The Role of Flour Lipids in Baking

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ABSTRACT

Certain lipid-extracting solvents, including water-saturated butanol, are unsuitable for studying the role of lipids in baking since they alter the functional properties of flour protein. Other solvents, such as chloroform and petroleum ether, do not affect the properties of flour components. About three-fourths of the flour lipid may be removed by cold solvent extraction. Most of the remaining lipid occurs in the starch granules and does not appear to play an important role in baking. Curves of loaf volume as a function of lipid content for several flours with a range of properties all showed minima at lipid contents intermediate between those of the defatted and whole flours. Polar and nonpolar lipid fractions have different effects on loaf volume. Variations in loaf volume as a result of different lipid treatments become apparent only during the baking stage in the oven. Lipid content and bromate level both affect loaf volume but appear to act independently.

The role that the natural flour lipids play in baking has been a controversial topic. Many studies have shown that lipids exert an important effect in the baking process althought the results obtained by different workers have often appeared to be conflicting. Some of the possible reasons for this have been recognized. For example, different baking processes may give rise to varying degrees of response from the lipid component. In particular, where baking formulations include shortenings or other lipid additives, the effect of the natural flour lipid may be obscured. Conversely, the effects of adding lipids to whole flour are difficult to interpret owing to the presence of natural lipid. Another source of uncertainty is concerned with whether the techniques used always allow lipid to be extracted from flour and restored without alteration of the functional properties of the flour components, including the lipid itself.

The present work was aimed at clarifying the role of lipid in baking. For this, several flours with a range of properties were chosen for study so as to permit general conclusions. The plan was initially to study the baking behavior as a function of the amount of lipid present in the flour. Evaluation of baking behavior was primarily by accurate measurements of loaf volume. Non-flour lipid additives were not used in the formulation except for certain reference loaves, which were included in order to allow comparison with commercial baking practice. It was regarded of utmost importance to evaluate the validity of the extraction and reconstitution techniques in order to ensure that any variations in baking behavior observed could be reliably ascribed to changes in lipid content only. For this reason, a number of independent checks were devised.

MATERIALS AND METHODS

Materials

The flours used were commercial baker's flours. Their protein contents and farinograph data are given in Table I.

Two grades of commercial starch were used. Their average granule diameters, calculated from photomicrographs, were 22 μ (coarse) and 3 μ (fine). One sample of commercial gluten (70% protein) was used. These samples of starch and gluten were obtained from Fielder's Starches Pty. Ltd., Sydney.

Glutens were washed from flours using a Simon gluten washer. The temperature of the gluten was maintained at 10°C. or below during the washing. Starch and water-solubles were separated by centrifugation and all fractions were freeze-dried. The recovered starch thus contained both prime starch and "squeegee" fractions.

All solvents were A.R. grade except chloroform and ethyl acetate which were laboratory reagent grade. Acetonitrile was used without further purification, while

TABLE I. PROTEIN CONTENTS AND FARINOGRAPH DATA FOR FLOURS USED

Flour	Protein % on 13.5% Moisture	Development Time min.	Farinograph Water Absorption %	Breakdown B.U.
A	13.7	7.0	69.9	40
B	12.8	5.5	61.5	65
C	12.7	4.0	67.9	85
D	12.1	4.5	65.1	70

all other solvents were distilled before use. Ether was peroxide-free and dried over anhydrous calcium chloride.

Extraction and Analysis of Lipid

For extraction of lipid from flours, 2.2 liters of solvent were added to 1.75 kg. of flour and the slurry stirred vigorously with an electrical stirrer for 3 min. The slurry was filtered and the procedure repeated three times on the residual flour. Further batch extractions removed negligible amounts of lipid. Following a comparison with Soxhlet and column methods of extraction, the batch extraction method was adopted since it was found to extract at least as much lipid as the other methods and was more convenient for scaling up. Chloroform was used as the extracting solvent unless otherwise stated. The filtrate was evaporated in a rotary evaporator at 40°C. and the lipid stored under nitrogen in a stoppered flask.

For extraction of starches, 200 ml. of methanol was added to 50 g. of starch and refluxed for 1 hr. while being continuously stirred. The solution was then filtered hot and the process repeated with further 200 ml. quantities of methanol.

Flour lipid was separated into polar and nonpolar fractions by the method of Ponte and DeStefanis (1).

