Study of Some Factors of Macaroni Brownness[1]

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ABSTRACT

Brown index of semolina (BIS) has been defined as the reflectance at 550 nm. of a dry pressed disc of semolina, and potential brown index of semolina (PBIS) as the reflectance at 550 nm. of a sheeted and pressed disc of hydrated semolina. It was demonstrated that 25% of PBIS comes from the 0.5M NaCl-soluble components of semolina, 28% from the chloroethanol-soluble fractions, and 47% from the insoluble material. PBIS is highly correlated to semolina protein content ($r = 0.728^{**}$) and depends on the extraction yield of semolina. Brownness of pasta product is defined by the brownness of semolina (BIS), which seems to occur during kernel maturation, and by the brownness which develops during pasta processing, both resulting from oxidase activities. Selection of varieties with low peroxidase activity should improve the color of macaroni.

[1]Presented in part at the 57th Annual Meeting, Miami Beach, Oct.-Nov. 1972.

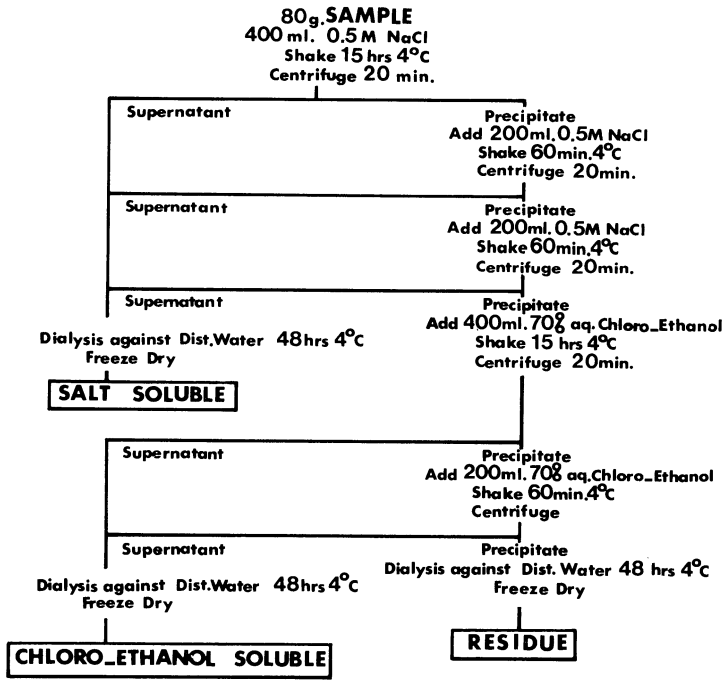

Fig. 1. Semolina fractionation procedure with 0.5M NaCl and 70% aqueous chloroethanol.

Color of pasta products is an important indicator of quality. Consumers tend to be attracted by products of amber-yellow color. This color is a combination of a yellow hue and a brown or grey hue. Various studies have shown that yellowness is a result of the natural carotenoid pigments, which are more or less oxidized by lipoxidases during pasta processing (1). The origin of brownness is less well known.

According to Matsuo and Irvine (2), as confirmed by Walsh (3), a brown cupric-soluble protein is responsible for the difference of browning observed on macaronis made from different durum wheat varieties. Menger et al. (4) suggest that during pasta processing flavons could be partially oxidized by polyphenoloxidases, causing formation of brown components. According to our recent research, a highly significant correlation between the peroxidase or polyphenoloxidase activity in semolina and the brownness of pasta product has been demonstrated (5). Moreover, polyphenoloxidases have been shown to be responsible for chapatti browning (6). Irvine (1) distinguishes two types of brownness, inherent brownness and the brownness resulting from high extraction levels, and states that the latter may, at least partially, be due to enzyme action.

The purpose of this work, as part of a general study on the improvement of pasta color quality, is to determine the origin of macaroni brownness and to define the part played by various technological and agronomic factors.

