



MINI REVIEW

# Pasta Brownness: An Assessment

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## ABSTRACT

Pasta colour is an essential factor in assessing pasta quality. It results from a desirable yellow component, an undesirable brown component and, under some drying conditions, a red component. The cause of pasta brownness is complex and its biochemical and technological basis is still a matter of controversy. This paper is a comprehensive review of the literature data in the light of results which have been recently obtained in our laboratory. Pasta brightness (L) is an indicator of the attenuation of the light reflected by pasta samples. Brownness is usually defined as 100-L, and brownish pasta is characterised by a low L value and a dominant wavelength in the 578 nm region. The contributions of cultivar and location to the variance of L are about 15% and 65%, respectively. Within the same cultivar, L decreases when the protein and ash contents increase but the basis of these relations are not known. Pasta brownness is the result of an inherent brownness of the endosperm (the dominant parameter in the case of semolina scarcely contaminated by the peripheral parts of the grain), of the degree of purity of the semolina and of Maillard reactions when pasta are dried at high temperature. Inherent brownness of semolina could be due to a water-soluble copper protein (Matsuo's brown protein) and/or to the action of oxidising enzymes which would take place during grain maturation. The brown colour of spaghetti increases sharply with the ash content of the milling streams. Whether such brownness results from the inherent brownness of milling streams or from the action of polyphenol oxidase is not known. Kneading and extrusion of pasta have no significant effect on brownness. The formation of brown 'melanoidin' pigments due to the development of Maillard reactions is related to the reducing-sugar content of pasta and the drying parameters. Recommendations for future research are given, which include further genetic and physicochemical investigations of Matsuo's brown protein, the evolution of polyphenoloxidase activity during durum wheat grain maturation and the relationship between pasta brownness and the PPO activity of milling streams.

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*Keywords:* durum wheat, semolina, pasta, brownness, oxidising enzymes, processing conditions, drying.

## INTRODUCTION

Pasta products which have excellent nutritional and safety quality have been known in Mediterranean countries for many centuries and are eaten and enjoyed everywhere. Cooking quality and appearance are the two most important factors in assessing pasta quality. The appearance of pasta is determined by three groups of parameters: colour, specks (brown specks from the grain pericarp, and black specks from ground ergot and surface

discoloration such as black point) and surface texture (checking, smoothness, white spots, streaks, air bubbles).

Colour is a psychological phenomena resulting from the interaction of the light source, object being viewed, eye and brain. Colour is composed of two chromatic attributes (hue and purity) and one luminous factor (brightness). Hue refers to the spectral composition of light leaving the object. Purity (or saturation) is the amount of colour present: the higher the saturation, the lower the

greyness. The brightness (or lightness) refers to the capacity of an object to reflect or transmit light<sup>1</sup>.

Pasta colour results from a desirable yellow component, an undesirable brown component and, under some drying conditions, a red component<sup>2,3</sup>.

The contribution of the semolina components to the yellowness of pasta products is well documented since the pioneering work by Irvine and Anderson<sup>4</sup> which demonstrated that variation in the yellow colour of macaroni is considerably greater with variety than with environment, and that the yellow component is related to the presence of carotenoid pigments and lipoxygenase activity in the semolina. Recent work has confirmed these early findings<sup>5</sup>. The brown colour tends to mask the yellow colour when it reaches substantial values<sup>6</sup>.

The red component<sup>7</sup> is the result of Maillard, or carbonyl-amino, reactions<sup>8-10</sup> developed between proteins and sugars. It increases with the content of furosine in pasta, which is a product of the Maillard reaction<sup>11</sup>.

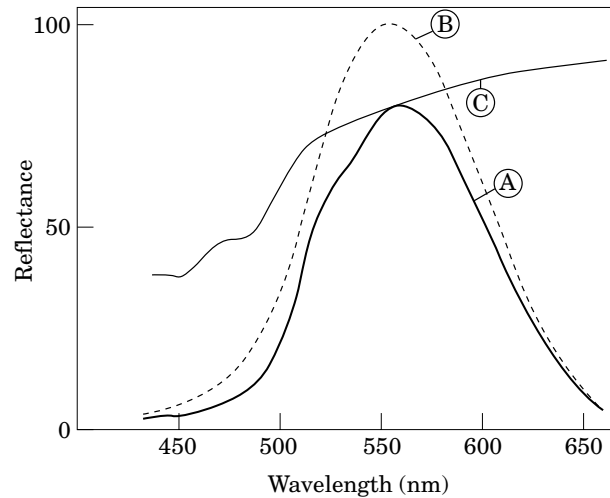
The cause of browning is more complex and its biochemical and technological basis are still a matter of controversy. The purpose of this paper is to review the literature in the light of results which have recently been obtained in our laboratory.

## BRIGHTNESS AND BROWNNESS

If the concept of pasta yellowness, which is directly related to the final amount of yellow pigments in pasta, is easily understandable, the concepts of brightness and brownness are sometimes confusing and need some comments.

To an observer, as shown in Figure 1, the colour appearance of spaghetti (curve A) is the result of the interactions between eye visibility (curve B), i.e. the relative luminance of spectra colours emitted at an identical level of energy, and spaghetti reflectance (curve C). The human judgement is based on this interaction.

Curve A is differentiated from curve B by two main characteristics. Firstly, a global flattening of curve B, which is easily determined by the spaghetti reflectance at 550 nm. The greater the flattening (and therefore the lower the reflectance at 550 nm), the lower the brightness of the sample. Secondly, a slight inflection is present at 480 nm, which is related to the spaghetti yellowness.



**Figure 1** Physiological response to spaghetti reflectance<sup>18</sup>  
A: Spaghetti appearance; B: Eye visibility; C: Spaghetti reflectance.

Pasta brightness (L) is an indicator of the overall attenuation of the light reflected by spaghetti samples when illuminated by sunlight or overcast daylight. Brownness is usually defined as 100-L. As the opposite of yellowness, brownness is not linked to any specific change in the spaghetti reflectance curve. That is one of the reasons why its study is complicated.

## DETERMINATION OF PASTA BROWNNESS

Numerous direct and indirect methods have been suggested to predict brownness of pasta products. The simplest method of prediction is the assessment of semolina brownness by visual inspection (by a trained technician or a panel) or reflectometry. Measurements are made on semolina or on semolina pressed discs<sup>12,13</sup>. Pressure is applied to improve the surface smoothness of the semolina disc and so to eliminate the disturbing effect of the semolina particle size.

Alternatively, a rapid method based on wheat flour samples which were made into slurries with water, with the colour read in an Agtron Reflectance Spectrophotometer, has also been suggested. Various grades of wheat flours were graded on colour basis. When blends of flours were read in the Agtron, linear relationships between the percent of one ingredient and the Agtron colour reading were found. A simple and rapid method for determining the percentage composition of a two-component blend is described. It is necessary

to establish only one standard curve if the same batches of ingredients are used throughout the operation. The degree of bleaching of flours with benzoyl peroxide was followed by this colour technique<sup>14</sup>.

Intermediate in complexity is the disc method, initially proposed by Fifield *et al.*<sup>15</sup> and further improved by others<sup>16-18</sup>. It consists of manufacturing pasta discs from semolina under standardised conditions (hydration, mixing, sheeting and pressing) and measuring their colour parameters. Its main advantages are speed of analysis and the small amount of sample required for each analysis (less than 50 g), and allowing routine analysis in breeding programmes or in commercial mills.

