Purification of Sucrose Esters by Ultrafiltration

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ABSTRACT

A sucrose ester product containing glycerides and free fatty acids has been separated into a sucrose ester rich fraction and a glyceride-fatty acid rich fraction by ultrafiltration using a benzene or carbon tetrachloride solution and a polysulfone membrane which normally separates solutes above and below a molecular weight of 10,000.

INTRODUCTION

Sucrose ester products can be prepared readily by the soap-catalyzed interesterification of molten sucrose and a mixture of mono-, di-, and triglycerides (1). The unreacted sucrose and alkali-metal ions from the soaps can be removed easily. However, removal of glycerides and free fatty acids by standard procedures such as fractional crystallization was found to be either too involved or inefficient. An investigation was undertaken to further purify a sucrose ester product by removing glycerides and free fatty acids by ultrafiltration.

EXPERIMENTAL PROCEDURES

The sucrose ester product was prepared by heating to 185 C a mixture consisting of 34.8 g palmitin (mono-, di-, and tri-palmitin, 0.336 equivalent of fatty acid per 100 g), 10.0 g potassium oleate, and 2.5 g lithium oleate and then adding slowly, with stirring, 50.0 g powdered sucrose. Vacuum was applied for 10 min to remove free glycerol. The resulting sucrose ester product was distributed between water and 1-butanol, and the water layer was removed. Distilled water was added to the alcohol layer, the pH adjusted to 5 with orthophosphoric acid, and the acidified water layer removed. The alcohol layer was then washed twice with distilled water. The sucrose ester product recovered from the alcohol was free of unreacted sucrose, alkali metal ions, and a sizable proportion of the color bodies.

A PM-10 Diflow membrane (Amicon Corp., Lexington, MA), which consists of a film of anisotropic polysulfone on a layer of open-celled microporous sponge (2), was used for the ultra-filtration. The apparent radius of the pores in the film is about 20 Å, and normally these partition solutes above and below a mol wt of 10,000. The membrane, which measured 25 mm in diameter, was mounted in a filter holder (Millipore No. XX50-025-00, Millipore Filter Corp., Bedford, MA), and the assembly was mounted in a constant temperature cabinet maintained at 50 C. Overhead nitrogen at a pressure of 20 psig was used to force the solvent through the membrane at a flow rate up to 8 drops/min. The membrane was prewashed according to the manufacturer's instructions and then was prerinsed with 5 ml of the solvent to be used in the test.

One gram of the semi-refined sucrose ester product (free of unreacted sucrose and alkali metal ions) was dissolved in 10 ml warm carbon tetrachloride (Run 1) or 10 ml warm benzene (Run 2), poured into the filter holder, and filtered under nitrogen pressure. The material left on the membrane was flushed with 3 ml of the solvent used in the run. The filtrates from the run were combined and the solvent was evaporated under dry nitrogen at 50-60 C. The residue on the membrane was recovered by washing with warm solvent and then removing the solvent by evaporation. The fractions were weighed and analyzed.

Thin layer chromatographic analyses for glycerides and free fatty acids were conducted by spotting each sample, as a 5% solution in chloroform, on a silicic acid plate (Silica Gel 60, EM reagents No. 5763) and developing with a solution of petroleum ether-diethyl ether-glacial acetic acid (90:30:1 v/v), essentially according to Malins and Mangold (3). The chromatogram was visualized by spraying with an aqueous solution containing 3% cupric acetate and 8% orthophosphoric acid and then heating for 20 min at 175 C (4).

Another thin layer chromatographic technique was used to analyze for sucrose esters. The samples were spotted on the silicic acid plate and the chromatograms were developed with a solution of toluene-ethyl acetate-95% ethanol (2:1:1 v/v) (5). The sucrose ester spots were visualized by spraying the developed and dried plate with a solution of urea (1 g), 85% orthophosphoric acid (4-5 ml), and water saturated 1-butanol (48 ml) and then heating at 110 C for 30 min (6).

Quantitative data were developed from the chromatograms with the aid of a Nester/Faust Model 900 Scanning Densitometer. Standards of known composition and calibration curves were used to quantify the spots in the chromatograms.

RESULTS AND DISCUSSION

Fatty acid composition of the semi-refined sucrose ester product was about 75% palmitic and 25% oleic. Based on data developed in other research, both acids were present in the different types of compounds in the product. The semi-refined product, which contained approximately 18% sucrose ester, 28% free fatty acids, and 54% glycerides (mono-, di-, and triglycerides), was selected for fractionation because it contained large proportions of the unwanted glyceride and free fatty acid by-products.