Lipid analyses on flour, gluten, starch, and lipid samples were carried out according to the standard AOAC acid hydrolysis method (2). The only modification was that samples were weighed directly into the Mojonnier tubes and subsequent hydrolysis and extraction performed without the need to transfer hydrolysate. Analyses were done in triplicate and averaged. The standard deviation of the method calculated from triplicate determinations on 60 flour samples was 0.15%.

Baking Test

The procedure was based on the standard no-time micro-baking test used by the Bread Research Institute of Australia.

Unless otherwise stated, the formulation for test loaves was as follows:

	g.
Flour (dry weight)	30.2
Yeast	0.81
Sodium chloride	0.65
Improver	0.16

The composition of the improver was 0.6% potassium bromate, 1.0% ascorbic acid, 10% ammonium chloride, 15% calcium sulfate, and 73.4% malt flour.

An aqueous suspension of the correct proportions of yeast, sodium chloride, and improver was prepared and stirred magnetically to keep it uniform. For each test loaf, 20.0 ml. of this suspension was placed in the mixing bowl. The previously weighed sample of flour with or without added lipid was introduced and the water content adjusted where necessary by pipetting a measured volume of water. The mixer was a four-pin planetary type, the mixing bowl having three pins and being designed for 35 g. of flour. After mixing for the required time, the dough piece was machine-moulded and placed in a sealed container within a cabinet maintained at 38°C. for an initial fermentation period of 20 min. It was then re-moulded, tinned, placed in a proofer (38°C., 98% r.h.) for 40 min., and baked at 185°C. for 17 min. Accurate proofing and baking times were maintained by the use of conveyor belts

in the respective equipments. Proof heights and loaf heights were measured at the end of the proofing and baking stages respectively. Loaf volumes were measured after cooling for 20 min. The apparatus and method of measurement are described elsewhere (3).

The lipid content of flours was varied by adding weighed amounts of extracted lipid to defatted flour. The hydrolysate lipid content (i.e., the percentage of lipid determined by the acid hydrolysis method) at each addition was calculated using the previously determined values for whole flour, defatted flour, and extracted lipid.

Each series of treatments for a particular flour were examined on the same day. Six replicate loaves were baked for each treatment and the order of baking shown to be of no significance. The loaf volume data were treated by analysis of variance and mean loaf volumes were plotted on the graphs.

RESULTS

Comparison of Lipid-Extracting Solvents

Flour B was extracted four times with each of a number of common lipid solvents. The hydrolysate lipid contents of the defatted flours are shown in Table II.

Effects of Solvents on Flour Properties

Preliminary experiments showed that certain solvents caused greatly extended mixing times for flour B. This effect has been observed previously by other workers (4,5). For a given solvent, the peak development time was independent of whether the flour was defatted in the normal way or mixed with solvent and the slurry allowed to evaporate to dryness without removal of lipid (solvent-treated flour). A thorough study was therefore made of the effects of commonly used lipid solvents

TABLE II. EFFECTS OF SOLVENTS ON LIPID EXTRACTION AND MIXING TIMES OF FLOURS

Flour	Solvent	Hydrolysate Lipid %	Peak Development Time min.
B	Control flour, untreated	2.20	4
	Petroleum ether	0.89	4
	Benzene	0.83	4
	Chloroform	0.67	4
	Benzene/chloroform (50/50)	0.77	4
	Dichloromethane	...	4
	Petroleum ether/ether (50/50)	0.88	4
	Ethyl acetate	...	4
	Water	...	4
	Acetonitrile	...	7
	Water saturated n-butanol	0.74	8
	Acetone/water (90/10)	0.99	10
	Ethanol/water (95/5)	0.57	24
	Ethanol/ether/water (40/40/20)	...	27
Gluten + starch	None		5
Gluten (solvent-treated) + starch	Ethanol/water (95/5)		12
Gluten + starch (solvent-treated)	Ethanol/water (95/5)		5

on the mixograms of flour B. Mixtures of commercial starch and gluten (85/15) were included in the study to ascertain which component was affected by the solvent. The results are given in Table II.

Some of the solvent-treated flours were baked under standard conditions and the resulting loaves were compared with those baked from the untreated flours. Loaves baked from flour which had been treated with ethanol/water (95/5) gave volumes of 100 cc. compared to volumes of 175 cc. for the control loaves. When doughs were mixed to peak consistency, loaf volume, although increasing to 135 cc., was still considerably lower than that of the control loaves. Similar results were obtained for flour samples whose mixing characteristics had been altered by treatment with other solvents. Flours which had been treated with chloroform or petroleum ether gave volumes identical to those of the control loaves.

