agents are the 1,2-diols. The hydroxyl content of the reduced lanolin is at least equal to if not greater than that of the saponification alcohols. About 5% of the alcohol fraction are diols (4, 15). Hydroxy acids have been reported (5) to comprise about 30% of the acid fraction, and these compounds upon reduction would yield 1,2-diols. It is logical to assume that the emulsifying properties of wool wax alcohols would be enhanced by the addition of the glycols formed by the reduction of the hydroxy acids of wool grease. It was found, on testing the reduced lanolin for its emulsifying properties (13) according to a procedure by Schulman and Cockbain, that they were equal to or better than those of wool wax alcohols obtained by saponification.

Summary

The sodium reduction technique has been modified for application to various grades of lanolin and wool grease. The improved process gives good yields of alcohols with low ester and acid numbers. The sterols present in the grease are not affected by the reduction. A recovery procedure is described which avoids the difficulties with extremely stable emulsions. The essential features of this procedure are the elimination of emulsion-stabilizing sodium soaps by precipitation with barium chloride prior to the washing of the reduction mixture and acetone extraction of the alcohols from the insoluble barium soaps.

Acknowledgment

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Some Effects of Semolina Lipoxidase Activity on Macaroni Quality[1]

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THE PROBLEM of assessing the macaroni-making quality of a sample of durum wheat or durum semolina is largely one of predicting the color of the macaroni which the sample will produce. The most reliable way of doing this is to process macaroni from the sample and to measure the color of the product, either visually or by using some type of instrument. This requires too long a time for some commercial applications and is not convenient in dealing with new varieties at early stages of development because of the small amount of wheat that can be spared for testing. Accordingly it is necessary to seek useful indirect methods of predicting macaroni color.

The desirable color for macaroni is a clear bright yellow. This results from the presence in the semolina of certain yellow carotenoid pigments. The problem, then, should be simply one of determining the amount of pigment in the semolina from which the macaroni is made. However when quality testing of durum wheats was first begun about 20 years ago, it was noted (1) that certain semolinas appeared to bleach badly during processing while others retained their color. For this reason no useful correlation between semolina pigment and macaroni color was found.

In seeking an answer to this problem some years ago, a study was made (5) of the rate at which semolina pigment was destroyed during mixing of macaroni doughs. As a result of this work it was postulated that durum wheats contained the enzyme lipoxidase and that it was the presence of this enzyme, in varying amounts, that gave rise to the variations in pigment loss during macaroni processing. In this brief review I will discuss the application of this hypothesis to the development of a simple prediction test which allows one to estimate the macaroni color of a sample of wheat or semolina of about 20 g.

The data in Figure 1 are taken from some of our earlier work and show that the rate of pigment oxidation during mixing for two samples of semolina which contain the same amount of pigment initially but which vary widely in macaroni-making quality; The methods have previously been described (5). The upper curve, showing rapid oxidation of pigment, is for a semolina yielding a pale macaroni; the lower curve, showing slow oxidation of pigment, is for a semolina yielding a yellow macaroni. Following this investigation we began working with a Warburg apparatus to find out if crude aqueous extracts of durum wheat or semolina showed any lipoxidase activity. Enzyme extracts were prepared by grinding the material with sand and water, followed by centrifuging (3); preparation of a suitable linoleic acid emulsion was eventually solved by using a non-ionic surface-active agent, Triton X-100 supplied by Rohm and Haas (3). The pH optimum for this enzyme-substrate system was found to be 6.5 in phosphate buffer. We found that these wheats did contain significant amounts of this enzyme and obtained the sort of results shown in Figure 2. These curves show the rate of oxygen uptake for aqueous extracts of semolinas, using the linoleic acid emulsion as substrate, at pH 6.5; they represent the same two types of semolina as those shown in Figure 1. The close corre-

