# Sucrose Monoesters and Diesters in Breadmaking[1]

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ABSTRACT

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Sucrose esters of nine fatty acids were synthesized in *N,N*-dimethylformamide solution by transesterification between sucrose and a methyl ester of a fatty acid. Sucrose monoester and diester fractions were purified from the crude products by chromatography on silica gel. The pure fractions were tested in breadmaking for their improving effects in microloaves baked from a soy-fortified, no-shortening formula. In the series of monoesters of saturated fatty acids of chain-length $C_8$–$C_{20}$, the $C_{16}$ and $C_{18}$ esters performed best at 0.25–0.38%, based on flour, whereas the $C_{12}$ ester was best at 0.5–0.75%. In the diester series, the $C_{12}$ diester at 1.0–1.5% gave excellent loaf volume and crumb grain. The diester fraction of sucrose palmitate alone performed poorly in improving loaf volume. However, sucrose dipalmitate and higher esters of sucrose palmitate increased the loaf-improving effects of sucrose monopalmitate. Thus, unfractioned sucrose palmitate was an excellent dough strengthener at 1.25–2.0%. Sucrose monocaprylate and monocaprate reduced dough mixing time by ~15%.

Pomeranz et al (1969) first reported that sucrose esters and other glycolipids (Chung et al 1978, Finney and Shogren 1971, Pomeranz 1969) overcome the deleterious effects of soy protein in bread. More recently, Chung et al (1976, 1978) found that commercial sucrose esters are able to completely replace the function of natural free lipids (petroleum-ether extracted) of flour in breadmaking. Furthermore, they found that the more hydrophilic sucrose esters gave better bread than did hydrophobic esters.

Besides carrying nonwheat protein in bread, sucrose esters, like other selected lipid surfactants, perform additional functions. They reduce the need for shortening, improve the tolerance of dough to physical abuse, and soften bread crumb (Chung et al 1976, 1978; Seib et al 1977). Sponge cakes are currently being made in Japan using sucrose esters (Kosaka and Yamada 1977).

Sucrose esters are produced commercially in several countries for food use. The Codex Alimentarius Committee of the Food and Agriculture Association of the World Health Organization set an acceptable daily intake of 0–2.5 g for sucrose esters of fatty acids and sucroglycerides (Lauridsen 1976). Furthermore, a directive of the European Economic Community in 1974 included sucrose esters on a list of emulsifiers authorized for food use by all members of the EEC (Lauridsen 1976). Sucrose esters are presently approved for food use in Japan, Italy, England, Belgium, Spain, Switzerland, and France, but not in the United States.

Sucrose esters of fatty acids can be synthesized by acylation of sucrose with an acid chloride or anhydride or by transesterification with a fatty acid ester (Colbert 1974, Kollonitsch 1970, Rizzi and Taylor 1978). Only the transesterification reaction is used commercially (Feuge et al 1970, Kosaka and Yamada 1977, Osipow et al 1956, Osipow and Rosenblatt 1967).

Commercial sucrose esters are complex mixtures of monoesters, diesters, and higher esters that contain fatty acids with various chain lengths. Acylation of sucrose with a single fatty acid potentially gives 255 different esters, including eight mono-, 28 di-, 56 tri-, 70 tetra-, 56 penta-, 28 hexa-, and eight heptaesters, and one octaester.

Our objective was to prepare sucrose esters of pure fatty acids, separate them into pure monoester and diester fractions, and compare their functions in bread.

## EXPERIMENTAL AND RESULTS

### General

Solutions were evaporated under reduced pressure below 60° C. Thin-layer chromatography was done on plates coated with silica gel G (Brinkman Instruments, Inc., Westbury, NY). After a plate was developed in chloroform and methanol (4:1, v/v), components were located by spraying with 50% aqueous sulfuric acid and charring on a hot plate.

Proton-noise, decoupled carbon-13 spectra were recorded at 25.2 MHz on a Varian XL-100-15 spectrometer fitted with a Nicolet 1080 data system. The spectra were obtained at 30° C in methyl sulfoxide-$d_6$ solution (approximately 0.5*M*) with 12-mm sample tubes and a pulse delay time of 9 sec. Chemical shifts are reported in ppm downfield from the signal of tetramethylsilane. Sucrose was analytical reagent grade. Methyl esters of 99% purity, except for the 95% purity of methyl laurate, were obtained from the following sources: methyl caprylate and caprate, Nuchek Preparations, Elysian, MN; methyl laurate and oleate, Eastman Kodak Co., Rochester, NY; methyl myristate and stearate, Aldrich Chemical Co., Milwaukee, WI; and methyl arachidate and linoleate, Sigma Chemical Co., St. Louis, MO. Commercial sucrose esters, Dai-Ichi F-160B and Ryoto P-1670 were obtained,

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respectively, from Dai-Ichi Kogyo Seiyaku Co. Ltd., Kyoto, Japan, and Dai-Nippon Sugar Manfacturing Co. Ltd., Tokyo, Japan. Reagent grade *N,N*-dimethylformamide (DMF) and benzene (Fischer Scientific, Fairlawn, NJ) were dried over calcium hydride and filtered before use.

