Chapter 6

# Browning Reactions in Foods

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## I. INTRODUCTION

Browning reactions in food are widespread phenomena which take place during processing and storage. These reactions occur during the manufacture of meat, fish, fruit, and vegetable products, as well as when fresh fruits and vegetables are subjected to mechanical injury. Browning affects the flavor, appearance, and nutritive value of the food products involved. However, for certain foods, browning is an important part of the preparation process. For example, in the manufacture of coffee, tea, beer, and maple syrup, and in the toasting of bread, it enhances the appearance and flavor of these products. Browning, to a limited degree, is considered desirable in apple juice, potato chips, and French fries. To control or inhibit these reactions it is important to understand the mechanisms involved.

Three browning mechanisms appear to be involved in foods, as shown in Table 6.1. Ascorbic acid browning can proceed either by the enzyme ascorbic acid oxidase or by direct atmospheric oxygen and oxidation of ascorbic acid.

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**TABLE 6.1** Mechanisms of Browning Reactions

| Mechanism | Requires Oxygen | Requires Amino Group in Initial Reaction | pH Optimum |
|---|---|---|---|
| Maillard | − | + | Alkaline |
| Caramelization | − | − | Alkaline, acid |
| Ascorbic acid oxidation | + | − | Slightly acid |

## II. NON-ENZYMATIC BROWNING

During the preparation and processing of foods, one soon becomes acquainted with the phenomenon of browning associated with heated and stored products. This phenomenon, referred to as non-enzymatic browning, distinguishes it from the enzyme-catalyzed reactions described in Chapter 10. The importance of this reaction in the production of foods is amply illustrated by its contribution to the flavor, color, and aroma of coffee, caramel, bread, and breakfast cereals. Careful control must be exercised to minimize excessive browning, which could lead to unpleasant changes in the food product. In recent years there has been considerable focus on the deleterious effects of non-enzymatic browning reactions in food (Nursten, 2005). Of particular concern is the toxicity and potential mutagenicity of some of the intermediates formed (Aeschbacher *et al.*, 1981; Lee *et al.*, 1982; Sugimura *et al.*, 1988; Mottram *et al.*, 2002; Tareke *et al.*, 2002; Friedman, 2003). However, not all the intermediates formed are deleterious as some appear to exert considerable antioxidant activity (Yamaguchi and Fujimaki, 1974; Kawashima *et al.*, 1977; Lingnert and Eriksson, 1980; Eichner, 1981; Lingnert and Hall, 1986; Yen and Hsieh, 1995; Yoshimura *et al.*, 1997; Wagner *et al.*, 2002, 2007; Tagliazucchi *et al.*, 2010a, b).

Since the second edition of this book a large number of papers have been published on non-enzymatic browning systems. Nevertheless, our knowledge of this area remains fragmentary. Current evidence still supports the existence of three major pathways: Maillard reaction, caramelization, and ascorbic acid oxidation.

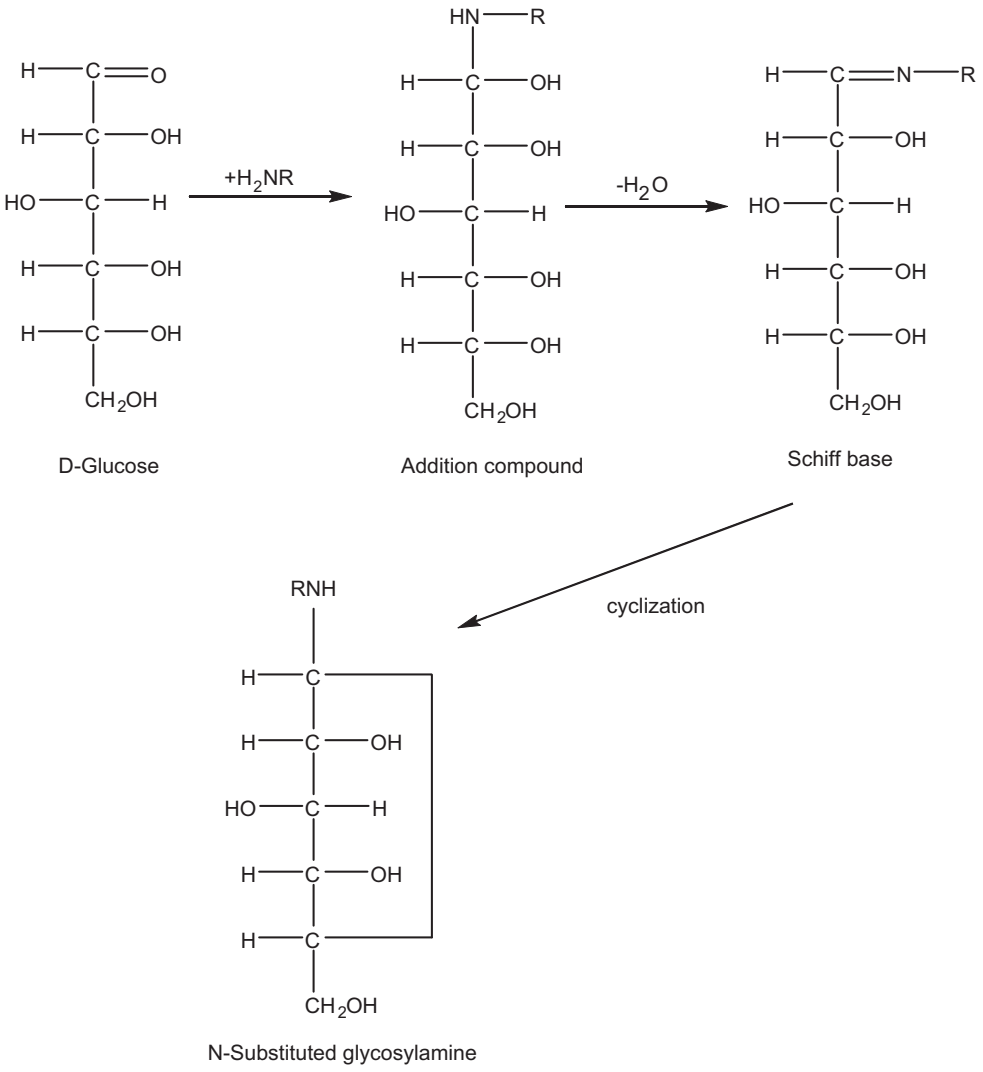
### A. Maillard Reaction

The formation of brown pigments and melanoidins was first observed by the French chemist Louis Camille Maillard (1912) following the heating of a solution of glucose and lysine (Finot, 2005). This reaction was subsequently referred to as the Maillard reaction and essentially covers all those reactions involving compounds with amino groups and carbonyl groups present in foods. These include amines, amino acids, and proteins interacting with sugars, aldehydes, and ketones, as well as with products of lipid oxidation (Feeney *et al.*, 1975; Hidalgo and Zamora, 2004a, b, 2005; Kwon *et al.*, 1965; Montgomery and Day, 1965). The general mechanism of browning was first proposed by Hodge (1953) and subsequently reviewed by Ellis (1959), Heyns and Paulsen (1960), Reynolds (1963, 1965, 1969), Baltes (1973), Namiki (1988), and Ledl and Schleicher (1990). In spite of the volumes of research on this reaction, the original reaction sequence (Scheme 6.1) proposed by Hodge (1953) still remains valid.

The importance of this reaction in living systems has also been the subject of extensive studies over the past 30 years. This reaction can also occur *in vivo*, originally being referred to as non-enzymatic glycosylation, and later as glycation (Tessier, 2010). The random damage to extracellular proteins in the human body, as a result of glycation, has important implications for aging and chronic diseases such as diabetes (Brownlee, 2001).

#### *1. Carbonylamino Reaction*

The first step in the Maillard reaction involves condensation between the α-amino groups of amino acids or proteins and the carbonyl groups of reducing sugars: this defines the carbonylamino reaction. The initial product is an addition compound which rapidly loses water to form a Schiff base followed by cyclization to the corresponding N-substituted glycosylamine:

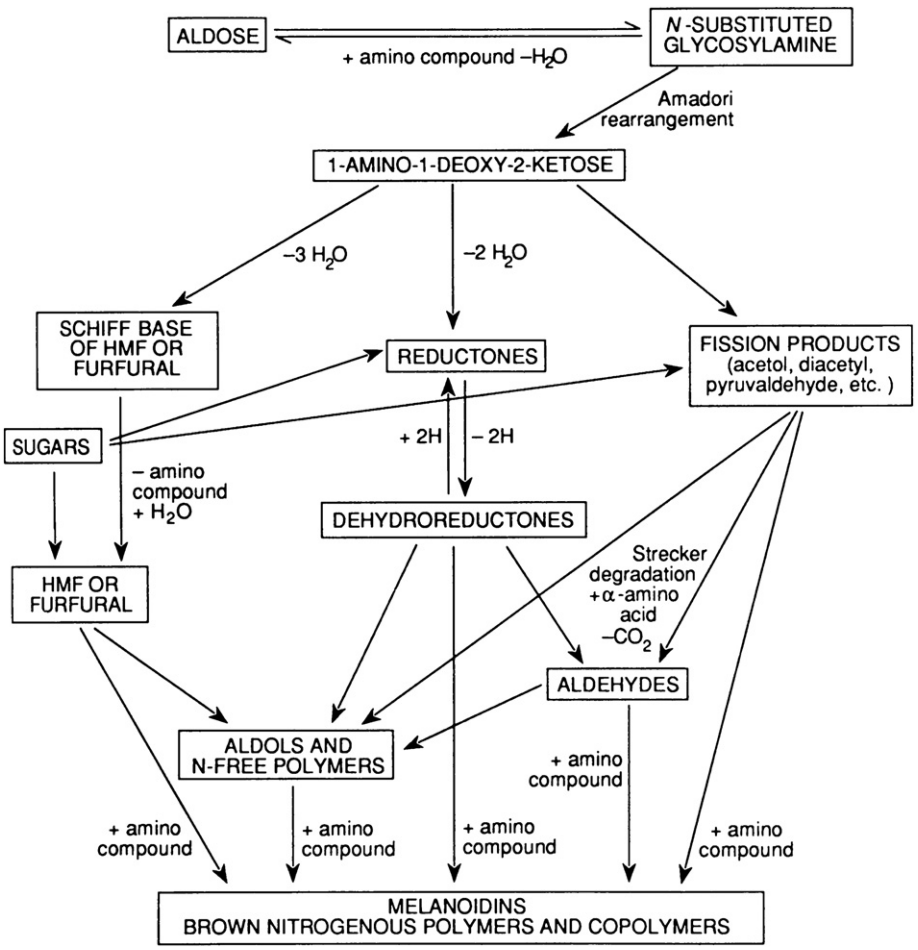



These reactions are all reversible as an equilibrium exists for these compounds in aqueous solution.