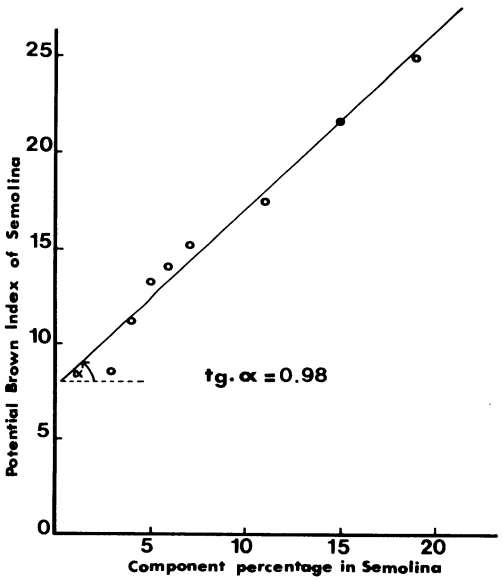

Fig. 2. Diagrammatic determination of the brownness capacity of the semolina salt-soluble proteins extracted from the durum wheat variety Wells.

MATERIALS AND METHODS

Source of Semolinas

Separate lots of durum wheats (nine varieties from several test fields) were analyzed. Mills employed were the Brabender Jr. mill, fitted for semolina processing with a laboratory-made purifier attachment (7), and a semi-industrial laboratory mill (8). One sample was ground on a commercial mill.

Brown Index of Semolina (BIS)

Semolina (5 g.) was pressed into a 5-mm.-thick disc by applying a pressure of 450 kg. per cm.^{2} for 2 min. The BIS was calculated from the disc reflectance at 550 nm. by the equation BIS = 100 log. (reflectance 550 nm).

A Bausch and Lomb Spectronic 20 spectrophotometer with a color analyzer reflectance attachment was used.

Potential Brown Index of Semolina (PBIS)

PBIS was determined as reported by Alause and Feillet (9). Discs of pasta were prepared by mixing 10 g. semolina with 3 ml. of deionized water; after sheeting, two discs were cut from the sheet of dough, allowed to rest 2 hr., then pressed (80 kg. per cm.^{2}) and sheeted into 0.8-mm.-thick discs. The PBIS of semolina was calculated from the disc reflectance at 550 nm. by the equation PBIS = 100 log. (reflectance 550 nm.).

The color of a pasta product processed industrially from semolina corresponds to the color of the experimental pasta disc prepared from the same semolina. Hence the PBIS concept provides direct, useful information on the value of semolina for pasta processing (9).

TABLE I. BROWNNESS DISTRIBUTION AMONG SEMOLINA FRACTIONS[1]

Fractions	Browning Capacity	Std. Dev.[2]	Weight[3] % of semolina	Std. Dev.[2]	Browning[4] Contribution	Std. Dev.[2]
0.5M NaCl-soluble	0.64	0.23	5.6	1.7	25.3	3.6
70% Chloroethanol-soluble	0.50	0.17	7.2	1.3	28.2	10.2
Residue	0.07	0.02	87.2	2.0	46.5	10.7

[1]Values are means of duplicate analyses of 14 samples.
[2]Standard Deviation (for the 14 samples).
[3]Total adjusted to 100.
[4]Expressed in PBIS

Semolina Fractionation

Samples of semolina were fractionated by successive extractions into salt-soluble, chloroethanol-soluble, and residual fractions with 0.5M NaCl and 60% chloroethanol (Fig. 1).

Brownness Capacity of Semolina Component

The browning capacity of a component was defined as the increase of the PBIS due to 1 g. of that component in 100 g. of semolina. It is equal to the slope (tg. α) of the regression curve between the component percentage in the semolina and PBIS (Fig. 2).

In the case of semolina fractions, the regression curve was obtained from the PBIS determination of semolina reconstituted with different amounts of the components studied.

Brownness Contribution of a Component

By multiplying the brownness capacity of a component by its concentration in the semolina, its brownness contribution to the PBIS was determined.

