materials

Sucrose palmitate products were prepared in the laboratory by interesterifying molten sucrose with a mixture of mono-, di-, and tripalmitins in the presence of potassium and lithium oleates (10). The soaps and glycerides were made from commercial fatty acids of about 96% and 98% purity, respectively.

The crude sucrose ester reaction product was distributed between 1-butanol and distilled water and acidulated with dilute orthophosphoric acid to a pH of 5-6 to destroy the soaps. The butanol layer was extracted three times with distilled water. This procedure removed unreacted sucrose and alkali metal ions from the sucrose esters.

For two of the three runs where a chromatographic column was used, the sucrose ester product was enriched with purified sucrose esters isolated from another product.

The following adsorbents were examined for their ability to fractionate the partially purified ester products:

1. Silicic acid A (Silicar CC-7, No. 7034, 200-325 mesh, Mallinckrodt Chemical Works, St. Louis, MO)
2. Silicic acid B (Silica Gel, 0.05-0.20 mm, Merck, Darmstadt, West Germany)
3. Silicic acid C (Adsorbosil 5-P, Applied Science Laboratories, State College, PA)
4. Activated carbon, acidic (Nuchar C-115-A, Industrial Chemical Sales, New York, NY)
5. Aluminum oxide (No. 71707, Merck and Co., Inc., Rahway, NJ)
6. Bleaching clay, neutral (BC Clay, Bennett Clark Co., Nacogdoches, TX)

The solvents employed as eluents in the fractionations were of reagent grade. The other compounds employed were also of reagent grade unless indicated otherwise.

Fractionations

Two series of fractionation experiments were conducted. In the first series (runs 1-15), screening tests were made to compare the effectiveness of different solvents and adsorbents in separating sucrose esters from free fatty acids and unreacted glycerides.

For these screening tests, 2 g of dry adsorbent was distributed evenly over the surface of a 15 ml, fine fritted, glass filtering funnel mounted on a 125 ml suction flask. To obtain a uniform thickness, the adsorbent was applied as a slurry in solvent over the ca. 2.9 cm^2 of filtering area while the flask was connected to the house vacuum line. A plug of glass wool was placed on top of the adsorbent to prevent disturbing the bed. The semirefined ester product (freed of unreacted sucrose and alkali metal ions) was accurately weighed out and dissolved in 35 ml of the solvent or mixture of solvents to be used in the attempted elution of the glycerides and free fatty acids. The warm (ca. 45 C) solution of semirefined product was poured into the funnel while house vacuum was applied, and 40 ml of the same solvent or solvent mixture was then passed through the adsorbent. The two eluates were combined. The sucrose esters were extracted by passing 75 ml of the more polar solvent or solvent mixture, usually methanol-chloroform (40:60, v/v), through the adsorbent. Passage of the solvents through the adsorbent required less than a minute. Solvents were removed from the solutions by distillation under vacuum and by stripping with dry nitrogen under vacuum at 80-90 C.

The second series of fractionation experiments (runs 16-18) was conducted under more carefully controlled conditions, using a water-jacketed chromatographic column (Fig. 1). The glass rod attached to the upper disk of fritted glass facilitated placement of this disk on top of the bleaching clay to avoid disturbing the bed of clay when the eluents were added. Each column consisted of a 20 g layer of bleaching clay and a 2 g layer of diatomaceous earth. For each run the column was packed with the clay and diatomaceous earth, and wetted by passing benzene through it. While the column was held at 50 C, the semi-purified sucrose ester product dissolved in 25 ml benzene was put on the column. The amounts of product were 10 g, 10 g, and 5 g for runs 16, 17, and 18, respectively. Benzene, 125-150 ml, was passed through the column to elute glycerides and free fatty acids, followed by 125-150 ml anhydrous ethanol to elute the sucrose esters. A nitrogen pressure of 6-12 in. of water was maintained on the column, which usually forced the solvents through over a