The most elaborate prediction procedure is to process semolina into pasta, usually spaghetti, and then determine the colour of the final product by visual inspection or reflectometry. This can be considered as a reference method, but it is time-consuming, expensive, and needs special equipment (pasta press, dryer).

The measurement of colour by visual inspection and comparison against standard samples is subjective, and its many shortcomings are immediately apparent (differences among judges, lack of precision in describing colour). Instrumental methods to eliminate these errors have therefore been developed. The oldest and most tedious method was the use of the Munsell spinning disk colorimeter<sup>15</sup>. Use of a reflectance measuring spectrophotometer was introduced by Matz and Larsen<sup>19</sup>. Two types of equipment have been used: scanning spectrophotometers, enabling the sample reflectance to be determined at any selected wavelength; and tristimulus colorimeters<sup>19,104</sup>, giving three readings, X (red value), Y (green value) and Z (blue value); easily combined to give the value *a* which indicates redness when it is positive, the value *b* which indicates yellowness when positive, and the value L which indicates brightness.

Taking advantage of the characteristics of the pasta reflectance curve (Figure 1), Alause and Feillet<sup>18</sup> calculated the yellowness and the brownness of pasta discs from the equations:

$$BI \text{ (brown indices)} = \text{brownness} = 100 - \text{reflectance}_{550 \text{ nm}}$$

$$YI \text{ (yellow indices)} = \text{Yellowness} =$$

$$100 (\text{reflectance}_{480 \text{ nm}} - \text{reflectance}_{550 \text{ nm}})$$

Using a spectrophotometer with a reflectance attachment, Matsuo and Irvine<sup>21</sup> applied the 10 selected ordinates method<sup>22</sup> to determine the dom-

**Table I** Semolina and pasta discs brightness (L) of durum wheat varieties samples

Varieties	Semolina discs	Pasta discs
Bidi 17	87.3	59.4
Agridur	88.3	59.2
Exeldur	88.6	59.3
Ardente	88.7	59.6
Exodur	89.1	63.3
Galadur	89.1	61.8
Lloyd	89.2	63.4
Néodur	89.2	61.8
Ixos	89.4	61.8
Excalibur	89.6	63.5
Duriac	90.8	65.1

inant wavelength (DWL), purity and brightness: brightness gives a measure of the degree of surface dullness; an increase in DWL indicates an increase in degree of browning; purity is an indication of hue or colour intensity and is related to pigment content. A mathematical method has been developed that allows direct calculation of DWL from trichromatic coefficient if DWL lies between 550 and 600 nm<sup>23</sup>.

Brownish pasta is characterised by a low L value, by a dominant wavelength in the 578 nm region and by a high brown indices (BI). In semolina streams, DWL and L of pasta are highly correlated ( $r = -0.984$ ,  $n = 16$ )<sup>24</sup>; the same relation was not found when comparing a large set of durum wheat semolina samples ( $n = 120$ )<sup>25</sup>. BI was shown to be highly related to L<sup>18</sup>.

### The relationship between semolina and pasta brownness

Kobrehel *et al.*<sup>13</sup> showed that BI of semolina (measured on a semolina pressed disc as described above) is highly correlated to BI of pasta discs ( $r = 0.86^{**}$ ,  $n = 60$ ). Further studies were undertaken recently in our laboratory and confirmed the previous results. The comparison of semolina and pasta discs' brightness (L) of 11 durum wheat varieties (Table I) showed a high correlation between the two series of values ( $r = 0.84$ ); 136 lines, the progenies of three crosses between three durum wheat varieties (Ixos × Lloyd; Néodur × Lloyd; Néodur × Primadur), kindly provided by P. Roumet (Station de Génétique et d'Amélioration des Plantes, INRA, Montpellier) were also analysed. The cor-

relation coefficients for semolina and pasta discs' brightness were highly significant ( $p=0.01$ ) and ranged from 0.748 to 0.874 with an overall correlation of 0.837.

The fact that pasta brightness is highly correlated to semolina brightness strongly supports the hypothesis of Irvine<sup>26</sup> who distinguished two types of brownness in pasta: inherent brownness of endosperm and brownness resulting from high extraction levels. Further work is required to understand the molecular basis of endosperm or 'pure semolina' brightness and to determine the genetic and environmental control of this attribute. These points will be discussed below.

Furthermore, screening durum wheat lines on the basis of a high semolina brightness value is easy and useful to improve the colour quality (high brightness) of pasta products. The 'semolina disk method', as described by Kobrehel *et al.*<sup>13</sup>, was recommended to measure semolina brightness. No relationship was found between semolina and spaghetti brown indices when measurements were made on semolina without compression into a disc<sup>27</sup>. That might be explained by a 'particle size effect' on readings.

## DURUM WHEAT CHARACTERISTICS

### Genetics and environment

Work carried out in different countries, mainly Canada, France, Italy and U.S.A. has shown that pasta brightness depends on the cultivar and the growing conditions of durum wheats. Earlier Mediterranean varieties such as Montferrier and Bidi 17 were known for their high brownness, while North American varieties such as Lakota and Wells had low BI (Table II). During the last 40 years, breeders have taken advantage of this finding to breed new durum wheat varieties with low browning potential.

The relative influences of genetic and agronomic factors are not fully understood. According to Grignac<sup>105</sup>, comparison of the brown indices of five durum wheat varieties grown in different locations for four years showed that brownness was much more affected by the environmental conditions than yellowness. The brown indices increased when the grain was grown or stored under poor conditions. The sensitivity of durum wheat to adverse conditions was higher with Mediterranean varieties.

The contributions of cultivar, year and location

**Table II** Brown indices of durum wheat varieties with North American or Mediterranean origins<sup>27</sup>

North American origin	Brown indices
Adur	11.0
Mandon	11.5
Leeds	12.0
Lakota	12.0
Sentry	12.0
Nugget	12.0
Wells	12.5
Stewart 63	12.5
Mediterranean origin	Brown indices
Montferrier	15.5
Bidi 17	16.5
Chili 961	18.0
Candeal	18.0
Lez	18.0
Oued Zenati	18.5

to the variance of pasta brightness, calculated by Matsuo *et al.*<sup>25</sup> on 30 cultivars grown at two locations for two years, were found to be 15.7, 0.9 and 67.7%, respectively. Autran *et al.*<sup>28</sup> analysed a large data set (112 durum wheat samples: 36 breeding lines and five cultivars grown in 1983 and 1984, grown either in two locations in the north of France, or two locations in the south of France, or both). They confirmed that the influence of the cultivar was not as dominant in determining brightness variability as in determining yellowness<sup>105</sup>. They found that the genotype was responsible for 12.6% of the variability, the location for 67.9% and other factors for 19.5% (with the pasta yellow indices, these values were 86.6, 8.5 and 4.9%, respectively).

### Protein composition

The protein content of wheat or semolina affects pasta brownness: for a given cultivar, the higher the protein content, the higher the brownness. The effect of protein content on pasta brownness was first noted by Grignac<sup>105</sup> and by Alause and Feillet<sup>18</sup> who analysed 17 samples of the durum wheat variety Montferrier grown in different locations and showed that BI increased by 1.2 when the protein content increased by 1.