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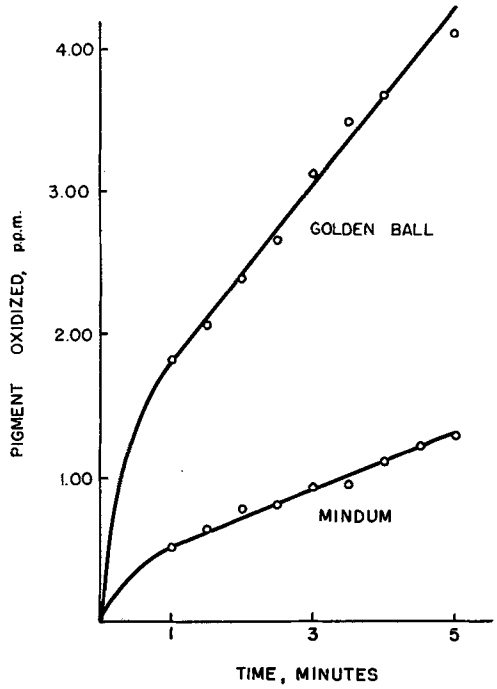

FIG. 1. Rate of pigment oxidation during mixing of macaroni doughs for two varieties of durum wheat.

spondence of the sets of curves in these two figures suggest that our working hypothesis was correct, and this has been verified in other ways which need not be discussed here.

While both of these experiments were made with semolinas milled from the same varieties, Golden Ball and Mindum, different samples of each variety were used in the two experiments. The similarity in behavior of different samples of the same variety has been noted in many other experiments, and it has been established (3) that the amount of this enzyme present in wheat is a varietal characteristic. Environmental variation in lipoxidase is very small as compared with varietal variation whereas other characteristics of wheat, such as yield per acre, bushel weight, or protein content, may vary more widely

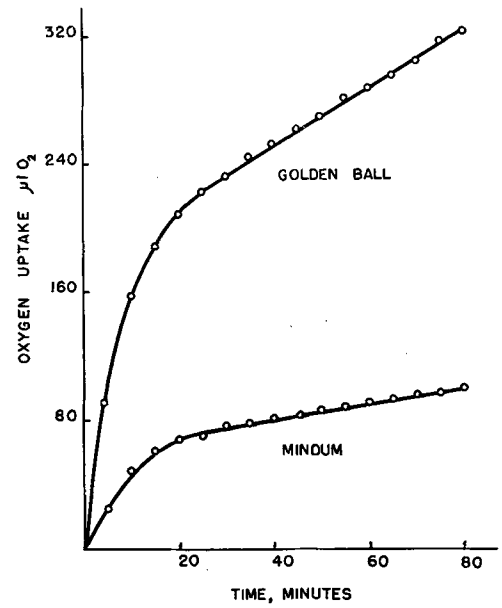

FIG. 2. Rate of oxygen uptake by lipoxidase extracts of two varieties of semolina, using linoleic acid as substrate.

with environment than with variety. Because of the limited effect of environment, it is possible to distinguish good varieties from poor varieties of durum wheat, in a general way, by lipoxidase measurement alone even though samples may come from different areas, where growing conditions may vary widely. It is even possible to distinguish between good and poor varieties when the wheat is so shrunken as to preclude identification in other ways. This technique is proving very useful for the badly rusted crops which are currently being harvested.

FOLLOWING upon this preliminary work, we studied the kinetics of the lipoxidase system as it occurs in wheat (2) and developed suitable manometric assay methods for the enzyme in wheat and in semolina which are described in detail in two subsequent papers (3, 4). With this tool the next step was to work with a large number of durum wheat samples, including both plant breeders' material and commercial carlots, to see if we could improve the prediction of the amount of pigment in macaroni by measuring not only the pigment content of the semolina but also its lipoxidase activity. Pigment content was determined by an overnight extraction of 8 g. of material with 40-ml. of water-saturated n-butyl alcohol. The extract is filtered, and its transmission is measured in an Evelyn colorimeter, using a 440 mμ filter. Pigment concentrations are reported as p.p.m. calculated as β carotene.

