A Solvent-free Synthesis of Sucrose Polyesters

GEORGE P. RIZZI, Winton Hill Technical Center, The Procter & Gamble Company, Cincinnati, Ohio 45224
HARRY M. TAYLOR, Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio 45247

ABSTRACT

A solvent-free reaction system is described for making sucrose polyesters (SPE) by interesterification of sucrose and long chain fatty acid methyl esters. The process avoids the usual toxic solvents by using a novel two-stage reaction sequence. In the first stage a 3:1 mole ratio of methyl esters to sucrose is reacted in the presence of potassium soaps to form a one phase melt containing mainly lower esters of sucrose. In the second stage more methyl esters are added and reacted to produce SPE in yields up to 90% based on sucrose. Sucrate ion generated in situ with alkali metal hydrides or Na-K alloy proved to be a superior catalyst for formation of sucrose esters during both stages.

INTRODUCTION

Long chain fatty acid esters of sucrose have been proposed as novel surfactants and emulsifiers in food systems (1). These reports have dealt with mono or partially acylated sucrose whose functionality resulted from their combined hydrophilic/lipophilic nature. The more highly substituted sucrose esters, i.e., sucrose polyesters (SPE), have received less attention in the literature.

Recent studies by Mattson and co-workers have demonstrated viable uses for the higher esters of sucrose as noncaloric dietary fats (2-4) and as agents for reducing plasma cholesterol (5). In connection with these proposed uses, a method was sought to prepare food-quality sucrose polyesters (SPE). Usually sucrose esters with a high degree of substitution, i.e., 6-8 acyl residues/molecule, are prepared in heterogeneous reactions involving solid sucrose and highly reactive acylating agents like acid chlorides, anhydrides, or aryl esters. Alternatively, SPE can be prepared by interesterification, but higher temperatures and toxic solvents like dimethylacetamide, dimethylformamide, or dimethylsulfoxide are required. The latter materials are difficult to remove at levels compatible with current consumer standards.

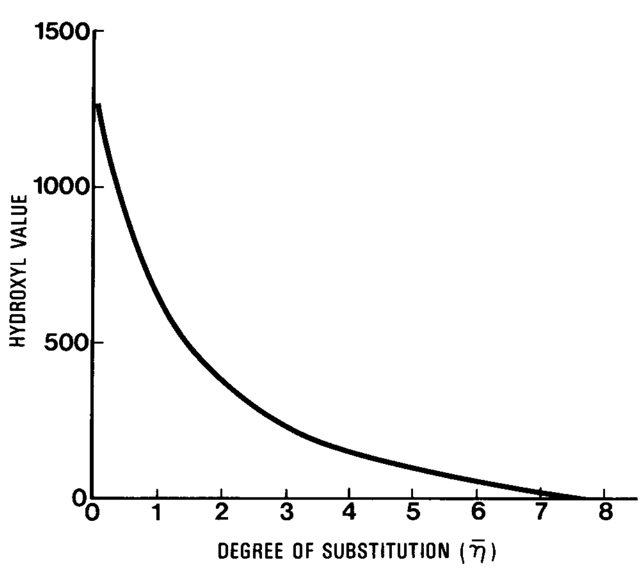

FIG. 1. Theoretical hydroxyl values corresponding to oleic acid esters of sucrose.

A more practical route to SPE was suggested by recent publications of Feuge et al. (6). Feuge showed that sucrose (S) could be solubilized and react with long chain methyl esters (ME) if comparable chain length fatty acid soaps were present. The soaps apparently catalyzed the interesterifications since no other agents were added for this purpose.

Rational modification of the procedure set forth by Feuge led to moderate yields of the desired SPE; however, relatively large amounts of soap were required, and the high reaction temperature (160-170 C) led to some sucrose degradation and a dark-colored product which ultimately was difficult to purify. Subsequently we found that sucrate ion (generated by addition of catalytic amounts of alkali metals or their hydrides to the customary mixture of S, ME, and soap) greatly facilitated the production of SPE (7). Under these conditions, homogeneous reactions were obtained with as little as 3% soap, and high conversions to easily refinable SPE were achieved at temperatures as low as 130 C.