Further analysis of 225 samples (nine varieties,

**Table III** Effect of protein content on the brown indices of durum wheat varieties<sup>13</sup>

Variety	Number of samples	Correlation coefficient <sup>a</sup>	Brown indices increase due to 1% protein increase
Agathé	16	0.84**	1.18
Montferrier	39	0.69**	0.92
Bidi 17	39	0.72**	0.77
Durtal	39	0.67**	0.70
Lakota	29	0.44**	0.50

<sup>a</sup> Between protein content and brown indices of semolina  
 $p=0.01$  for \*\*

several locations and two harvests) confirmed this result<sup>13</sup>. The pasta brownness increased when the protein content increased. The slope of the regression curve depended on the variety (Table III).

Dexter *et al.*<sup>29</sup> grew cultivars at three levels of soil fertility by applying 0.56 and 224 kg/ha of ammonium nitrate fertiliser. They found that spaghetti brightness decreased concomitantly with an increase in DWL when the N fertiliser level was increased.

These findings are important because they demonstrate that increasing the protein content to improve the spaghetti cooking quality<sup>3</sup> is detrimental to the colour, and that some cultivars are more sensitive to the increase in protein content. No data are available to relate this sensitivity to the brown indices of durum wheat varieties, and the basis of this relation is still unknown. Endosperm paste reflectance at 540 nm (a measure of the brightness) of white wheat flour was found to be negatively correlated with the protein content of the endosperm<sup>30</sup>. Baik *et al.*<sup>31</sup> found that the discoloration of dough for oriental noodles is affected by protein content, and suggested that protein could be involved in at least three ways: as a marker for an unknown component, through an effect on hardness or through an effect on the rate of water binding during dough processing. The relationship found between protein content and polyphenol oxidase activity in bread wheat<sup>32</sup> might be the basis for the negative effect of protein content on brownness. Irrespective of the basis, breeding new durum wheat varieties with a low relationship between protein content and brownness is an useful and feasible goal for the future.

Using fractionation and reconstitution assays, Kobrehel *et al.*<sup>13</sup> found that 25% of the pasta brownness arose from the semolina components

soluble in 0.5 M NaCl, 28% from the chloro-ethanol soluble fractions and 47% from the insoluble material. A correlation was found between the gluten content and the brown indices of semolina extracted from two varieties, Lakota and Bidi, and enriched in gluten<sup>33</sup>. Varieties high in albumin and glutenin and low in globulin tended to show low brightness<sup>34,35</sup>. It would be interesting to compare pasta and gluten brownness, but no data are available.

The relationship between protein quality (as assessed by gluten tenacity) and brownness is controversial. Grignac<sup>105</sup> found a high correlation between gluten tenacity and pasta brownness and, according to Laignelet<sup>36</sup>, brownness cannot be separated from good cooking quality and strong gluten in durum wheat cultivars. However, cultivars released in many countries since this time show that breeding can improve cooking quality without adverse effects on colour, as already noted by Matsuo *et al.*<sup>25</sup>. It is today accepted that the pasta brown indices are not related to the 'protein quality'.

### Ash content

Matsuo *et al.*<sup>25</sup> found a highly negative correlation between wheat ash content and spaghetti brightness ( $r = -0.82$ ,  $n = 120$ ). Because a significant correlation was found by Feillet<sup>37</sup> between the ash and protein contents of durum wheat kernels ( $r = 0.90$ ,  $n = 300$ ), the relation between ash content and brownness could be explained either by an unknown functional effect of ash on brownness or by an indirect functional effect of protein on brownness. The second hypothesis is improbable because there was no evidence of a relationship between ash content and protein content when

**Table IV** Colour of semolina and spaghetti from developing durum wheats<sup>40</sup>

Varieties	Stewart 63				DT 411				Candeal			
	24	17	10	0	24	17	10	0	27	17	10	0
Days pre-ripe												
WE 400 nm	0.23	0.17	0.12	0.09	0.27	0.18	0.08	0.10	0.57	0.35	0.28	0.27
Brightness	37.5	52.2	49.4	48.4	44.6	51.0	49.5	44.0	34.8	47.7	46.0	43.7
DWL	578.8	576.3	577.3	577.0	577.5	577.1	577.3	577.7	580.2	577.5	578.0	578.2

WE 400 nm = absorbance at 400 nm of semolina water extract

DWL = dominant wavelength

protein varied in function of crop management conditions<sup>29</sup>.

### Kernel immaturity, sprouting and heat damage, starchy and shrunken kernels, and bleaching

Harris *et al.*<sup>38,39</sup> reported that semolina milled from durum wheat damaged by sprouting or immaturity give rise to brownness in macaroni.

During kernel development, rapid changes in the nature of the semolina components were noted by Dexter and Matsuo<sup>40</sup>: the absorption at 400 nm of the water-soluble extract of semolina decreased, as did the content of the brown coloured component identified by Matsuo and Irvine<sup>21</sup> as responsible for the inherent brownness of semolina (see below); the brightness increased and the DWL (dominant wavelength) decreased sharply between 24 and 17 days before maturity.

The lower brightness and longer DWL of spaghetti produced from immature samples were confirmed in further work (Table IV).

The effect of sprouting on brownness was studied by Matveef<sup>41</sup>, Dick *et al.*<sup>42</sup>, Matsuo *et al.*<sup>43</sup> and Combe *et al.*<sup>44</sup> who reached the common conclusion that pasta brownness was slightly influenced by sprouting, as illustrated by the data given in Table V. The overall appearance was affected.

No relationship was found between spaghetti brightness or DWL and vitreousness while a slight decrease in brightness and a pronounced shift in DWL were noticed in shrunken kernels<sup>45</sup>. A low level of bleaching by adverse weather conditions, involving only the discoloration of the kernel seed coat, did not affect the semolina properties or the spaghetti colour<sup>46</sup>. Durum wheat cultivars downgraded because of *Fusarium*-damaged kernels gave duller semolina, the deterioration in pasta colour being discernible by eye<sup>47</sup>. Besides an undesirable

**Table V** Effect of sprouting (as determined by the Hagberg Falling Number) on pasta brownness<sup>44</sup>

Varieties	Falling Numbers	Brownness
Capdur	484	33.5
Capdur	258	33.2
Capdur	123	35.0
Primadur	466	35.7
Primadur	232	37.5
Cando	236	41.5
Cando	165	39.6
Cando	140	39.0
Cando	73	40.5

increase in semolina speckiness, the effect of smudge (a dark-brown or black discoloration of the kernel associated with fungal pathogen) and blackpoint and of mildewed kernels was a slight deterioration of spaghetti colour, particularly from mildewed kernels (an average decrease of spaghetti brightness from 45.4 to 43.4). At a high level of ergot, spaghetti colour deteriorated rapidly: because of its dark colour, ergot has a pronounced effect on brightness<sup>48</sup>. The poor refinement of semolina from severely frosted durum wheats resulted in duller and browner spaghetti<sup>49</sup>.

Dexter *et al.*<sup>50</sup> tempered and artificially dried durum wheat grains (Wascana and Medora varieties) at various temperatures (50 °C to 80 °C) and relative humidities (final moisture content: 15.5 and 13.5%) to impart a range of heat damage. They found no major detrimental effect of the treatments on pasta brownness and DWL, and all samples gave satisfactory results. However, there were some significant changes in sample brightness when the drying temperature was above 70 °C.