Test Baking

Loaf volume-lipid content relations were measured for flours A, B, and C at optimum dough-handling conditions as assessed by a baker. In addition, for flours

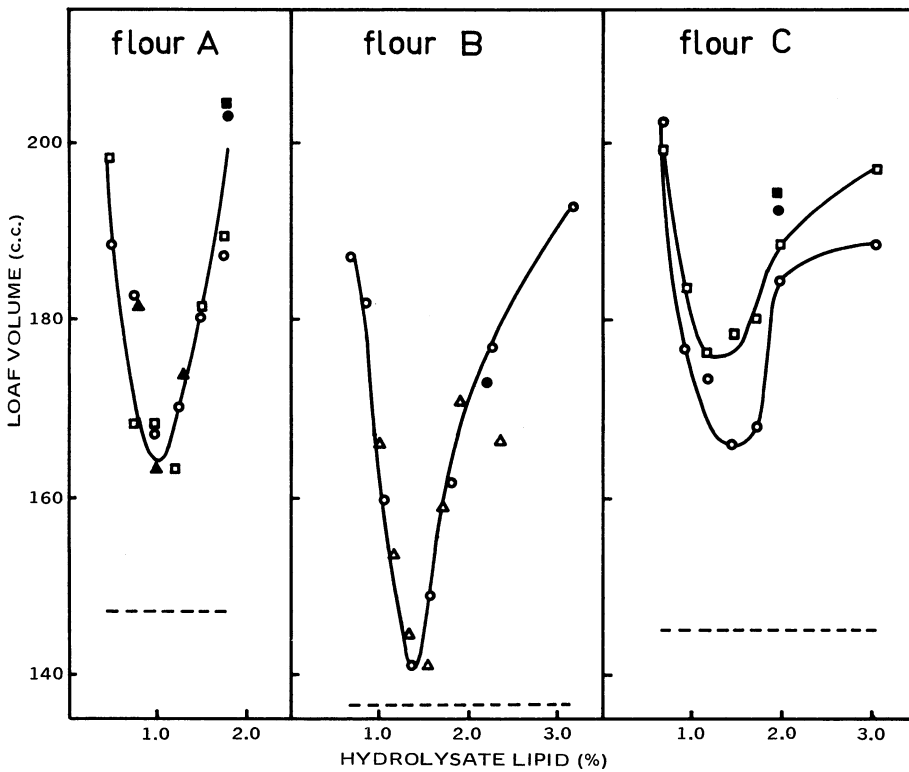

Fig. 1. Loaf volume vs. hydrolysate lipid content for flours A, B, and C. Open squares, maximum loaf volume conditions; open circles, optimum dough-handling conditions; solid squares, whole flour, maximum loaf volume conditions; solid circles, whole flour, optimum dough-handling conditions; open triangles, petroleum ether as defatting solvent; solid triangles, additions of lipid extracted from flour B to defatted flour A; dashed line, volume at end of proofing.

A and C, the relations were measured at maximum loaf volume conditions. The results are plotted in Fig. 1. The choice of conditions for each flour was made by systematically varying both mixing time and water content and observing the effects on measured loaf volume and dough-handling characteristics. The mixing times (min.) and water contents (parts water per 100 parts dry flour) at optimum dough-handling conditions were 5 and 83.2 for flour A, 3.5 and 81.5 for flour B,

