Effect of Certain Surfactants on the Starch in Bread[1]

R. R. ROACH[2] and R. C. HOSENEY[3]

ABSTRACT

Addition of Tristearin (C_{18}TG) improved loaf volume in a manner similar to that of shortening. Triolein (C_{18}'TG), when used to replace shortening in the breadmaking formula, improved volume only slightly, probably because less solid fat was present. Using the hydrated form of monoglycerides (MG) was more effective than blending the MG with the flour in a high-speed mixer or adding them as is. Light micrographs of starch isolated from bread showed that MG or sodium stearoyl lactylate (SSL) added to the formula reduced the swelling of starch, whereas shortening did not. If the effect of MG on crumb firmness relates to their effect on starch swelling, then the mechanism of softening for MG is different than that for shortening. The SSL had a somewhat different effect in this limited water system than it had in an excess water system. The effect appeared to be similar to that in the excess water system heated to a lower temperature. Studies with bread made from defatted flour showed that MG reduced crumb firmness, whereas shortening did not. This supports the idea that the mechanisms by which these two lipids reduce crumb firmness are different

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Many studies (Osman and Dix 1960, Gray and Schoch 1962, Harbitz 1983, Tester and Morrison 1990) on properties of granular starch have used systems in which water was not a limiting factor (an excess water system). It is not clear whether the results from this type of system can be applied directly to those from a limited water system. Researchers have found differences in starch properties when the water content was reduced. Eliasson (1980) and Burt and Russell (1983) used differential scanning calorimetry (DSC) to show that, in a starch and water system, the gelatinization temperature of starch (an endothermic transition) increased as water content was reduced below 30%. Similarly, Derby et al (1975) showed that when water content went below a certain level, increasing percentages of starch granules retained birefringence at a given temperature.

Preparing concentrated starch gels for a study of limited water systems is difficult (Schoch and French 1947, Ghiasi et al 1983). A gradient of starch gelatinization can occur. The starch granules near the heat source may begin to gelatinize and swell. A water gradient develops in the system as water flows from the ungelatinized granules to the gelatinized granules. Thus, the granules near the heat source are gelatinized and swollen, whereas those away from it may not be gelatinized at all.

Bread provides a limited water system that does not have a large gradient of gelatinization, apparently because the gluten slows the movement of water. However, the starch granules in bread are embedded in a gluten network. This makes examining the starch difficult. Using an enzyme to degrade the protein may provide a method to remove the network (Derby et al 1975, Morrison et al 1984) and make characterization of the granules easier. Granules isolated from limited or excess water systems can be observed by light or scanning electron microscopy.

As a dough-bread system is heated above a certain temperature and the granules swell, the viscosity of the dough may increase, restrict expansion, and eventually set the crumb structure. Swollen starch granules or soluble material also may increase associations with proteins. Interaction among various components also may relate to crumb firming, which occurs over time.

Fatty compounds, such as monoglycerides (MG), can reduce the swelling and solubility of starch (Lord 1950, Leach et al 1959, Gray and Schoch 1962). These compounds also decrease the level of firmness and firming rate of bread crumb (Krog and Jensen 1970, Lagendijk and Pennings 1970). These facts suggest a correlation between starch swelling or solubility and crumb firmness.

The firming phenomenon in bread has been attributed to the retrogradation of the amylopectin fraction of starch rather than the amylose portion (Schoch and French 1947). Lagendijk and Pennings (1970) reported that various MG reduced the firmness of bread crumb but complexed with amylose rather than amylopectin. They suggested that the complexed amylose was less flexible and, thus, had less ability to interact with other amylose or amylopectin molecules. Thus, retrogradation of the starch would be reduced, leading to a reduced rate of firming.