## 2. Mechanism of the Carbonylamino Reaction

The formation of the N-substituted glycosylamine involves condensation of the amine group of the amino acid with a carbonyl group of a reducing sugar. This reaction is not necessarily restricted to α-amino acids and can involve the participation of other amino groups found in peptides and proteins. This is facilitated when the pH of the medium is above the isoelectric point of the amino group, thus producing basic amino groups.

The protein molecules are composed of many amino acids joined covalently by peptide bonds, in which the amino acids are presumably unavailable for interaction. Harris and Mattil (1940) observed that lysine provided the majority of free amino groups in proteins, in the form of ε-amino groups, which were the main participant in this reaction. While this is true, other amino acids with additional amino groups could also participate, for example, arginine. As the temperature is increased, many more amino acids are rendered unavailable, which cannot be explained by the cleavage of the peptide bonds, a process which appears to be slight even at fairly high temperatures. Horn *et al.* (1968) found it difficult to explain the rapid and extensive destruction of amino acids in proteins in the presence of sugars simply on the basis of the free amino groups present. A common group such as the imide group of the peptide bond was suggested to be involved, in which the hydrogen of this group was replaced by a carbohydrate moiety. The resulting complex was thought to render the amino acid involved unavailable or prevent enzymatic hydrolysis of the peptide bond itself.



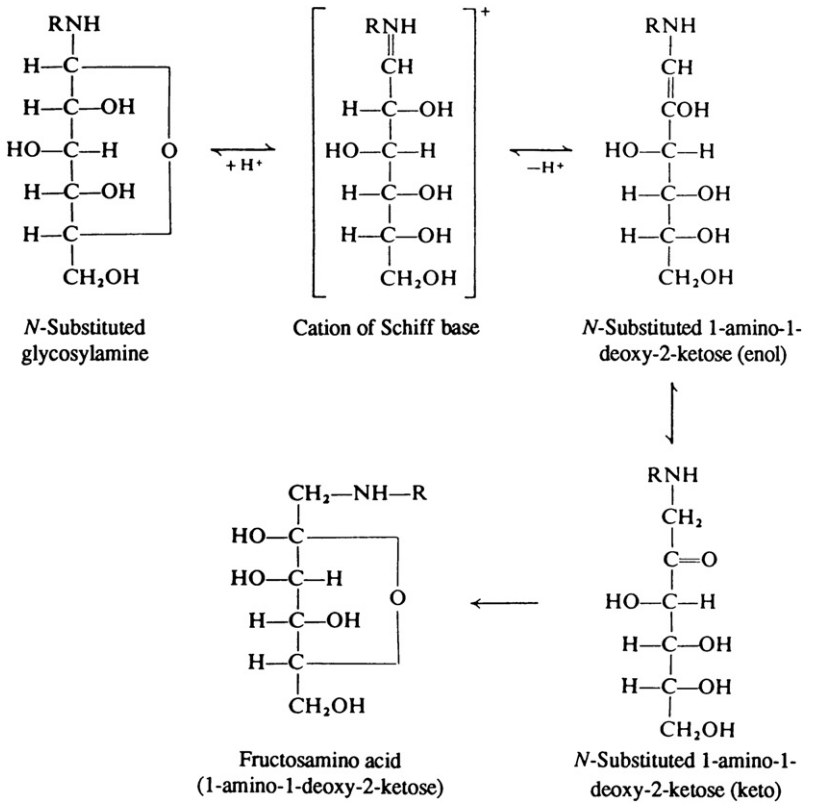

**SCHEME 6.1** Non-enzymatic browning *(based on Hodge, 1952) (Nursten, 1981).*

In addition to the mechanisms discussed here, the possibility of anhydride linkages between carboxylic and amino groups was suggested earlier by Harris and Mattil (1940). It was later proposed that these linkages might arise from the interaction between the ε-amino groups of lysine and free dicarboxylic acids in the protein chain. Patton *et al.* (1954) proposed that such linkages could involve aspartic and glutamic acids in the protein.

Besides proteins, oligopeptides have also been identified in a variety of natural and artificial protein hydrolysates such as seafood, coffee beans, soy, and wheat gluten (Aaslyng *et al.*, 1998; Ludwig *et al.*, 2000). Kim and Lee (2009) found that the Maillard reaction rate was affected by the length of the peptide chain. In particular, the reaction between glucose and diglycine was far greater than with glycine or triglycine. This suggested that the reaction rate may be greatly affected by the extent of hydrolysis of the peptide bond and its stability as the heating time is increased. On the other hand, it has been reported that although the diglycine−glucose mixtures had a higher degree of browning, followed by glycine−glucose and triglycine−glucose, the overall reactivity of peptides for flavor formation was determined to be glycine > triglycine > diglycine (Lu *et al.*, 2005). Thus, chain length could be an important factor affecting the reaction and the formation of Maillard reaction products (MRPs).

### *3. Amadori Rearrangement*

The final condensation product in the carbonylamino reaction is the N-substituted glycosylamine. It soon became evident, however, that this compound was extremely unstable and underwent a series of rearrangements, which explained why the reducing power for a casein−glucose system was of the same order as the original glucose (Lea and Hannan, 1950). These changes involved isomerization of the N-substituted glycosylamine to the corresponding fructose−amino acid. The transition from an aldose to a ketose sugar derivative (Scheme 6.2) is referred to as the




**SCHEME 6.2** Amadori rearrangement.

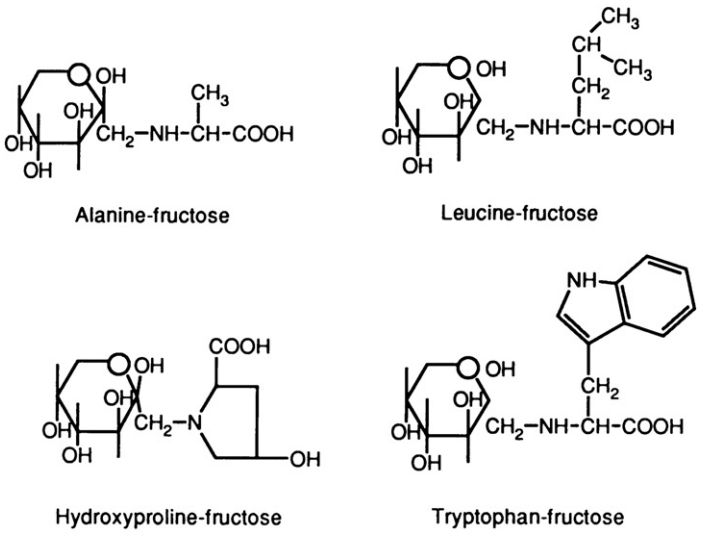
Amadori rearrangement (Weygand, 1940) and involves protonation of nitrogen at carbon 1 (C1). In the case of ketones and amines, ketosylamines are formed which then undergo the Heyns rearrangement to form 2-amino-2-deoxy aldoses (Reynolds, 1965) by protonation of the oxygen at C6 (Kort, 1970).

The Amadori rearrangement has been demonstrated for a series of glucose–amino acid complexes synthesized by Abrams *et al.* (1955). The reactions leading up to the formation of 1-amino-1-deoxy-2 ketone are all reversible. In fact, these products are quite stable and have been identified in freeze-dried peaches and apricots (Anet and Reynolds, 1957), tomato powder (Eichner *et al.*, 1994), soy sauce (Hashiba, 1978), and milk (Finot *et al.*, 1968). Moll *et al.* (1982) isolated and purified a number of Amadori compounds from crude extracts of Maillard reaction systems using high-performance liquid chromatography (HPLC). These included Amadori compounds of alanine–fructose, leucine–fructose, hydroxyproline–fructose, and tryptophan–fructose, the structures of which are shown in Scheme 6.3. Lee *et al.* (1979) followed the development of MRPs during the processing of apricots and found that the level of Amadori compounds reached a maximum prior to the development of any brown color. In foods containing proteins and glucose, one of the Amadori compounds formed is ε-fructosyl–lysine or furosine (Olano and Martinez-Castro, 1996). The most significant consequence of this reaction is the loss of available lysine (Henle *et al.*, 1991a). Milk, with lactose as the major carbohydrate, forms lactulosyl–lysine when heated. Amadori compounds, such as furosine, are used to assess the quality of a variety of food products such as dairy, eggs, cereals, vegetables, tomatoes, infant cereals, honey, and dehydrated fruits (Molnar-Perl *et al.*, 1986; Resmini and Pellegrino, 1991; Hildago *et al.*, 1998; Guerra-Hernandez *et al.*, 1999; Sanz *et al.*, 2000, 2001, 2003). Gokmen *et al.* (2008) showed that the formation of furosine in cookies was highly correlated with the initial water content of the dough under the same baking conditions.

Yaylayan and Locas (2007) recently showed that 4-hydroxy-alkenals can be formed in a non-lipid system from 2-deoxyribose catalyzed by amino acids. These are important, including lipid peroxidation products that can form Schiff base adducts with nitrogen nucleophiles, such as amino acids and proteins, and then undergo vinylogous Amadori rearrangement. While these Amadori intermediates do not contribute directly to browning or flavor, they result in a loss of nutritional value due in large part to the unavailability of the ε-amino group of lysine (Mauron, 1970; Finot and Mauron, 1972; Hurrell and Carpenter, 1974, 1981; Dworschak, 1980; Friedman, 1982; Lee *et al.*, 1982; Plakas *et al.*, 1988).

Amadori compounds readily undergo acid hydrolysis, so several direct and indirect methods of analysis have been developed (Silvan *et al.*, 2006). Early methods for the direct analysis of Amadori compounds used column

**SCHEME 6.3** Amadori compounds. *(Reprinted with permission from Moll* et al.*, 1982. Copyright © by the American Chemical Society.)*




chromatography in an amino acid analyzer (Ellis, 1959; Reynolds, 1959; Moller *et al.*, 1977; Ciner-Doruk and Eichner, 1979; Henle *et al.*, 1991b). This method has since been replaced by HPLC coupled with electrochemical and/or diode array detector. Amadori compounds can also be measured by fast atom bombardment and tandem mass spectrometry (Staempfli *et al.*, 1994). Recently, Davidek *et al.* (2005) developed a high-performance cation-exchange chromatography coupled to tandem mass spectrometry or electrochemical detection as an efficient method for analyzing Amadori compounds derived from hexose and pentose sugars. Indirect measurement of Amadori compounds uses rapid colorimetric or fluorimetric methods (Silvan *et al.*, 2006).