**Table VI** Brownness (100-L) of durum wheat milling stream<sup>52</sup>

Colour Durum wheat variety	Brownness			Ash content (% db)		
	Agathé	Durtal	Valdur	Agathé	Durtal	Valdur
<i>Semolina</i>						
S1 (central endosperm)	17.3	18.1	17.6	0.75	0.63	0.79
S2 (medium endosperm)	19.1	17.9	19.3	0.92	0.73	0.95
S3 (central endosperm)	16.8	17.0	17.5	0.68	0.60	0.67
S4 (medium endosperm)	18.3	17.4	19.0	0.95	0.83	0.85
S5 (peripheral endosperm)	25.5	22.5	22.4	1.38	1.10	1.14
S6 (peripheral endosperm)	24.9	22.5	23.6	1.43	1.16	1.34
<i>Break flours</i>						
B1 (1 <sup>st</sup> break)	34.7	22.4	31.6	2.11	0.81	1.75
B2 (2 <sup>nd</sup> break)	30.3	20.0	27.5	2.14	0.98	1.68
B3 (3 <sup>rd</sup> break)	30.7	22.6	27.1	2.80	1.32	2.19
B4 (4 <sup>th</sup> break)	35.6	27.7	32.5	3.33	1.99	2.75
<i>Scratch rolls flours</i>						
D1 (1 <sup>st</sup> roll)	25.7	21.2	24.0	2.16	1.25	1.77
D2 (2 <sup>nd</sup> roll)	30.4	24.9	27.1	2.85	1.63	2.22
D3 (3 <sup>rd</sup> roll)	26.7	21.5	26.0	2.64	1.44	2.35
D4 (4 <sup>th</sup> roll)	34.3	28.8	31.3	2.99	2.34	2.96

## PROCESSING CONDITIONS

### Milling

The aim of semolina milling is to separate and remove the germ and the outer layers of the kernel (aleurone layer, pericarp) from the endosperm and to obtain the maximum amount of semolina with the highest purity, i.e. with the lowest ash content.

Milling yields and milling conditions (tempering, break system, efficiency of purifiers, extraction rate) are known to have marked effects on flour and semolina properties. Irvine and Anderson<sup>6</sup> found that the brown colour of macaroni increased sharply with the ash content of semolina fractions; they hypothesised that the best score was related to the removal of aleurone material and of bran particles.

Semolina ash and extraction rate have a pronounced effect on spaghetti brightness and dominant wavelength: reflectance measurements show a progressive tendency towards lower brightness in the spaghetti as extraction rate increases due to an increasing amount of non-endosperm material in the semolina; at high extraction, spaghetti becomes browner and duller<sup>24,51</sup>. Other data<sup>52,53</sup> confirm these findings (Table VI).

Comparing three commercial mills, Matsuo and Dexter<sup>24</sup> found the following relation between ash content and brightness of semolina streams:

$$\text{Spaghetti brightness} = -19.55 \text{ ash content} + 59.95.$$

When durum wheats were pre-processed according to the Tkac procedure (which involves the removal of bran layers by sequential friction and abrasion passages using rice polishers), Dexter *et al.*<sup>54</sup> found that the ash content of semolina decreased and that the pre-processing had a slightly beneficial effect on spaghetti brightness.

### Pasta making

Pasta production is a simple operation. Semolina is hydrated, mixed, extruded to give pasta of the desired shape, and the fresh pasta is dried. During the process, semolina components undergo several modifications, mainly oxidations, which might contribute to the final colour of the pasta.

The two potential stages of brownness development during pasta processing are dough formation, including kneading and extrusion, and drying.

#### *Dough development: hydration, mixing and extrusion*

An instrumented pasta press was used to analyse the effects of experimental parameters (hydration, temperature and shearing) on colour characteristics of spaghetti by Abecassis *et al.*<sup>55</sup> They found that production factors had little influence on the colour of pasta but that they did affect cooking quality. Under the most extreme pro-

**Table VII** Effect of drying conditions on pasta brownness

Time (hours)		6			18		
		30	60	90	30	60	90
Bidi 17	RH = 100	14.2	15.4	17.8	14.3	14.8	27.5
Bidi 17	RH = 50	13.8	13.6	13.2	13.3	13.8	18.6
Montferrier	RH = 100	11.6	13.1	15.5	13.8	12.6	26.1
Montferrier	RH = 50	12.9	11.9	11.5	11.5	12.1	17.7

RH = relative humidity

cessing conditions, the brown pasta indices ranged from 35.4 to 37. However, the presence of a pre-die plate before the die in the extrusion worm had a tendency to increase the brown indices of pasta. In contrast with studies from Medvedev *et al.*<sup>56</sup>, no improvement of pasta brightness was found upon increasing the extrusion temperature.

Five process variables (water absorption, barrel temperature, screw speed, mixing time and water temperature) were investigated by Debbouz and Doetkott<sup>57</sup> to determine their effects on pasta quality. Contour plots showed that spaghetti brightness improved slightly at lower water absorption (30.5–31%) and lower barrel temperature (35–45 °C) and at intermediate screw speed (25 rev/min). Spaghetti yellowness showed similar trends, except that it increased at higher barrel temperatures.

### Drying conditions

It was reported that spaghetti dried at high temperature showed a tendency to 'browning'<sup>37,33,58,59</sup> due to a Maillard-type reaction<sup>9</sup>. Feillet *et al.*<sup>33</sup> showed that applying a high temperature (90 °C) for 18 h dramatically increased the brownness of pasta. However, when the temperature was kept at or below 60 °C, the brownness was not greatly affected by time or humidity (Table VII).

Similar results were obtained by Dexter *et al.*<sup>60</sup> who showed no significant effects of drying conditions on pasta brownness as measured by the brightness and the dominant wavelength value, except a slight decrease in the brightness of spaghetti dried at high temperature.

Using a larger set of samples including 'brown' and 'bright' varieties, Abecassis *et al.*<sup>61</sup> found that pasta brownness is not affected by the drying conditions (at low, medium and high temperature)

**Table VIII** Effect of drying at low, medium and high temperature on pasta brownness (nine durum wheat varieties and two commercial semolina)<sup>61</sup>

Drying temperature	37 °C (low)	70 °C (medium)	90 °C (high)
Z11	30.2	30.7	30.4
Cando	31.2	31.9	30.5
Kidur	31.6	31.5	31.9
Mondur	31.9	31.7	31.8
Tomclair	32.7	32.3	31.9
Capdur	33.0	33.6	33.8
Tomclair	33.0	33.4	33.1
Cando	33.5	33.2	31.5
Agathé	33.9	34.4	33.8
SSSE 1 (South France)	35.1	35.3	34.8
SSSE 2 (North France)	35.9	35.6	34.6
Mean	32.9	33.1	32.56
Standard deviation	1.7	1.6	1.6

Low temperature: 30 h at 37 °C

Medium temperature: 10 h at 70 °C

High temperature: 90 min at 90 °C

(Table VIII). In this work, the high temperature was applied at the beginning of the drying cycle in conditions which were not optimum for the development of the Maillard reactions. This could explain why the brightness was not affected.

De Stefanis and Sgrulletta<sup>62</sup> and D'Egidio and Pagani<sup>11</sup> also reached the conclusion that brownness was not affected by drying temperature.