By combining these findings, one can propose that the MG, which reduced starch swelling or solubility to the greatest extent, also may be the most effective antifirming agent in bread. However, other fatty materials such as triglycerides (TG) also decrease the firmness and firming rate of bread crumb (Hoseney 1986). The question can be raised as to whether or not these compounds affect the swelling and solubility of starch in bread. If they do not, then other factors may be important to crumb firmness. Examining the effect of fatty materials on the swelling and solubility of starch in various systems may provide insight on how they reduce firming.

The objectives of this study were to determine the effect of various lipids on the baking quality and firming of bread and to attempt to relate this to the morphology of starch granules isolated from bread.

MATERIALS AND METHODS

Materials

Two commercial bread flours (donated by Cargill Flour Milling, Wichita, KS) with protein contents of 10.9 and 11.3%, moisture contents of 13.56 and 13.47%, and ash contents of 0.45 and 0.45% were used for making bread.

Commercially available lipids and surfactants examined included a powdered distilled monoglyceride (PMG) (Amidan ESK, Grinsted Products, Industrial Airport, KS), a hydrated monoglyceride (HMG) (Panatex, donated by ADM Arkady, Olathe, KS), and sodium stearoyl lactylate (SSL) (Emplex, American Ingredients Co., Kansas City, KS). Additional lipids (donated by Grünau, Illertissen, Germany) included monoglyc-

[1]Contribution 95-295-J, Kansas State Agricultural Experiment Station, Manhattan, KS. 66506.

[2]Present address: Keebler Company, Elmhurst, IL.

[3]Graduate research assistant and professor, respectively, Department of Grain Science and Industry, Kansas State University, Manhattan, KS 66506. Fax: 913/532-7010.

eride samples with hydrocarbon chains of 18 carbons (C_{18}MG) and monounsaturated 18 carbons (C_{18}'MG) and two triglycerides with chains of 18 (C_{18}TG, tristearin) and monounsaturated 18 (C_{18}'TG, triolein) carbons. The shortening used was partially hydrogenated soybean and cotton seed oils containing mono- and diglycerides.

Methods

Hydration of monoglycerides. The C_{18} and C_{18}'MG were hydrated by combining 2.0 ± 0.001 g with 20 ml of water at room temperature. The C_{18}MG was solid at room temperature. Small particles of the MG were produced by scraping the large sample with a metal spatula. The desired amount of MG particles was weighed and added to the water. The C_{18}'MG was not as hard at room temperature and scraping produced shavings that were added to the water. The hydrated MG were heated in a 75°C water bath for 10 min. Samples were swirled by hand frequently during heating and after removal from the bath during cooling.

The MG and TG (2% fwb) were blended with flour using a high-speed mixer (Stein Mill) before mixing the dough. Shortening was omitted from the formula when these lipids were added. The control contained 3% shortening (AACC formula) that was not blended with the flour before mixing the dough. As shown later, 2% MG or TG gave loaf volumes equal to 3% shortening. Also included was a treatment with no added lipid.

Breadmaking. The straight-dough bake test procedure (AACC 1983) was followed to produce bread. Doughs were mixed to optimum (minimum mobility) in a National Special 100-g pin mixer (TMCO-National Mfg. Co., Lincoln, NE). The dough was fermented in a proof cabinet (TMCO-National Mfg.) at 30°C and 90–95% rh for 90 min. During the fermentation, the dough was sheeted at a gap of 3/16 in. after 52 and 75 min. At the end of the fermentation (90 min), the dough was sheeted at a gap of 5/16 in. and then molded in a drum molder (Thomson Co., Beltsville, NJ). The dough piece was panned (top: 77- × 142 mm; bottom: 62- × 126 mm; depth: 57 mm) and then proofed at 30°C and 90–95% rh for 33 min. The proofed dough was baked in a 12-1 pound electric reel oven (TMCO-National Mfg.) at 218°C for 24 min. Immediately upon removal from the oven, the loaf was weighed and the volume was taken by rapeseed displacement. Triplicates were baked for all treatments.