## *4. Conditions for the Maillard Reaction*

### a. pH and Buffers

The carbonylamino reaction can develop in acidic or alkaline media, although it is favored under alkaline conditions, where the amine groups of the amino acids, peptides, and proteins are in the basic form. Increasing the pH also ensures that more of the hexoses are in the open chain or reducing form (Burton and McWeeney, 1963). A higher pH environment intensifies Maillard browning in most instances. More browning was observed in leucine−glucose (Renn and Sathe, 1977), lysine−glucose (Ajandouz and Puigserver, 1999), lysine−fructose (Ajandouz *et al.*, 2001), and proline−glucose (Blank *et al.*, 2003) systems. Similar effects were observed for microwave-irradiated samples (Yeo and Shibamato, 1991a; Zamora and Hidalgo, 1995). When extrusion cooking was used, the effects of pH were temperature dependent. Volatile compounds increased with decreasing pH at 180°C but increased with rising pH at 120°C (Ames *et al.*, 2001). The role of buffers in non-enzymatic reactions has been shown to increase the rate of browning for sugar−amino acid systems as a result of their influence on the ionic environment in which the reaction takes place. For example, Lee *et al.* (1984) monitored the formation of the Amadori compounds monofructosyllysine (MFL) and difructosyllysine (DFL) in glucose−lysine mixtures at different temperatures and pH. Their results, as shown in Figure 6.1, indicate pseudo-first-order plots for MFL and DFL formation, which increased from pH 4 to 8. This pattern was similar to that observed for pigment formation.

A plot of pigment formation as a function of pH, however, showed a parabolic curve with break points at pH 6 and 5 for systems heated at 100°C and 110°C, respectively (Figure 6.2). Using a glycine−glucose model system, Bell (1997) showed that phosphate buffer enhanced the browning rate and loss of amino acid at pH 7 and 25°C while citrate buffer had only a minimal effect. The catalytic ability of the phosphate buffer was attributed, in part, to its ability to act as a base catalyst for Amadori rearrangement.

### b. Temperature

The temperature dependence of this reaction has been demonstrated in a number of quantitative studies, where increased rates were reported with rise in temperature. Lea and Hannan (1949) found that the decrease in free amino

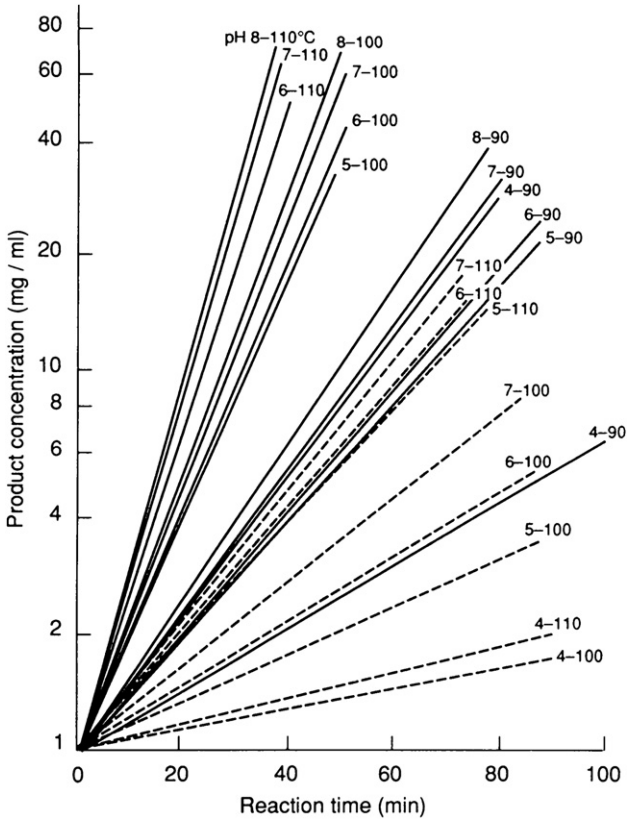



**FIGURE 6.1 Formation of monofructosyllysine (MFL) (—) and difructosyllysine (DFL) (– –) as a function of reaction time at various temperatures and pH.** All lines were drawn for best fit of the data points. *(Reprinted with permission from Lee* et al.*, 1984. Copyright © by the American Chemical Society.)*

nitrogen for a casein–glucose system conformed to the Arrhenius equation over a temperature range of 0–80°C, where a linear relationship existed between the rate of reaction over this range. The α-amino nitrogen loss possessed 29 cal/mole activation energy in the casein–glucose system, while an increase in activation energy from 26 to 36 cal/mole was noted by Hendel *et al.* (1955) during the browning of dehydrated potato products with increased humidity. Using the formation of hydroxymethylfurfural (HMF) as a measure of progress of the Maillard reaction, Dworschak and Hegedüs (1974) noted an increase in the activation energy for lysine from 29.4 to 34.8 cal/mole when milk powder was heated while increasing the humidity from 2.45 to 5.7%. The amount of HMF produced, however, decreased from 43.6% to 34.6%. Hurrell and Carpenter (1974) noted that the loss in ε-amino lysine groups in an albumin–glucose system at 37°C over 30 days was almost equivalent to that in the same system heated at 121°C for 15 minutes. In both cases the loss in ε-amino groups was 80%, thus emphasizing the importance of duration of storage as well as temperature. Horak and Kessler (1981) monitored the loss of lysine residues during the heating of milk at 160°C and described the loss as a second order reaction. A semilog plot of lysine retention during heating of the glucose–lysine model systems at 69°C was shown by Lee *et al.* (1984) to be linear during the first 2 hours, with an extrapolated decimal reduction time *D* (time required for a 90% reduction of lysine at 69°C) of 3.5 hours (Figure 6.3).

More volatile compounds were detected as xylose and glucose were reacted at increasing temperatures (Benzing-Purdie *et al.*, 1985). The high-molecular-weight products formed were characterized by different lengths of aliphatic carbons and fewer unsaturated carbons. A leucine and glucose system also exhibited a greater browning rate at 122°C than at 100°C (Renn and Sathe, 1997). Similarly, mixture of glucose and glycine generated more volatile compounds at elevated reaction temperatures from 100°C to 300°C (Tehrani *et al.*, 2002).

### c. Moisture Content

The Maillard reaction proceeds rapidly in solution, although complete dehydration or excessive moisture levels inhibit this process (Wolfrom and Rooney, 1953). Lea and Hannan (1949, 1950) recorded the optimum moisture level

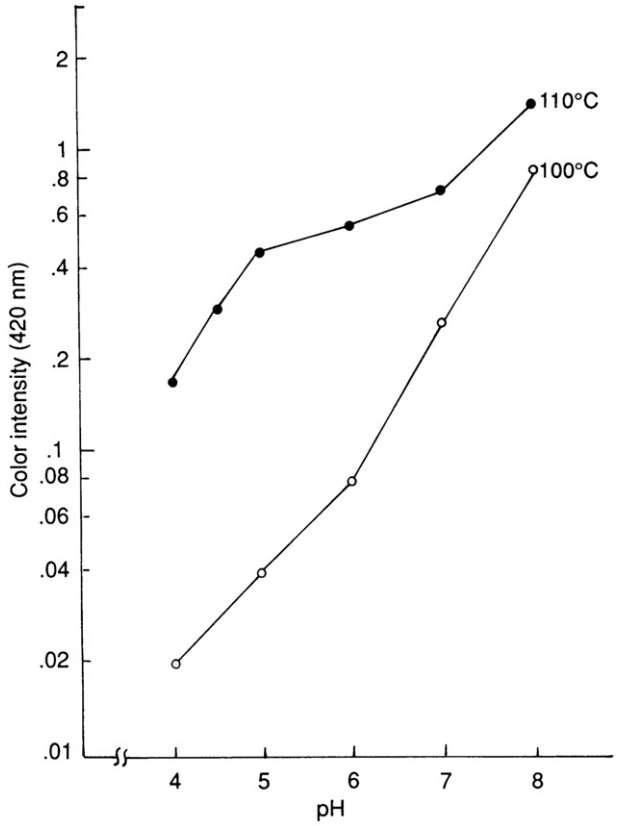



**FIGURE 6.2 Changes in pigment formation as a function of pH.** *(Reprinted with permission from Lee* et al.*, 1984. Copyright © by the American Chemical Society.)*

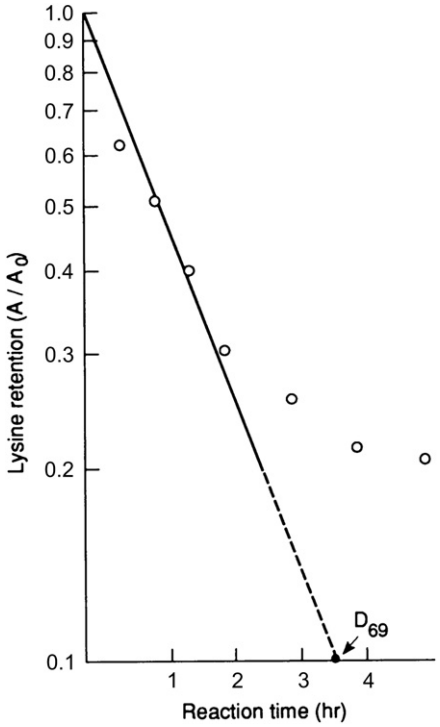



**FIGURE 6.3 Lysine retention as a function of reaction time.** $D_{69}$: time required for a 90% reduction in the concentration of lysine at 69°C. *(Reprinted with permission from Lee* et al.*, 1984. Copyright © by the American Chemical Society.)*

for a casein–glucose system and found that the maximum loss of free amino groups occurred between 65% and 70% relative humidity, which corresponded to a level at which the reactants were still in a comparatively dry state. Loncin *et al.* (1968) monitored browning in milk powder at 40°C as a function of water activity ($a_w$) and lysine over a period of a day. Their results, shown in Figure 6.4, show that the loss of lysine paralleled the extent of browning with a maximum between $a_w$ of 0.6 and 0.7. An increase in humidity was also shown by Dworschak and Hegedüs (1974) to cause an increase in the loss of lysine and tryptophan with the concomitant increase in HMF formation and browning. In general, it appears that this reaction is favored at an optimum moisture content corresponding to fairly low moisture levels (Danehy, 1986).

Investigations into the effect of water on volatile MRPs showed that both quantitative and qualitative changes occurred in the volatile profile of a meat flavor model system with different moisture levels (Hartman *et al.*, 1984a, b). The maximum amount of volatiles was observed at an $a_W$ of 0.72. The kind of major volatiles also differed: sulfur-containing compounds were present in the high water system while dehydration-type products predominated in the low water system. In a glycine–glucose model system, the presence of water drastically increased the amount of volatiles, with furans as the predominant product (Ames *et al.*, 2001). Moisture content also affected the Maillard reaction when microwave heating was used (Yeo and Shibamoto, 1991b; Peterson *et al.*, 1994).