The relation of the pigment content of macaroni to that of the semolina from which it was made, for semolinas milled from 227 different wheats, is shown in Figure 3. No useful prediction can be obtained

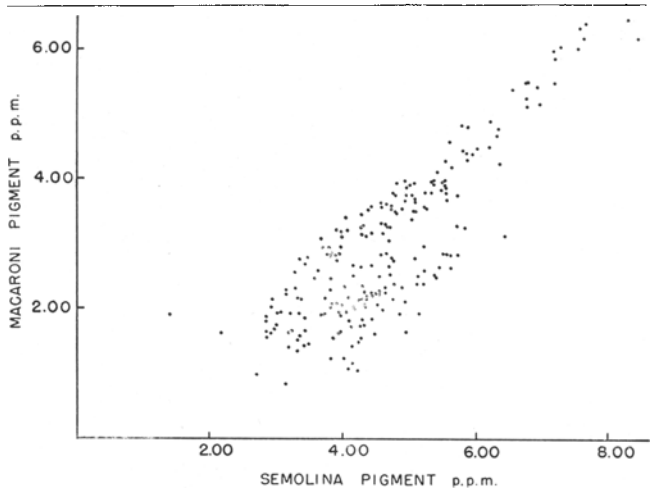

FIG. 3. Relation between pigment content of semolina and pigment content of the corresponding macaroni.

from these data. However, by utilizing as well the data for semolina lipoxidase, a multiple regression can be calculated, relating macaroni pigment to both semolina pigment and semolina lipoxidase (3); and this yields an equation from which macaroni pigment can be predicted from the other two measurements. The result of plotting these predicted values against actual macaroni pigment values is shown in Figure 4; this technique improves the prediction considerably. The prediction equation is

$$P_m = 0.669 + 0.726\,P_s - 0.042\,L_s$$

where P_m is predicted macaroni pigment, p.p.m.; P_s is semolina pigment, p.p.m.; and L_s is semo-

lina lipoxidase activity calculated as μl of oxygen per minute, per gram of semolina.

The standard error of prediction of macaroni pigment from these measurements is 0.38 parts per million. This type of prediction test should be very useful to mills, for control of semolina quality, and to purchasers of semolina in products control.

The same procedure can be followed for wheat itself rather than semolina (4) although one would not expect quite the same degree of precision since the semolina stage is being bypassed. Figure 5 shows the relation between wheat pigment and the pigment content of macaroni processed from it for 137 wheat samples. Applying the same multiple regression tech-

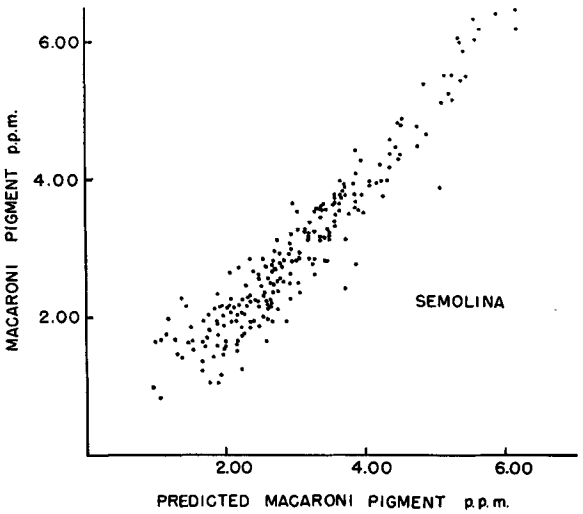

FIG. 4. Relation between macaroni pigment as predicted from data on semolina and experimental macaroni pigment values.

nique, but using wheat data in place of semolina data, and again plotting predicted values against actual values for macaroni pigment, the results shown in Figure 6 are obtained. Again there is a very significant improvement in the regression as a result of adding in the lipoxidase factor. The prediction equation for wheat is

$$P_m = 0.807\ P_w - 0.0105\ L_w - 0.383$$

where P_m again is predicted macaroni pigment, p.p.m.; P_w is wheat pigment, p.p.m.; and L_w is wheat lipoxidase activity μl O_2/min./g.

The standard error of prediction with this equation is 0.48 p.p.m. This prediction test should prove valuable to plant breeders; the test requires only 20 g. of wheat and, by scaling down, could be done on wheat samples as small as 10 g. The wheat prediction test should also be useful to millers for wheat selection.