The chromatograms of the sucrose esters (Fig. 1 and Table I) reveal that the ultrafiltration membrane was effective in separating sucrose esters from both carbon tetrachloride and benzene solution. The semi-refined sucrose ester product in carbon tetrachloride solution was separated into a membrane-impermeable fraction containing 75.1% sucrose esters and a membrane-permeable fraction containing 7.4% sucrose esters.

When the benzene solution was filtered, the membrane-impermeable fraction contained 60.0% sucrose esters, while the membrane-permeable fraction contained 9.2% sucrose esters. This was still a good separation.

The urea-containing reagent used to visualize these chromatograms does not react with fatty acids and glycerides; therefore, all of the spots shown in Figure 1 were produced by sucrose esters. Because the visualizing reagent reacts with the sucrose moiety, the amount of color bodies produced decreases as the molecular weight of the sucrose esters increases. Thus, relatively faint spots in the region of the higher sucrose esters represent sizable proportions of these esters.

The sucrose ester fraction removed from the carbon tetrachloride solution by the ultrafiltration membrane (chromatogram 3) was not as rich in sucrose monoesters as was sample SMD, a mixture consisting entirely of sucrose esters, mostly mono- and diesters. The semi-refined sucrose ester product contained a larger proportion of higher esters of sucrose than did sample SMD.

Chromatograms showing the proportions of glycerides and fatty acids are reproduced in Figure 2. In these chro-

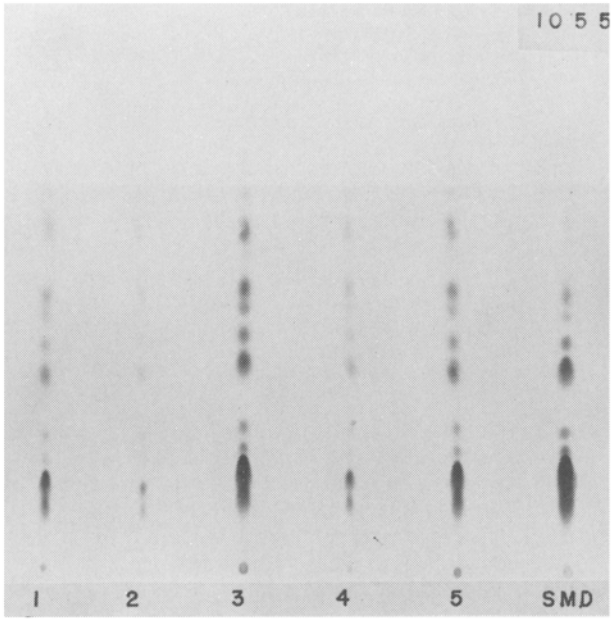

FIG. 1. Thin layer chromatograms of sucrose esters, 150 μg samples: 1, semi-refined sucrose ester product; 2, membrane-permeable fraction of carbon tetrachloride solution; 3, membrane-impermeable fraction of carbon tetrachloride solution; 4, membrane-permeable fraction of benzene solution; 5, membrane-impermeable fraction of benzene solution; and SMD, 100% sucrose esters, mostly mono- and diesters of palmitic and oleic acids. A, sucrose monoesters; and B, sucrose di- and higher esters.