MATERIALS

Commercial methyl oleate and methyl laurate were redistilled before use. Methyl esters of soybean oils were obtained by sodium methoxide catalyzed methanolysis of refined and bleached oils which had been partially hardened to iodine values of 107 and 57; the methyl esters were freshly distilled before use. Sucrose was commercial cane sugar which was reduced to the consistency of fine talcum powder on a lab-scale hammermill before use. Anhydrous, alkali metal soaps were obtained by saponification of methyl esters in aqueous methanol containing a slight excess of ester; the products were vacuum dried, washed with hexane, and redried prior to use. Crystalline sucrose monooleate was obtained by reacting excess sucrose with methyl oleate in the presence of sodium methoxide (8). Sucrose octaoleate was prepared by the method of Hess (9). Sodium/potassium alloy, Na-K and 56% sodium hydride dispersed in mineral oil were obtained from Metal Hydrides Inc., Beverly, MA. Filtrol clay was obtained from Filtrol Corp.

PRODUCT STRUCTURE PROOF AND METHODS FOR ANALYSIS

The high molecular weight of SPE made it impossible to establish structure proof by the usual physico-chemical methods. Instead a degradative approach was used wherein SPE was methanolized back to the predicted amounts of fatty acid methyl esters and sucrose. The approximate degree of esterification ($\tilde{n}$) in isolated SPE was determined indirectly by a standard hydroxyl value (HV) determination and reference to a calculated plot of HV vs $\tilde{n}$ (Fig. 1). Qualitative compositions of SPE were routinely determined by thin layer chromatography (TLC) on silica gel plates using three separate solvent systems designed to span the wide range of polarities involved (Table I). Reference "compounds" for TLC were obtained by column chromatographic fractionation of a crude SPE sample with individual HV determinations on the fractions; in this way R_f ranges could be bracketed for approximate $\tilde{n}$ values. In addition, pure samples of sucrose monooleate and octaoleate were available by alternate synthesis. A rapid analysis of ME re-

TABLE I

Thin Layer Chromatographic Behavior of Sucrose Oleates[a]

No. oleate groups/sucrose	70:30:1 Hexane-ether-HOAc	75:25:1 Pet. ether-ether-HOAc	96:4:1 Benzene-MeOH-HOAc	85:15:2:1 $CHCl_3$-MeOH-water-HCOOH
8	92[b]	100	100	100
7	27-60	32-80	100	100
6	9-21	14-29	58-91	100
5	0-5	4-12	22-56	100
4	0	0	15-22	90-100
3	0	0	~5	~85
2	0	0	0	43-75
1	0	0	0	19-32
Methyl oleate	62	97	100	100
K-oleate	43	59	39-50	81

[a] Analyses performed on Silica Gel G coated glass plates nominally eluted at 25 C; spots visualized by spraying with 50% H_2SO_4 and heating at 150 C.

[b] R_f x 100.

TABLE II

Sucrose Polyester (SPE) Synthesis Using K-oleate Catalyst[a]

Final mole ratio			K-oleate as % of sucrose	Reaction time, hr	Temperature	SPE yield[b]
Sucrose	Methyl oleate	K-oleate				
1.00	9.6	0.25	23	21	165 C	0.4
1.00	9.6	0.50	47	19.5	165 C	50
1.00	9.6	1.60	150	5.5	175 C	50
1.00	8.9	1.60	150	6.0	170 C	37

[a] Reactions were run under 5 mm Hg pressure; about one-half the methyl oleate was added initially and reacted to form a clear solution before adding the balance.

[b] The percent yield is based on the weight of methanol insoluble product, assuming the material to be sucrose octaoleate.

maining in the crude product utilized proton magnetic resonance spectroscopy (PMR). A mixture of product and an internal standard (triphenylmethane) was analyzed at 60 MHz, and the percent ME was determined via the area ratio of methyl ester protons to phenyl ring protons.