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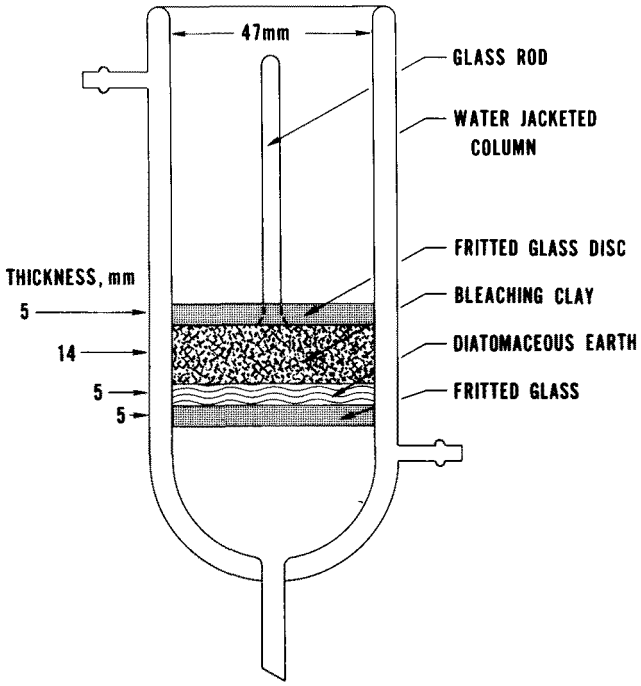

FIG. 1. Chromatographic column employed in fractionations (runs 16-18).

period of 2-3 hr. Fifteen-milliliter fractions were collected during each run. The fatty material recovered from each fraction was weighed and analyzed.

Analysis

The semirefined sucrose ester products and their fractions, together with standards, were analyzed by thin layer chromatography (TLC), and the plates were scanned with a densitometer to obtain quantitative values. The TLC analyses for glycerides and free fatty acid consisted of spotting the samples on 20 x 20 cm plates (Silica Gel 60, No. 5763, EM Reagents, Elmsford, NY) and developing with a mixture of petroleum ether-diethyl ether-glacial acetic acid (90:30:1, v/v). The developing mixture was a modification of that used by Malins and Mangold (13). The developed chromatograms were visualized by spraying with a copper acetate-orthophosphoric acid reagent and charring at 175 C for 20 min (14), which charred all of the spots on the TLC plates. Chromatograms of the sucrose esters were obtained in a similar manner, except that the developing mixture consisted of toluene-ethyl acetate-95% ethanol (2:1:1, v/v) (15), and visualization was accomplished by spraying with urea-phorphoric acid-1-butanol reagent and heating at 110 C for 30 min (16). The urea reagent, unlike the copper acetate reagent, was specific for the sucrose esters, producing blue-gray spots. Calibration curves were developed and used in the quantifications.

RESULTS AND DISCUSSION

Because a single fatty acid can form 255 different sucrose esters of 8 degrees of acylation, not every compound can be identified and quantified to a TLC chromatogram. Also, the presence of large numbers of closely related compounds tends to streak the chromatograms. Therefore, the products and fractions were analyzed for sucrose monoesters as a group and for the di- and higher sucrose esters as a group. The latter were quantified by using calibration data for sucrose dipalmitates, which resulted in some inaccuracy. This, however, does not affect the utility of the data. The percentages in Table I and in the last three columns of Table II were normalized; that is, the quantities were adjusted proportionately to total 100%.

The sucrose ester product employed in run 16 contained 17% sucrose esters (mostly mono- and diesters) and 83% glycerides and free fatty acids. For runs 17 and 18, this product was enriched with a sucrose ester fraction which analyzed 65% sucrose monoesters and 35% sucrose di- and some higher esters. The enriched product contained 50% glycerides and free fatty acids and 50% sucrose esters.

Under the interesterification conditions employed, the oleic acid from the soap interchanged with the palmitic acid from the glycerides, and both acids were present in each type of compound produced.

Among the three silicic acids used in the screening tests (Table II), only silicic acid A adsorbed all of the sucrose monoesters and none of the free fatty acids and glycerides (runs 1, 12, and 13).

None of the silicic acids completely adsorbed the di- and higher sucrose esters. Proportionately, the higher esters were adsorbed less than were the diesters. In sucrose ester products prepared for use as emulsifiers, the higher esters are found in relatively low proportions and are less surface active than are the lower esters; therefore, the tendency not to adsorb these esters would be desirable. Should it become desirable to recover the higher esters, this can be accomplished. Passing the recovered glyceride fraction through a second layer of adsorbent always separated the sucrose esters from the glycerides.

As anticipated, the silicic acid could be reused (runs 1 and 2). In fact, the reused silicic acid performed better than it did originally. This observation agreed with earlier results obtained on bleaching oils in solvents and regenerating the clay with an alcohol. In a sense, the reused silicic acid had been freshly activated.

Silicic acid A performed well as a fractionating medium up to ratios of 1:2 of sucrose ester product to adsorbent (runs 1, 3, and 4). Undoubtedly the high mol wt of the sucrose esters coupled with the presence of a number of hydroxyl groups per molecule made possible their selective adsorption at relatively high ratios of product to adsorbent, making this technique practical for large scale use.

