STUDIES ON THE BREADMAKING PROPERTIES OF WHEAT-FLOUR NONPOLAR LIPIDS[1]

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ABSTRACT

Cereal Chemistry 53(5): 636-642

Total lipids of a commercial wheat flour were separated into polar and nonpolar fractions. When added at the dough stage, the nonpolar lipids were detrimental in baking. Nonpolar lipids were fractionated into steryl esters, triglycerides, free fatty acids, and diglycerides, each of which was then tested in three dough systems: 1) defatted flour, 2) intact flour, and 3) intact flour with 3% lard. When added to either the defatted or intact flour, the deleterious effects were caused by the free fatty acids. However, in the presence of 3% lard the ill effects were not as evident as in the other two systems. Within the fatty acids class, detrimental effects in bread were directly related to linoleic acid. Complementary studies showed that the free fatty acids both increased the peak viscosity and delayed the peak time of starch during the gelatinization cycle.

Over the years, cereal chemists have shown an active interest in the role of wheat lipids in breadmaking (1–4). Early research in lipid functionality was often directed at the extraction of flour lipids, followed by their incorporation into dough systems. Frequently, lipids were extracted with solvents of different polarities from flours of varying extraction rates, then baked by different procedures. As one would expect from such practices, the results reported in the literature have been quite contradictory (4).

In the last several years, one area of agreement on lipid functionality has emerged. Investigations by Pomeranz *et al.* (5), as well as by our laboratory (6), have shown that polar lipids exert a loaf-volume improving effect when added to dough; specifically, it appears that the galactolipids are primarily responsible for the improving effect (7,8).

The objective of the present work was to determine which class of nonpolar lipids was directly responsible for poor baking performance.

MATERIALS AND METHODS

Materials

Commercial baker's patent flour was used throughout this study (12.0% protein, 0.45% ash on 14% moisture basis).

The solvents used were reagent grade.

Starch gelatinization properties were studied with the Brabender Visco-Amylograph® (9).

Palmitic acid (94.9%) was obtained from Mallinckrodt, PX25.

Linoleic acid (79.5%) was obtained from MCB, LX300.

Fractionation of Polar and Nonpolar Lipids

Lipids were extracted from wheat flour with a mixture of ethanol-benzene (1:1

[1]Presented at the 56th Annual Meeting, Dallas, Oct. 1971.

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v/v). Solvents were removed on a Flash evaporator at a temperature less than 40°C (vacuum). The recovered lipids were redissolved in benzene (1.3% flour solids basis), then adsorbed on activated silica gel (550°C/30 min). The nonpolar fraction was eluted with benzene, while the polar lipids were desorbed with 95% methanol. The nonpolar fraction (60% of the total lipids) consisted mainly of steryl esters, triglycerides, free fatty acids, diglycerides, and traces of monoglycerides, while the polar fraction (40%) was mostly made up of glycolipids and phospholipids (6).

Fractionation of Nonpolar Lipids

Nonpolar lipids were fractionated into various classes at ambient temperature as shown in Fig. 1. Ten grams of lipids was mechanically shaken for 5 min with 50 ml of the aqueous methanolic solution. After the residue settled, the supernatant was decanted in another flask. This technique was used until the insolubles consisted of triglycerides and steryl esters only (six times). Under separate conditions, the obtained methanolic insolubles were further fractionated into steryl esters and triglycerides with 50 ml of an aqueous acetone solution (six times), as described previously. The insoluble white granular material consisted of steryl esters. Sufficient methanol was added to the methanolic solubles (50:5 v/v) until a 95% concentration was obtained. Six hundred milliliters of normal heptane (pre-equilibrated with 95% methanol) was added to the solubles; the mixture was shaken vigorously for several minutes in a separatory funnel, and after phase separation, the heptane extract was siphoned. Fresh heptane was added and mixed, and this technique was repeated until the heptane removed all the diglycerides (three times). The free fatty acids remained in 95% methanol.