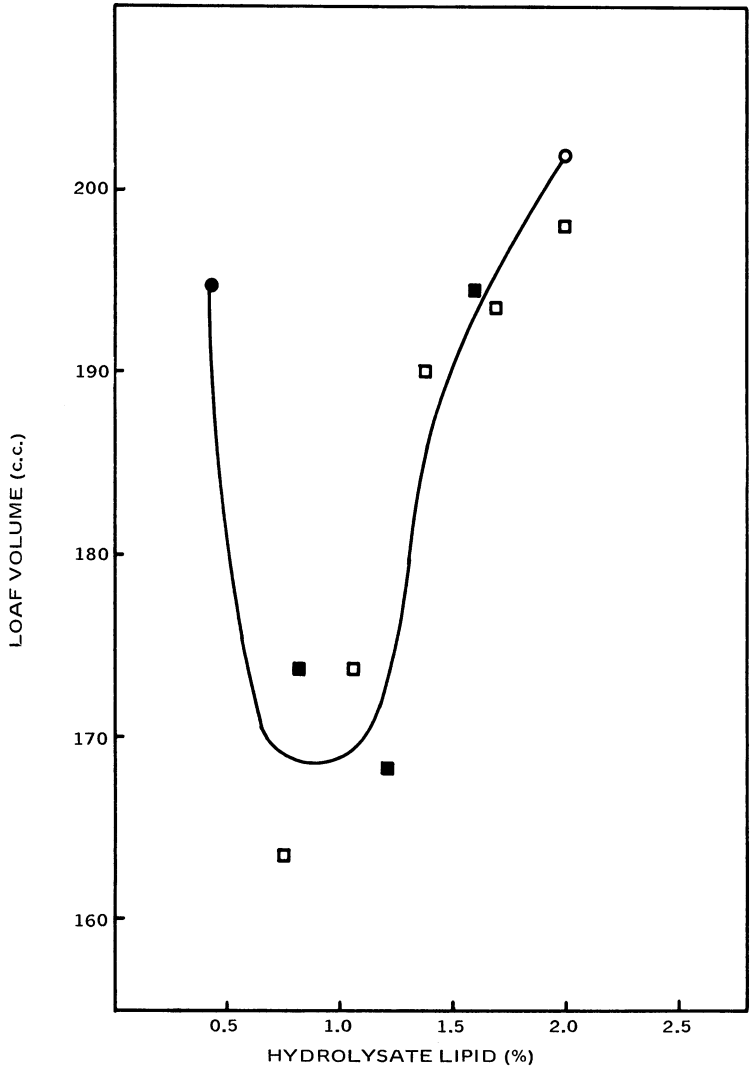

Fig. 2. Loaf volume vs. hydrolysate lipid content of flour D. Baking conditions: 3.5 min. mixing time, 81.5 parts water per 100 parts dry flour. Open squares, addition of extracted lipid to defatted flour; solid squares, mixtures of defatted and whole flours; solid circles, defatted flour; open circles, whole flour.

and 2.75 and 83.2 for flour C. Corresponding data at maximum loaf volume conditions were 6 and 89.5 for flour A and 4 and 88.4 for flour C. A comparison between the use of chloroform and petroleum ether as defatting solvents was carried out for flour B (Fig. 1). Loaves baked from defatted flours were much whiter than those from whole flour and had an extremely fine texture. As lipid was added to defatted flour, the texture of the resulting loaves became coarser until the point of minimum loaf volume, after which it progressively improved.

For a particular flour, the proof height was constant, independent of the treatment. Plots of loaf volume vs. oven spring (baked loaf height minus proof height) were found to be linear. The volume at zero oven spring (i.e., the volume of the dough piece at the end of the proofing stage) was determined for each flour from the regression relationship.

Analyses of variance on the results of each test series yielded an average standard deviation per mean loaf volume of 4.5 cc.

Mixtures of Defatted and Whole Flours

Mixtures of whole and defatted flour D in different proportions were prepared and the loaf volume-lipid content relationship measured. The results are shown in Fig. 2. Corresponding results for which the lipid content was varied in the usual way by additions of extracted lipid to the defatted flour are shown for comparison.

TABLE III. DISTRIBUTION OF LIPID IN FLOUR FRACTIONS

Flour	Fraction	% of Fraction Separated from Flour	% H.L.[a] in Fraction	% H.L.[a] in Flour
B	Gluten	11.8	9.32	1.10
H.L. = 2.20%	Starch	80.4	1.07	0.86
	Water-solubles	7.8	1.75	0.14
B	Gluten	12.9	2.05	0.26
Petroleum ether-defatted	Starch	78.3	0.88	0.69
H.L. = 0.89%				
B	Gluten	13.3	1.15	0.15
Chloroform defatted	Starch	78.0	0.78	0.61
H.L. = 0.67%				

[a]H.L. = Hydrolysate lipid content.

TABLE IV. EFFECT OF METHANOL EXTRACTION OF STARCH ON LOAF VOLUME

	% H.L.[a] of Starch (before extraction)	% H.L.[a] of Starch (after methanol extraction)	Loaf volumes (cc.) Whole Flour	Reconstituted with Methanol-Defatted Starch	Reconstituted with Defatted Starch + Methanol-Extracted Lipid
Petroleum ether-defatted flour B	0.88	0.34	190	190	192
Starch (coarse) + gluten	0.56	0.35	223	221	223

[a]H.L. = Hydrolysate lipid content.