How will the new methods of vacuum processing affect the usefulness of the lipoxidase measurement? The answer seems to be that they will not affect it. We recently investigated a series of 12 semolinas of widely varying quality and found that the macaroni pigment was identical for normal and vacuum mixed samples. This confirms similar findings from earlier work on the rate of pigment oxidation in macaroni doughs. The pronounced improvement in macaroni color that results from vacuum processing seems to be entirely due to a much smoother macaroni surface and to the increased translucency which results from absence of air bubbles in the macaroni.

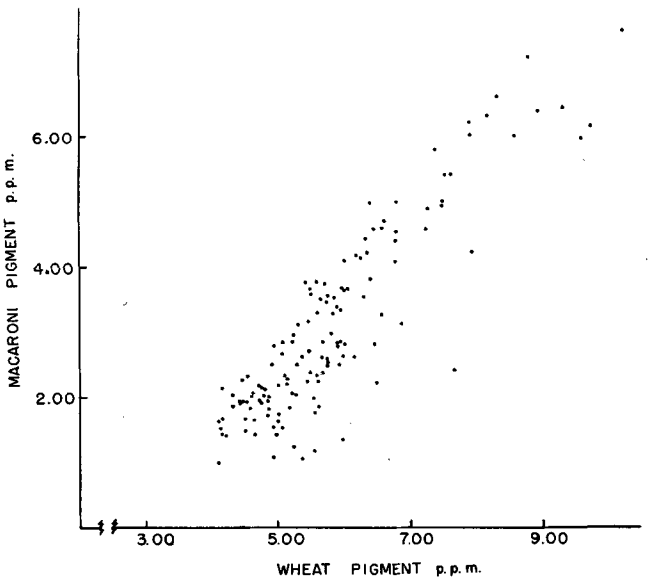

FIG. 5. Relation between pigment content of wheat and pigment content of the corresponding macaroni.

These prediction tests are concerned with estimating macaroni pigment content while the ultimate goal is estimating macaroni color. How good is macaroni pigment as a measure of macaroni color? The answer seems to be that it is the best single parameter measure that we have. On the other hand, no single parameter will suffice to measure all possible macaroni colors encountered in commerce. Fortunately the great majority of commercial samples can be characterized very largely by a single parameter, yellowness. An additional parameter is necessary to deal with brownness. Working with a reflectance spectrophotometer, we have calculated values of dominant wavelength, purity, and brightness in the C.I.E. system for about 100 semolinas and the corresponding

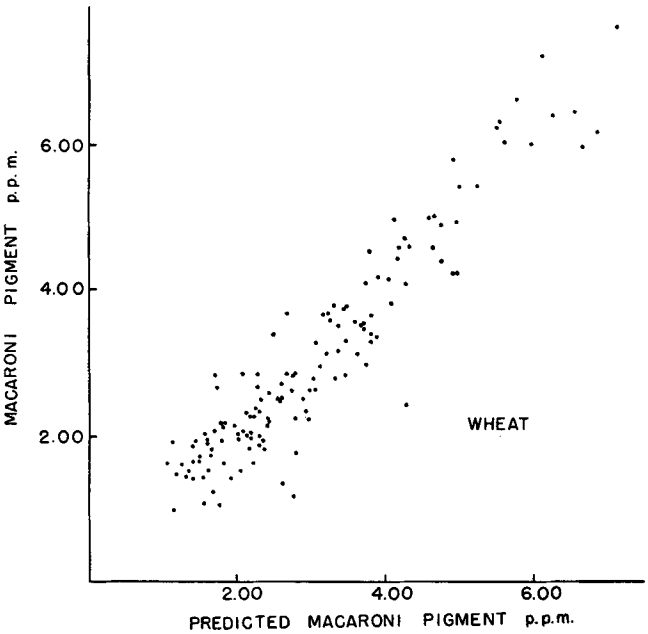

FIG. 6. Relation between macaroni pigment as predicted from wheat data and experimental macaroni pigment values.

