

# Influence of Solvent on Degree of Acylation in the Formation of Sucrose Esters<sup>1</sup>

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## ABSTRACT

Sucrose palmitates were prepared by the interesterification of sucrose and methyl palmitate in different solvents. The ratio of methyl palmitate to sucrose in dimethylformamide (DMF) solution was varied so that the effect on yield and ester composition could be evaluated. When sucrose esters were prepared in DMF, the palmitoyl groups approximated a random distribution when only penta- and lower esters were formed. When the proportion of palmitoyl groups was increased, hexa- through octaesters were formed, but the yield was less than that calculated for a random distribution. The interesterification of sucrose and methyl palmitate in solvents other than DMF, but under otherwise identical reaction conditions, yielded different reaction products. Only traces of sucrose esters were produced in hexamethylphosphoramide and formylmorpholine. Reactions in dimethylsulfoxide and N-methyl-2-pyrrolidinone yielded larger percentages of higher esters than were obtained in DMF. However the distribution was far from random.

## INTRODUCTION

In preparing sucrose palmitates by interesterifying 1 mole sucrose with 1-4 moles methyl palmitate in dimethylformamide (DMF) solution, it was observed that the distribution of the fatty acid groups in the ester mixture was approximately random (1).

Hass (2) reported the preparation of sucrose tetra- through hexalinsedate by interesterifying 1 mole sucrose with 6-8 moles methyl linseedate in DMF. Bobalek et al. (3) obtained similar results using a ratio of 1 mole sucrose to 12 moles methyl ester of fatty acids. Only small amounts of octaesters were detected in the reaction mixtures.

Bares and Zajic (4) evaluated the relative effect of DMF and dimethylsulfoxide (DMSO) on the interesterification of sucrose with methyl palmitate. They found that the reaction mixture reached equilibrium in DMSO in one-third the time required for the same reaction to equilibrate in DMF. However only a 1:1 mole ratio of sucrose to methyl palmitate was used.

Komori et al. (5) investigated additional sucrose solvents. They studied the effect of formyl- and acetylpyrrolidines and morpholines on interesterification. Their purpose was to evaluate procedures for making monoester products using 1.5-3 moles sucrose per mole methyl

palmitate. They did not compare the equilibrium compositions obtained with those obtained in DMF or DMSO.

The present investigation was undertaken to establish whether or not the higher esters of sucrose could be obtained in good yield by interesterifying in DMF or one of several other solvents for sucrose (6).

## EXPERIMENTAL PROCEDURES

The interesterification of sucrose and methyl palmitate in the selected solvent was conducted essentially according to the laboratory procedure given by the Sugar Research Foundation for preparation of sucrose distearate (7). This procedure required 1000 ml DMF, 6.0 g anhydrous K<sub>2</sub>CO<sub>3</sub> (as catalyst), 171.2 g (0.5 mole) sucrose and 270.5 g (1 mole) methyl palmitate. When the mole ratio of methyl palmitate to sucrose was raised to 7:1 and 12:1, the amount of solvent was doubled to avoid, as far as possible, two-phase mixtures.

The solvents used were DMF and hexamethylphosphoramide (HMPA) (Eastman Kodak Co.), DMSO (J.T. Baker Chemical Co.), N-methyl-2-pyrrolidinone (Aldrich Chemical Co.) and formylmorpholine prepared according to Komori et al. (5).

Pressure was adjusted to allow the solvent to reflux in the distillation column while a temperature of 90 C was maintained in the reaction vessel. The pressures required are shown in Table I.

The reaction was continued for 5-6 hr, although the amount of methanol collected in the trap did not increase after 3-4 hr. Previous work (4,8) indicated such reaction times to be sufficient at the catalyst level used.