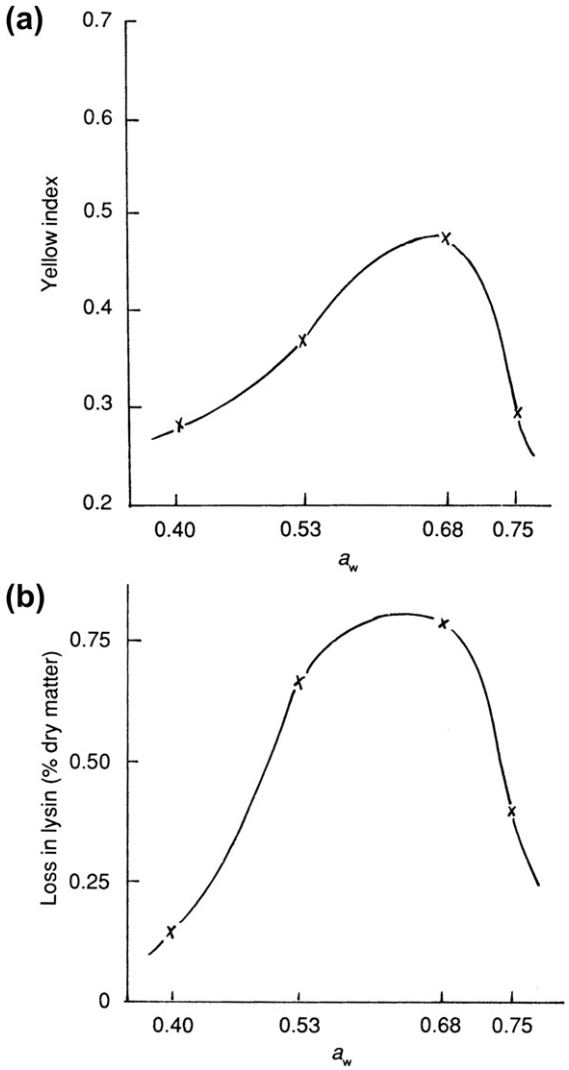



**FIGURE 6.4 (A) Color change and (B) loss of free lysine of milk powder kept at 40°C for 10 days as a function of water activity ($a_w$).** *(Loncin* et al.*, 1968).*

### d. High Pressure

High-pressure processing has gained much attention because of its minimal effect on food flavor and nutrient quality. However, in combination with other factors, high pressure may lead to some flavor variation.

According to Hill *et al.* (1996), the effect of high pressure on the Maillard reaction varied depending on the pH of the medium. In a glucose and lysine system with pH ranging from 7.0 to 7.5, high pressure had insignificant effects. However, at a higher pH, high pressure hastened the Maillard reaction, with the opposite effect observed at a lower pH. This suggested that pressure induced the ionization of the acid groups in the system, resulting in a lower pH and a subsequent rate reduction. This pH dependency on the effect of pressure on the browning reaction was confirmed by Moreno *et al.* (2003).

Pressure could also change the reaction profile of a system. For example, when glucose−lysine solutions (with initial pH 10.1 and incubated at 60°C) were subjected to atmospheric pressure or 600 MPa, significant quantitative differences in the reaction products were observed (Hill *et al.*, 1998). High pressure also enhanced the formation of tetramethylpyrazine under weak acidic conditions (Huang *et al.*, 1996). Moreno *et al.* (2003) indicated that Amadori arrangement products formed more rapidly and subsequently degraded under high pressure, resulting in an increase in intermediate and advanced reaction products.

### e. Pulsed Electric Field and Ultrasound

Using an asparagine−glucose model system, Guan *et al.* (2010a) showed that applying a pulsed electric field at an intensity above 30 kV/cm resulted in a dramatic increase in the formation of MRPs. Guan *et al.* (2010b) also reported that ultrasonic treatment, at high intensities, can be used to promote the Maillard reaction in a glycine−maltose model system. However, the length of time used in their study (100 minutes) for the ultrasonic treatment was impractical for a commercial process, so further studies are needed for this to become a viable process.

### f. Sugars

Reducing sugars are essential ingredients in these reactions, providing the carbonyl groups for interaction with the free amino groups of amino acids, peptides, and proteins. The initial rate of this reaction is dependent on the rate at which the sugar ring opens to the oxo or reducible form. Burton and McWeeny (1963) monitored the concentration of the oxo form of the sugar using polarography and found that it increased with increasing pH. The amount of the oxo form was much higher for pentoses than hexoses, thus explaining the greater reactivity of pentoses in browning systems. This was confirmed by Spark (1969), who found that the order of reactivity was greater for aldopentoses than aldohexoses while reducing disaccharides were considerably less reactive. Tu and Eskin (1973) noted that reducing sugars exerted an inhibitory effect on the hydrolysis of casein by trypsin because of the unavailability of certain essential amino acids resulting from non-enzymatic browning reactions. They found that xylose exerted the greatest inhibitory effect, followed by fructose and glucose. Katchalsky (1941) reported that fructose did not condense with amino acids in dilute solution, although scientists have since confirmed that a definite interaction does take place (Heyns and Breuer, 1958; Heyns and Noack, 1962, 1964). D-Fructose has also been reported by Shallenberger and Birch (1975) and Bobbio *et al.* (1973) to brown at a much faster rate than glucose during the initial stages of the browning reaction, but it then falls behind. This was confirmed by Reyes *et al.* (1982) using model systems containing glucose−glycine and fructose−glycine (1:1 molar ratio) at 60°C, pH 3.5, and held for 280 hours. The fructose system browned at a faster rate during the first 80 hour period but was subsequently taken over by the glucose system. The consumption pattern of glucose and fructose paralleled the rate of browning (Figure 6.5). The difference in losses was attributed to the greater polymerization of the glucose-derived melanoidins as measured by the formation of a haze after 240 hours of storage compared to the fructose system, which remained essentially clear. A similar haze formation was noted for a sucrose−glycine system (1:1 molar ratio) resulting from the hydrolysis of sucrose and the release of glucose.

Using a shrimp hydrolysate, Laroque *et al.* (2008) examined the effect of five reducing sugars (ribose, xylose, arabinose, glucose, and fructose) on the kinetics of the Maillard reaction at 55°C and pH 6.5. The pentose sugars were all more reactive than the corresponding hexose sugars, with ribose being the most active, followed by xylose and arabinose (Figure 6.6).

### g. Metals

The formation of metal complexes with amino acids can influence the Maillard reaction. This reaction was catalyzed by copper and iron, and inhibited by manganese and tin (Ellis, 1959; Markuze, 1963). Inhibition of browning in

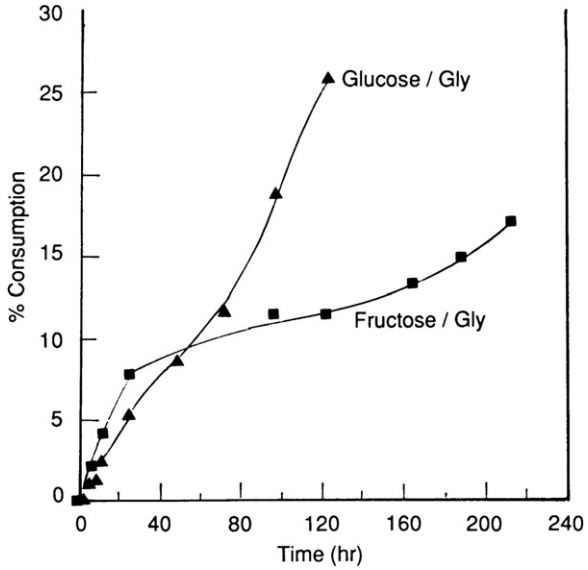



**FIGURE 6.5 Consumption of glucose and fructose in the glucose and fructose–glycine systems during storage at 60°C and pH 3.5.** % Consumption represents the percentage individual sugar lost (Reyes *et al.*, 1982). *(Copyright © by the Institute of Food Technologists.)*

glucose–glycine model systems by trace metals was reported by Bohart and Carson (1955). Using an ovalbumin–glucose mixture Kato *et al.* (1981) examined the effect of $Na^{+}$, $Cu^{2+}$, $Fe^{2+}$, and $Fe^{3+}$ on the rate of browning at 50°C and 65% relative humidity. Figure 6.7 shows that an acceleration of browning occurred in the presence of $Cu^{2+}$ and $Fe^{3+}$, while $Na^{+}$ had no effect. $Fe^{3+}$ was more effective than $Fe^{2+}$ in accelerating the browning reaction, which suggested that the first step was an oxidation activation resulting in a reduction of the metal. The more rapid browning of a dried egg white–solid glucose system was attributed by both Kato *et al.* (1978) and Watanabe *et al.* (1980) to the presence of trace metals in the egg white. In addition to the catalytic effect of iron on the browning reaction (Hashiba, 1979), it was shown that iron also participated as a chromophore of the pigment (Hashiba, 1986). The possible interaction of iron with hydroxypyridone and hydroxypyranone, both capable of chelating iron, in the melanoidin polymer may be responsible for color formation. The presence of these heterocyclic compounds was reported previously by Tsuchuda *et al.* (1976) after the pyrolysis of non-dialyzable melanoidins.