### Preparation of Sucrose Esters

Fatty acid esters of sucrose were prepared by transesterification using a modified Hass-Snell procedure (Kosaka and Yamada 1977, Lemieux and McInnes 1962). Sucrose (20.5 g, 60 mmoles) was dissolved in anhydrous DMF (300 ml), and the solution was placed in a three-necked round-bottomed flask (500 ml) mounted above a magnetic-stirring hot plate. The reaction vessel was placed in an oil bath at 80° C and the pressure above the DMF solution was lowered to ~65 mm Hg. After the sucrose was dissolved by vigorous stirring, a solution of sodium in methanol (1 *M*, 4.0 ml) was injected through a rubber septum with a hypodermic syringe. A solution of a methyl ester of a fatty acid (20 mmoles) in dry benzene (20 ml) was injected into the reaction vessel. The reaction mixture was maintained at 80° C and ~65 mm Hg for 3 hr, during which time methanol, benzene, and a portion of DMF distilled from the reaction mixture. The mixture was evaporated to dryness, and the residue dissolved in warm *n*-butanol (50 ml). The butanol solution was extracted three times with 5% aqueous sodium choloride solution and the butanol phase dried over anhydrous sodium sulfate. After evaporation of the butanol, the solid product was dried under vacuum. The yields of the sucrose esters are given in Table I.

### Purification of Sucrose Monesters and Diesters

Sucrose monoesters and diesters were isolated and purified from the crude sucrose esters with silica gel (100–200 mesh, grade 923, Fisher Scientific, Fairlawn, NJ) column chromatography. Columns (30 × 650 mm) were developed by gravity flow (1–2 ml/min) with either 95:5 or 98:2 (v/v) chloroform/methanol. Solvents were distilled. Sucrose ester (5 g) was dissolved in chloroform (50 ml), and the solution was added to silica gel (25 g) and evaporated to dryness. The dry mixture was ground and mixed gently using a mortar and pestle and then applied to the top of a column of silica gel (200 g). Elution of the components from a column was followed using thin-layer chromatography. In a typical run, 5 g of crude sucrose ester gave approximately 1.5 g of chromatographically pure sucrose monoester and approximately 0.1 g of pure diester, which were dried to constant weight under vacuum. Typical data for the isolation of sucrose monopalmitate and dipalmitate are given in Table II.

### Characterizing Purified Sucrose Monoesters and Diesters

The sucrose content of each purified ester was determined with thiobarbituric acid (Tanaka et al 1975). Saponification equivalents were determined on 200 mg of sucrose ester by hot alcoholic potassium hydroxide (30-min reflux) followed by adding cold water and titrating with 0.03 *M* sulfuric acid (Robertson et al 1962). The effect of sucrose esters on yeast activity was tested before all bake tests by the AACC gassing power procedure (AACC 1961). Sucrose ester (0.05 g), flour (10 g), and 2 ml of aqueous yeast suspension (0.3 g of yeast) were used in each test. Data characterizing the sucrose esters are given in Table III.

**TABLE I**
**Yields of Crude Sucrose Esters**

| Ester | Amount | Yield[a] |
|---|---|---|
| Caprylate | 5.8 | 67.4 |
| Caprate | 6.4 | 65.0 |
| Laurate | 6.7 | 64.0 |
| Myristate | 7.0 | 64.0 |
| Palmitate | 8.0 | 67.0 |
| Stearate | 8.2 | 68.0 |
| Oleate | 6.2 | 51.0 |
| Linoleate | 6.2 | 50.8 |
| Arachidate | 8.5 | 66.8 |

[a] Yield based on methyl ester of fatty acid as limiting reagent and assuming product is entirely monoester.

### Characterization and Purification of Commercial Sucrose Esters

The monoester and diester fractions of two commercial sucrose esters, Ryoto P-1670 and Dai-Ichi F-160B, were separated and purified as described. In a typical run, 5 g of a commercial sucrose ester gave approximately 1.9 g of chromatographically pure sucrose monoester and 0.2 g of pure sucrose diester. The sucrose and fatty acid contents of the monoester and diester fractions are given in Table III.

The fatty acids in the commercial sucrose esters, before and after purification, were determined by a modification of the AOCS (1976) method. Commercial sucrose ester (1 g) or its monoester fraction (1 g) was heated at 70° C for 30 min in 10 ml of 1% methanolic potassium hydroxide. After cooling and neutralizing with 1% aqueous hydrochloric acid, the methyl esters were extracted with petroleum ether. The organic phases were combined and washed with water, dried over anhydrous sodium sulfate, and concentrated to 1 ml. The concentrate was analyzed by gas-liquid chromatography with a column packed with diethyleneglycol succinate on chromosorb G. The methyl esters were detected by

**TABLE II**
**Column Chromatographic Separation of Sucrose Monopalmitate and Dipalmitate from Crude Sucrose Palmitate (5 g) with Either 95:5 or 98:2, v/v, Chloroform/Methanol**

| Solvent | Fraction No. | Cumulative Volume (ml) | Weight (g) | Esters Present[a] | | |
|---|---|---|---|---|---|---|
| | | | | Monoester | Diester | Higher |
| 95:5 | 1 | 875 | 1.40 | + | + | + |
| | 2 | 1,024 | 0.13 | − | + | + |
| | 3 | 1,169 | 0.10 | − | + | − |
| | 4 | 2,369 | 0.80 | + | + | − |
| | 5 | 5,269 | 1.60 | + | − | − |
| 98:2 | 1 | 900 | 1.20 | + | + | + |
| | 2 | 1,650 | 0.15 | − | + | + |
| | 3 | 2,250 | 0.19 | − | + | − |
| | 4 | 4,850 | 1.10 | + | + | − |
| | 5 | 9,050 | 1.48 | + | − | − |

[a] Determined by mobility on thin-layer chromatography using chloroform/methanol (4:1, v/v). $R_f$ values for monoesters, diesters, and higher esters of sucrose were 0.31, 0.42, and <0.05, respectively.