The bleaching clay performed practically as well as did

TABLE I

Composition of Semirefined Sucrose Ester Products

Component	Amount (% by wt)		
	Runs 1-15	Run 16	Runs 17-18[a]
Sucrose monoesters	21	10	32
Sucrose di- and higher esters	48	7	18
Monoglycerides	1	9	4
Diglycerides	10	22	15
Triglycerides	9	24	14
Free fatty acids	11	28	17

[a]Mixture of purified sucrose esters and product used in runs 17 and 18.

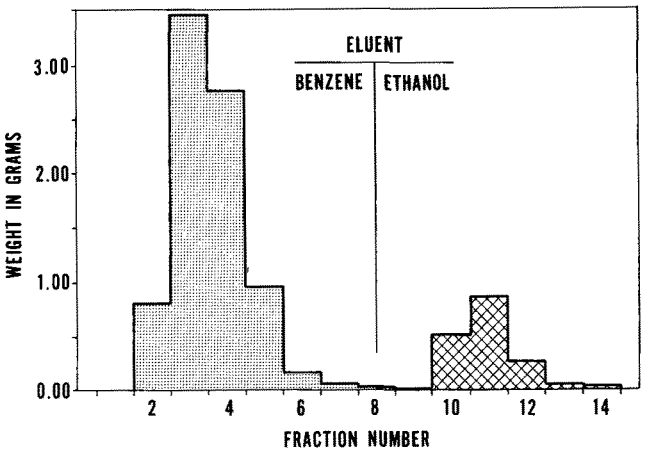

FIG. 2. Run 16, fractionation of 10 g sucrose ester product with 20 g bleaching clay.

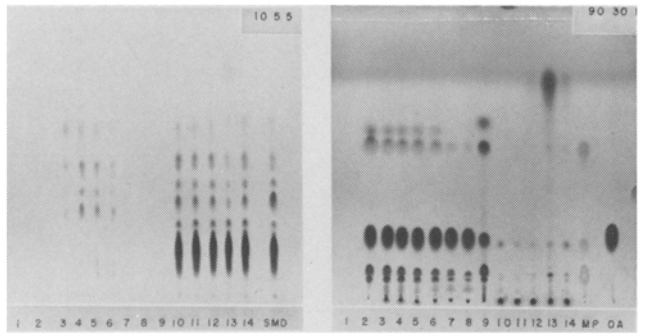

FIG. 3. Thin layer chromatograms of sucrose ester (left) and glycerides plus free fatty acids (right) in fractions 1-14, run 16, Figure 2. All samples, 150 μg. SMD means glyceride- and fatty acid-free concentrate of sucrose esters, mostly mono- and diesters; MP = mixture of mono-, di-, and tripalmitates, plus palmitic acid; OA = oleic acid.

the best silicic acid (runs 1, 3, 9, and 10) when 25% and 35% product, based on weight of adsorbent, were employed. At 50% product the bleaching clay retained a higher proportion of sucrose esters than did silicic acid A (runs 4 and 11), but it also retained some glycerides and free fatty acids.

Neither the activated carbon nor the aluminum oxide performed as well as did the best silicic acid (runs 1, 14, and 15), and both retained sizable proportions of sucrose esters after being washed with methanol-chloroform.

Ethanol and methanol eluted sucrose esters from the silicic acid as rapidly as did the methanol-chloroform mixture, which was found to be a good solvent mixture for sucrose esters. Benzene (run 7) was the most effective solvent for separating the glycerides and free fatty acids from the sucrose esters and was the only solvent which did not elute di- and higher sucrose esters when the adsorbent was used as received. Petroleum ether was inferior to benzene in removing glycerides and free fatty acids.

Using the chromatographic column with 20 g of bleaching clay, 10 g of semirefined sucrose ester product containing 17% sucrose esters was separated cleanly into two fractions (Fig. 2). TLC analyses of the fractions for sucrose esters (Fig. 3, left) revealed that the benzene eluted practically no sucrose monoesters and only minor amounts of higher sucrose esters, mostly in fractions 4 and 5. The ethanol effectively eluted the sucrose esters, fractions 10-14. The large, dark spot closest to the origin and the small spot just above it were produced by sucrose monoesters. The remaining spots in the sucrose ester chromatograms of fractions 10-14 were produced by the di- and