macaronis. Over the entire range of colors encountered, dominant wavelength was remarkably constant, and the purity and brightness values were sufficient to establish the macaroni colors observed. Of these two, brightness varied significantly only for samples which were brownish in color; otherwise purity alone would suffice to establish the color. Purity values for macaroni are very closely correlated with macaroni pigment values, and either will serve equally well as the color index for prediction tests. We have worked out the prediction test to yield macaroni purity values; but, except under special circumstances, we feel that macaroni pigment values are more readily understood and meaningful. It is also possible, with semolina, to use a single reflectance measurement in place of the semolina pigment determination, along with the semolina lipoxidase measurement, to predict either purity of macaroni or macaroni pigment.

Summary

It has been established that durum wheats contain lipoxidase and that the presence of this enzyme is responsible for the low correlation between the pigment content of semolina and the color of macaroni. By taking account of the lipoxidase factor and using a multiple regression equation, it is possible to predict macaroni pigment or percentage of purity of macaroni from measurement of semolina reflectance, semolina pigment, or wheat pigment.

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Ethanolamines and Other Amino- and Hydroxyl-Containing Compounds in the Refining of Rice Oil[1]

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THE COMMERCIAL REFINING of crude rice oil with sodium hydroxide in the usual manner (3) generally results in losses that are much greater than would be expected from the characteristics of the oils.

While rice oils processed entirely under carefully controlled laboratory or pilot plant conditions have given refining losses similar to those of cottonseed oils with comparable free fatty acid content (6, 7, 13), the usual commercial losses are of such a magnitude as to make it very difficult, if not impossible, to refine rice oil economically.

Considerable effort has been expended in attempts to find a practical method of reducing these losses. The Japanese, in particular, have done a great amount of work on the refining of rice oil (8, 9, 10, 11, 12). In this country attempts have been made to refine rice oil, using special techniques (4, 13) and the many methods developed for decreasing the refining losses of other vegetable oils. However, as far as is known, no practical commercial method applicable to rice oil has been reported.

When normal refining procedures are employed, the foots formed from crude rice oil are unusual in their inability to cohere and settle out of the oil cleanly. The soapstock is usually composed of small individual grains. These grains settle very slowly, occlude considerable oil, and are almost as fluid as the oil itself. Without the use of special techniques for the separation of the soapstock, the refining loss on a comparatively good rice oil (content of free fatty acids, 5.5%) could be in excess of 50.0%. Centrifugation of the mixture or refining in solvents increases the yield of refined oil but still results in losses of about 25 to 30%. Similar reductions in refining loss may be obtained in the laboratory by simply filtering the mixture through a 100-mesh stainless steel screen (5).

The peculiar behavior of rice oil foots has been attributed to some unknown material in the crude oil that tends to emulsify the oil under the conditions of refining. Light non-settling foots are thus formed. In the past year the major objective of the research on rice oil in this laboratory has been to isolate and to identify this unknown material. The results of the initial phase of this work will be the subject of a forthcoming report.

Recently, in the preparation of liquid floor polishes containing high concentrations of rice wax in the solid portion, it was noted that the emulsions would invariably grain out as though no emulsifying agent were present whenever a triethanolamine soap was used as the emulsifying agent. The use of morpholine instead of triethanolamine, or carnauba wax instead of rice wax, resulted in stable emulsions. Apparently the triethanolamine was effectively neutralizing the emulsifying properties of the mixture.

Therefore an investigation of the effect of triethanolamine and related compounds in the refining of crude rice oil was undertaken. As a result of this investigation enough information has been gathered to provide the basis for future development of the problem. No attempt has been made to present a complete commercial process for the refining of rice oil.

Materials and Methods

Three samples of clarified crude rice oil and one of unclarified crude rice oil were obtained from commercial processors. The clarified oils, used in most of the work, were filtered through diatomaceous earth to insure uniformity of successive samples of each oil and to remove the last traces of solid wax. The unclarified rice oil was used as received. The clarified crude oil having a free fatty acid content of 5.5% was used to establish the preferred refining condi-

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