The ability of monovalent and divalent cations to prevent the formation of acrylamide in a fructose–asparagine model system was reported recently by Gokmen and Senyuva (2007). Divalent cations, such as $Ca^{2+}$ and $Mg^{2+}$, were

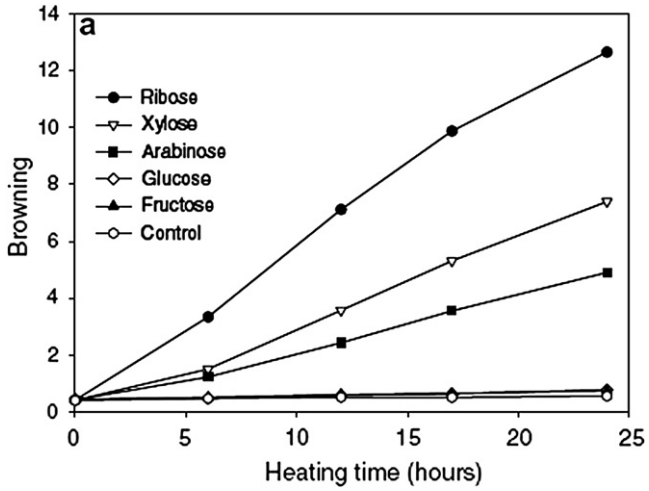



**FIGURE 6.6 Effect of different sugars on the development of browning in a shrimp hydrolysate.** Browning development is expressed as absorbance at 420 nm × dilution factor *(Laroque* et al., *2008).*

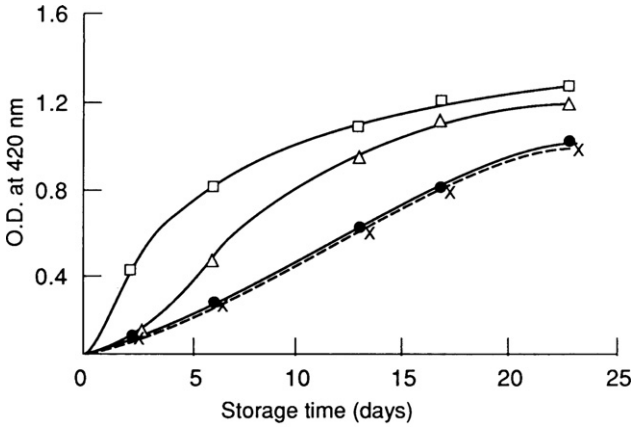



**FIGURE 6.7 Effect of $Na^+$, $Cu^{2+}$, and $Fe^{3+}$ additions on the browning color development in ovalbumin–glucose (OVG) mixtures.** (●) OVG, (×) OVG–Na; (□) OVG–Cu; (Δ) OVG–Fe. *(Reprinted with permission of Kato* et al.*, 1981. Copyright © by the American Chemical Society.)*

able to completely stop the formation of acrylamide compared to the monovalent cations, $Na^+$ and $K^+$, which only reduced acrylamide formation by half. One explanation was the ability of the cations to affect the rate of decomposition of one of the acrylamide precursors, for example the reducing sugars.

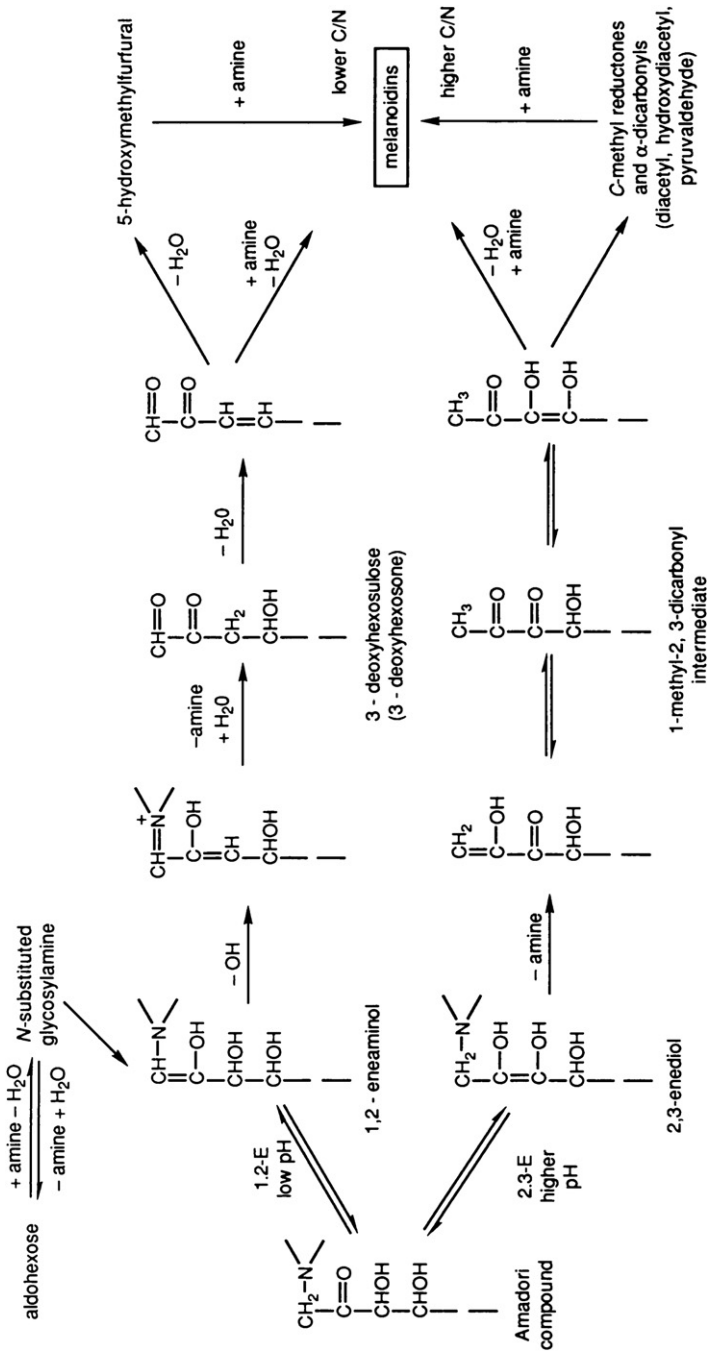
## III. PIGMENT FORMATION

### A. Via Amadori Compounds

The reactions involved in the conversion of 1-amino-1-deoxy-1-ketose derivatives to brown pigments or melanoidins are extremely complex and incompletely understood. Nevertheless, three distinct pathways have been proposed, two of which are directly involved in pigment formation (Scheme 6.4). They involve different labile intermediates, which are the enol forms of the Amadori compounds. In one pathway, enolization of 1-amino-1-deoxy-2-ketose occurs at 2 and 3 positions to irreversibly produce 2,3-enediol. This then undergoes a series of changes including the loss of the amine from C1 to form a methyl dicarbonyl intermediate (Hodge, 1953; Hodge *et al.*, 1963; Simon and Heubach, 1965). The second pathway involves formation of 1,2-eneaminol from the Amadori product in which a hydroxyl group is lost at C3, followed by deamination at C1 and addition of water to form 3-deoxyhexosulose (Anet, 1960, 1964; Kato, 1962). Both hexose derivatives, 1-deoxyhexosulose and 3-deoxyhexosulose, are very reactive and will undergo retro-aldolization to form α-dicarbonyls such as glyoxal, methylglyoxal, and 2,3-butanedione (Weenen and Apeldoorn, 1996). The subsequent reactions are complex and involve a series of aldol condensation and polymerization reactions. The final products are nitrogenous compounds which give rise to the dark brown pigmentation. A low pH favors the 1,2-eneaminol pathway while a high pH favors the pathway involving the conversion of 2,3-enediol to reductones and the subsequent fragmentation to furaneol and pyrones.

### B. Alternative Pathways

The formation of free radicals in browning mixtures of carbonyl compounds and amines or amino acids was first reported in the 1970s by Namiki *et al.* (1973), Namiki and Hayashi (1975), and Hayashi *et al.* (1977). The generation of free radicals during the initial stages of the carbonylamino acid reaction for D-glucose–aminobutyric acid isomers was established by Milic *et al.* (1978, 1979, 1980). Namiki and Hayashi (1981) reported that model systems with alanine and arabinose gave rise to electron spin resonance spectra with 17 and 23 lines. These simple signals were attributed to the presence of *N*,*N*-dialkyl pyrazine cation radicals, which were detected prior to the formation of Amadori compounds. These researchers proposed the formation of a $C_2$ sugar fragment as the precursor of this radical, which was confirmed by isolation and identification of glyoxal dialkylimine. This pointed to an alternative pathway for browning in which the sugar moiety of the Schiff base was cleaved prior to the Amadori rearrangement, leading to the formation of glycolaldehyde alkylimine or its corresponding eneaminol (Scheme 6.5) (Namiki and Hayashi, 1983). Further research by Hayashi and Namiki (1986) confirmed the formation of methylglyoxal dialkylimine, a $C_{2n}$ compound, during the initial stages of the Maillard reaction. The formation of this $C_2$ compound was




**SCHEME 6.4** Maillard reaction: two major pathways from Amadori compounds to melanoidins *(based on Hodge, 1967) (Nursten, 1981).*

thought to arise directly from the Amadori rearrangement. Glycoaldehyde and methylglyoxal, which represented the $C_2$ and $C_3$ sugar fragments, exhibited much higher browning rates, corresponding to 2000 and 650 times faster than those of glucose, fructose, or xylose when heated with β-alanine (Table 6.2). Another $C_3$ compound, glyceraldehyde, also showed close to a 2000-fold increase in the rate of browning compared to the corresponding sugars. Hayashi and Nimiki (1986) presented a summary of the early stages of browning in which they concluded that, under acidic conditions, the traditionally accepted pathway involved osone formation via the Amadori rearrangement. Under alkaline conditions, however, they largely attributed the increase in browning to sugar fragmentation to $C_2$ and $C_3$ fragments (Scheme 6.6). Danehy (1986), however, suggested that this pathway be considered as a concomitant one occurring along with the established Maillard reaction scheme.