TABLE II

Operational Details and Compositional Data for Runs 1-15

Run number	Adsorbent	Product to adsorbent (%)	Eluent[a]		Product recovered (%)		Composition of recovered fraction (%)				
							Glyceride fraction		Sucrose ester fraction		
									Sucrose esters		
			Glycerides	Sucrose esters	Glyceride fraction	Sucrose ester fraction	Sucrose monoesters	Sucrose di- and higher esters	Mono-	Di- and higher	Glycerides plus free fatty acids
1	Silicic acid A	25	PE-DE	M-C	42.3	57.7	0	15	28	72	0
2	Silicic acid A (reused)	25	PE-DE	M-C	45.3	53.8	0	Tr	40	60	0
3	Silicic acid A	35	PE-DE	M-C	55.5	42.3	0	32	32	68	0
4	Silicic acid A	50	PE-DE	M-C	33.7	47.2	4	35	39	61	0
5	Silicic acid A	25	PE-DE	Methanol	40.1	57.0	0	16	31	69	0
6	Silicic acid A	25	PE-DE	Ethanol	42.3	57.5	Tr	11	24	76	0
7	Silcici acid A	25	Benzene	M-C	42.7	57.5	Tr	0	26	74	0
8	Silicic acid A	25	PE	M-C	32.4	64.4	22	27	13	60	27
9	Bleaching clay	25	PE-DE	M-C	54.6	42.6	Tr	15	44	56	0
10	Bleaching clay	35	PE-DE	M-C	50.7	44.6	Tr	19	41	56	0
11	Bleaching clay	50	PE-DE	M-C	39.5	58.1	Tr	21	37	49	14
12	Silicic acid B	25	PE-DE	M-C	42.1	57.9	9	12	27	60	13
13	Silicic acid C	25	PE-DE	M-C	34.5	38.4	2	5	33	67	Tr
14	Activated carbon	25	PE-DE	M-C	33.8	46.1	5	17	26	47	27
15	Aluminum oxide	25	PE-DE	M-C	21.5	31.8	6	29	23	55	22

[a]PE-DE = petroleum ether-diethyl ether (90:30, v/v); PE = petroleum ether; M-C = methanol-chloroform (40:60, v/v); Tr = trace.

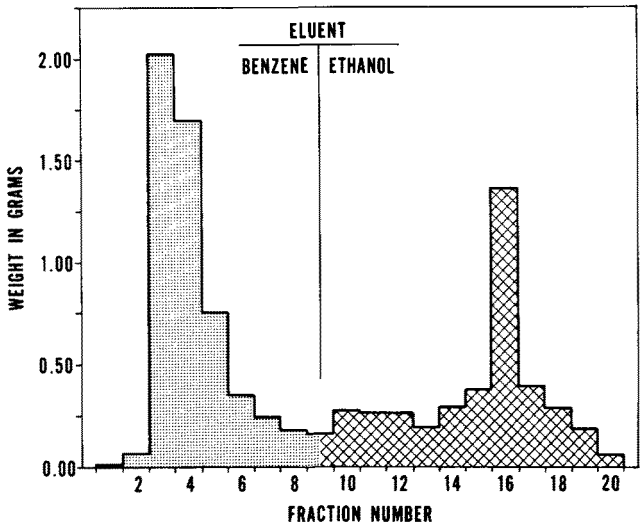

FIG. 4. Run 17, fractionation of 10 g sucrose ester product (50% sucrose esters) with 20 g bleaching clay.

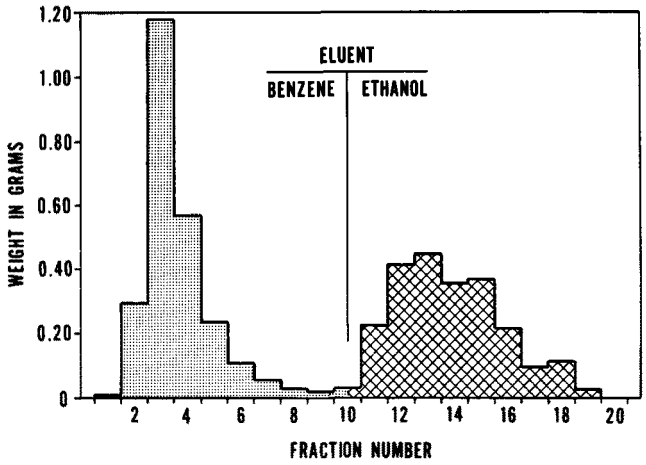

FIG. 5. Run 18, fractionation of 5 g sucrose ester product (50% sucrose esters) with 20 g bleaching clay.

higher esters of sucrose.