Baking Studies

A conventional laboratory sponge-dough process, yielding two 1-lb loaves per dough, was used. Details of this procedure have been previously reported (10). To determine which class of the nonpolar lipids caused loaf-volume deterioration, three dough systems were studied which differed in flour and lipid

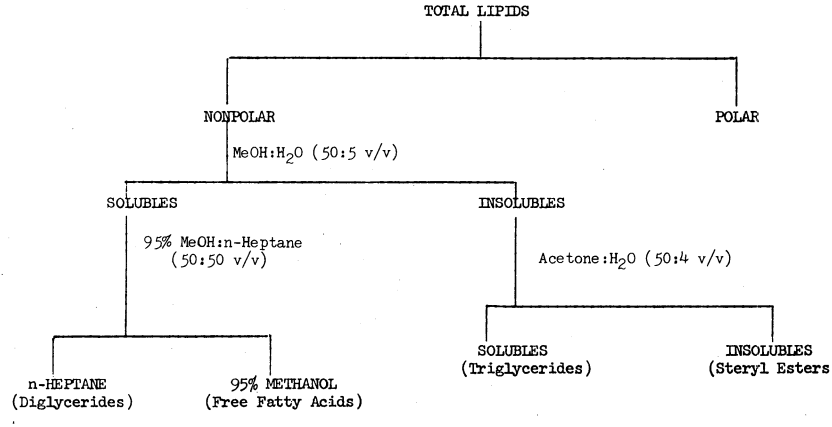

Fig. 1. Solvent fractionation of various classes of the nonpolar lipids. All solvent mixtures were premixed prior to extraction.

TABLE I
Composition of the Nonpolar Fraction[a]

Lipid Class	%
Steryl esters	6.0
Triglycerides	58.4
Free fatty acids	20.6
Diglycerides	10.0
Monoglycerides	2.0
Origin	3.0

[a]Nonpolar lipid solids basis.

TABLE II
Effect of Lipid Fractionation on Bread Volumes

Lipid System	Loaf Volume cc
Intact flour	2704
Intact flour + nonpolar fraction	2663
Intact flour + reconstituted nonpolar classes[a]	2557

[a]To accentuate the effects, lipids were added at a level of 50% above that found in flour.

TABLE III
Effect of Various Lipid Classes on Bread Volumes

Lipid System[a]	Loaf Volume, cc		
	Defatted flour 0% lard	Intact flour 0% lard	Intact flour 3% lard
Control	2434	2606	2721
Nonpolar fraction (intact)	2684	2581	2647
Steryl esters	2639	2590	2712
Triglycerides	2681	2639	2741
Diglycerides	2561	2610	2704
Free fatty acids	2376	2569	2712

[a]Lipids were added at the level found in flour.

TABLE IV
Effect of Fatty Acids on Bread Volume

Lipid System	Loaf Volume, cc		
	Defatted flour 0% lard	Intact flour 0% lard	Intact flour 3% lard
Control	2602	2639	2733
Palmitic acid (1×)	2512	2647	2733
Palmitic acid (3×)	2569	2598	2725
Linoleic acid (1×)	2458	2577	2782
Linoleic acid (3×)	2196	2278	2655

addition as follows: 1) defatted flour (pet ether), no lard added; 2) intact flour with no lard added; and 3) intact flour with 3.0% lard. Various lipid classes were added directly to the flour at the dough stage, at a level of 50% higher than that found in the native state, to enhance the effects. The data reported herein are the mean of at least duplicate determinations conducted on separate days.

Thin-Layer Chromatography (tlc)

A slurry made up of 30 g of silica gel (Quantum Industries), 10 g of Kieselguhr G (Merck), and 100 ml of distilled water was deposited on 20 × 20-cm glass plates with a Desaga applicator (0.5 mm thick, wet). The tlc plates were allowed to air-dry overnight at ambient temperature. Nonpolar lipids were separated into classes with the solvent system benzene-acetic acid-water (99.0:0.9:0.1 v/v/v, using the ascending technique. The lipids were sprayed with 50% sulfuric acid, then heated at 200°C for 30 min.

Condition of Starch in Bread

The degree of starch swelling in the bread crumb was examined with the Brabender Amylograph®. The procedure suggested by Yasunaga *et al.* (11) was employed in our studies: 100.0 g of bread crumb was soaked in 460 ml of dilute amylograph buffer for 1 hr at 30°C. The bread was blenderized for 1 min at low speed, then immediately transferred to the amylograph bowl. The starch gelatinization cycle was conducted as usual.

