

could be made from less flour. Whether this same property of greater capacity to hold moisture during baking, giving a heavier loaf of the same size, is a desirable one in flour for home-baking will depend upon whether a moist or a dry bread is preferred. If capacity to hold moisture during baking gives similar capacity to hold moisture after baking and so prevent the rapid drying-out of the bread, this would be a desirable quality. Experiments to determine whether this be true are planned and will be carried out in this laboratory at an early date.

### Conclusions

From the results of these comparative tests, we must conclude that no single test which was tried is capable of giving conclusive evidence as to the baking quality of flour. Any of the processes which have yet been suggested for testing flour must be supplemented by a baking test if final and accurate conclusions are to be reached.

The baker's sponge tests appear to afford little evidence of value except in the case of low-gluten flours. In as much as these tests require nearly as much actual work and fully as much care and attention as the complete baking tests, it appears that they may well be abandoned in favor of the latter.

The writer is indebted to Mr. A. L. Glover and to Mr. H. B. Berry for assistance in this study, in carrying on the nitrogen determinations and the sponge and baking tests respectively.

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## CORN OIL—ITS POSSIBLE USE AS AN ADULTERANT IN LARD AND ITS DETECTION.

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The statement is frequently made that corn oil is used as an adulterant in lard. On what authority this claim is made, we have not been able to ascertain. Both Lewkowitsch<sup>1</sup> and Allen<sup>2</sup> state that the oil is used for this purpose and it is probable that American authors have accepted these statements. Although I have conferred with a great many food analysts, I have never yet found one who has found a definite case of such adulteration. There may be two reasons for this: In the first place it may not be used for this purpose; or, in the second place, the chemist may have failed to recognize it, although present, because no accurate method has been worked out for its detection. The following work was carried out with a view to determining whether corn oil may be so used and if so to determine some method for its detection.

To determine the effect of the presence of corn oil in lard, three samples

<sup>1</sup> Chemical Analyses of Oils, Fats and Waxes, 373.

<sup>2</sup> Commercial Organic Analysis, 2, I, 144.

of pure lard were mixed with definite amounts of corn oil and the resulting mixtures tested by substituting them for lard in making various forms of pastry. The samples of lard used were as follows: (1) Sample of leaf lard rendered in the laboratory; (2) Sample rendered in the laboratory from the whole fat; (3) Sample of pure country lard. From these samples mixtures were made containing respectively 2, 4, 6, 8 and 10 per cent of the oil. No samples were tested containing more than 10 per cent. of the oil, since it could hardly be used in larger amounts without its presence being indicated by its physical properties (color, odor and taste). Through the kindness of Miss Minnie A. Stoner, Professor of Domestic Science in the Ohio State University, these samples were thoroughly tested by using them as a substitute for lard in making various kinds of pastry and such foods as require lard as an essential ingredient. In accordance with the results obtained, Professor Stoner reports that in all the trials, as palatable products were obtained by the use of the mixtures of corn oil and lard as when pure lard was used and that she would be unable to distinguish between the forms of pastry made from the mixture on the one hand and from the pure lard on the other. In addition to these tests, lard containing as high as 15 per cent. of corn oil was employed as a substitute for lard in making the pastry used in a number of boarding clubs and private homes and no adverse reports were offered. No physiological tests were carried out but considering the source of the oil and its similarity to wholesome vegetable oils, there can be little doubt as to its food value. Whether corn oil is actually used as an adulterant of lard or not, the above results show that lard containing as high as 10 per cent. of the oil might easily pass for the pure product.

So far as we have been able to find out, no definite tests have been reported for the detection of corn oil in lard. The only statements made are that the presence of corn oil would be *indicated* by the iodine number and the refractive index, both of which would be abnormally high. When we consider, however, the wide variation of these constants in different samples of pure lard it is certain that many samples of lard containing small amounts of corn oil would give constants that would come within the limits of pure lard. Moreover, it would be possible to materially reduce the values of both the constants by the addition of from 5 to 10 per cent. of beef stearin, this being the maximum amount of the stearin which might be present and escape detection. A number of the mixtures of lard and oil were made and analysed to determine to what extent the oil would be indicated by abnormally high iodine number and index of refraction. The lard was rendered in the laboratory from the whole fat of the hog. The corn oil used was the ordinary refined product. It had a specific gravity of 0.9245 at 15°, an iodine number of 125.4 and an index of refraction of 1.4727 (20°). The following results were obtained:

			Iodine Number	Butyro-refractometer reading at 40.
Pure lard.....			60.92	49.25
98.5 per cent. lard	+	2.5 per cent. corn oil.....	61.73	49.85
95 "	"	" + 5 " " " " .....	62.28	50.45
92.5 "	"	" + 7.5 " " " " .....	62.86	50.55
90 "	"	" + 10 " " " " .....	65.78	50.75
85 "	"	" + 15 " " " " .....	68.58	51.35
95 "	"	" + 2.5 " " + 2.5 bee <sup>c</sup> -stearin	59.25	48.65
90 "	"	" + 5 " " + 5 " " "	60.10	48.95
85 "	"	" + 7.5 " " + 7.5 " " "	61.92	49.25
80 "	"	" + 10 " " + 10 " " "	62.52	49.45
70 "	"	" + 15 " " + 15 " " "	66.20	50.45