TABLE V. VARIATION OF LOAF VOLUME WITH LIPID CONTENT AND BROMATE LEVEL

Bromate p.p.m.	Loaf Volumes (cc.) Hydrolysate lipid content (%)				
	1.00	1.26	1.59	2.00	2.20
30	183	149	182	182	187
70	193	161	194	191	191
130	198	161	195	199	200
255					195

Lipid not Removed by Solvent Extraction of Flour

Flour B, petroleum ether-defatted flour B, and chloroform-defatted flour B were separated into gluten, starch, and water-soluble fractions and hydrolysate lipid determinations were made on each fraction. The results are summarized in Table III. Differences between the lipid content of the flour and the sum of the lipid contents of the components are well within the error expected from the standard deviation of the method of analysis. Hydrolysate lipid contents of two commercial starch samples differing in average granule size were measured and found to be 0.66 (coarse starch) and 0.75% (fine starch).

Commercial starch (coarse) and the starch fraction separated from petroleum ether-defatted flour B were each extracted seven times with boiling methanol. The initial and final hydrolysate lipid contents of the starches were measured and are shown in Table IV. The extracted starch samples were then reconstituted, the commercial sample with commercial gluten and the flour B fraction with the gluten and water-soluble fractions of flour B, and test loaves were baked. The results are shown in Table IV.

Variation of Bromate Level

The loaf volume-lipid content relationships were measured for flour B using several different levels of bromate in the formulation. The results are shown in Table V.

Effect of Lipid Fractions

The chloroform extract of flour B was separated into "polar" and "nonpolar" lipid fractions. The loaf volume-lipid content relationships were measured by additions of the fractions to chloroform-defatted flour B. The results are plotted in Fig. 3.

Effect of Lipids on Rheological Properties of Doughs

Alveograms were measured for flour B, defatted flour B, and defatted flour B with the lipid content adjusted to that corresponding to minimum loaf volume. The alveograms of the three samples were the same within experimental error.

DISCUSSION

The present results show that roughly three-fourths of the total lipid can be removed from flours by cold solvent extraction (Table II). Because of this incomplete extraction, the hydrolysate lipid method is superior to solvent

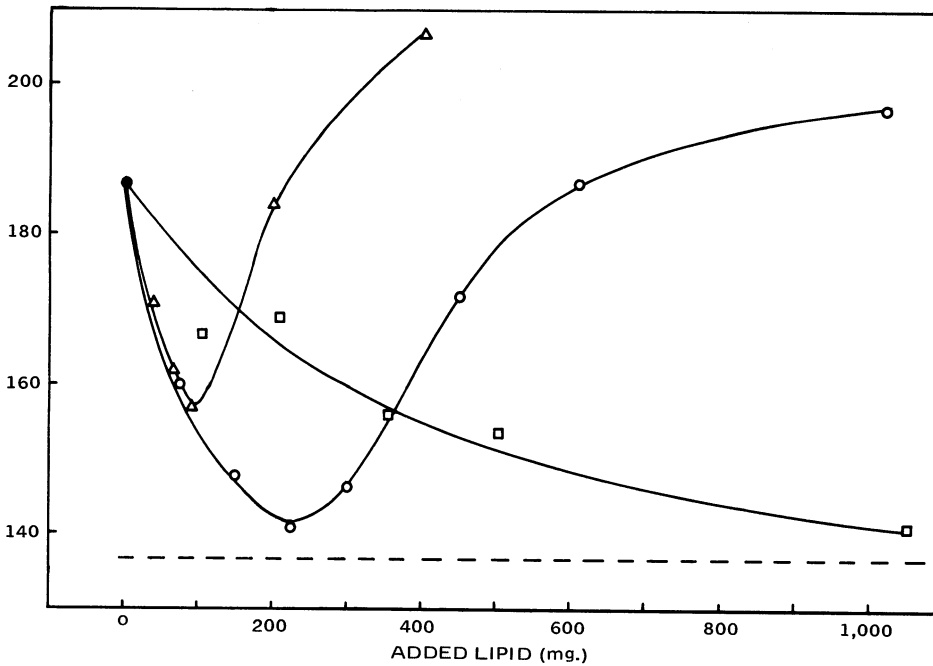

Fig. 3. Effects on loaf volume of additions of polar and nonpolar lipid fractions to defatted flour B. Circles, whole lipid; triangles, polar lipid; squares, nonpolar lipid; dashed line, volume at end of proofing stage.