Peroxidase Activity Determination

Peroxidase activity of samples was determined spectrophotometrically according to the method of Honold and Stahmann (10), with some modifications. The assay mixture consisted of 1.5 ml. citrate-phosphate buffer, pH 4.2; 1.5 ml. deionized water; 1 ml. 0.02M guaiacol, 0.5 ml. crude enzyme extract; and 0.5 ml. 0.02M H_2O_2 added at zero time. The increase in absorbance was measured at 465 nm.

Analytical Analysis

Ash content and protein content (N $\times$ 5.7) were determined according to Matveef (8). Moisture content was evaluated with a semiautomatic Brabender oven.

RESULTS AND DISCUSSION

Brownness Distribution in Semolina Fractions

As shown in Table I, the mean values of the brownness capacities of 14 samples are 0.64 for the 0.5M NaCl-soluble fraction, 0.50 for the 60% chloroethanol-soluble fraction, and 0.07 for the residue; the standard deviation of each of these values is between 0.23 and 0.02.

TABLE II. BROWNNESS CONTRIBUTION OF SEMOLINA FRACTIONS EXTRACTED FROM FIVE DURUM VARIETIES (AVERAGE OF TWO ANALYSES)

Variety	PBIS[2]	Brownness Contribution[1]			Brownness[1] Recovery
		0.5M NaCl Fraction	60% Chloroethanol Fraction	Residue	
Montferrier	15	25	19	49	93
Bidi 17	14	25	17.5	59.5	102
Wells	13	30	18	48	96
LF 129	12.5	23	16	63	102
311	11	25	23	51	99

[1]Values expressed in PBIS.
[2]Potential Brown Index of Semolina.

From the amount of these fractions in semolina, their contributions to the brownness of the product were calculated to be 25.3, 28.2, and 46.5%, respectively. According to these results, brownness of pasta products is approximatively distributed in the three analyzed fractions in the ratios 1:4, 1:4, and 1:2. This distribution is a function of the origin of the samples (Table II).

No correlation was found between PBIS and distribution of brownness in the three fractions. The brownness contribution of the 0.5M NaCl fraction, expressed in PBIS %, appears sufficiently constant to explain the finding of Matsuo and Irvine (2), according to whom the degree of brownness can be surmised from the absorbance at 400 nm. of an aqueous extract of semolina.

Since a high correlation between the peroxidase activities in semolina and the brownness of its pasta product exists (5), it is suggested that the browning capacities of the semolina fractions reflect their peroxidase or substrate content. This hypothesis is sustained by the correlation between the peroxidase activities of the 0.5M NaCl-soluble fraction and its brownness capacity (0.866**); unfortunately, the enzymatic activities cannot be measured after the chloroethanol extraction. However, we have shown by enzymatic digestion of the starch in the residue of the variety Bidi 17 that 66% of the brownness is recovered in 5.6% of the residue. This residual brown fraction has a browning capacity equal to 2.0; its protein content is 38% (dry weight).

Effect of Protein Content on PBIS

The effect of protein content on PBIS was first mentioned in a preliminary study of 17 samples of the durum wheat variety Montferrier grown in different locations (9). Analysis of 225 samples (9 varieties harvested in 1971 and 1972 in several places) confirms this result (Fig. 3).

There is a highly significant correlation between PBIS and protein content of semolina ($r = 0.716^{**}$). Hence, as the regression curve shows ($y = 0.90x + 0.46$; y = PBIS; $x = N \times 5.7$), PBIS increases when the protein content increases. This conclusion is in good agreement with previous results reported in this work.

Table III shows that the PBIS increase depends also on the variety of wheat. Thus our results confirm the investigations of Grignac (11).

From these data, it should also be emphasized that the improvement of cooking quality with the increase of protein content could cause the color deterioration of pasta products.