Maximum and minimum numbers for pure lard (Lewkowitsch) 59. to 68.8 ..... 44.8 to 53

The results are not in exact proportion to the amount of corn oil present, probably due to the imperfect mixing, but the samples represent about what one would expect to find in commercial products. It will be seen that so far as the iodine number and the butyro-refractometer reading are concerned all of the above samples would pass for pure lard. The iodine number of the sample of pure lard used is near the minimum but it represents about the average iodine number of a large number of analyses of commercial lards. If the iodine number of the lard used were near the maximum, of course some of the above samples would give abnormally high figures for the constants. Another complication arises as to just what numbers shall be considered the maximum and minimum ones for the constants of pure lard, since the different investigators do not agree with reference to them.

The maximum and minimum numbers for the butyro-refractometer readings are so far apart that the determination of this constant would rarely give any indication of the oil unless present in such large amounts that its physical properties would serve for its detection.

A number of analyses were also made to determine whether or not a partial separation of the oil might not take place during the solidification of the melted product, in which case the last portion of the fat to solidify would give an abnormally high iodine number. Two samples were prepared containing 10 per cent. of corn oil and the iodine number of the mixture as well as of portions of the molten fat as solidification proceeded were determined.

Portion	Iodine Number	
	Sample 1	Sample 2
" 1. ....	62.20	63.69
" 2. ....		63.20
" 3. ....	61.39	63.53
" 4. ....		63.54
" 5. ....	61.44	63.38
" 6. ....	61.16	63.13

These results show that no separation of the oil occurs and hence its presence could not be detected in this way.

A number of color tests<sup>1</sup> have been proposed but none of them proved satisfactory. The presence of the corn oil in the lard influences the color tests but the differences were no more marked than were the differences between certain samples of pure lard.

Finally an effort was made to detect the oil by separating the unsaponifiable product and to determine its character according to Bomer's acetate method.<sup>2</sup> The unsaponifiable product in corn oil has been variously regarded as cholesterol<sup>3</sup>, phytosterol<sup>4</sup>, and sitosterol<sup>5</sup>. While the question as to its identity can not be regarded as definitely settled, it will be termed sitosterol when reference is made to it, in accordance with the view of Gill and Tufts<sup>6</sup>, who made a study of it and suggested that its detection might serve to indicate the presence of corn oil in mixtures. The percentage of sitosterol in corn oil is much larger than the percentage of cholesterol in lard and this together with the fact that the melting points of the acetyl derivatives of the cholesterol and sitosterol are so far apart ( $113^{\circ}$  and  $127^{\circ}$ - $128^{\circ}$  respectively) render it possible to detect even very small amounts of corn oil present in lard.

The method of separation of the unsaponifiable products used was essentially that of Bomer<sup>7</sup> with some slight modification to insure a rapid separation of the ether in making the ethereal extractions. The process used is as follows: 100 grams of the fat are saponified by the addition of 200 cc. of an alcoholic solution of potassium hydroxide made by dissolving 200 grams of the hydroxide in 1000 cc. of a 70 per cent. (by volume) solution of alcohol. The flask containing the solution is connected with a return condenser and heated on the water bath for two hours. The solution is then transferred to a 2-liter separatory funnel, 800 cc. of water added and the cool solution extracted first with 1000 cc. of ether and then three times with 500 cc. each time. If after shaking the liquid with ether, a foam forms on the surface, it is necessary to add more water; otherwise the ether will not as a rule separate. The ethereal extracts are combined and the ether removed by distillation. The resulting residue is then heated for 15 or 20 minutes with 20 cc. of the potassium hydroxide solution. After diluting the resulting liquid with 50 cc. of water and cooling, the solution is extracted first with 50 cc. of ether and then three times with 20 cc. each time. The ethereal extract is separated and washed twice with water using about 25 cc. each time. The ether is then distilled off and the resulting residue crystallized from alcohol until a perfectly white product is obtained. The crystals obtained were very

<sup>1</sup> Vulte and Gibson, *This Journal*, 22, 462.

<sup>2</sup> *Z. Nahr.-Genussm.*, 4, 865.

<sup>3</sup> Hoppe-Seyler, *Bull. soc. chim.* [2] 6, 342. Hopkins, *This Journal*, 20, 948.

<sup>4</sup> Vulte and Gibson, *This Journal*, 23, 2.

<sup>5</sup> Gill and Tufts, *This Journal*, 25, 251.

<sup>6</sup> Gill and Tufts, *This Journal*, 25, 254.