The solvent used in an interesterification and the unreacted sucrose were removed from the reaction mixture by dissolving it in *n*-butanol and washing with a 10% solution of sodium chloride in water (7). The *n*-butanol was evaporated under vacuum. The mixed sucrose esters and unreacted methyl palmitate were dissolved in chloroform and filtered to remove any solid sodium chloride. The chloroform was removed by stripping with dry nitrogen at subatmospheric pressure.

Hydroxyl values of the ester preparations were determined by AOCS Method Cd 13-60 (9). Unreacted methyl palmitate was determined by separating it from the sucrose esters by means of a silicic acid column. The column was made with 24 g silicic acid (Mallinckrodt, 100 mesh) suspended in a solution of 2% ethyl ether in petroleum ether. About 0.5 g sucrose ester dissolved in 15 ml of the same solution was put on the column, which then was washed with 150-200 ml of additional solution. The eluate was evaporated to dryness in tared test tubes. The residue was weighed and reported as methyl palmitate, although it was found that butyl palmitate (ca. 1% of the material on the column) also was present, probably the result of ester interchange during the removal of *n*-butanol after purification of the ester mixture. The sucrose esters remained adsorbed on the silicic acid column. No sucrose esters were detected in the eluate from the column.

Sucrose esters were determined by the quantitative thin layer chromatography (TLC) method of Weiss et al. (1). Some degree of uncertainty was associated with the identity of specific spots for the tetra- through heptaesters. However TLC analyses of all the products were compared,

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TABLE I

Vapor Pressure of Solvents in Reaction Mixtures at 90 C

Solvent	Pressure, mm Hg
DMF	95
DMSO	24-30
N-Methyl-2-pyrrolidinone	16-20
HMPA	6
Formylmorpholine	6-7

TABLE II  
Esterification Level of Sucrose Ester Products Prepared in Different Solvents

Solvent	Mole ratio, methyl palmitate-sucrose	Hydroxyl content total product, wt %	Methyl palmitate removed, wt %	Hydroxyl content, methyl palmitate free basis, wt %	Palmitic acid groups per molecule sucrose ester <sup>a</sup>
Dimethylformamide	1:1	14.0	—	14.0	1.8
	2.2:1	10.3	—	10.3	2.4
	4:1	5.6	5.5	5.9	3.7
	7:1	3.4	40.2	5.7	3.8
	12:1	0.9	40.1	1.5	6.4
Dimethylsulfoxide <sup>b</sup>	7:1	2.1	17.0	2.5	5.6
	12:1	1.5	53.6	3.3	5.0
N-Methyl-2-pyrrolidinone	7:1	2.3	19.4	2.8	5.3
Hexamethylphosphoramide <sup>c</sup>	7:1	—	—	—	—
Formylmorpholine <sup>c</sup>	7:1	—	—	—	—

<sup>a</sup>Calculated from hydroxyl value.

<sup>b</sup>Reaction product slightly immiscible at 7:1 ratio, more immiscible at 12:1.

<sup>c</sup>Yield of sucrose esters very low.

and the conclusions about relative molecular weights are valid. Also the average degrees of acylation calculated from the TLC data agree within experimental error with those calculated from hydroxyl values. Sucrose octapalmitate prepared by the acylation of sucrose with palmitoyl chloride in pyridine-chloroform solution (10) was used to locate octapalmitate on the TLC plates.

## RESULTS AND DISCUSSION

The sucrose ester products obtained were compared for free hydroxyl content and average number of palmitoyl groups per molecule of sucrose ester. The results are recorded in Table II.

When the ratio of methyl palmitate to sucrose was increased to 4:1 and above for reactions in DMF, unreacted methyl palmitate was found in the reaction product. As this ratio was increased markedly, the average number of palmitoyl groups per molecule of sucrose ester increased very slowly.