**SCHEME 6.5** Alternative pathway for browning *(Namiki and Hayashi, 1983)*.

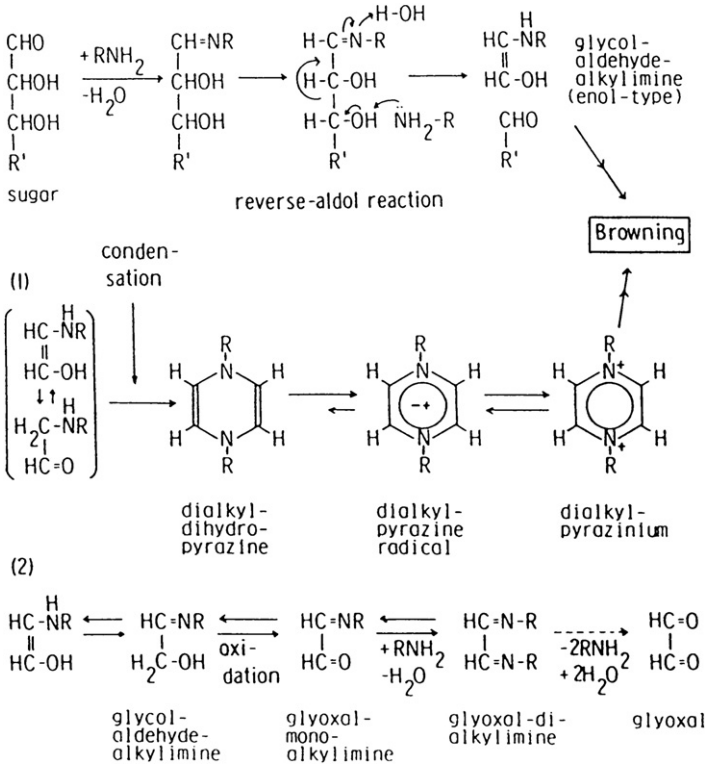


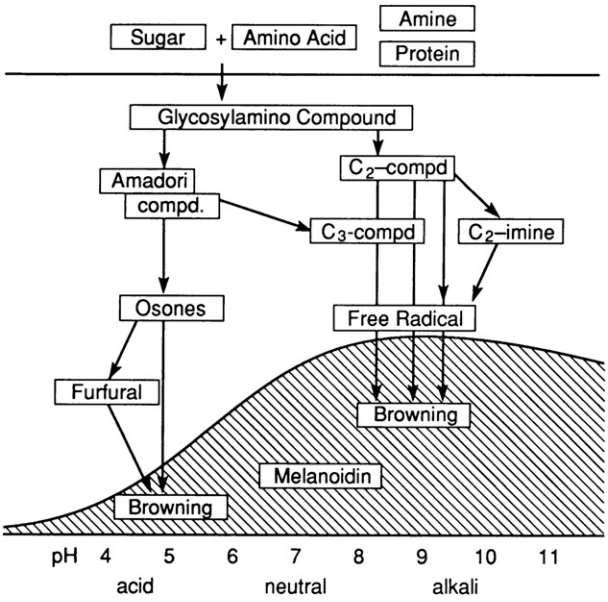

**TABLE 6.2** Browning Rates of β-Alanine with Sugar or Carbonyl System

| Sugar or Carbonyl Compound | Reaction Temperature (°C) | Browning Activity[a] (liters/min) | Relative Value |
|---|---|---|---|
| Glucose | 95 | 0.019 | 1 |
| Fructose | 95 | 0.014 | 0.74 |
| Xylose | 95 | 0.166 | 8.74 |
| Xylose | 80 | 0.037 | |
| Methylglyoxal | 80 | 2.77 | 654.3 |
| Glyceraldehyde | 80 | 8.33 | 1967 |
| Glyoxal | 80 | 0.515 | 121.6 |
| Glycoaldehyde | 80 | 8.93 | 2109 |

[a]*Browning rate measured as change in absorbance at 420 nm.*
From Hayashi and Namiki (1986).

## C. Strecker Degradation

The third pathway in the Maillard reaction is concerned with the oxidative degradation of amino acids in the presence of α-dicarbonyls or other conjugated dicarbonyl compounds formed from Amadori compounds. This reaction is based on the work originally carried out by Strecker over a century ago in which he observed the oxidation of alanine by alloxan, a weak oxidizing agent. The reaction, now referred to as the Strecker degradation, is not directly concerned with pigment formation but provides reducing compounds essential for its formation (Rizzi, 2008). The initial reaction involves the formation of a Schiff base with the amino acid. The tuatomeric




**SCHEME 6.6** Different pathways for melanoidin formation depending on reaction pH *(Hayashi and Namiki, 1986)*.

end-form then decarboxylates to produce the eneaminol, which then undergoes hydrolysis to the corresponding aldehyde with one carbon less, together with a 1-amino-2-keto compound (Scheme 6.7). The aldehydes formed during the Strecker degradation reaction contribute to flavor. Some of these aldehydes are listed in Table 6.3 together with their flavor characteristics. At one time aldehydes were considered to be directly responsible for the flavor of roasted foods, although they are now recognized to have a contributory role as auxiliary flavor compounds (Reynolds, 1970; Hodge *et al.*, 1972). Van Praag *et al.* (1968) showed that it is the secondary products of Strecker degradation that are responsible for the strong aroma of cocoa.

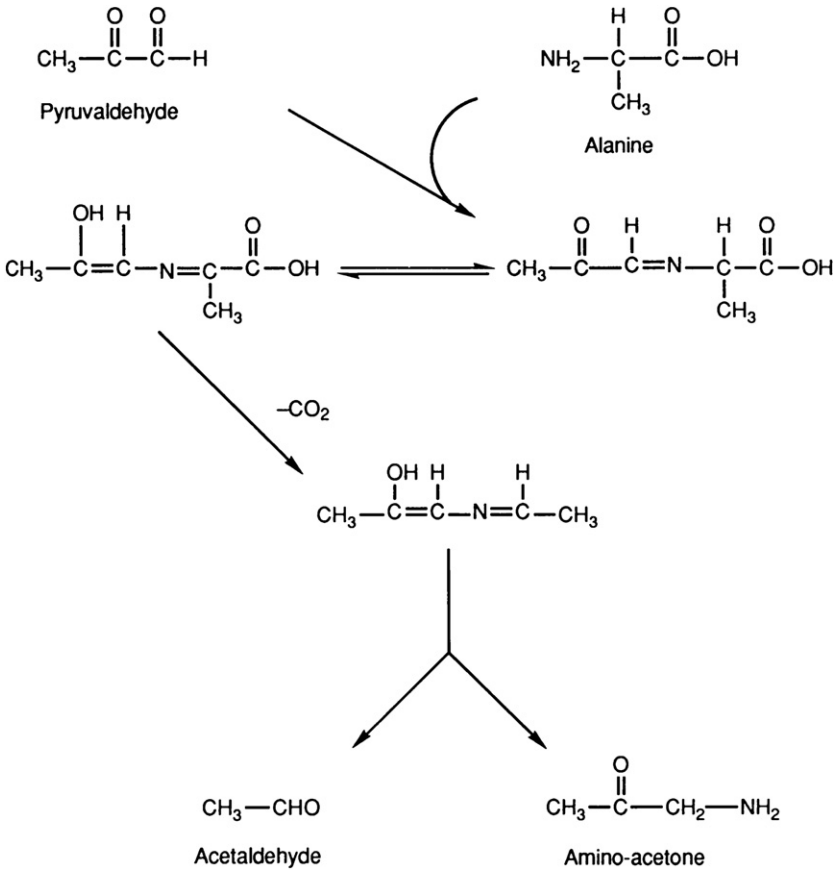
Hodge *et al.* (1972) similarly noted that the contribution of the Strecker aldehydes isobutyric, isovaleric, and methional to roasted food aroma was only auxiliary. Condensation of the intermediates formed by Strecker degradation produced many heterocyclic compounds, pyrazines, pyrrolines, oxazoles, oxazolines, and thiazole derivatives responsible for the flavor of heated foods (Hodge *et al.*, 1972; Maga and Sizer, 1973; Maga, 1982).

The generation of flavor compounds by the Maillard reaction has been based primarily on mixtures of sugars and amino acids. Izzo and Ho (1992) first pointed out that the formation of aroma from amino acids bound in proteins and peptides has not been investigated, as in the absence of free amino acids, the Strecker degradation reaction cannot take place. As pointed out by van Boekel (2006), the situation has not changed, as research has still not generated peptide- or protein-specific flavor compounds.

### *1. Strecker Degradation Reaction and Acrylamide Formation*

Tareke *et al.* (2002) first detected the neurotoxin and carcinogen acrylamide in heated foods. The consumption of high-acrylamide food was shown to be associated with a higher incidence of ovarian, endometrial, breast, and kidney cancers in humans (Hogervorst *et al.*, 2007, 2008; Olesen *et al.*, 2008). This led to extensive research to improve the accuracy of its analysis as well as to understand better its formation and subsequent reduction in foods (Locas and Yaylayan, 2008; Anese *et al.*, 2010; Knol *et al.*, 2010; Pedreschi *et al.*, 2010; Kotsiou *et al.*, 2011). Acrylamide appeared to be formed by the thermal degradation of asparagine in the presence of carbonyl compounds (Zamora *et al.*, 2011). Scheme 6.8 outlines the role that Strecker aldehydes and α-keto acids play in the conversion of asparagine to acrylamide. Asparagine is first decarboxylated to 3-alkylaminopropionamides or 3-amino-propionamide, which requires carbonyls (Yayalayan *et al.*, 2003), and then deaminated to form acrylamide. Fortunately, various methods have been developed which prevent the formation of acrylamide in heated foods (Amrein *et al.*, 2007; Yuan *et al.*, 2011).

**SCHEME 6.7** Strecker degradation reaction *(Adapted from Schonberg and Moubacher, 1952).*



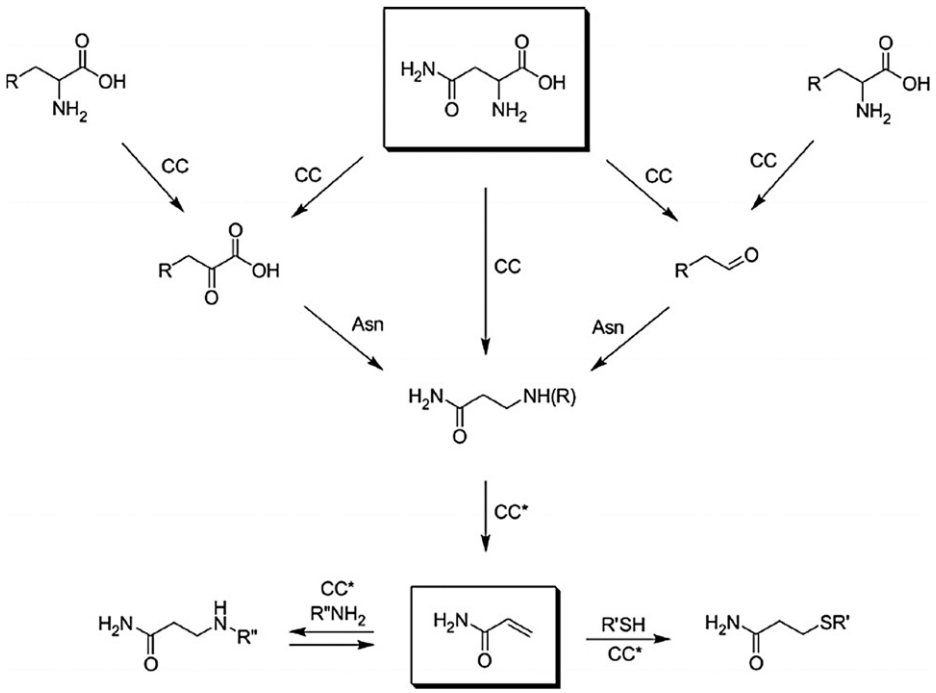

## IV. HETEROCYCLIC COMPOUNDS

### A. Pyrazine

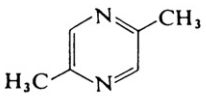
Among the heterocyclic compounds formed from the Strecker degradation products are the pyrazines. These are very potent flavored compounds which have been identified in almost all processed foods, including beef products, soy products, processed cheese, coffee, potatoes, tea, and roasted pecans (Maga and Sizer, 1973; Maga, 1981, 1982). Dawes and Edwards (1960) identified a number of substituted pyrazines in sugar–amino acid model systems including 2,5-dimethylpyrazine and trimethylpyrazine.