**TABLE III**
**Characterization of Sucrose Monoesters and Diesters**

| Sucrose Ester | Fatty Acid (% of theory) | Sucrose (% of theory) | Gassing Power[a] (cc) |
|---|---|---|---|
| Monocaprylate | 96.9 | 95.7 | 368[b] |
| Monocaprate | 98.2 | 96.0 | 368[b] |
| Monolaurate | 96.4 | 95.0 | 370[c] |
| Monomyristate | 99.0 | 97.0 | 360[c] |
| Monopalmitate | 97.9 | 100.2 | 375[c] |
| Monostearate | 99.8 | 100.1 | 370[c] |
| Monoarachidate | 95.0 | 100.5 | 370[c] |
| Monooleate | 99.5 | 95.0 | 380[c] |
| Monolinoleate | 94.0 | 96.2 | 370[b] |
| Monoester Dai-Ichi | 98.0[d] | 96.0[d] | 375[b] |
| Monoester Dai-Nippon | 97.0[d] | 96.0[d] | 375[b] |
| Dicaprylate | 93.4 | 94.1 | 365[b] |
| Dilaurate | 92.8 | 98.2 | 350[b] |
| Dipalmitate | 98.0 | 95.2 | 375[b] |
| Distearate | 99.0 | 94.8 | 380[b] |
| Diester Dai-Ichi | 94.8[d] | 93.9[d] | 380[b] |
| Diester Ryoto | 94.0[d] | 94.0[d] | 375[b] |

[a] Gassing power for the control of one run was 375 cc. On a different day, when a different supply of yeast was used, gassing power values were normalized by multiplying observed value by the ratio of 375 cc over the gassing power observed for a control.
[b] Gassing power values normalized.
[c] Gassing power determined when control was 375 cc.
[d] Calculated assuming the commercial sucrose esters contained only palmitic acid.

flame-ionization. They were identified by comparing their retention times to those of known standards, and the weight percentages of the fatty esters were calculated, assuming an identical response factor for all esters. The results are given in Table IV.

### Na Content

The sodium contents of commercial sucrose esters and their monoester fractions were determined by atomic absorption spectrophotometry (Perkin-Elmer model 460, Norwalk, CT). Samples (50–100 mg), except for 10.0 mg of crude Dai-Ichi, were digested in a mixture of concentrated nitric acid (1.0 ml) and sulfuric acid (2.0 ml). The digest was cooled, made to volume (10.0 ml) with distilled water, and analyzed in duplicate. The results are given in Table V.

### Baking

The effects of sucrose esters in breadmaking were measured by the modified microbake test (10 g of flour) described by Shogren et al (1969). The dough formula was as follows: wheat flour (regional baking standard) or a composite flour (9:1 mixture by weight of the wheat flour and a defatted soy flour, Ardex 550 of Archer Daniels Midland Co., Decatur, IL), 10 g; water, amount varied to give uniform dough consistency and handling properties; yeast, 0.35 g; shortening, 0.3 g, or sucrose ester, variable; salt, 0.15 g; barley malt 54 DU/g (20° C), 0.075 g; and L-ascorbic acid, 50 ppm. The dry ingredients (flour and sucrose ester) were blended in a Stein mill for 30 sec. In loaves containing shortening, the shortening was a commercial hydrogenated vegetable oil. After being mixed to the point of minimum mobility (optimum), the dough was fermented 120 min, with punches at 69 and 103 min, and molded at 120 min. The dough was panned, proofed to height (30° C, 90% rh) and baked at 230° C for 13 min. Loaf volume was determined by dwarf-rapeseed displacement immediately after the bread was taken from the oven. Loaf volumes were reported as the average of triplicate loaves. Seven control loaves baked from a standard wheat flour and 3% shortening had a mean loaf volume of 74.8 cc with a standard deviation of 1.43 cc, whereas 17 loaves baked from the composite flour in a no-shortening formula with 0.75% Dai-Ichi sucrose ester had a mean volume of 77.5 cc with a standard deviation of 1.54 cc. After cooling, loaves were cut and crumb grains evaluated. All loaves with volumes exceeding 70 cc had satisfactory crumb grain.


**Fig. 1.** Fourier-transform c.m.r. partial spectra showing only the $C_{2'}$ region of sucrose monomyristate **(A)**, monopalmitate **(B)**, and monostearate **(C)** isolated from a transesterification reaction in *N,N*-dimethylformamide.

## DISCUSSION

Sucrose esters were synthesized from methyl esters of purified fatty acids, and after column chromatography on silica gel, pure fractions of sucrose monoesters and diesters were obtained. Breadmaking with those fractions permitted us to determine the chain length of fatty ester that functioned best by itself. However, the fractions of monoester and diester tested in this investigation were still mixtures of several compounds. Positional isomers were not resolved on the columns of silica gel. But we did use $^{13}C$ nuclear magnetic resonance (NMR) spectroscopy to show that the isomeric composition of the pure monoester fractions of the various fatty esters probably were the same. We assumed that all the diesters also had the same positional composition.

We synthesized the sucrose esters using a modification (Lemieux and McInnes 1962) of the original Hass-Snell procedure (Osipow et al 1956). In an extensive investigation of the transesterification reaction, Lemieux and McInnes (1962) found that, when sucrose and a methyl ester of a fatty acid reacted in the presence of a soluble catalyst in *N,N*-dimethylformamide, the composition of the sucrose ester remained constant throughout the reaction. Thus, no matter when the reaction is stopped, the products isolated from different reactions will contain the same kinds and amounts of positional isomers. The composition of a mixture also should be independent of the chain length of the fatty acid.