Bread firmness. Bread firmness was measured according to method 74-09 (AACC 1983). The TA-XT2 Texture Analyzer (Texture Technologies, Scarsdale, NY) was used instead of the Instron universal testing machine. Bread slices were cut to a thickness of 25 mm using a miter box. The plunger diameter was 38 mm. The crosshead speed was 1.7 mm/sec. Data from the TA-XT2 were transmitted to a personal computer through an I/O card and analyzed with Analisa and XT.RA Dimensions software (Texture Technologies). Firmness measurements were taken at 25% compression (6.25 mm). Measurement were made on three slices from each loaf. A minimum of three loaves were tested for each treatment.

Enzymatic isolation of starch. Pronase E (0.01 g, ≈40 Sigma units) was added to ≈200 ml of distilled water. A pup loaf was sliced in a miter box that produced five slices. The crust was removed (≈5 mm into crumb) from the center slice and an adjacent slice. The entire trimmed crumb from the center slice was used with an amount of the adjacent slice to obtain 10 g of crumb. The weighed crumb was torn into small pieces (≈5–10 mm in diameter) and added to the enzyme-water solution. The combined suspension was stirred with a magnetic stir bar, creating a vortex extending to near the bottom of the beaker, for 1.5 hr at room temperature. The suspension then was poured onto a 100-mesh screen resting on a 4,000-ml breaker. The beaker used for digestion was rinsed until clean with distilled water from a wash bottle. A rubber spatula and distilled water were used to flush the digested starch through the screen. Very little material was removed with the screen. It mainly assisted in breaking apart aggregated starch particles in the digested crumb. The contents (digested starch, enzyme-water solution, rinse water) of the beaker were transferred to a 1,000-ml centrifuge tube. The beaker then was rinsed with distilled water, which was poured into the centrifuge tube. The sieved suspension was centrifuged at 1,000 × g for 15 min. The supernatant was discarded. The centrifugate was transferred to 60-ml centrifuge tubes. Approximately 40 ml of distilled water was added to the precipitate and stirred with a metal spatula for ≈1 min to help remove residual solubilized protein. The resulting suspension was centrifuged at 1,100 × *g* for 10 min. This was slightly more force than was used for the large tubes. The tailings (dark, upper layer) were scraped off of the starch (white, lower layer) to recover samples of starch for examination.

Light microscopy. Diluted samples of excess-water starch suspensions or enzymatically degraded bread crumb were examined by light microscopy. No additional treatment was required.

Hydration capacity of bread crumb. Crust was removed from a loaf of bread within 4 hr after baking. The crumb was torn by hand into pieces and placed into a plastic bag to allow the moisture to equilibrate throughout the crumb. A portion of crumb (5.0 ± 0.001 g) was weighed and torn into smaller pieces (3–6 mm) and placed in a 125-ml Erlenmeyer flask. Distilled water (50 ml) was added to the flask containing the crumb. The suspension was stirred vigorously with a magnetic stir bar for ≈30 min. The stir bar then was removed, and the suspension was transferred to a preweighed 60-ml centrifuge cup. The sample was centrifuged at 1,000 × *g* for 10 min. The supernatant was decanted, and the tube with the centrifugate was reweighed (±0.001). Moisture content of the crumb was determined by method 44-15A (AACC 1983). At least triplicate determinations were made.

The hydration capacity (HC) was calculated as: hydration

TABLE I
Effect of Various Lipids and Form of Addition on Loaf Volume[a]

Treatment	Loaf Volume (cm^3)
Bake 1[b]	
Control: 3% shortening, unblended	960 a
No shortening	683 d
C_{18}MG: 2%, blended[c]	905 b
C_{18}'TG: 2%, blended	743 c
Bake 2[b]	
Control: 3% shortening	918 a
No shortening	700 c
C_{18} MG: 2%, as is	835 b
C_{18} MG: 2%, hydrated	907 a
C_{18}TG: 2%, as is	915 a

[a] Values within the same bake followed by the same letter were not statistically different at the 5% level.
[b] Bakes 1 and 2 were on different days with different flours.
[c] C_{18}MG = monoglyceride with 18 carbons; C_{18}TG = triglyceride with 18 carbons; C_{18}'TG = triglyceride with monounsaturated 18 carbons.