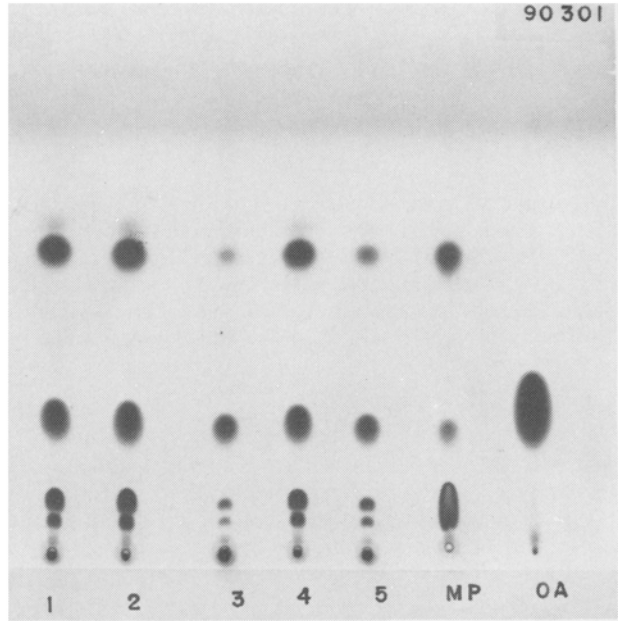

FIG. 2. Thin layer chromatograms of glycerides and fatty acids, 150 μg samples: 1, semi-refined sucrose ester product; 2, membrane-permeable fraction of carbon tetrachloride solution; 3, membrane-impermeable fraction of carbon tetrachloride solution; 4, membrane-permeable fraction of benzene solution; 5, membrane-impermeable fraction of benzene solution; MP, mixed palmitins (60% di-, 21% mono-, 17% tri-, and 2% free palmitic acid); and OA, oleic acid. A, sucrose esters and monoglycerides; B, diglycerides; C, free fatty acids; and D, triglycerides.

matograms, the sucrose esters remained at the origin, and monoglycerides barely moved away from the origin. In Figure 2, chromatograms 1 through 5, the tight group of two sizable spots just above the origin was produced by 1,2- and 1,3-diglycerides; the next spot by fatty acids; and the spot farthest from the origin, by triglycerides. On comparing chromatograms 1, 2, and 3 (Fig. 2), it is apparent that the triglycerides and diglycerides were removed more effectively from the sucrose esters than were the free fatty acids, which probably complex to some extent with sucrose esters. The distribution of the monoglycerides between the two fractions cannot be established easily from chromatograms of the type represented in Figure 2, but close examination of a number of such chromatograms revealed that the monoglycerides behaved about like the diglycerides. In sucrose ester products of the type fractionated, the content of monoglycerides is always considerably lower than that of di- or triglycerides.

Neither benzene nor carbon tetrachloride seemed to adversely affect the ultrafiltration membrane.

In exploratory tests, unsuccessful attempts were made to fractionate by ultrafiltration crude sucrose ester products containing soap and free sucrose.

Carbon tetrachloride and benzene were employed because they were the only solvents which did not damage the ultrafiltration membrane and were also good solvents for glycerides and free fatty acids.

While carbon tetrachloride would be an undesirable solvent for processing sucrose esters for food use, benzene has been used for this purpose. However, it may be possible to develop other ultrafiltration membranes which permit the use of other solvents.

The PM-10 membrane which was used normally separates solutes in water into a fraction above and a fraction below about 10,000 mol wt. Yet, under the conditions employed with the sucrose ester product, this membrane retained sucrose monopalmitates of mol wt 581 and passed triglycerides of mol wt 807 and higher. Even though we recognize that molecular shape influences permeability and that the permeability of the membrane to solutes decreases

TABLE I

Composition of Semi-Refined Sucrose Ester Product and Fractions Obtained by Ultrafiltration

	Composition, wt %		
	Sucrose esters	Glycerides	Free fatty acids
Semi-refined sucrose ester product starting material	18.0	54.0	28.0
Membrane-permeable fraction, CCl_4 soln.	7.4	61.0	31.6
Membrane-impermeable fraction, CCl_4 soln.	75.1	9.2	15.7
Membrane-permeable fraction, benzene soln.	9.2	67.6	23.2
Membrane-impermeable fraction, benzene soln.	60.0	24.7	15.3

when a nonaqueous solvent is substituted for water, the ability of the membrane to retain sucrose esters is nevertheless unexpected. The sucrose esters apparently do not form true solutions in benzene and carbon tetrachloride. Instead, they probably form micelles which are too large to pass through the holes in the membrane. Data obtained in attempting to determine the molecular weight of sucrose esters in benzene solution support this probability.

REFERENCES

1. Feuge, R.O., H.J. Zeringue, Jr., T.J. Weiss, and Mona Brown, JAOCS 47:56 (1970).
2. Michaels, A.S., and R.W. Baker, U.S. Pat. 3,526,588 (1970).
3. Malins, D.C., and H.K. Mangold, JAOCS 37:576 (1960).
4. Fewster, M.E., B.J. Burns, and J.F. Mead, Jr., Chromatogr. 43:120 (1969).
5. Gee, M.J., Ibid. 9:278 (1962).
6. Kroller, E., Fette Seifen Anstrichm. 65:482 (1963).

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