**TABLE 6.3** Aromas and Volatile Compounds Produced from L-Amino Acids in Maillard Reaction Systems

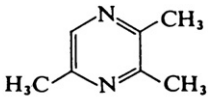
| Amino Acid | Volatile Compound | Aroma |
|---|---|---|
| Alanine | Acetaldehyde | Roasted barley |
| Cysteine | Thiol, $H_2S$ | Meaty |
| Valine | 2-Methylpropanal | |
| Leucine | 3-Methylbutanal | Cheesy |
| Lysine | | Bread-like |
| Methionine | Methional | |




**SCHEME 6.8** Schematic role of carbonyl compounds and amino acids in the formation and elimination reactions of acrylamide. CC means that the presence of a carbonyl compound is required; CC* means that carbonyls play a role in the reaction *(Zamora* et al.*, 2011)*.



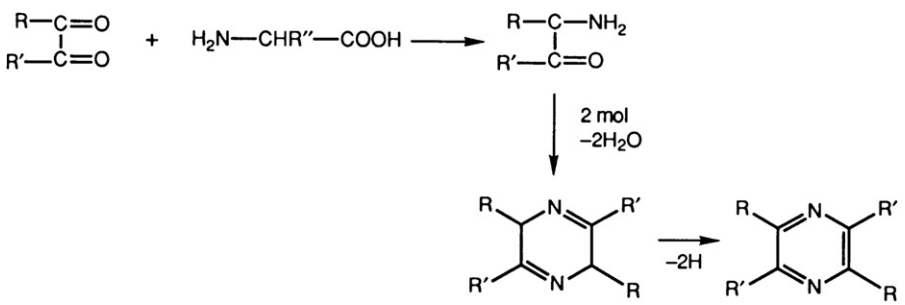
2,5-Dimethylpyrazine



Trimethylpyrazine

Koehler *et al.* (1969) showed that the C-ring in the substituted pyrazines was derived from the fragmentation of sugars. Koehler and Odell (1970) monitored the formation of methylpyrazines and dimethylpyrazines from sugar–asparagine systems. They noted that fructose gave the highest yields while arabinose gave the smallest yields of these compounds. This suggested that the yields and distribution patterns of pyrazine rings were determined by the nature of the sugar. Shibamato and Bernard (1977), using sugar–ammonia model systems, found similar distribution patterns of pyrazines for both pentose and aldose sugars. Only in the case of the aldose sugars was the level of unsubstituted pyrazines higher, although higher yields were obtained in the presence of the pentoses. One of the major pathways leading to the formation of pyrazines is illustrated in Scheme 6.9, involving condensation of amino-ketones.

Koehler *et al.* (1969) proposed an alternative pathway involving Strecker degradation in which the bound amino acid nitrogen was the main contributor to nitrogen in the pyrazine rings. Condensation of two 2-carbon sugar fragments with nitrogen produced pyrazine, while a similar reaction involving condensation of a 2-carbon fragment with a 3-carbon sugar fragment produced methylpyrazine. The formation of dimethylpyrazine was attributed to the

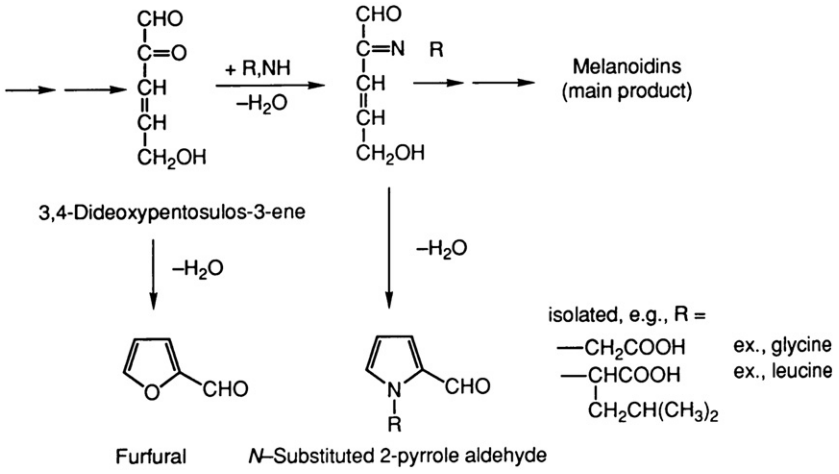



**SCHEME 6.9** Formation of pyrazines *(Shibamato and Bernard, 1977)*.

condensation of two 3-carbon sugar fragments and nitrogen. Wong and Bernhard (1988) examined five different nitrogen sources (ammonium hydroxide, ammonium acetate, ammonium formate, glycine, and monosodium glutamate) for the formation of pyrazines. They concluded that the nitrogen source had a marked effect on both the amount and types of pyrazines formed during non-enzymatic browning, as suggested earlier by Koehler and Odell (1970) and Koehler *et al.* (1969). Since there is more than one amino acid in foods, competition between amino acids to generate pyrazines can occur. To investigate this competition, a $^{15}N$ isotope-labeled glycine was used as a reference with another test amino acid (glutamine, glutamic acid, asparagines, aspartic acid, lysine, arginine, phenylalanine, or isoleucine) added to compete with glycine in the production of pyrazines (Hwang *et al.*, 1995). They found that the reaction mixture containing lysine had the highest yield of pyrazines, with the reaction mixture containing arginine producing the lowest yields. These results indicated that lysine was able to increase the reactivity of glycine. Consequently, the variety and quantity of pyrazine formation appeared to depend on the reactivity and type of amino acids used.

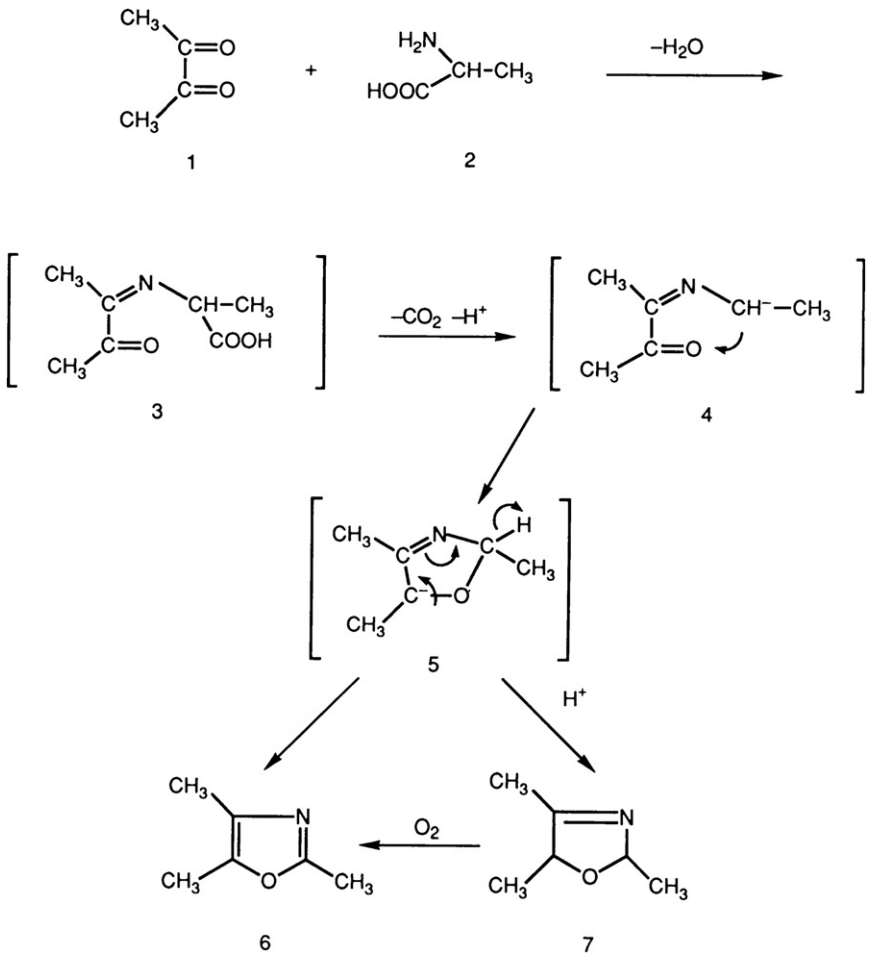
## B. Pyrroles

Pyrroles are an important group of heterocyclic compounds formed during the browning of foods (Hodge, 1953). One of the pathways leading to their formation involves cyclization of methyldicarbonyls to 2,4-dideoxypentulose-3-ene, which cyclizes to furfural or reacts with an amino acid at C2 to form a Schiff base, which then cyclizes to N-substituted pyrrole-2-aldehyde (Kato and Fujimaki, 1968). The formation of pyrrole derivatives has since been identified in a number of sugar–amino acid systems (Ferretti and Flanagan, 1971, 1973; Shigematsu *et al.*, 1972; Rizzi, 1974). Shaw and Berry (1977) reported the formation of 2-acetylpyrrole and 5-methylpyrrole-2-carboxyaldehyde in fructose–alanine model systems. This pathway is shown in the diagram below, in which the 3-deoxyhexulose derivative underwent Strecker degradation with the amino acid leading to the formation of 1-amino-3-deoxy-2-ketose. Further changes included enolization and dehydration, resulting in the formation of 2-acetylpyrrole.




## C. Oxazoles and Oxazolines

Oxazoles and oxazolines have been identified among the flavor volatiles of coffee (Stoeffelsman and Pypker, 1968), baked potato (Coleman *et al.*, 1981), and roasted peanuts (Lee *et al.*, 1981). The role of these compounds in the flavor of foods has been reviewed by Maga (1978, 1981). One such compound, 2,3,5-trimethyl-2-oxazole, was identified in the volatiles of boiled beef (Chang *et al.*, 1968) and canned beef stew (Peterson *et al.*, 1975). The latter researchers also reported the presence of the corresponding oxazoline (2,4,5-trimethyl-3-oxazoline). The role of the Strecker degradation reaction in the formation of these compounds was first suggested by Rizzi (1969), in which 2-isopropyl-4,5-dimethyl-3-oxazoline was formed from D-histidine and 2,3-butadione (diacyl). The formation of oxazoles and oxazolines by Strecker degradation was confirmed by Ho and Hartman (1982) to explain the presence of these compounds in the flavor volatiles of meat and roasted peanuts. These researchers proposed the pathway in Scheme 6.10 to explain the mechanism for the formation of 2,4,5-trimethyloxazole and 2,4,5-trimethyloxazoline

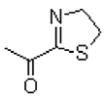


**SCHEME 6.10** Formation of 2,4,5-trimethyloxazole and 2,4,5-trimethyl-3-oxazoline from the reaction of DL-alanine and 2,3-butanedione. *(Reprinted with permission from Ho and Hartman, 1982. Copyright © by the American Chemical Society.)*

from DL-alanine and butanedione. Elimination of water resulted in an unstable Schiff base which then underwent decarboxylation to the corresponding anion followed by cyclization to the 3-oxazolinide ion. Protonation or loss of hydride ion was thought to produce the 2,4,5-trimethyloxazoline. The corresponding oxazole was attributed to the oxidation of the oxazoline or loss of hydride.