TABLE II
Effect of Added C_{18}MG[a] Content on Loaf Volume[b]

Treatment	Loaf Volume (cm^3)
Control	952 a
No fat	675 d
0.5% C_{18}MG	880 c
1.0% C_{18}MG	908 b
1.5% C_{18}MG	943 a
2.0% C_{18}MG	945 a

[a] Added as a hydrate, but reported weight is of the monoglyceride. C_{18}MG = monoglyceride with 18 carbons.
[b] Values followed by the same letter were not statistically different at the 5% level.

capacity = grams of centrifugate/grams of solids.

Hydration capacity of starch isolated from bread crumb was based on the weight of the centrifugate from the enzyme-isolated starch described above. When determining HC, no samples were taken for microscopy so tailings were not removed. The HC values were determined by dividing the weight of centrifugate by an amount of solids as described in method 44-15A (AACC 1983) for bread moisture content.

Defatting flour. Flour was defatted with 2–2.5 L of petroleum ether with a Soxhlet apparatus. A large thimble was lined with filter paper, then filled with ≈350 g of flour. A mantle was used to heat the system and cause the petroleum ether to drip at a rate of ≈6 drops/10 sec. The sample was extracted for at least 12 hr, dried at room conditions (≈23°C), then reextracted for another 12 hr with new petroleum ether, and finally redried at room conditions. Of course, petroleum ether only removes the free lipids. The moisture of the defatted flour was determined according to method 44-15A (AACC 1983).

RESULTS AND DISCUSSION

Effect of Various Lipids on Loaf Volume

Addition of shortening to the breadmaking formula was shown to increase volume (Table I). A volume increase also was caused by C_{18}MG and C_{18}'TG. However, the latter gave only a small increase in volume, possibly because of the low solid fat content at mixing and fermentation temperatures. It is generally believed that a certain amount of solid fat is necessary at each of these stages to obtain a positive effect on loaf volume (Baker and Mize 1942, Knightly 1977). The C_{18}MG improved loaf volume over that with no added shortening or lipid, but not to the extent of the shortening or C_{18}TG.

The C_{18}TG effectively replaced the shortening in bread. The hydrated C_{18}MG caused the average loaf volume to increase over that with no added fat. The C_{18}MG appeared to influence loaf volume to a greater extent when applied in the hydrated form. This is not surprising because other studies have shown its effect on other properties, such as crumb firmness, is influenced by the form in which it is added to the dough (Krog and Jensen 1970).

Because the C_{18}MG improved loaf volume, various levels were examined to determine if it could replace shortening. The more effective hydrated form was used. At 1.5–2.0%, the C_{18}MG had an effect similar to that of shortening at 2.0–3.0% (Table II).

Effect of Hydrated C_{18} and C_{18}'MG on Crumb Firmness

MG are used widely in commercial bread formulas to reduce crumb firmness. These generally are composed of a mixture of C_{16} and C_{18}MG. The bread formula (method 10-10B, AACC 1983) contained 3% shortening and 1% of the hydrated C_{18}MG. The MG was used at 1% because of some difficulty in achieving significant effects with lower levels (0.25 and 0.5%). In an initial test, 1% C_{18}MG significantly reduced crumb firmness (Fig. 1). C_{18}'MG also was tested in bread at 1% to determine whether it reduced crumb firmness, and it was at least as effective at reducing crumb firmness as was the C_{18}MG (Table III). On day 1 after baking, both MG reduced crumb firmness significantly below that of the control. On day 5, C_{18}'MG reduced crumb firmness below that of the control, but the bread with C_{18}MG was not significantly less firm.