EXPERIMENTAL PROCEDURES AND RESULTS

Sucrose/ME/Soap Reactions

Small-scale reactions were run in 50 or 100 ml three-necked, round-bottomed flasks equipped with thermometers, graduated dropping funnels with stopcocks, a vacuum take-off line leading to a dry-ice acetone cooled trap, manometer and vacuum pump, and provisions for magnetic stirring. Heat was supplied by an external, electrically heated oil bath. In a typical reaction, sucrose (0.687 g, 0.002 mole), K-oleate (1.026 g, 0.0032 mole), and methyl oleate (2.2 g, .0074 mole) were stirred and heated to 150-160 C at 8 mm Hg pressure. Methanol evolved as bubbles, and the mixture became homogeneous after about 2 hr. At this point more methyl oleate (3.52 g, 0.0118 mole) was added in portions, and the reaction temperature was gradually raised to 180 C over 2.5 hr. The final mixture was stirred 1 hr at 180 C taking a total reaction time of 5.5 hr. The product was washed with hexane to separate 0.673 g of K-oleate. Evaporation of hexane gave 6.7 g of oil which was separated into methanol soluble (3.8 g) and methanol insoluble (2.5 g) components. TLC analysis showed the former material to be methyl oleate and lower sucrose esters, and the latter was SPE with $\tilde{n}$ of ~6-8. The yield of SPE was 51% assuming the product to be sucrose octaoleate. Similar experiments led to the data in Table II. We found that yields of desirable, higher SPE ($\tilde{n}$ ~6-8) fell drastically as the soap level was decreased much below 50% of the sucrose used.

Sucrose/ME/Sucrate Ion Reactions

A 1 liter resin kettle equipped with a mechanical stirrer, thermometer, dropping funnel and a distillation head arranged for vacuum takeoff was charged with sucrose (25.5 g, 0.0745 mole), methyl esters derived from soybean oil [iodine value of 107] (73.5 ml, 0.224 mole), and anhydrous K-soap derived from the same methyl esters (10.0 g). The mixture was stirred and degassed at 15 mm Hg pressure for 1.25 hr at 95 C. After cooling to 55 C, NaH (0.178 g of 56% dispersion in mineral oil, 0.004 mole) was added, and the mixture was reacted at 145-148 C at 15 mm for 2 hr during which time all the sucrose appeared to dissolve. After adding a second 0.178 g portion of NaH and reacting another 1.5 hr at 150 C, TLC analysis indicated the presence of sucrose mono and diesters. The mixture was cooled somewhat, diluted with an additional 297.0 ml of methyl esters, reheated to 150 C/10 mm Hg for 1 hr, treated with a third 0.178 g portion of NaH, and finally reheated and reacted at 150 C/10 mm Hg for 3 hr. During 7.5 hr about 25-30 ml of liquid distilled into the cooled, vacuum traps. The crude reaction product was treated with 1 ml of acetic acid and washed by stirring and decantation with 9 x 600 ml of methanol. Ice cooling greatly facilitated the separation of the lower, more dense SPE phase. The clear, pale brown SPE was freed of last traces of methanol under vacuum prior to bleaching with 10 g of Filtrol clay at 100 C/2.5 hr. The mixture of SPE and clay was dissolved in hexane, filtered, and the filtrate was evaporated under vacuum to give 143.2 g of pale yellow product. The SPE had an HV of 18.7 ($\tilde{n}$ = 7.25), and the yield based on sucrose was 86%. Results from other experiments are summarized in Table III. Reactions were generally started with mixtures of sucrose and methyl esters in a 1:3 mole ratio containing 0-15% K-soaps, and a single dose of catalyst. When the sucrose all dissolved, additional methyl esters were added to lower the final S/ME mole ratio to 1:11.8.

TABLE III

Effect of NaH and K-soaps on Sucrose Polyester (SPE) Synthesis[a] with Soybean Derived Methyl Esters

Wt % K-soap[b]	Wt % NaH[c]	Reaction time, hr	SPE yield (%)[d]
0	.5	16	0, no reaction
1	.5	3	12
2	.5	3	25
5	.5	3	70
5	.05	3	0, only lower esters found
5	.06	16	45
5	.05 (x2)[e]	6	86

[a] Reaction conditions: 140-145 C/5 mm Hg; initial S/ME ratio 1:3, decreased to 1:11.8 after sucrose solubilized.

[b] Expressed as % soap in final reaction mixture.

[c] Expressed as % of initial S/ME/K-soap charge.

[d] Yield based on wt of MeOH insoluble product and theoretical amount of octaester; $\tilde{n}$ was typically 7.0-7.5 for 6+ hr runs.