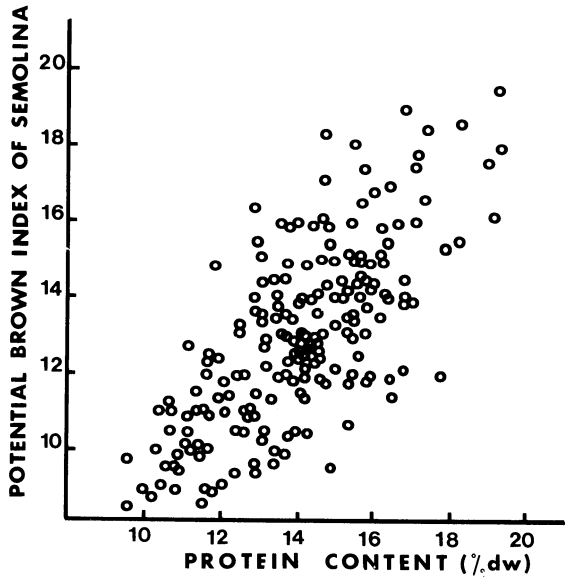

Fig. 3. Effect of protein content (N × 5.7) on the PBIS (r = 0.728**).

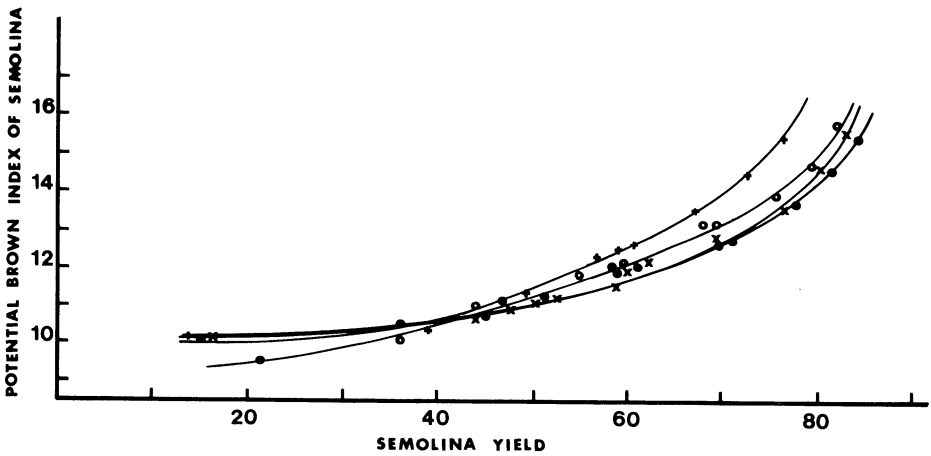

Fig. 4. Effect of semolina yield on PBIS.

Potential Brown Index of Semolina Streams

Semolina streams from a commercial mill were analyzed. Results are shown in Table IV.

Ash content, PBIS, peroxidase activity, and absorption 400 nm., according to Matsuo and Irvine (2), increase simultaneously. PBIS is highly correlated to ash content (r = 0.98**) in agreement with the work of Gillis (12) who showed that

TABLE III. VARIETAL INFLUENCE ON THE MODIFICATION OF POTENTIAL BROWN INDEX OF SEMOLINA DUE TO INCREASING PROTEIN CONTENT (IN RANGE OF USUAL PROTEIN CONTENT)

Variety	Number of Samples	Mean Value N × 5.7 % d.b.	Mean Value PBIS	Correlation Coefficient[1]	PBIS Increase due to 1% Protein Increase d.b.
Agathe	16	12.4	13.0	0.841**	1.18
Montferrier	39	14.4	15.0	0.695**	0.92
Bidi 17	39	14.7	15.2	0.725**	0.77
Durtal	39	11.5	13.0	0.669**	0.70
Lakota	29	12.3	14.1	0.443**	0.50

[1]Between protein content (N × 5.7) and Potential Brown Index of Semolina (PBIS).