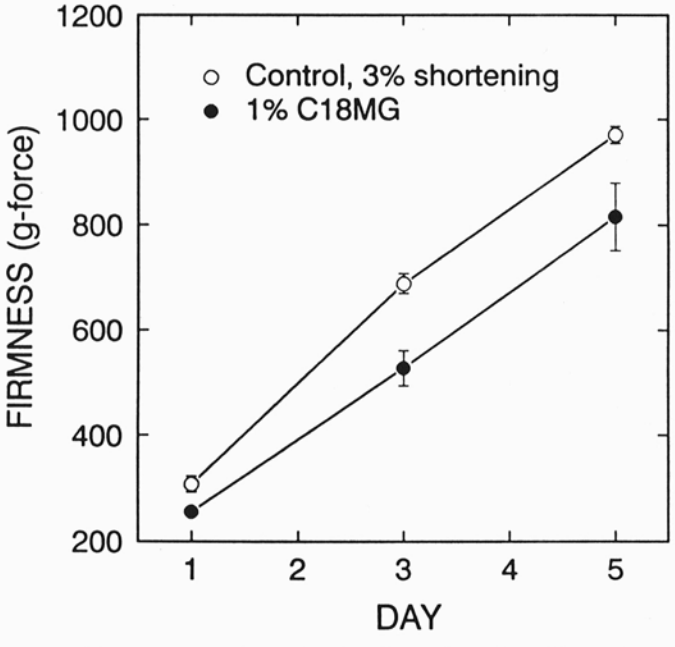

Fig. 1. Effect of monoglyceride with 18 carbons (C_{18}MG) on bread crumb firming. The treatment containing C_{18}MG also contained 3% shortening.

TABLE III
Effect of 1% C_{18}'MG on Crumb Firmness[a]

Treatment	Firmness (*g*-force)	
	Day 1	Day 5
Control	361 a	866 a
C_{18}MG	315 b	764 ab
C_{18}'MG	306 b	684 b

[a] Values followed by the same letter within a column were not statistically different at the 5% level. C_{18}MG = monoglyceride with 18 carbons; C_{18}'MG = monoglyceride with monounsaturated 18 carbons.

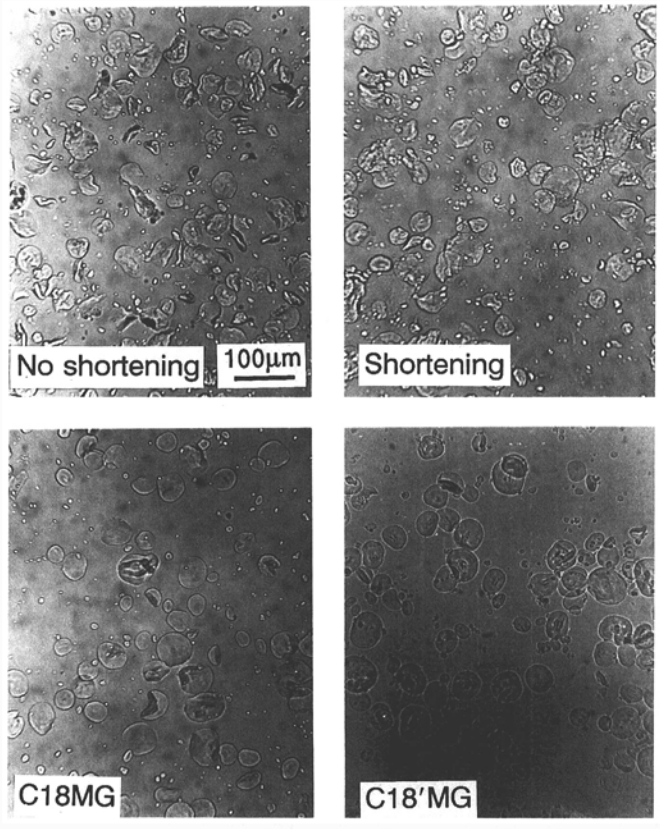

Fig. 2. Light micrographs of the effect of shortening, monoglyceride with 18 carbons (C_{18}MG) and monounsaturated 18 carbons (C_{18}'MG) on the swelling of starch in bread crumb.