We investigated the composition of the sucrose monoester fractions with $^{13}C$ NMR spectroscopy. The partial, proton-decoupled spectra of sucrose monostearate, monopalmitate, and monomyristate in methyl sulfoxide-$d_6$ are shown in Fig. 1.

The anomeric carbon[4] ($C_{2'}$) of the fructose moiety in sucrose resonates at 103.4 ppm (downfield from tetramethylsilane) in

[4]The carbons in the D-fructose portion of the sucrose molecule are numbered with a prime notation.

**TABLE IV**
**Fatty Acid Compositions of Commercial Sucrose Esters and Their Monoester Fractions**

| Sucrose Ester | Fatty Acids (weight %) | | | |
|---|---|---|---|---|
| | $C_{12}$ | $C_{14}$ | $C_{16}$ | $C_{18}$ |
| Ryoto, P-1670 | Trace | Trace | 79 | 21 |
| Monoester fraction | Trace | Trace | 77 | 23 |
| Dai-Ichi, F-160B | Trace | 5 | 36 | 59 |
| Monoester fraction | None | 8 | 51 | 41 |

**TABLE V**
**Sodium Content of Commercial Sucrose Esters and Their Monoester Fractions**

| Sucrose Ester | Weight of Digested Sample (mg) | Sodium Concentration in Digest Made to 10.0 ml ($\mu$g/ml) | Sodium Stearate Content[a] (%) |
|---|---|---|---|
| Dai-Ichi F-160B | 10.0 | 10 | 10[b] |
| Monoester fraction | 50.0 | 0.5 | 0.1 |
| Ryoto P-1670 | 100.0 | 17 | 1.7 |
| Monoester fraction | 100.0 | 1 | 0.1 |
| Blank | 0 | 0 | 0 |
| Control, sodium acetate | 17.84 | 50[b] | ... |

[a]Calculated assuming the sodium was present as sodium stearate (7.5% Na) in sucrose ester.
[b]Digest diluted with water to 100.0 ml instead of 10.0 ml.

water, and the chemical shift is the same when the solvent is methyl sulfoxide (Binkley et al 1972). The $C_{2'}$ region in the spectra of all three sucrose monoesters in Fig. 1 showed two identical major peaks (104.1 and 104.4 ppm), one minor peak (102.4 ppm), and traces of two others (103.2 and 105.0 ppm). The carbonyl region of each spectrum (~173 ppm) also showed five resolved signals with the same relative intensities as those for the $C_{2'}$ carbon. The $C_{2'}$ signals of the monopalmitate (Fig. 1B) were almost identical to those of the monostearate (Fig. 1C), which indicates that both those monoesters are composed of identical proportions of the same isomers. However, the $C_{2'}$ signals of sucrose monomyristate (Fig. 1A) differed somewhat from those of the other two monoesters, which indicated different proportions of the two major isomers in the monomyristate ester. The difference in composition could stem from some change, like that of reaction temperature, in the esterification reaction.

Signals in $^{13}C$ NMR normally do not yield quantitative information, but they can be integrated in a fully-relaxed spectrum of a mixture of positional isomers (Koerner et al 1973, Allerhand et al 1971). To insure a fully relaxed $^{13}C$ spectrum, we used a delay time of 9 sec between the radiofrequency pulses, which ensures relaxation of $C_{2'}$; it has a relaxation time of ~1 sec in a sucrose derivative (Hall et al 1977).

In equilibrium-controlled reactions, the primary hydroxyls of carbohydrates are approximately 10 times more reactive than are secondary hydroxyls (Rowland et al 1966). Transesterification of sucrose then should yield a monoester fraction containing mostly three isomers, sucrose 6-acylate, sucrose 6'-acylate, and sucrose 1'acylate. Furthermore, the proportion of the last isomer should be small because the 1'-OH in sucrose is sterically hindered and is much less reactive than the 6-hydroxyl and 6'-hydroxyl (Kahn 1977, Reinfeld and Klaudianos 1968).

Using the $C_{2'}$ and $C_{4'}$ signals in the proton-decoupled spectrum made possible the deduction that sucrose monopalmitate is predominantly a 6:3:1 mixture of sucrose 6-palmitate, sucrose 6'-palmitate, and sucrose 1'-palmitate (Seib et al 1977). Thus, the breadmaking effects of the sucrose monoesters we measured in this work stem from combined effects of mostly the 6-acylate and 6'-acylate isomers.

To conduct our baking tests, we purified the monoester fraction of sucrose esters made from nine fatty acids, including the seven common saturated acids from $C_8$ through $C_{20}$ and the two unsaturated oleic and linoleic acids. We also purified the corresponding diesters of the common $C_8$–$C_{16}$ acids. The purified esters contained no Kjeldahl nitrogen and gave 93–100 and 95–100% of the theoretical amounts of fatty acid and sucrose, respectively. Furthermore, none of the sucrose esters adversely affected yeast fermentation as determined by a gassing power test. Typically, yields of chromatographically pure monoesters and diesters were ~25 and 3%, respectively, based on the fatty acid ester as limiting reagent (Table II).

A microloaf bake test was used to evaluate the dough-strengthening effect of the sucrose esters. Most bake tests were done with a no-shortening formula and a composite wheat-soy flour. The composite flour formula was used rather than a wheat flour formula because loaf volume of bread baked from the composite flour is approximately twice as sensitive to the improving effect of surfactants as is loaf volume of bread from white flour. A loaf volume of 73 cc for a microloaf is considered acceptable for the type of bread eaten in the United States.