TABLE IV. CHEMICAL DATA AND PBIS ON COMMERCIAL SEMOLINA STREAMS

	Semolina Streams							
	3rd-Break semolina	4th-Break coarse semolina	4th-Break fine semolina	6th-Break semolina	7th-Break semolina	Scratch semolina	Exhaust flour	Low-grade flour
Ash Content, % d.b.	0.61	0.79	1.18	1.29	1.43	1.86	2.77	3.15
PBIS	9.2	11.6	12.0	13.1	13.8	16.3	20.3	26.0
Peroxidase activity	0.07	0.13	0.25	0.32	0.44	0.69	0.32	0.58
Absorption, 400 nm.[1]	0.102	0.165	0.260	0.298	0.375	0.560	0.400	0.550

[1]According to Matsuo and Irvine (2).

the color reflectance of flour at 546 nm. can be used accurately in determining ash content. The correlation coefficient values between absorption 400 nm. and PBIS ($r = 0.81^{**}$) and absorption 400 nm. and peroxidase activity ($r = 0.97^{**}$) must be emphasized.

Peroxidase activity of the third-break semolina is very low. Consequently, under normal processing conditions, PBIS of this fraction is due to the browning of the semolina rather than to the development of brownness during manufacturing under the influence of enzyme activity. Up to a certain extent, PBIS of this high-grade semolina is similar to the so-called "inherent brownness" discussed by Irvine (1).

The high PBIS of the low-grade mill products is easily explained by their high peroxidase content; the high PBIS of the exhaust flour compared to its peroxidase activity could be due to the presence of dusty impurities in this product.

Quantitative data were obtained by milling of four durum wheats on a semi-industrial laboratory mill (8). Figure 4 shows the relation between the semolina yield and PBIS.

Comparison between BIS and PBIS

Figure 5 shows that the brown index of semolina is highly significantly correlated to the potential brown index of semolina ($r = 0.863^{**}$).

As shown by the slope of the regression curve (tg. $\alpha = 1.36$), it appears that the development of brownness during pasta processing becomes greater as the value

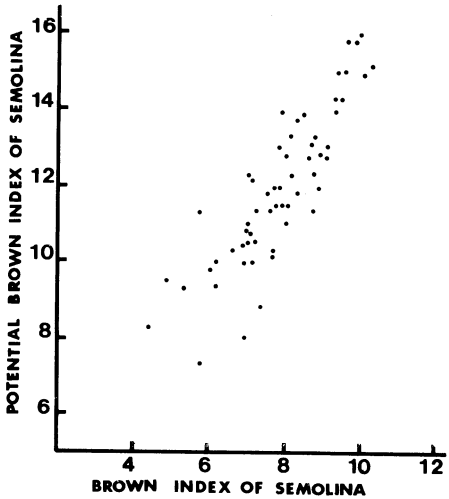

Fig. 5. Relation between brown index of semolina and potential brown index of semolina.

TABLE V. EFFECTS OF ASCORBIC ACID, THIOUREA, AND CATECHOL ON BROWNNESS OF MACARONI

Addition	PBIS				Peroxidase Activity of Semolina
	Water (control)	Ascorbic acid (300 p.p.m.)	Thiourea (300 p.p.m.)	Catechol (250 p.p.m.)	
Montferrier	18.7	16.0	17.3	19.5	0.440
Bidi 17	18.2	15.4	16.0	19.0	0.445
Wells	17.5	16.0	17.2	18.3	0.158
Leeds	17.2	15.2	16.2	18.5	0.141
Durtal	13.8	12.6	13.6	15.8	0.052
Lakota	12.4	11.6	12.3	14.3	0.042

of semolina brownness increases. This could be explained by the high peroxidase activity of the sample with high BIS (5).

Influence of Additives on PBIS

The addition of oxidase inhibitors as thiourea (300 p.p.m.) or ascorbic acid (300 p.p.m.) keeps the macaroni from browning during manufacturing. The addition of catechol (250 p.p.m.), easily oxidized by peroxidases and polyphenoloxidases, increases the development of brownness (Table V).

Analyses of variance of PBIS data (Table VI) showed that apart from the additives, varieties were a highly significant source of variation of PBIS.