[e] Catalyst added at 0 hr and 3 hr.

TABLE IV

Atmospheric Pressure Sucrose Polyester (SPE) Syntheses[a]

Reaction temperature, C	Reaction time, hr		Inert gas		SPE yield (%)[b]
	Stage I	Stage II	Sparge	$\tilde{n}$	
130-132	3.5	6.0	No	7.0	69
145-150	2.0	6.0	No	7.1	90
145-150	3.0	6.0	Yes	6.5	90

[a] Reactions were run in two stages: stage I 90 wt % of 1:3 mole ratio S/ME plus 10 wt % K-soap derived from ME plus 0.2% NaH reacted; stage II a second 0.2% NaH plus more ME added to lower S/ME ratio to 1:16. ME was methyl esters derived from soybean oil (IV=57).

[b] Yield based on wt of methanol insoluble product, amount of S used and molecular wt of SPE calculated from $\tilde{n}$.

Syntheses of SPE were also accomplished at atmospheric pressure using the NaH generated sucrate ion catalyst, Table IV. Moderate to high yields of highly substituted sucrose were obtained in small-scale reactions by simply allowing methanol to distill off spontaneously. Argon sparging and vacuum seemed to be more important in larger-scale reactions in which a more efficient removal of methanol is required to displace various equilibria in the direction of products.

Disproportionation of Sucrose Monooleate

A mixture of crystalline sucrose monooleate (1.216 g, 0.0020 mole), methyl oleate (0.015 mole), and Li-oleate (0.00020 mole) was heated at 130 C and 5 mm Hg to yield a clear, water white solution. On further heating at 145 C and 5 mm Hg/2 hr a solid was precipitated, which was isolated from the cooled mixture by $CHCl_3$ addition and filtration. The solid proved to be pure sucrose by infrared analysis and subsequent conversion to the known octaacetate derivative. The yield of sucrose (0.281 g) was 82% based on the stoichiometry predicted by a 2 SE1 → S + SE2 disproportionation reaction. TLC analysis of the $CHCl_3$ solubles indicated mainly sucrose dioleates, methyl oleate, and soap. Similar reactions run at 170 C gave bad charring of the solid sucrose and no observable higher ester formation.

DISCUSSION

Soap Catalyzed SPE Reactions

In our initial attempts to extend the soap assisted sucrose ester synthesis to yield higher esters it became obvious that a lower reaction temperature was desirable to avoid excessive sugar degradation. Melting point data on mixtures containing alkali metal oleates showed a minimum fusion point with about 40% K-oleate and 60% sucrose of ca. 160 C. However, mixtures of K-oleate and sucrose would not react under the usual interesterifying conditions when fatty acid methyl esters (ME) were present in the correct stoichiometric amount to form fully acylated SPE. The great insolubility of sucrose in ME evidently favored the disproportionation of initially formed partial esters with an ultimate loss of sugar to caramelization. This effect was dramatized in a separate reaction between pure sucrose monooleate and methyl oleate catalyzed by Li-oleate. Under interesterifying conditions, sucrose initially dissolved but later precipitated as the reaction proceeded (cf above). Apparently the combined hydrophobic nature of the forming partial esters and ME induced the sugar to separate in crystalline form.

The problem of disproportionation was solved by first reacting sucrose with a smaller molar proportion of ME to build up a substantial amount of lower esters prior to adding the bulk of ME required. Homogeneity was achieved in a firststage reaction and maintained during subsequent reaction with excess ME to give moderate yields of higher SPE. The method still had some drawbacks in that relatively high temperatures still were required, and significant amounts of soap in the crude product portended difficult purification and recycle problems.

Sucrate Ion Catalyzed SPE Reactions

An obvious solution to the problem of high temperature was to choose a better interesterification catalyst. Initial work with alkali metal alkoxides or carbonates added to the usual S/ME/soap mixtures showed little promise, probably because of their poor solubility. These materials led to excessive soap buildup, caramelization, and SPE which was difficult to purify by customary means, i.e., alkali refining, clay bleaching, etc.