### PHYSICO-CHEMICAL BASIS OF BROWNNES

Pasta brownness may arise from naturally coloured brown molecules present in the endosperm or in the outer layer of the kernel, enzymatic reactions (polyphenol oxidases and, possibly, peroxidases),



**Table IX** The ash content, pasta brownness and water soluble absorption at 400 nm of commercial semolina streams<sup>13</sup>

	Ash content % db	Pasta brownness	Absorption 400 nm
3 <sup>rd</sup> break semolina	0.61	9.2	0.102
4 <sup>th</sup> break coarse semolina	0.79	11.6	0.165
4 <sup>th</sup> break fine semolina	1.18	12.0	0.260
6 <sup>th</sup> break semolina	1.29	13.1	0.298
7 <sup>th</sup> break semolina	1.43	13.8	0.375
Scratch semolina	1.86	16.3	0.560
Exhaust flour	2.77	20.3	0.400
Low grade flour	3.15	26.0	0.550

and non-enzymatic reactions. These possibilities have stimulated specific investigations.

### Brown-coloured compounds

According to Matsuo and Irvine<sup>21</sup>, water extracts of semolina which produce brownish macaroni are invariably reddish brown, whereas extracts of semolina which yield bright macaroni are generally very pale yellow. Moreover, the colour of macaroni processed from the good colour quality variety, Mindum, was not substantially affected by the removal of water-soluble materials (WSM), while the removal of WSM from the poor quality variety, Taganrog, markedly improved its macaroni colour. This finding was confirmed by Walsh<sup>20</sup> and by Matsuo *et al.*<sup>25</sup> who found a highly significant correlation between pasta brightness and the absorption of an aqueous extract of semolina at 400 nm. The influence of cultivar was dominant on the absorption at 400 nm of the water extract<sup>25</sup>.

Studying bread wheat flours intended for the manufacture of Chinese noodles, Miskelly<sup>63</sup> showed that noodle brightness and the content of Matsuo's brown pigment were correlated ( $r=0.47$ ;  $p=0.001$ ), and that the brown pigment content of a single cultivar varied with the location and the year of culture.

Kobrehel *et al.*<sup>13</sup> found a strong correlation between the absorption at 400 nm of the water soluble fraction and the brown indices of semolina streams ( $r=0.81$ ;  $p=0.001$ ) (Table IX).

The component responsible for the brown reddish colour of water extracts was isolated and characterised<sup>21</sup>. It is a basic protein (Table X) which shows an absorption maximum at 400 nm (as well as a typical protein absorption at 280 nm) and has a copper content of 0.4 mg/g. Matsuo

and Irvine<sup>21</sup> suggested that the brownish colour resulted from the reaction of this protein with a reducing agent in the presence of copper, and claimed that this type of reaction was responsible for the inherent brownness of certain varieties of durum wheat. Interesse *et al.*<sup>64</sup> determined the amino-acid composition of a wheat *o*-diphenolase of wheat (Table X), which is also a copper protein. With the exception of the tryptophan content, of which the accuracy of determination was dubious in the sixties, the amino-acid compositions of these two proteins were very similar, suggesting that they are related, if not identical. The content of basic (lysine, arginine, histidine) and hydrophobic

**Table X** Amino-acid compositions (residues per 10 000 MW) of the Matsuo reddish water soluble protein P1<sup>21</sup> and of wheat *o*-diphenolase P2<sup>64</sup>

Amino-acid	P1	P2
Tryptophan	0.1	1.0
Lysine	3.3	5.2
Histidine	1.7	1.7
Arginine	4.0	3.5
Aspartic acid	6.4	9.4
Threonine	3.5	5.2
Serine	4.5	7.7
Glutamic acid	11.2	10.4
Proline	5.8	6.3
Glycine	6.8	8.3
Alanine	6.6	7.7
Cystine	3.2	2.8
Valine	5.0	5.6
Methionine	1.1	1.4
Isoleucine	2.8	3.5
Leucine	5.5	6.6
Tyrosine	2.0	3.5
Phenylalanine	2.4	3.5

(proline, valine, isoleucine, leucine, phenylalanine) residues of the wheat *o*-diphenolase are 11.4 and 27.7% respectively, compared to 13.5 and 32.1% in the Matsuo basic protein (Mbp).

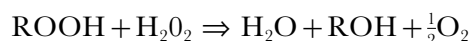
While paper chromatography analysis showed that phenols were not associated with this 'copper protein'<sup>21</sup>, the possibility that Mbp is the product of reactions between polyphenol oxidases (PPO) and their substrates during kernel maturation cannot be ruled out. The work of Kruger<sup>65</sup> on the change of PPO activity during kernel maturation provides some evidence to support this hypothesis (see below). Moreover, this is consistent with the statement of McCallum and Walker<sup>66</sup> that a relationship could exist between bran pigmentation and *o*-diphenolase activity.

### Oxidases

Lipoxygenase, peroxidase, polyphenol oxidase and catalase activities are related to pasta colour and cooking behaviour. The roles of peroxidase and polyphenol oxidase in the discoloration of pasta and Chinese noodles have been particularly studied<sup>67</sup>.

#### Peroxidases

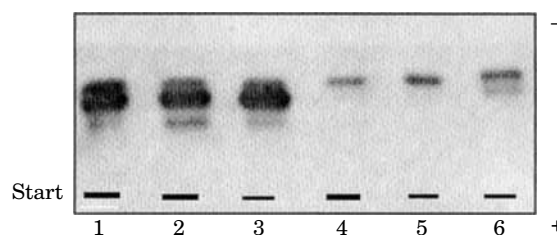
Peroxidases are enzymes catalysing the general reaction:



Peroxidases are not specific in their reactions, and catalyse the oxidation of a large number of phenols and aromatic rings which occur naturally in plant tissues. They appear to be the most stable enzymes in plants (it is generally accepted that if peroxidase is destroyed, then it is unlikely that other enzymes will have survived)<sup>68</sup>.

By analysing 56 durum samples made of seven cultivars (Mediterranean and North American types) grown in different locations, Kobrehel *et al.*<sup>69</sup> found a high correlation ( $r=0.840$ ;  $p=0.01$ ) between pasta brown indices and peroxidase activity. This finding stimulated new studies on the composition and properties of durum wheat peroxidases.

The peroxidase composition of bread wheats, as determined by polyacrylamide gel electrophoresis (PAGE) at pH=8.6, depends on genetic characteristics and is not modified by growing conditions. Eight peroxidase isoenzymes were detected in PAGE (pH=8.9), two of which migrated toward the cathode at pH 8.9, Honold and Stahmann<sup>70</sup>



**Figure 2** Peroxidase PAGE (pH=8.6) patterns of durum wheat varieties: (1) Bidi 17; (2) Montferrier; (3) Agathé; (4) Lakota; (5) Wells; (6) Leeds<sup>72</sup>.

and six cathodic bands, Kobrehel and Gautier<sup>71</sup>. By analysis of nulli-tetrasomic lines, it was shown that genes on chromosomes 7D, 4B and 7A encode the two faster and the major peroxidases, respectively. In durum wheat, three isozymes were identified in the Mediterranean varieties Bidi 17, Montferrier and Agathé, while varieties Lakota, Mandon, Leeds and Wells have only two, one major (the fastest moving) and one minor<sup>69,72</sup> (Fig. 2). The total peroxidase activity of the grains is about eight times higher in the first group of durum wheat varieties than in the second<sup>73</sup>.