extraction methods for the estimation of the total lipid content of flours. Although different solvents were found to extract different amounts of lipid, our results suggest that the terms "free" and "bound" lipid (on the basis of those portions which are removed by successive extractions with petroleum ether and water-saturated butanol) may be misleading. This is because there appears to be a portion of the total lipid associated with the nonstarch components, which may be extracted to a greater or lesser degree by cold extraction using common lipid solvents. Another portion of the lipid is associated with the starch fraction and is very difficult to remove although successive extractions with boiling methanol remove a significant amount. Evidence has been presented that this lipid is distributed uniformly throughout the starch granules (6,7). Our results tend to confirm this finding; for example, the lipid contents of two starch samples of very different average granule size did not differ significantly as might be anticipated if the lipid were concentrated at the surface of the granules. The difficulty of removing this lipid makes it hard to evaluate its effect in baking. From the experiments described in Table IV, however, it does not seem to play an important role in baking. This is not unexpected if we consider that most of the volume change occurs during baking when this lipid is not present in the continuous matrix of the dough.

Chloroform was chosen as the main lipid extracting solvent since it removed a comparatively high proportion of lipid without affecting flour properties.

Petroleum ether is also suitable although it does not extract as much lipid as chloroform. Certain solvents, such as those containing alcohols, altered the functional properties of flours and were therefore not used for investigations into the role of lipids. These solvents do not extend mixing times of doughs because of removal of lipid, as has occasionally been believed, but because they induce a change in the properties of the gluten fraction of the flour. Hoseney et al. (8) have attempted to overcome this problem by premixing their defatted flours to restore the rheological properties of the doughs. We have preferred to avoid any possible uncertainties introduced by this procedure by using only extracting solvents which do not alter the rheological properties of the flour components.

For all flours studied, the loaf volume varied with lipid content in a characteristic manner, passing through a minimum at a lipid content intermediate between that of the fully solvent defatted and whole flours. That the same curve was obtained whether the lipid content was varied by adding extracted lipid to defatted flour or by adding increasing amounts of whole flour to defatted flour confirms that the curves do not result from artifacts, introduced during the lipid extraction and addition steps. Essentially the same curve was obtained whether petroleum ether or chloroform was used as the extracting solvent except that, with the latter, the range of measurement was extended to lower lipid contents. Many of the apparently conflicting results in the literature may be rationalized on the basis of a loaf volume-lipid content curve with a minimum at an intermediate lipid content. Whether a defatted flour gives loaves with better or worse volume and texture than the whole flour depends, in a very sensitive manner, on the amount of lipid which has been extracted from the flour. This depends, in turn, on the method of extraction, the nature of the extracting solvent, and the particular flour used. At lipid contents approaching those of the whole flour, it was found that loaves reconstituted from defatted flour and extracted lipid were in some cases smaller than expected. Reproducibility also tended to be slightly poorer in this region. This may be due to problems in dispersion of the lipid and requires further study.

In agreement with previous workers (9,10), the differences in loaf volume, as a result of different lipid treatments, became apparent during baking in the oven. Until the end of the proofing stage, no differences could be measured between any treatments for a given flour. Some workers have suggested that lipids may be involved in oxidation mechanisms (11) and the bromate reaction (12). Our results showed no interaction between lipid and bromate, i.e., the roles of lipid and bromate are apparently independent.

When flour lipids are split into two fractions, additions of these fractions to defatted flour produce dramatic effects on loaf volume. It would be more correct to refer to these fractions as "more polar" and "less polar" since only minute amounts of truly nonpolar compounds occur in flour. The "more polar" fraction contains more of the higher melting point lipids. Our results agree qualitatively with those of other workers, particularly those of Daftary et al. (13). These workers observed beneficial effects of their polar lipid fraction at all additions. However, we have observed different results by extending the range of measurements to lower lipid contents using chloroform-extracted flour (see Fig. 3). Further fractionation of the lipid complex is needed in order to further advance our understanding of their effects.

Although there has been much speculation about the role of lipids, little sound evidence has been obtained with regard to their function in baking. This is hardly

surprising since the effects of lipids on loaf volume and texture have not been sufficiently defined. The present study has advanced our knowledge in this regard but further work is required to elucidate the reasons for the marked dependence of loaf volume on lipid type and content. It does appear significant, however, that variations in loaf volume, due to different lipid treatments, occur during a period of rapid expansion of the gas within the air cells of the loaves.

Evidence from the present study suggests that lipids do not contribute significantly to the bulk rheological properties of doughs, although results of other workers are conflicting on this point (14). On the other hand, lipids are tensioactive substances and the lipid complex of flour certainly contains a wide range of foaming and antifoaming agents. They may therefore be expected to play a highly important role in stabilizing the foam structure of dough.

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