The actual catalytic specie in sucrose interesterification is believed to be the sucrate ion (S^-) which is formed by added methoxide or carbonate ion according to (I) and (II).

$$CH_3O^- + S \rightleftharpoons S^- + CH_3OH \qquad (I)$$

$$CO_3^{=} + S \rightleftharpoons S^- + HCO_3^- \qquad (II)$$

Accordingly, Lemeiux found that for the formation of sucrose monomyristate the rate of interesterification was a function of methyl myristate and sucrate ion concentrations and independent of sucrose concentration (10). A general mechanism for sucrose interesterification is shown in (III) and (IV) where k_1 and k_{-1} represent second order rate constants for the forward and reverse reactions.

$$S^- + ME \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SE_1 + CH_3O^- \qquad (III)$$

$$CH_3O^- + S \rightleftharpoons CH_3OH + S^-, \text{ etc.} \qquad (IV)$$

If one assumes that S^- and SE_n^- as well as S and SE_n ($n < 8$) function interchangeably, the overall rate of forward reaction in terms of ME consumption is represented by (V).

$$-\frac{d\,(ME)}{dt} = k_1\,(ME)\,(S^-) + k_2\,(ME)\,(SE_1^-) + \ldots$$

$$= (ME) \sum_{n=1}^{n=8} k_n\, SE_{n-1}^- \qquad (V)$$

We found that sucrate ion generated irreversibly by adding NaH or Na-K alloy to a mixture containing 90 wt % of ME and S in a 3:1 mole ratio and 10 wt % of anhydrous K-soap derived from ME gave a homogeneous melt of lower SPE and starting materials in 2-3 hr at 130-145 C. The reaction succeeded with as little as 5% K-soap, but Na and Li soaps were less satisfactory over a wide concentration range. The intermediate reaction mixture dissolved in excess ME at 90 C, and at 130-145 C additional reactions took place to form higher SPE in good yields after 3-4 hr. Ratios of S to ME below 1:12 did not noticeably increase the yields or reaction rate. The reaction proceeded well with distilled ME derived from soybean oils previously hardened to IV's of 57 and 107 as well as with pure methyl oleate. Vacuum removal of methanol both with and without inert gas sparging did promote interesterification but in small-scale reactions simple atmospheric pressure distillation was found to be sufficient. Generally the K-soap was derived from its corresponding ME by saponification, however, certain modifications were possible. Sucrose polylaurate was successfully prepared from sucrose and excess methyl laurate in the presence of K-soap derived from soybean methyl esters. However, attempts to prepare SPE with soybean methyl esters in the presence of K-laurate led only to the formation of methyl laurate. Evidently the relatively high volatility of the laurate ester permitted its facile removal from the reaction mixture. The ester interchange between laurate and "soyate" is peculiar, and further study along these lines may yield clues regarding the actual reaction mechanism. In a series of controlled experiments it was determined that sucrate ion is apparently involved since NaH catalyzed mixtures of K-laurate and soybean methyl esters did not yield exchange.

ACKNOWLEDGMENTS

The authors wish to thank C.G. Birch for the TLC calibration data and Jack Wendel and Norvin Gullion for their technical assistance.

REFERENCES

1. McGinnis, R.A., "Sugar (Properties of Sucrose)," Kirk-Othmer Encycl. Chem. Technol., Vol. 19, 2nd Edition, A. Standen Executive Ed., 1969, pp. 151-155.
2. Mattson, F.H., and R.A. Volpenhein, J. Nutr. 102:1177 (1972).
3. Mattson, F.H., and R.A. Volpenhein, J. Lipid Res. 13:325 (1972).
4. Mattson, F.H., and R.A. Volpenhein, U.S. Patent 3,600,186 (1971).
5. Fallat, R.W., C.J. Glueck, R. Lutmer, and F.H. Mattson, Am. J. Clin. Nutr. 29:1204 (1976).
6. Feuge, R.O., H.J. Zeringue, T.J. Wiess, and M. Brown, JAOCS 47:56 (1970).
7. Rizzi, G.P., and H.M. Taylor, U.S. Patent 3,963,699 (1976).
8. Mattson, F.H., and G.A. Nolen, J. Nutr. 102:1171 (1972).
9. Hess, K., and E. Messmer, Chem. Ber. 54B:499 (1921).
10. Lemeiux, R.U., and A.G. McInnes, Can. J. Chem. 40:2376 (1962).

[Received September 12, 1977]