Kruger and LaBerge<sup>74</sup> found that most durum wheat varieties had major peroxidase isozymes with identical electrophoretic mobilities (PAGE pH=4.75) but some variation was present in the less intensely stained peroxidase isozymes of lower mobility. No variation in peroxidase isozyme pattern was observed in a variety grown at different locations.

The two major durum wheat peroxidases were isolated and their amino-acid composition determined by Jeanjean *et al.*<sup>75</sup>. The  $\text{Ca}^{2+}$  ion was shown as an activator of both isozymes. Two cathodic peroxidases purified by Iori *et al.*<sup>76</sup> by ion exchange chromatography are polypeptides of 39.7 and 38.6 kDa, respectively, with pHi above 9.3. Both are strongly activated by the calcium ion.

Up to 12 peroxidase enzymes are present in different parts of immature wheat kernels, and varied in quantitative amounts throughout kernel development, maturation and germination. Isozymes present in the pericarp and the green tissues decreased in intensity as the kernel matured, with those present in the aleurone, endosperm, scutellum and embryo increasing slowly<sup>74,77</sup>.

According to our own work, the peroxidase activity of durum wheat semolina (expressed as

**Table XI** Semolina peroxidase activities of durum wheat varieties grown in several locations

Varieties locations	Ixos	Ardente	222	Acalou	Néodur	126
Montpellier	3703	2713	2902	399	341	275
Castelnaudary	3966	2696	2852	305	337	267
Auzeville N	2444	1875	2082	269	318	245
Auzeville N-40	2743	2134	2062	270	301	236
Oraison N	2555	1786	2046	268	277	205
Oraison N-40	2108	1297	1739	235	228	155
Mean	2920	2084	2281	291	300	231
Standard deviation	743	552	479	57	43	45

All values are in absorbance units at 465 nm per gram and per minute. N and N-40 are two dosages of N fertiliser.

**Table XII** Peroxidase activities of durum wheat milling streams

Products	Peroxidase
1 <sup>st</sup> break semolina	101
2 <sup>nd</sup> break semolina	277
3 <sup>rd</sup> break semolina	139
4 <sup>th</sup> break semolina	208
5 <sup>th</sup> break semolina	408
6 <sup>th</sup> break semolina	837
Total semolina	257
Coarse bran	218
Fine bran (purifiers)	440
Fine bran (scratched rolls)	591
Middlings	1054

All values are in absorbance units at 465 nm per gram and per minute.

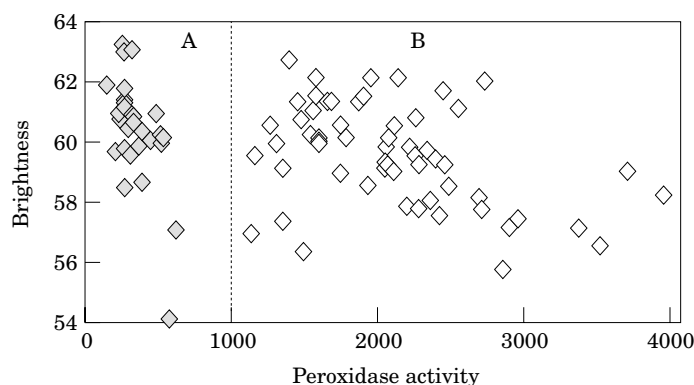
absorbance units at 465 nm per gram and per minute) is genetically determined and influenced by the environmental factors (Table XI). Accordingly, durum wheat cultivars can be classified into two main families according to their peroxidase activities.

Peroxidase activity was found five to be 13 times higher in bran than in bread wheat flour<sup>70</sup>. It was found that the peroxidase activity of durum wheat milling streams increases with the advancement of the milling process, from the 1<sup>st</sup>–3<sup>rd</sup> break semolina to the fine brans and middlings (Table XII). These data suggest that the aleurone layer is particularly rich in peroxidases, as in many other enzymes. When comparing peroxidase activity and brown indices of commercial semolina streams, Kobrehel *et al.*<sup>13</sup> demonstrated a high positive correlation ( $r=0.97$ ;  $p=0.01$ ) between the two characteristics.

In pasta dried at high temperature, the total peroxidase activity decreased, and the composition of isoperoxidases, as revealed on polyacrylamide gel electrophoresis, underwent various modifications<sup>78</sup>.

Despite strong correlation between pasta brownness and semolina peroxidase activities found by Kobrehel *et al.*<sup>69</sup>, and its confirmation by Taha and Sagi<sup>79</sup> who analysed six cultivars grown in one location for three years, it is unlikely that the semolina peroxidase plays a significant role, if any, in pasta brownness development. The following arguments support this assumption: as in bread-making<sup>80</sup>, the action of peroxidases during pasta processing is uncertain because the formation of hydrogen peroxide, their primary substrate, is questionable; while the content of peroxidase in semolina is important in some durum wheat varieties, little or no effects was noted on the brownness value of pasta during drying, when it would be expected that an enzymatic reaction would be sensitive to humidity and temperature of the products. Indeed, the fact that the brownness intensity is independent of the temperature applied during pasta manufacturing suggests that the principal causes of brownness do not have an enzymatic origin; pasta brownness is highly correlated to semolina brownness, indicating that enzymatic browning is at most a secondary phenomenon in the development of pasta brownness; peroxidase activity is mainly dependent on genetic factors, contrary to pasta brownness which mainly depends on environmental factors.

This assumption is strengthened by the poor correlation that we found between the peroxidase activity and the pasta brightness of a set of the 136



**Figure 3** Peroxidase activity and pasta brightness of 86 durum wheat semolina samples.

line described above ( $r = -0.37$  and  $r = -0.40$ , respectively) and of a set of 86 semolina samples isolated from 15 varieties grown in six locations ( $r = -0.37$ ) (Fig. 3). Even when grouping the samples of the latter set according to their peroxidase activity (group A with PO activity inferior to 1000; group B with PO activity superior to 1000), the correlation coefficients were only slightly improved ( $r = -0.6$  and  $r = -0.4$ , respectively).

The discrepancy between this conclusion and the work of Kobrehel *et al.*<sup>69</sup> may be explained by the fact that the samples examined in 1972 were representative of a limited numbers of durum wheat varieties, three Mediterranean and four American types. It is suspected that the relation found in 1972 was due to a genetic linkage, and not to a functional one. Similarly, it was demonstrated<sup>81</sup> that the high correlation between gluten tenacity and pasta brownness found by Grignac<sup>105</sup> was due to the specific background of the cultivars examined in his study.

### Polyphenol oxidases

Polyphenol oxidases (PPO) catalyse the oxidation of phenolic compounds in presence of molecular oxygen. They occur widely in plants and cause enzymatic browning in food material through an initial oxidation of phenols into quinones. Quinones readily undergo self-polymerisation or condensation with amino acids or proteins via their amino groups to form complex brown polymers<sup>82</sup>.

Polyphenol oxidase was partially purified from the bran fraction of mature grains of tall and dwarf varieties of wheat. The specific activity of the enzyme in dwarf wheats was distinctly higher than in tall varieties<sup>83</sup>. Interesse *et al.*<sup>64</sup> purified and characterised a *o*-diphenolase of wheat flour (Table

X). The optimum pH for wheat flour *o*-diphenolase was found to be around pH = 8.6 by McCallum and Walker<sup>66</sup>. Interesse *et al.*<sup>84</sup> found two maxima, at pH = 6.9 and pH = 5.3.