The dough-strengthening effects of the saturated sucrose monoesters as manifested by loaf-volume improvement in a no-shortening bread are shown in Fig. 2. In general, increasing the concentration of a sucrose monoester increased loaf volume up to a maximum. Beyond that, adding more sucrose monoester caused loaf volume to decline. At low concentration, the potency of each sucrose monoester differed, as did the overall capacity for loaf-improvement of any given ester.

Loaf volume responded rapidly to the addition of small amounts (0.25%)[5] of the monopalmitate and monostearate esters but somewhat less rapidly to the monocaprylate, monocaprate, monolaurate, and monomyristate esters. The $C_{16}$ and $C_{18}$ esters gave a maximum loaf volume at ~0.38%, whereas the $C_8$–$C_{14}$ esters gave an optimum volume at ~0.5%. The behavior of the arachidate monoester was unique. It was much less potent at low levels and did not perform well until its concentration reached ~0.9%. However, it had the greatest capacity for improving loaf volume of all the saturated monoesters.

The differences in the optimum levels of the sucrose monoesters shown in Fig. 2 cannot be explained entirely by differences in their molecular weights. For example, 0.5% by weight of sucrose monocaprylate is equivalent to 0.57% sucrose monolaurate and 0.68% sucrose monoarachidate. At those concentrations, the loaf volumes read off the curves in the right-hand graph of Fig. 2 are 71, 73, and 67 cc for the $C_8$, $C_{12}$, and $C_{20}$ esters, respectively. In addition, more molecules of surfactant are in 0.25% sucrose monolaurate than in 0.25% sucrose stearate, yet the monostearate was a more effective improver (71 cc) than was the monolaurate at 0.25% (66 cc).

Viewed as shown in Fig. 3, the data in Fig. 2 show that at low levels, sucrose monopalmitate and monostearate are the surfactants of choice. But at higher levels (0.5–0.75%), sucrose monolaurate had the greatest capacity for dough strengthening.

Sucrose monocaprylate and monocaprate reduced the mixing

[5]Concentrations of sucrose esters in a formula are given in "baker's percentages." Thus, 0.5% sucrose monoester means 0.5 g of ester added to 100 g of flour (14% mb).

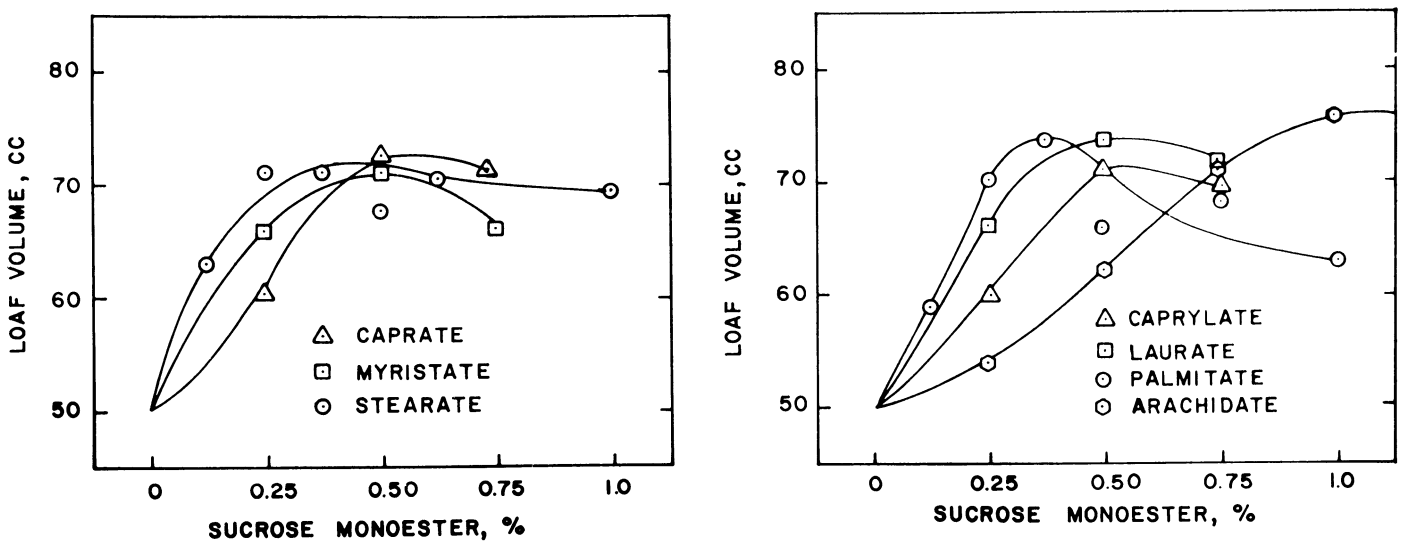


**Fig. 2.** Loaf volumes of microloaves (10 g of flour) baked from a no-shortening formula and a 9:1 mixture of wheat and soy flours. A control loaf with 3% shortening gave a loaf volume of 71.2 cc.

times of doughs by about 15%. None of the other sucrose esters significantly affected mixing.

The effect of unsaturation of the fatty acids on the functioning of the sucrose monoesters in bread is shown in Fig. 4. Sucrose monooleate performed slightly better than did sucrose stearate, but sucrose monolinoleate performed worse.

Commercial sucrose esters generally contain a high proportion of myristates, palmitates, stearates, and possibly traces of oleates. The dough-conditioning effects of the sucrose monoesters of those common fatty acids are shown in Fig. 5. The similarity in improving effects of the monoesters of all three common, saturated fatty acids is apparent.