At a 7:1 mole ratio, DMSO produced more of the higher esters than did DMF. At a 7:1 ratio in DMSO, two phases were present at the start of the reaction, the reactants became homogeneous after about 2 hr, and a small amount of second phase (indicated by a slight haze) again formed toward the end of the reaction. At a 12:1 ratio in DMSO, the formation, disappearance and reformation of two phases was more pronounced; this result had an adverse effect on the yield of sucrose esters and the level of acylation, as seen in Table II. When higher esters are to be

prepared, DMSO evidently has an advantage over DMF under relatively limited reaction conditions.

The use of N-methyl-2-pyrrolidinone with a 7:1 ratio of methyl palmitate to sucrose also resulted in the formation of two phases at the start of the reaction. Because of the limited solubility of esters in N-methyl-2-pyrrolidinone and the similarity of the sucrose ester products obtained with it and DMF, no other ratios of methyl palmitate to sucrose were evaluated for this solvent. The use of hexamethylphosphoramide (HMPA) and formylmorpholine as solvents was entirely unsatisfactory, since the yields of sucrose esters were very low.

A number of experiments in addition to those recorded in Table II were conducted. The substitution of sodium methoxide for potassium carbonate in interesterifications in DMF did not affect the amount or distribution of esters in the final product. Increasing the catalyst concentration and extending the reaction time when HMPA was used did not produce any significant change in the amount and composition of the sucrose esters.

In Table III is recorded the composition of the sucrose esters in the various solvents as determined by TLC analysis. Random distribution was calculated for several ratios of methyl palmitate to sucrose. Experimentally determined compositions were found previously (1) to compare well with random distribution up to mole ratios of 4:1.

Departure from random distribution at ratios of 7:1 and higher was great. The percentage of octaester was particularly low. Variation of products in different solvents at the

TABLE III  
Composition of Sucrose Ester Products Prepared in Different Solvents

Solvent	Mole ratio of methyl palmitate-sucrose	Sucrose ester composition, wt %								Palmitoyl groups per molecule sucrose ester <sup>a</sup>
		Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	
Dimethylformamide	1:1	43.5	35.7	16.4	4.4	0.0	0.0	0.0	0.0	1.4
	2.2:1	15.3	33.2	26.4	16.8	8.3	0.0	0.0	0.0	2.4
	4:1	0.6	10.5	16.2	27.6	20.3	19.6	5.2	0.0	4.0
	7:1	0.4	2.1	4.0	10.4	31.8	33.8	17.5	0.0	5.2
	12:1	0.0	0.0	1.3	4.5	17.9	43.7	29.4	3.2	5.9
Dimethylsulfoxide	7:1	0.0	0.9	1.6	4.9	17.2	43.3	29.1	3.0	5.8
N-Methyl-2-pyrrolidinone	7:1	0.0	0.0	1.7	4.6	19.6	53.9	20.2	0.0	5.8
Hexamethylphosphoramide	7:1	Traces mono-, di-, triesters								
Formylmorpholine	7:1	Some mono-, di-, triesters								
Random distribution (calculated)	1:1	49.2	34.7	12.8	2.8	0.4	0.0	0.0	0.0	
	2.2:1	16.0	30.0	29.4	17.1	6.1	1.4	0.2	0.0	
	4:1	1.3	6.9	17.9	27.4	25.9	15.0	4.9	0.7	
	7:1	0.0	0.0	0.0	0.5	4.5	16.5	36.5	42.0	

<sup>a</sup>Calculated from thin layer chromatography data.

7:1 ratio ranged from practically no sucrose ester in HMPA to a total of almost 75% hexa- and heptaesters in DMSO and N-methyl-2-pyrrolidinone. The composition of the products obtained with the different solvents under otherwise similar conditions differed markedly.

It is recognized, of course, that the eight hydroxyl groups of sucrose do not possess equal reactivities. Some are relatively unreactive under interesterification conditions. Also, as the degree of acylation increases, the reactivity of the residual hydroxyls decreases. Under the interesterification conditions used in the current investigation, the reactivity of the residual hydroxyls of hexa- and heptaesters was insufficient to result in any appreciable degree of acylation.

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