We have especially studied, according to Dahle's method (13), the use of citric acid and ascorbic acid for color stabilization. It should be noted that the concentration of ascorbic acid used in this method is one-third that used in the previous study. Analysis of variance of PBIS data concerning these experiments is shown in Table VII.

TABLE VI. ANALYSIS OF VARIANCE OF PBIS DATA

	Degree of Freedom	Mean Squares for PBIS
Varieties (V)	5	17.9247**
Additives (A)	3	10.4061**
V × A	15	0.19708

TABLE VII. INFLUENCE OF ASCORBIC AND CITRIC ACIDS ON PBIS VALUE: ANALYSIS OF VARIANCE

	Degrees of Freedom	Mean Squares for PBIS
Varieties (V)	5	13.280**
Additives (A)	3	1.826**
Ascorbic acid, 0.01%	1	4.085**
Citric acid, 0.01%	1	0.305
Interaction, ascorbic and citric acids	1	1.088**
Triplicates	2	0.528
V × A × T	61	0.199

Here also it appears that the variety is the principal source of variation of PBIS value. Addition of ascorbic and citric acids diminishes PBIS value to a high degree of significance.

CONCLUSION

Our results so far suggest that the initial brownness of semolina and the brownness developed during pasta processing have the same enzymatic origin. Thus semolina brownness (BIS) could be due to action of oxidizing enzymes which takes place during the kernel maturation. Hence the macaroni brownness (PBIS) would be the sum of browning developed during grain maturation and pasta processing. The data obtained for semolina streams are in good agreement with this conclusion. Therefore wheat varieties having a low peroxidase content should be selected in order to reduce the browning of semolina and pasta products.

Acknowledgment

We are indebted to Christiane Mercier for performing the enzymatic digestion of starch.

Literature Cited

1. IRVINE, G. N. Durum wheat and pasta products. In: Wheat: Chemistry and Technology, ed. by Y. Pomeranz (Rev.); chap. 15, p. 777. Amer. Ass. Cereal Chem.; St. Paul, Minn. (1971).
2. MATSUO, R. R., and IRVINE, G. N. Macaroni brownness. Cereal Chem. 44: 78 (1967).
3. WALSH, D. E. The proteins of durum wheat: Their influence on spaghetti quality. PhD. Thesis. North Dakota State University (1969).
4. MENGER, A., CLEVE, H., and ANDER, E. Versuche zur Verbesserung der Teigwaren Quälitat durch Wärmebehandlung der Getreiderohstoffe. Brot Gebaeck 9: 179 (1969).
5. KOBREHEL, K., LAIGNELET, B., and FEILLET, P. Relation entre les activites peroxydasiques et polyphenoloxydasiques des bles durs et le brunissement des pates alimentaires. C. R. Acad. Agr. 14: 1099 (1972).
6. ABROL, Y. P., and UPRETY, D. C. Studies on darkening of whole wheat meal dough. Curr. Sci. 39: 421 (1970).
7. ALAUSE, J. Description d'un petit sasseur de laboratoire. Bull. E. F. M. 241: 36 (1971).
8. MATVEEF, M. Determinazione in semola dei grani duri; metodi utilizzati nel laboratorio di technologia dei grani duri a Montpellier. Tecn. Molit. 14: 341 (1966).
9. ALAUSE, J., and FEILLET, P. Metodo semplice ed obiettivo per la previsione del colore delle paste alimentari. Tecn. Molit. 21: 511 (1970).

10. HONOLD, G. R., and STAHMANN, M. A. The oxidation-reduction enzymes of wheat. IV. Qualitative and quantitative investigations of the oxidases. Cereal Chem. 45: 99 (1968).
11. GRIGNAC, P. Amelioration de la qualite des varietes de ble dur. Ann. Amelior. Plant. 20: 159 (1970).
12. GILLIS, J. A. Photoelectric method of determining flour color. Cereal Sci. Today 8: 40 (1963).
13. DAHLE, L. K. Color stabilization in wheat products. U.S. Patent 3,503,753 (1970).

[Received August 13, 1973. Accepted March 12, 1974]