Effect of Lipids on Starch Swelling and HC of Crumb

Martin (1990) showed that the HC was lower for crumb from bread containing shortening or MG than for crumb from bread with no shortening. This suggested a relationship to less swelling of the starch granules in the bread with MG or shortening. However, micrographs from the current study did not show the same correlation (Fig. 2). Rather, starch from bread crumb with shortening was similar in appearance to that of bread made without shortening, and both were more swollen than the starch from crumb of bread made with MG (PMG, Fig. 3).

Sodium stearoyl lactylate (SSL) is a surfactant that reduces crumb firmness. It also reduced starch swelling (Fig. 3). This raised an interesting point. In an excess water system at 95°C, SSL had no significant effect on starch swelling (data not shown). However, bread also reaches 95°C. This suggests that the behavior of SSL may be somewhat different in a limited water system when compared to that of an excess water system.

Attempts to reproduce Martin's (1990) HC results showing similarity between crumb with shortening and crumb with MG were not successful. The results did not show any differences in HC between crumb without shortening, with shortening, or with MG (data not shown).

In an effort to more accurately measure the HC of starch in bread crumb, the crumb was treated enzymatically to degrade the gluten matrix. The HC measurements on starch isolated from control bread (3% shortening) and bread with no added fat were not different (Table IV). Thus, shortening at 3% did not reduce the HC of the starch. However, C_{18}MG at 1 or 2%, HMG, and SSL decreased the HC compared to the control. Apparently, the effects of shortening and MG on the HC of starch were not similar. Therefore, HC does not appear to explain how both compounds reduce the firmness of bread crumb.

While making the measurements, we observed that the distinction between the tailings and prime starch became greater as the level of MG increased. The shortening and no-shortening centrifugates were similar and did not show as distinct a difference between the tailings and starch. The starch layer from the treatments with MG was whiter and more opaque than the starch layer from the shortening or no shortening treatments. This whiter, more opaque appearance of suggested that the starch was less swollen and supported the findings for HC of the isolated starches.

Effect of Shortening and Distilled MG on Loaf Volume and Crumb Firmness of Bread Made with Defatted Flour

No significant difference occurred in volume or crumb firmness between bread made with 3% shortening and bread made with 2% distilled MG (Table V). All bread made with defatted flour had significantly lower volumes than those made with regular flour. The volume of bread made from defatted flour without shortening was statistically the same as that of bread made from defatted flour with MG or shortening. However, bread made from defatted flour supplemented with MG had a larger volume than bread made from the same flour with shortening. This suggested that the added lipids (MG or shortening) operate by different mechanisms when used with defatted flour.

Bread made with defatted flour and supplemented with MG had firmness values significantly lower than those for bread made with defatted flour with no added lipid and similar to those for bread made with regular flour plus MG or shortening. However, addition of shortening did not reduce firmness of bread made from defatted flour. This lack of an effect of shortening on crumb firmness of bread made with defatted flour also was reported by Rogers et al (1988).

Summary

Addition of C_{18}TG improved loaf volume in a manner similar to that of shortening. This is not surprising because shortening is comprised largely of triglycerides. Addition of C_{18}'TG to replace shortening in the breadmaking formula improved volume slightly, probably because less solid fat was present. Addition of C_{18}MG, in a hydrated form at 1.5–2.0% effectively replaced shortening as far as loaf volume was concerned. Using the hydrated form was more effective than blending the MG with a high-speed mixer with the flour or adding it as is.