RESULTS AND DISCUSSION

When total flour lipids (1.3% flour solids basis) were adsorbed on activated silica gel, the nonpolar lipids were eluted with benzene (60.0% of total lipids), while those of greater polarity were eluted with 95% methanol (40%) (6). As noted previously, the objective of this study was to fractionate the nonpolar lipids into major classes and add each one to a flour system to determine the class that impairs loaf volume. Table I shows the percentage composition of the nonpolar lipid fraction. Figure 1 describes the scheme employed to fractionate the various classes of lipids in sufficient quantities for the baking tests.

Solvent fractionation of the various lipid classes is demonstrated in Fig. 2. The purity of each class of lipids was estimated densitometrically at better than 85% by using pure lipid classes as standard, which had been isolated by preparative tlc.

Before initiating the baking studies of the nonpolar lipids, tests were performed to demonstrate whether native properties were altered during lipid extraction and class fractionation. Baking data, obtained on both the nonpolar and reconstituted nonpolar lipid classes, are shown in Table II. As expected, the intact nonpolar fraction lowered the loaf volume of bread. When fractionated nonpolar lipid classes were reconstituted at a level of 50% above that found in flour, loaf volume was further depressed.

To determine which class of lipids caused loaf volume deterioration in baking, three dough systems were considered: 1) doughs made with defatted flour and no lard, 2) those made with intact flour and no lard, and 3) those made with intact flour and 3% lard. Results obtained from this study are presented in Table III.

Under the described experimental conditions, removal of the nonpolar lipids

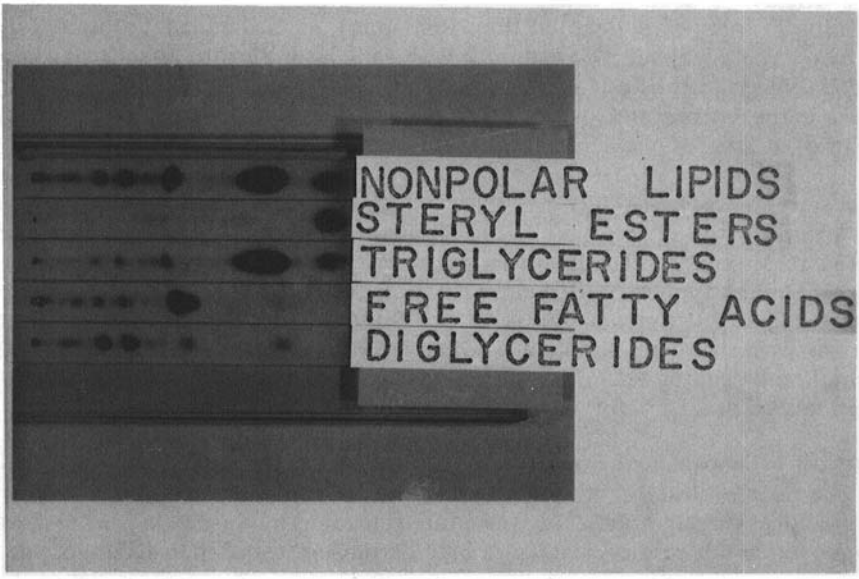

Fig. 2. A tlc illustration of the major classes of nonpolar lipids, as obtained by the solvent fractionation scheme described in Fig. 1. These lipid classes were studied in breadmaking.