Studying U.S. and Australian wheats grown in the U.S.A. and in Australia, Baik *et al.*<sup>32</sup> found that the PPO activity was affected by the cultivar and growing location. For a single cultivar, small kernels contained less PPO than did large kernels and PPO activity correlated with grain protein ( $r = 0.571$ ;  $p = 0.1$ ) and flour protein flour ( $r = 0.832$ ;  $p = 0.001$ ). Durum wheats have significantly lower polyphenol oxidase<sup>85</sup> and tyrosinase activities<sup>86</sup> than bread wheats but there are overlaps in tyrosinase activities between the two species. Differences in substrates specificity have been noted between bread wheat varieties<sup>65</sup>. According to Park *et al.*<sup>87</sup>, growing locations contribute more to variation in flour PPO activity than does variation among genotypes for hard bread wheat, the converse of what we have observed with durum wheat peroxidases.

Numerous studies have indicated that high levels of PPO in the grain endosperm of bread wheat have a deleterious effect, causing discoloration of chapatties<sup>88,89</sup> and oriental noodles<sup>31,90</sup>. A strong correlation between *o*-diphenol oxidase activity and flour colour grade (Kent-Jones test) was found by McCallum and Walker<sup>66</sup>; nevertheless, Park *et al.*<sup>87</sup> found that the correlation of flour L value with flour PPO activity in both white and red wheat samples was not significant. However, these results are not contradictory because water must be added to flour (as in the Kent-Jones test) to allow the development of enzymatic browning.

Several reports imply a role for polyphenol oxidases in pasta brownness. For instance, Menger

**Table XIII** Polyphenol oxidase activity (PPO) of semolina and granulars, and brightness and dominant wavelength (DWL) of spaghetti processed from semolina and granulars<sup>54</sup>

Durum wheat Products	N° 1 CWAD				Ontario Durum			
	Semolina		Granulars <sup>a</sup>		Semolina		Granulars	
PPO, units/g	23	9	25	11	8	6	16	9
Brightness%	49.7	50.2	48.3	49.8	35.8	39.1	33.6	38.8
DWL, nm	577.3	576.6	577.4	576.9	581.1	579.6	582.2	580.1

<sup>a</sup> semolina and flours combined.

*et al.*<sup>91</sup> showed that flavones could be partially oxidised by polyphenol oxidases during pasta processing, causing the formation of brown components. Kobrehel *et al.*<sup>69</sup> found that pasta brownness was related to PPO activity when activities were determined by densitometry of stained isozymes previously separated by PAGE, but no relationship were found when activities were determined by spectrophotometric analysis of coloured compounds formed in the presence of catechol. However, comparing two milling process, Dexter *et al.*<sup>54</sup> concluded that, because of the low level of PPO found in semolina, it was unlikely that PPO activity was a major factor determining spaghetti colour, at least under their experimental conditions (Table XIII). The correlation coefficient between PPO activity and brightness was 0.395. In the same way, no correlation could be found by Kruger<sup>65</sup> between the PPO isozyme composition of durum wheat and brownness. The PPO activity would be too low in purified semolina to influence the pasta brownness value and in these products pasta brownness would be almost exclusively dependent on inherent brownness of the semolina.

Polyphenol oxidase activities were determined at various stages in the growth and maturation of durum wheat kernels by Kruger<sup>65</sup>. PPO activity initially appeared during early kernel growth, remained throughout development, and then decreased to a low level on kernel maturation. Polyacrylamide-slab electrophoresis of immature kernel extracts indicated that up to 12 PPO isozymes were present, located in different parts of the kernel. Upon germination, PPO activity increased. Grain dissection indicated that a large part of the PPO in the immature wheat kernel was present in the endosperm. As phenolic compounds are abundant in immature endosperm, we propose that the action of PPO on these phenols

**Table XIV** Polyphenol oxidases levels in mill streams of the bread wheat cultivar Glenlea<sup>92</sup>

Stream	PPO level
B1	299
B2	189
B3	133
B4	339
S1	25
S2	12
M1	22
M2	45
M3	55
M4	66
M5	127
M6	122
Shorts duster	1401
Bran flour	366

B1–B4 = first through fourth breaks, S1–S2 = first and second sizings, M1–M6 = first through sixth middlings. All values are in nmol of O<sub>2</sub>/min/g.

could lead to the formation of quinonoid compounds and be at the origin of the inherent brownness of the endosperm.

The amount in PPO of bread wheat flour depends on the way the bread wheat is milled<sup>70</sup>. Hatcher and Kruger<sup>92</sup> have determined polyphenol oxidase (PPO) levels in individual and pooled millstreams of five Canadian bread wheat cultivars. Enzyme activity increased with increasing bran contamination in the millstreams (Table XIV). Less than 10% of the total grain PPO activity was present in cumulative flour streams corresponding to 70% extraction, after which the amount of the enzyme rapidly increased. PPO activity was

linearly correlated with ash content (up to 2.0% ash). Their results confirmed those of Marsh and Galliard<sup>93</sup> showing that PPO is closely associated with the outer layers of the grain. According to Baik *et al.*<sup>32</sup>, wheat flour contains on the average 3% of the PPO of the wheat grain.

If the PPO activity is distributed in the different regions of the durum wheat grain as it is in bread wheat grain regions, PPO might be involved in pasta brownness when semolina is contaminated by outer regions of the grain. In this case (i.e. poor purification of semolina and high extraction rate), the development of brownness would be partly related to enzymatic reactions, and so sensitive to humidity and temperature (i.e. to pasta processing and drying conditions). However, whether such brownness results from the inherent brownness of milling streams or from the action of polyphenol oxidase is not known. Work is in progress in our laboratory to test this hypothesis.

#### *Effects of inhibitors and substrates of oxidases*

According to Kobrehel *et al.*<sup>13</sup>, addition of oxidase inhibitors such as thiourea (300 ppm) or ascorbic acid (300 ppm) prevents pasta from browning during processing. However, Irvine<sup>94</sup> reported that ascorbic acid, at a fairly high concentration (350 ppm), reduced yellow pigment losses, but caused browning in macaroni. These findings were confirmed by Matsuo and Irvine<sup>21</sup> but Menger<sup>95</sup> found that adding ascorbic acid had little effect on brownness. Ascorbic acid at the 500 ppm level retarded discoloration of Asian noodles<sup>31</sup>. The addition of citric acid diminished the brown indices value<sup>13,96</sup>. The action of L-ascorbic acid was confirmed by Walsh *et al.*<sup>97</sup> who showed that L-ascorbic is a fully competitive inhibitor of wheat lipooxygenase.

Conversely, the addition of catechol (250 ppm), which is easily oxidised, increases the development of brownness<sup>13</sup>. Furthermore, the addition of phenol L-tyrosine, DL-dihydroxyphenylalanine (dopa), catechol and chlorogenic acid results in discoloration of chapatties<sup>98</sup>.

### MAILLARD REACTION

The products of the Maillard reaction or non-enzymatic browning are the result of very complex reactions between the free amino groups of amino acids and reducing sugars which ultimately give rise to brown 'melanoidin pigment'. They cause

a reduction in nutritive value of foods and the development of specific tastes and colours. Menger<sup>99</sup> was the first to suggest that nonenzymatic browning in pasta could easily result from condensations involving soluble carbohydrates.