Light micrographs of starch isolated from bread showed that MG or SSL added to the breadmaking formula reduced the swelling of starch, whereas shortening did not. Thus, the effect on starch swelling was different. If the effect of MG on crumb firmness relates to their effect on starch swelling, then the mechanism of softening for MG is different than that for shortening.

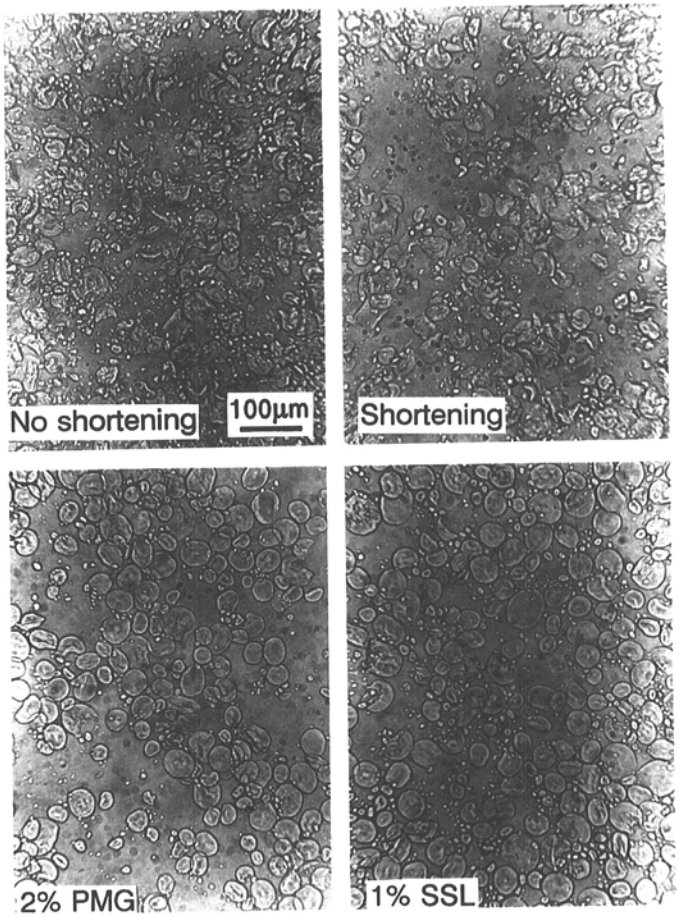

Fig. 3. Light micrographs of the effect of powdered distilled monoglyceride (PMG) and sodium stearoyl lactylate (SSL) on the swelling of starch from bread crumb.

TABLE IV
Hydration Capacity of Enzymatically Isolated Starch from Bread Crumb[a]

Treatment	Hydration Capacity[b]
No shortening	3.86 a
Control	3.79 a
1% C_{18}MG[c]	3.58 b
2% C_{18}MG	3.33 c
HMG[d]	3.24 c
SSL[e]	3.33 c

[a] Values followed by same letter were not statistically different at 5% level.
[b] Measured as g of centrifugate/g of solids.
[c] Monoglyceride with 18 carbons.
[d] Hydrated monoglyceride (MG).
[e] Sodium stearoyl lactylate

TABLE V
Effect of Distilled Monoglyceride (MG) and Shortening on Volume and Crumb Firmness of Bread Made With Defatted Flour[a]

Treatment	Volume (cm^3)	Firmness (Day 7) (*g*-force)
Control flour		
3% shortening	930 a	1,176 c
2% distilled MG	877 a	1,118 c
Defatted flour		
No shortening	720 bc	2,112 b
3% shortening	665 c	2,515 a
2% distilled MG	788 b	1,261 c

[a] Values followed by the same letter within a column were not statistically different at the 5% level.

SSL had a somewhat different effect in this limited water system than it had in an excess water system. The effect appeared to be similar to that in the excess water system heated to a lower temperature.

Studies with bread made from defatted flour showed that MG reduced crumb firmness, whereas shortening did not. This supports the idea that the mechanisms by which these two lipids reduce crumb firmness are different.

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