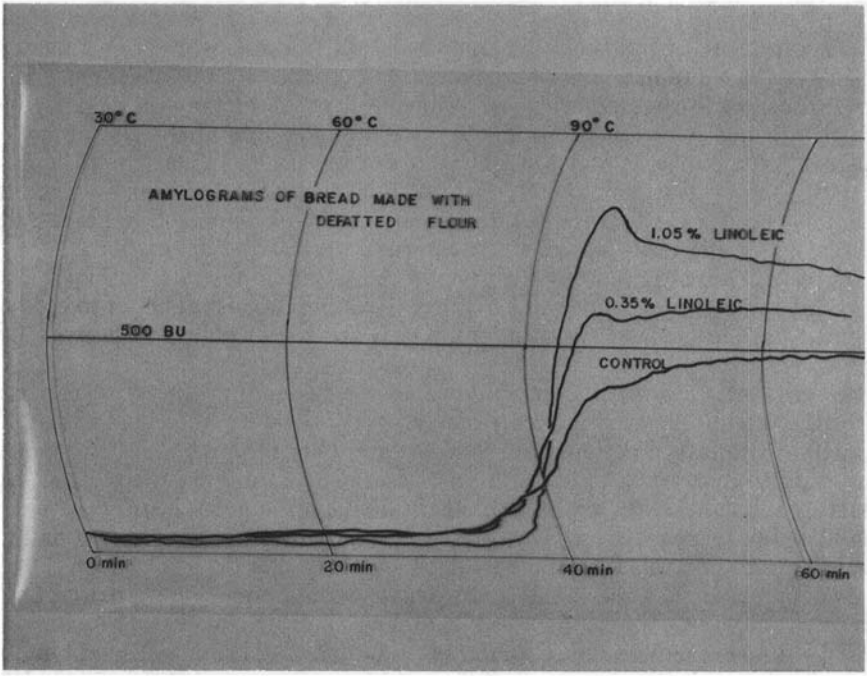

Fig. 3. Starch gelatinization patterns of bread made with 0.35 and 1.05% linoleic acid.

from flour seriously affected loaf volume. Close examination of the effects of the nonpolar lipid classes on loaf volume indicates that the steryl esters and triglycerides produced volumes similar to the intact nonpolar fraction. The diglycerides decreased loaf volume slightly. However, the addition of the free fatty acids brought about a substantial loss in volume. Data obtained strongly suggested that when using a defatted flour system, the free fatty acids were primarily responsible for poor baking performance.

As a second approach to the proposed study, an intact flour system was used. Again, the nonpolar fraction depressed loaf volume. The triglycerides improved it slightly, and the free fatty acids were deleterious in the system.

The third test system studied consisted of intact flour with 3.0% lard. When using defatted flour and intact flour without lard, the free fatty acids class of the nonpolar lipids was primarily responsible for volume depression in baking. However, when 3.0% lard was added to intact flour, these adverse effects were not obtained. It appears that lard masked the deleterious effects of the free acids in baking.

Since linoleic acid made up about 66% of the free fatty acids, the question arose whether the ill effects of the fatty acids were largely dependent upon the degree of saturation. To resolve this question, baking studies were conducted with palmitic and linoleic acid. Two levels were used. The lower level was similar to that used in previous studies, while the higher one was three times this level. Results obtained from this study are shown in Table IV. In all three dough systems, palmitic acid lowered loaf volume only to a small extent. No major changes were apparent at the higher level. When 3.0% lard was added to the intact flour, palmitic acid produced no major changes in loaf volume. Contrary to the findings of both defatted and intact flour systems, the lower level of linoleic acid in the presence of 3.0% lard showed some volume improvement. Linoleic acid caused serious deterioration when the higher level was used in the test system. Again, the presence of 3.0% lard during baking masked the ill effects of the unsaturated fatty acid.

Results reported herein are in agreement with those of Kozmin (12), who found that upon long storage the poor gluten properties of wheat were directly related to the level of linoleic acid present in the grain. Much work has been reported in the literature on the effects of lipids on gluten proteins, but relatively little effort has been made to study the effects of lipids on the starch

TABLE V
Effect of Lipids on Starch Gelatinization Properties of Defatted Flour

Lipid System[a]	Peak Viscosity BU	Peak Time min
Control	640	32
Nonpolar fraction (intact)	770	34
Steryl esters	630	31
Triglycerides	660	31
Diglycerides	650	31
Free fatty acids	750	38

[a]Lipids were added at the level found in flour.

fraction of flour. It is well known that this major flour component plays an important role in baking through its gelatinization properties. Therefore, it would be important to know how the nonpolar lipids affect the gelatinization properties of starch. A summary of these effects appears in Table V. To demonstrate the real effects of the test lipids, petroleum ether defatted flour was used for this study. Results show that the addition of steryl esters, triglycerides, and diglycerides had little or no effect on starch gelatinization. Nonpolar lipids and free fatty acids not only increased peak viscosity but also delayed peak time. In view of these results, the thought arises whether the ill effects of linoleic acid in baking may also be related to the effect of linoleic acid on the starch-swelling properties. One approach to this problem would be to examine the condition of the starch in the bread crumb, as illustrated in Fig. 3. Gelatinization patterns obtained on bread made with two levels of linoleic acid demonstrate that during breadmaking this fatty acid affected the starch properties of wheat flour. Peak viscosity of the bread crumb was directly related to the level of linoleic acid used in baking. In view of these and previous results, it is conjectured that the free fatty acids impart combined ill effects on both the gluten and the starch fractions of flour.

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[Received August 13, 1975. Accepted October 23, 1975]