The Maillard reaction can occur in pasta dried at high temperature and is related to the amount of furosine, a sensitive marker of the first stage of the reaction, and of lysylpyrrolaldehyde in dried pasta<sup>10</sup>. It causes a loss of available lysine<sup>100</sup>. The Maillard reaction was enhanced when the drying cycle includes temperature close to 80 °C or higher, and when pasta moistures values were close to 15% or lower<sup>10</sup>. Therefore, pasta browning (100 -L) is easily promoted by drying cycles including high temperature with low moisture content. Simultaneously, the value a (or redness) increased<sup>59,101</sup>.

The content of reducing sugars in paste semolina is a key factor of the intensity of the Maillard reaction<sup>10</sup> and is related to the semolina particle size<sup>102</sup>. The higher maltose content and the temperature at the final stage of the drying diagram, the greater the intensity of the Maillard reaction. Therefore, it is recommended to use low starch damaged semolina with minimal amylolytic activity.

### GENERAL DISCUSSION AND SUGGESTIONS FOR FUTURE RESEARCH

Pasta brownness is the result of a combination of wheat characteristics (variety, growing conditions), milling (tempering, extraction rate) and pasta drying conditions. The influence of cultivar on brownness is not as dominant as the influence of growing conditions (year, location, fertilization). The negative relationship between protein content and brightness, indicative of increased dullness and a tendency to browning, is highly significant, but has not yet been explained.

Pasta brownness has been attributed to a brown-coloured molecule in the endosperm, to enzymatic reactions, to Maillard reactions and to bran contamination.

Before the use of high temperature drying, Irvine<sup>26</sup> distinguished two types of brownness: inherent brownness of the endosperm and the brownness resulting from high extraction levels, and stated that the latter may be due at least partially to enzyme action. If a brownish discoloration develops during processing, it may be

attributed to oxidative reactions. Thus, differences in brownness between spaghetti are due either to differences in the colour of semolina resulting from differences in wheat quality or in extraction rate<sup>60</sup>, or both.

With the development of high temperature drying, the factors likely to influence the value of pasta are the value of endosperm brightness (or of inherent brownness of semolina)—the most important parameter in the case of semolina scarcely contaminated by the peripheral parts of the grain—and of brownness related to the extraction rate of semolina and drying of pasta. The following equation accounts for the brightness of the pasta products:

$$\text{Pasta brightness} = f [( \text{brightness of endosperm} ) - ( \text{brownness related to the rate of extraction} ) - ( \text{brownness related to the development of Maillard reaction} )]$$

'Endosperm brightness', a varietal characteristic, depends mainly on the conditions of grain development and decreases when the protein content increases. According to Matsuo and Irvine<sup>21</sup>, brownness arising from varietal characteristics of durum wheat is due to a water-soluble protein which exhibits an absorption maximum at 400 nm; this component is associated with copper. Therefore, the absorption of the water extract is related to the brownness of semolina<sup>25</sup>. Kobrehel *et al.*<sup>13</sup> suggested that the semolina brownness (equivalent to the inherent brownness of Irvine<sup>21</sup>) could be due to the action of oxidising enzymes which would take place during the kernel maturation. It needs to be determined whether the Matsuo's brown protein (Mbp) is a complex formed during grain maturation between PPO and their substrates. Under these conditions, endosperm PPO would not be in an active form.

The main arguments in favour of this hypothesis are the following: PPO activities in endosperm are substantial during grain maturation before decreasing to almost zero in the mature endosperm; grain maturation is accompanied by a marked decline in phenolics and flavanols, presumably due to the breakdown of cellular structure which would allow oxidizing reactions to take place<sup>66</sup>; the amino-acid composition of wheat PPO<sup>64</sup> and of Matsuo's protein are almost identical; bran pigmentation was considered to be produced by the action of *o*-diphenolase on flavanols<sup>103</sup>. A similar phenomenon could occur in the endosperm during grain maturation.

In further studies, it would be interesting: (a) to confirm the existence of a relationship between semolina brownness and the Mbp content of semolina (endosperm); (b) to elucidate the varietal and environmental effects on the Mbp content of semolina; (c) to explain why an increase in protein content of the grain results in a reduction in brightness; (d) to follow the evolution of PPO activity and Mbp content during grain maturation (comparisons between browning and non browning varieties would be useful); (e) to determine the physicochemical properties of Mbp.

If the role of Mbp is not confirmed, the origin of the inherent endosperm brownness would still need to be identified.

'Pasta brownness related to the rate of extraction' (PBRE) increases with the extraction rate of semolina. It might be related to the natural brown colour of kernel peripheral tissues (brans) and to semolina PPO activity, which might increase, as in bread wheat flour, as semolina is contaminated by outer histological layers of the grain rich in PPO.

With identical extraction rate, semolina PPO activity, and thus PBRE, would depend on the amount of PPO in the grain; on the distribution of the kernel PPO activity amongst the various histological parts of the grain (this could be a genetic characteristic); and on the ease to dissociation and separation of the various histological outer layers of the grain from the endosperm during milling, mainly the aleurone layer. Brownness would also depend on the colour, amount and size of contaminant bran particles.

PBRE, which might result from an enzymatic activity, should depend on the pasta manufacturing conditions (i.e. evolution of water activity and temperature values in the products; but also the pH and the oxygen concentration). Differences in PBRE values could also be explained by differences in the composition of phenolic compounds in the semolina. To our knowledge, there are no experimental data to support this assumption and the statement by McCallum and Walker<sup>66</sup> that bread wheat grains contain relatively low levels of oxidisable phenolics and that few, in any, *o*-diphenols are present deserves consideration.

It would be thus interesting (a) to determine the relations between PBRE values and PPO activities of the semolina at variable extraction rate; (b) to determine the evolution of PPO activity of the milling streams according to their histological origin and to determine the genetic and en-

vironmental effects on this distribution; (c) to examine the influence of the conditions of pasta manufacturing on PBRE values at different level of PPO activity; (d) to compare the inherent brownness of milling streams isolated from durum wheat cultivars of different genetic origin.

'Pasta brownness related to Maillard reactions' is reduced by milling durum wheat with low amylolytic activity, preventing the formation of damaged starch during milling, and avoiding the utilisation of high temperature at the end of the drying cycle.

To improve pasta brightness, the breeder would primarily aim to decrease the inherent semolina brownness and to break the relationship between brownness and protein content (aiming to breed durum wheat varieties with high colour and high cooking quality scores); and as a second aim, to decrease the polyphenol oxidase activity of the peripheral parts (aleurone and branny layer) of the kernel and/or the inherent brownness of milling streams to avoid pasta discoloration when the semolina purification is incomplete. The paucity of knowledge on the composition of wheat phenolics and the possibility of greater variability in *o*-diphenolase than in phenolic content<sup>66</sup> make breeding work aimed at modifying the phenolic composition of durum wheat endosperm more difficult.

Millers should avoid bran and aleurone layer contamination of semolina by optimal setting of the mill machines, mainly purifiers. Pasta manufacturers should control carefully the drying process parameters to avoid the development of the Maillard reaction when high temperature cycle is used.

### Acknowledgement

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