<sup>7</sup> *Z. Nahr.-Genussm.*, 21, (1898).

similar to those obtained by Tolman<sup>1</sup> from mixtures of lard and cotton seed oil. When crystallized slowly, the cholesterol from the samples of pure lard separated on the surface while the unsaponifiable products from the mixtures separated largely on the sides and bottom of the beaker. The purest products were obtained by dissolving the residues in small amounts of hot alcohol, chilling the resulting solution in ice water and at once filtering off the small crystals. The filter paper is then placed in a water oven until the crystals are perfectly dry in which state they will peel off from the paper. The acetyl derivative is then prepared by heating the crystals on a water bath with 2 or 3 cc. of acetic anhydride until they are dissolved. Sufficient water is then added to precipitate the derivative, which is filtered off and purified by crystallizing from alcohol. The product is then dried and its melting point determined. The following results were obtained :

	Melting point of acetyl derivatives
Pure lard.....	113°
" ".....	113°
Lard + 2 per cent. corn oil.....	120°-121°
" + 4 " " ".....	118°-119°
" + 4 " " ".....	122°-124°
" - 4 " " ".....	124°-125°
" - 6 " " ".....	125°-126°
" - 6 " " ".....	125°-126°
" - 8 " " ".....	125°-126°
" - 10 " " ".....	126°-127°
Pure corn oil.....	127°-128°

It is a noteworthy fact that the melting point of the acetyl derivative obtained from the lard containing even 2 per cent. of corn oil is markedly higher than the corresponding derivative from pure lard. This would indicate that in the process of purification the sitosterol is obtained nearly pure.

If the amount of corn oil present is higher than 4 per cent the process may be materially shortened. In such samples the liquid residue obtained after distilling off the ether from the first ethereal extract will, on cooling, deposit a solid which may be filtered off and converted directly into the acetyl derivative. The melting point of the derivative will be found to be about 125°.

The above method for detecting corn oil would of course fail in the presence of cotton seed oil. It is doubtful, however, whether the latter oil is used to any extent as an adulterant of lard at present, due undoubtedly to the ease with which it can be detected. In the examination of a large number of commercial samples of lard made during the last three years not a single sample was found adulterated with cotton seed oil.

The large amount of ether necessary for the extraction of the unsaponifiable products in the above process renders it an expensive one to

<sup>1</sup> This Journal, 27, 589.

carry out. The ether, however, may be largely recovered by distillation. An investigation is now being made in this laboratory with the hope of so modifying the method as to overcome the above objection.

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## REPLY TO CRITICISMS OF DRY LEAD DEFECACTION IN RAW SUGAR ANALYSIS<sup>1</sup>.

BY W. D. HORNE.  
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About the only objections which have been raised to the method<sup>2</sup> of defecating raw sugar solutions with anhydrous subacetate of lead, after making up the solution of the normal weight of sugar to 100 cc. and prior to polarizing, are those which Messrs. H. & L. Pellet have advanced. Of the seven objections originally raised<sup>3</sup> I answered all, but in the past few months Mr. H. Pellet has readvanced one of these in a new form and has presented a new objection<sup>4</sup>. His new claim is that the lead precipitate absorbs sufficient sugar from solution to slightly more than counterbalance the concentration of solution which one would expect to find due to the occupancy of space within the 100 cc. by the lead precipitate formed.

In the other objection it is urged that anhydrous subacetate of lead added to a sugar solution dilutes such solution to the extent of 0.37 cc. for each gram of reagent, causing through this dilution a corresponding lowering of polarization, and this also, he claims, just counterbalances the error due to the volume of precipitate. Experiments are cited to illustrate the first of these points in which a normal weight of raw sugar or syrup was dissolved in a small amount of water, defecated with lead subacetate solution and thrown upon the filter and then carefully washed free from sugar; filtrate and washings being made up to 100 cc. and polarized. These polarizations are said to be the same as or a little higher than those obtained in the usual way, from which he concludes that the precipitate occludes or adsorbs sugar. Obviously, this is only one of several explanations that might be given and if it can be shown that the precipitate does not adsorb sugar I am sure it must be admitted that Mr. Pellet's explanation is at fault and his deductions without weight.

To controvert this I dissolved 26.048 grams of a Cuban molasses sugar in a 100 cc. flask, added 12 cc. of a solution of basic acetate of lead at 24° Brix. to obtain a satisfactory clarification, made the whole up to 100 cc. and filtered on a dry paper. The loss on evaporation was found to

<sup>1</sup> Read before the N. Y. Section of the American Chemical Society, April 5, 1907.

<sup>2</sup> J. Am. Chem. Soc., 26, 186.

<sup>3</sup> Bull. assoc. chim. suc. dist., 23, 285-291.

<sup>4</sup> Internat. Sugar J., 8, 455.

<sup>5</sup> Bull. assoc. chim. suc. dist., 24, 473.