Analysis of the fractions for glycerides and free fatty acids (Fig. 3, right) revealed that nearly all of the glycerides were eluted in the first nine fractions. The ninth fraction contained only 0.01 g of product. In the TLC analyses for glycerides and free fatty acids, the sucrose esters remained at the origin. The monoglycerides, which were present in only minor amounts, moved just above the origin and were barely visible on the TLC plate. The largest spot in chromatograms 2-8 was produced by free fatty acids. The cluster of two spots just below the free fatty acid spots was produced by 1,2- and 1,3-diglycerides. The spots above those for the free fatty acids were produced by triglycerides and possible small amounts of esters of monohydric alcohols. Fraction 13, which weighed only 0.03 g, contained a compound of unknown composition.

When 10 g of the mixture containing 50% sucrose esters and 50% glycerides and free fatty acids was passed through the bleaching clay (run 17) (Fig. 4), sucrose ester fractions, 10-19, weighing 3.99 g and glyceride-free fatty acid fractions, 1-9, weighing 5.51 g were collected. However, the sucrose ester fractions all contained some glycerides and free fatty acids. The glyceride-free fatty acid fractions 3-9 contained di- and higher esters of sucrose, and fraction 3-5 also contained some sucrose monoesters. When 2 parts of bleaching clay was loaded with 1 part of the 50% sucrose

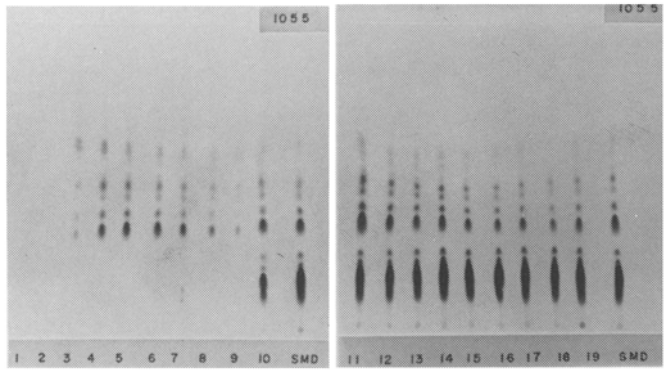

FIG. 6. Thin layer chromatograms of sucrose esters in fractions 1-19, run 18, Figure 5. Sample size, 150 μg. SMD means concentrate of sucrose esters (mostly mono- and diesters) free of glycerides and fatty acids.

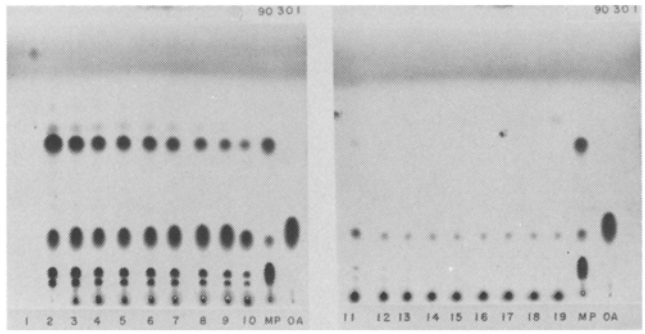

FIG. 7. Thin layer chromatograms of glycerides and free fatty acids in fractions 1-19, run 18, Figure 5. Sample size, 150 μg. MP means mixture of mono-, di-, and tripalmitin and palmitic acid; OA = oleic acid.

ester mixture, the limit for good adsorption apparently had been exceeded.

Loading 5 g of the mixture containing 50% sucrose esters on 20 g bleaching clay, run 18, did result in good fractionation (Fig. 5). The glyceride-fatty acid fractions, 1-10, weighed 2.53 g, whereas the sucrose ester fractions, 11-19, weighed 2.48 g.

On analyzing all of the fractions from run 18 for sucrose esters (Fig. 6), only one of the first nine contained sucrose monoesters and in trace amounts. The first nine fractions, mainly fractions 4-7, contained some di- and higher esters of sucrose.

On analyzing the fractions represented in Figure 5, only small proportions of glycerides and free fatty acids were found in sucrose ester fraction 11 (Fig. 7). Virtually no glycerides and only minute amounts of free fatty acids were found in sucrose ester fractions 12-19.

Adsorption techniques of the type commonly employed in analytical determinations prove to be quite effective in removing free fatty acids and glycerides from sucrose ester products. The ratios of product to adsorbent which can be employed are high enough to make such separations potentially useful in the large scale production of sucrose esters.

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