In previous work with commercial samples of sucrose esters in soy-fortified bread, Pomeranz et al (1969) observed that 0.5% sucrose dilaurate gave a pup loaf (100 g of flour) of acceptable volume (955 cc vs 933 cc for a 3% shortening control), whereas 0.5% sucrose dipalmitate gave an unacceptable volume of 840 cc. Our results of work with pure sucrose diesters (Fig. 6) verify those earlier findings. Generally, the diesters of the short-chain fatty acids ($C_8$, $C_{10}$, and $C_{12}$) gave dough strength sufficient to produce acceptable soy-fortified bread. In fact, sucrose dilaurate at 1.0–1.5% showed the greatest dough-strengthening capacity of all the pure sucrose esters we examined.

An unfractionated or crude sample of sucrose palmitate improved loaf volume more than either its monoester or diester fraction alone (Fig. 7). Optimum levels and corresponding loaf volumes for the palmitate esters were as follows: 2% crude sucrose palmitate, 81.2 cc; ) 0.38% sucrose monopalmitate, 71.8 cc; and 3% sucrose dipalmitate, 69.5 cc. Those results indicate that at low concentrations of crude ester, the beneficial effect of the monoester fraction is diluted by the higher ester fractions. However, at high

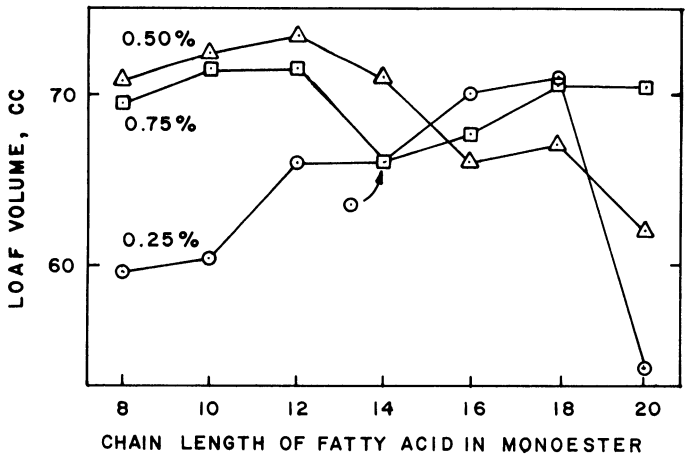


**Fig. 3.** Loaf volumes of microloaves vs chain lengths of saturated fatty acids in sucrose monoesters.

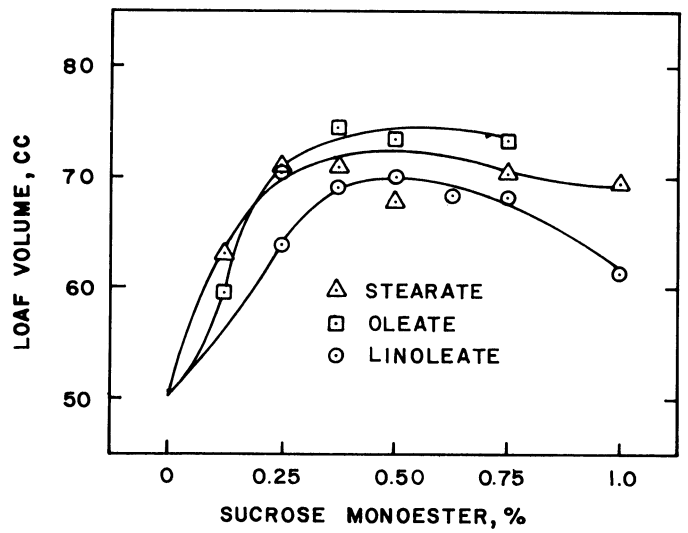


**Fig. 4.** Loaf volumes of microloaves baked with sucrose monoesters of $C_{18}$ fatty acids.

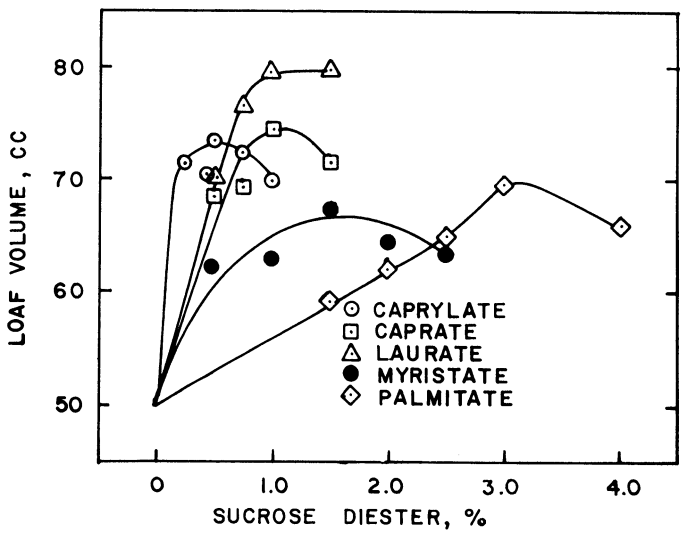


**Fig. 6.** Loaf volumes of microloaves baked with sucrose diesters.

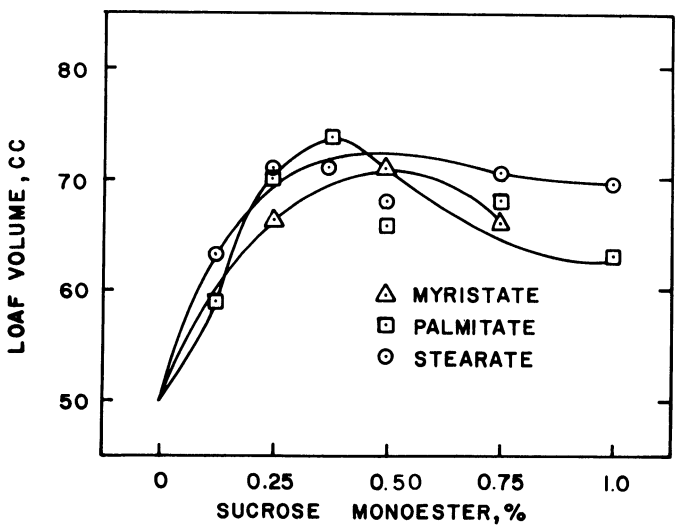


**Fig. 5.** Loaf volumes of microloaves baked with sucrose monoesters of the saturated fatty acids that occur most abundantly in nature.

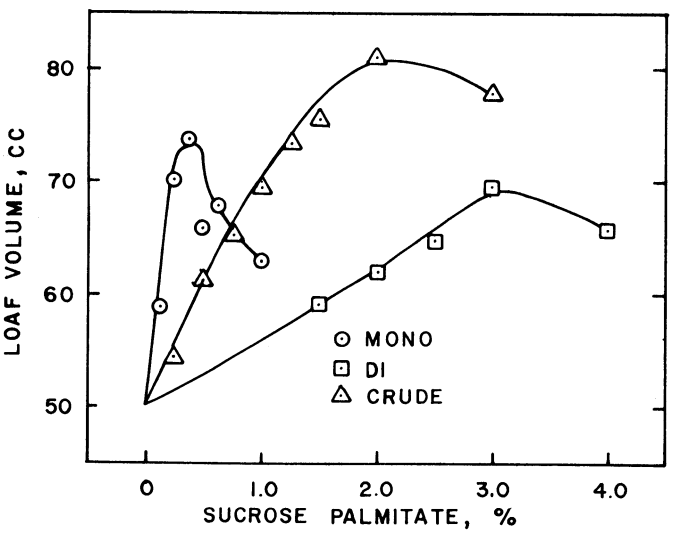


**Fig. 7.** Loaf volumes of microloaves baked with crude sucrose palmitate, the sucrose monopalmitate fraction, and the sucrose dipalmitate fraction.

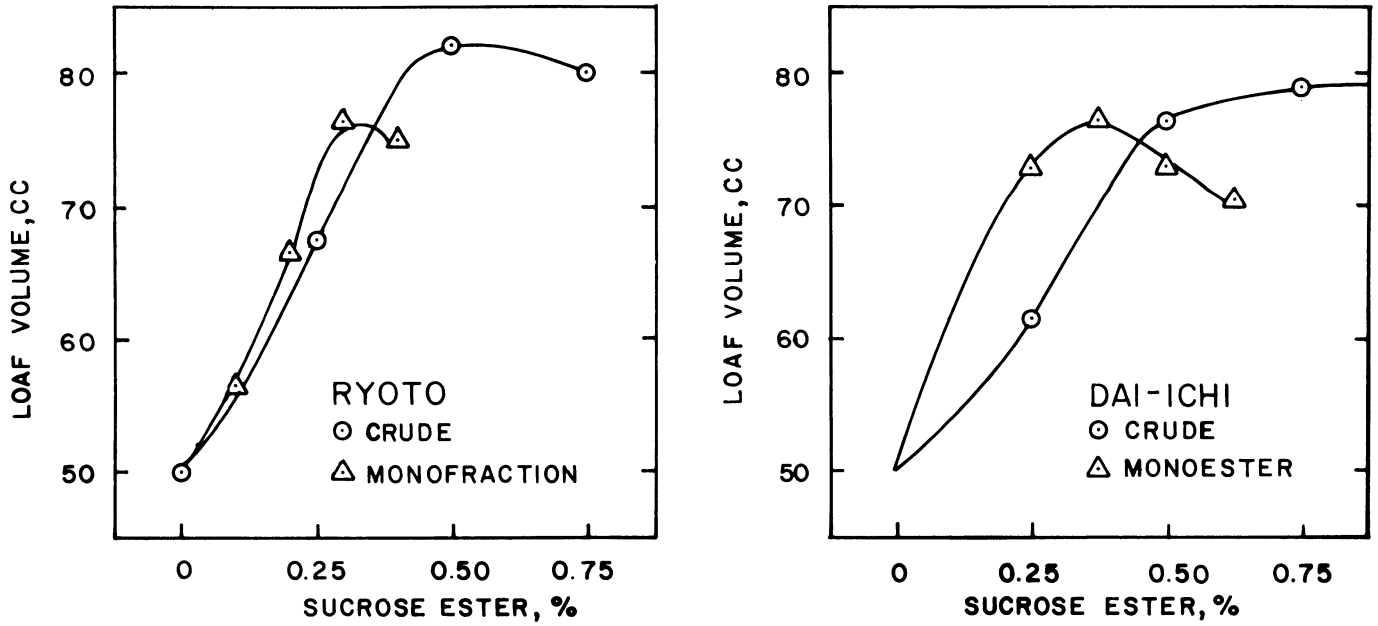


**Fig. 8.** Loaf volumes of microloaves baked with commercial sucrose esters and their purified monoester fractions.

levels of crude ester, the mono and higher ester fractions behave synergistically to produce excellent bread.

The loaf-improving action of crude sucrose palmitate is similar to the combined effects of flour lipids and shortening, as Chung et al (1978) demonstrated, and shortening does not improve loaf volume in the absence of flour lipids, especially the polar lipids. In the same manner, sucrose monopalmitate appears to add to the polar lipid phase in the dough and thereby make the higher esters of sucrose functional. Sucrose dipalmitate is hydrophobic, much like shortening, so the dipalmitate must be carried by the monopalmitate.

Crude sucrose stearate and arachidate had much lower capacities for dough conditioning than did crude sucrose palmitate. The optimum levels and corresponding loaf volumes for those esters and their purified monoesters were as follows: 3% crude sucrose stearate, 70 cc; 0.25% sucrose monostearate, 71 cc; 3% crude sucrose arachidate, 74.5 cc; 1% sucrose monoarachidate, 75 cc.

We also examined two commercial samples of sucrose esters. The sample from Dai-Ichi Kogyo Seiyaku, Ltd. was reported to be a mixture of 71% mono and 29% higher esters, with the fatty acids being 70% palmitic and 30% stearic. Dai-Ichi esters are reported to be synthezied by transesterification according to the Nebraska-Snell process, except that water is used as solvent instead of propylene glycol (Kosaka and Yamada 1977). The other commercial ester, obtained from Ryoto Co., Ltd., was reported to contain 78% monoester, 19% diester, and 3% higher ester, with the main fatty acid being palmitic. The method of producing Ryoto sucrose esters has not been revealed, although it may be related to the USDA method (Feuge et al 1970), which is licensed by the Ryoto Company (Kosaka and Yamada 1977).

The crude commercial esters were chromatographed on silica gel to obtain pure commercial monoester fractions. Fatty acid analysis of the commercial materials by gas-liquid chromatography showed that the fatty acid composition of the Dai-Ichi monoester fraction differed from that of its crude ester (Table IV). The pure monoester fraction contained 8% myristic (weight percent), 51% palmitic, and 41% stearic acids, whereas the crude ester contained 5% myristic, 36% palmitic, and 59% stearic acids. We used atomic absorption spectroscopy to show that the crude Dai-Ichi ester contained ~1% sodium (Table 5). The sodium is most likely present as sodium stearate, which is used in the esterification reaction to create a microemulsion (Osipow et al 1967). Chung et al (1976) previously reported that crude Dai-Ichi sucrose esters contained triglycerides and fatty acids.

From the sodium content, we calculated that the sample of crude Dai-Ichi ester contained ~10% sodium stearate, but the change in fatty acid composition between the crude ester and the pure monoester fraction indicated that the crude ester contained ~20% stearic acid. Apparently, one half the fatty acid was in the free acid form.

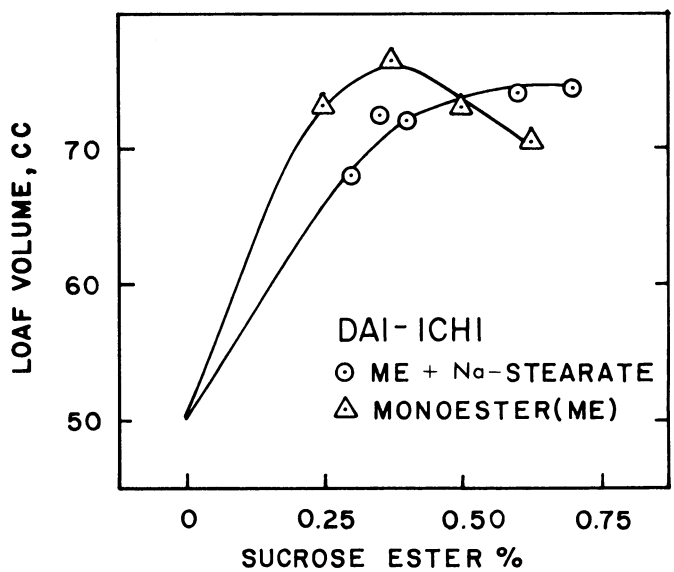


**Fig. 9.** Effect on loaf volume of adding sodium stearate to the monoester fraction of a commercial sample (Dai-Ichi) of sucrose stearate.

The fatty acid composition of the monoester fraction of the Ryoto sample was identical to that of the crude Ryoto ester (Table IV). The monoester fraction of the Ryoto product contained 77% palmitic and 23% stearic acids compared to 79% palmitic and 21% stearic acids in the crude ester.

The baking performances of the commercial sucrose esters are shown in Fig. 8. The Ryoto monoester fraction showed approximately the same potency as its crude ester (Fig. 8), but the crude Ryoto ester had more capacity to improve loaf volume. On the other hand, the monoester fraction of the Dai-Ichi ester was approximately 30% more potent as a dough strengthener than was the crude Dai-Ichi ester. The Dai-Ichi monoester, which was separated from sodium stearate and higher esters, gave a loaf volume of 75.6 cc at 0.38%, but 0.5% of the crude Dai-Ichi ester was needed to give a volume of 75.6 cc. The effect of sodium stearate on loaf volume is shown in Fig. 9. When loaves were baked with one part sodium stearate and three parts monoester fraction of Dai-Ichi

sucrose esters, volumes were generally depressed compared with those of controls baked with only the pure monoester. De Stefanis and Ponte (1976), baking white pan bread from dough to which they added ~0.5% palmitic or linoleic acid, found that palmitic acid had little effect on the loaves, whereas linoleic acid reduced loaf volume 13%.


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