## D. Thiazoles

Thiazoles are formed from sulfur amino acids. These compounds have been identified in coffee, roasted peanuts, cooked beef, and potato chips (Stoll *et al.*, 1967a, b; Walradt *et al.*, 1971; Buttery and Ling, 1974; Buttery *et al.*, 1983). The presence of 2-acetyl-2-thiazoline in beef broth was attributed by Tonsbeek *et al.* (1971) to the Strecker degradation reaction between cysteine and methylglyoxal followed by cyclization.

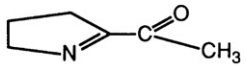


Hofmann and Schieberle (1995) later performed model experiments to gain a more detailed insight into the reaction mechanisms and intermediates governing the formation of 2-acetyl-2-thiazoline. The intermediates in the reaction path leading to 2-acetyl-2-thiazoline were identified as the odorless 2-(1-hydroxyethyl)-4,5-dihydrothiazole.

Formation of 3-thiazolines from an α-hydroxyketone involves the substitution of the hydroxyl group with a thiol group. This is followed by nucleophilic attack by the sulfur atom at the carbon atom of an imine intermediate formed

by the reaction between ammonia and an aldehyde. Subsequent ring closure, with the elimination of a molecule of water, gives the 3-thiazolines. Oxidation of the thiazoline results in the formation of the corresponding thiazole (Schutte, 1974).

The Strecker degradation reaction plays a key role in the production of important flavor compounds by condensation and cyclization of the different aldehydes formed. In addition to the heterocyclic compounds discussed there are many others, including pyrrolidines and pyridines. The isolation and chemical synthesis of 2-acetyl-1-pyrroline, a key compound responsible for the characteristic smell of cooked rice, provides another example of the role of Strecker degradation in flavor genesis (Buttery *et al.*, 1982, 1983). It is now confirmed that 2-acetyl-1-pyrroline is a Strecker degradation product of proline and is considered as a character impact compound also giving roasty odors to foods such as bread and popcorn (Schieberle, 1990; Adams and De Kimpe, 2006).




2-Acetyl-1-pyroline

In addition to these compounds, other heterocyclic and carboxylic compounds identified from heated sugar–amine systems include furanones, pyrrolinones, and cyclopentenones (Ledl and Fritsch, 1984).

## V. MAILLARD REACTION–LIPID INTERACTIONS

Lipids are common food components present intrinsically or added as ingredients. Their widespread occurrence unavoidably causes them to affect the Maillard reaction and to interact with its products. Major flavor changes occur as a consequence. The mechanism of flavor variation due to such interactions is being studied in both model and food systems.

Degradation products from lipid oxidation and the Maillard reaction give rise to certain aromatic compounds. Lipid oxidation results in the formation of aldehydes, etones, and other compounds. On the other hand, Strecker degradation in the Maillard reaction scheme produces other reactive intermediates that can react with lipid degradation products. The volatiles formed from these interactions include heterocyclic compounds containing oxygen, nitrogen or sulfur, with long-chain *n*-alkyl substituents (Whitfield, 1992).

The Maillard reaction and lipid oxidation products react to form pyrazines. Chiu *et al.* (1990) demonstrated the synthesis of pentylpyrazines or hexylpyrazines in a system containing ammonium acetate, acetol, and pentanal or hexanal. These alkyl-substituted pyrazines were also detected in fried potatoes (Carlin *et al.*, 1986), corn-based systems (Bruechert *et al.*, 1988), and fried chicken (Tang *et al.*, 1983). Interaction between 2,4-decadienal, a linoleic oxidation product, and cyteine or glutathione yielded long-chain alkyl dithiazines and trithiolanes (Zhang and Ho, 1989; Zhang *et al.*, 1994). Zhang and Ho (1989) also observed the formation of a large amount of 2-pentylpyridine in the model system containing glutathione instead of cysteine. They proposed that 2,4-decadienal was involved in a direct Schiff base formation with the amino group of cysteine or glutathione, followed by electrocyclic reaction and aromatization to form pentylpyridine. The relatively stable glutathione, rather than cysteine, provided more primary free amino groups for Schiff base formation and was responsible for the production of the larger amount of 2-pentylpyridine. The latter compound has been identified in deep-fried foods (Tang *et al.*, 1983) and meat (Mottram, 1985).

Sulfur-containing heterocyclic compounds are important to meat flavor (Mottram, 1998). A number of alkylthiazoles has been reported in meat (Hartman *et al.*, 1983; Tang *et al.*, 1983), with many alkyl-3-thiozolines and alkylthiazoles identified in cooked beef (Elmore *et al.*, 1997). The formation of these compounds was thought to be derived from α-hydroxyketones or α-diones, hydrogen sulfide, ammonia, and Strecker or lipid-oxidation derived aldehydes (Elmore and Mottram, 1997).

Phospholipids are often part of a food matrix. They are rich in polyunsaturated fatty acids, making them extremely prone to oxidation. Their presence was shown to alter the configuration of volatile products in a cysteine–ribose system (Farmer *et al.*, 1989). In this system, phospholipids caused a decline in the amount of sulfur-containing heterocyclic compounds.

Edible oils play a role in pyrazine production. Negroni *et al.* (2001) observed the opposite effects of edible oils on unsubstituted and substituted pyrazines in lysine–xylose–glucose model systems. Decreasing amounts of unsubstituted pyrazines were reported in the presence of olive, canola, or sunflower oil. In contrast, increasing levels of 2-methylpyrazine, 2,5-methylpyrazine, and 2,3-dimethylpyrazine were observed with olive, canola, and sunflower

oils. The sensitivity of the pyrazines was attributed to differences in the degree of unsaturation between the oils. However, this hypothesis remains to be tested using purified oils. Commercially available vegetable oils also contain different amounts and types of phenolic antioxidants which may influence the degree of lipid interactions in the Maillard reaction. As discussed earlier, Yayalan and Locas (2007) showed that important lipid peroxide products can form Schiff base adducts with nitrogen nucleophiles, such as amino acids and proteins; these can then undergo vinylogous Amadori rearrangements which can then cyclize and form pyrrole moieties. In the case of proline, however, this cyclization is prevented so that stable vinylogous Amadori rearrangement products (vARPs) are formed.

The Strecker degradation of amino acids by α-epoxyenals was reported by Hildago and Zamora (2004b), as part of their extensive studies on the interaction of lipid degradation products with amino acids and proteins. In their model studies with phenylalanine and 4,5-epoxy-2-decenal at 37°C overnight, products indicative of Strecker degradation occurring were identified by gas chromatography–mass spectrometry, including phenylacetaldehyde and 2-pentylpyridine.

Many foods exist as emulsions which affect the perception of aroma compounds. Van Ruth *et al.* (2002) reported that lower lipid and emulsifying fractions and greater particle diameter of oil–water emulsions enhanced the aroma release of alcohols, ketones, esters, aldehydes, terpenes, and sulfur compounds.

## VI. EFFECT OF POLYPHENOLS ON THE MAILLARD POLYMERS

Polyphenols are secondary metabolites of plants which are used in their defense against severe environments such as ultraviolet radiation or attack by pathogens. These compounds are generally classified as flavonoids, phenolic acids, lignans, and stilbenes. They are widely distributed in plant-based food products; however, their effects on the Maillard reaction have only recently been studied.

Certain polyphenols were recently shown to have trapping activity for reactive carbonyl species, indicating a new chemical characteristic of polyphenols (Jiang and Peterson, 2010; Lo *et al.*, 2006, 2011; Lv *et al.*, 2011; Sang *et al.*, 2007; Shao *et al.*, 2008). Reactive carbonyl species glyoxal, methylglyoxal, and 3-deoxyglucosone, generated by the Maillard reaction, are important intermediates for flavor and color formation. Trapping reactive carbonyl species by polyphenols can alter Maillard reaction pathways. For example, some flavor compounds normally generated in the Maillard reaction, such as pyrazine, methylpyrazine, 2,5-dimethylpyrazine, and trimethylpyrazine, were inhibited when epicatechin was added to a glucose–glycine model system (Totlani and Peterson, 2005). Using the glucose–glycine system, Noda and Peterson (2007) compared the trapping efficiency of flavan-3-ol epicatechin (EC), epigallocatechin (EGC), epigallocatechin gallate (EGCG), and several phenolic compounds (1,3,5-trihydroxybenzene, 1,2,3-trihydroxybenzene, and methyl gallate) on the formation of pyrazines. A similar significant reduction in pyrazine formation was observed for EC, ECG, and ECGC. Methyl gallate followed by 1,2,3-trihydroxybenzene was the least reactive, while 1,3,5-trihydroxybenzene proved to be the most effective. This suggested that the mechanism responsible for the inhibition was the carbonyl trapping activity on the A-ring of a flavonoid compound.

## VII. MELANOIDIN–MAILLARD POLYMERS

The final products formed in the Maillard reaction are polymers or melanoidins. Unlike the flavor and aroma compounds discussed earlier, the origin and nature of these polymers are poorly understood. Numerous studies have attempted to examine melanoidins in model systems, including Barbetti and Chiappini (1976a, b), Ledl (1982a, b), Ledl and Severin (1982), Velisek and Davidek (1976a, b), Imasato *et al.* (1981), and Bobbio *et al.* (1981). A study by Feather and Nelson (1984) attempted to isolate the Maillard polymers produced in model systems composed of D-glucose/D-fructose/5-(hydroxymethyl)-2-furaldehyde and glycine and D-glucose/D-fructose with methionine. Increasing amounts of water-soluble, non-dialyzable polymers with molecular weights greater than 16,000 were obtained for both glycine and methionine systems as a function of time (Figures 6.8 and 6.9). Elemental analyses (carbon, hydrogen, and nitrogen) of polymers prepared from glycine model systems were similar, which suggested that the amino acid was incorporated into the polymer. The polymer isolated from D-glucose/D-fructose and glycine was composed of sugar and amino acid minus three molecules of water. Detection of sulfur and nitrogen in polymers obtained from D-glucose and methionine also pointed to incorporation of the amino acid intact. The binding of metal ions to these melanoidins was evident by their greater solubility in tap water than in distilled water.

The nuclear magnetic resonance (NMR) spectra of these polymers suggested that some aromaticity was present. Feather and Huang (1986) examined the $^{13}$C-NMR spectra of water-soluble polymers produced from labeled

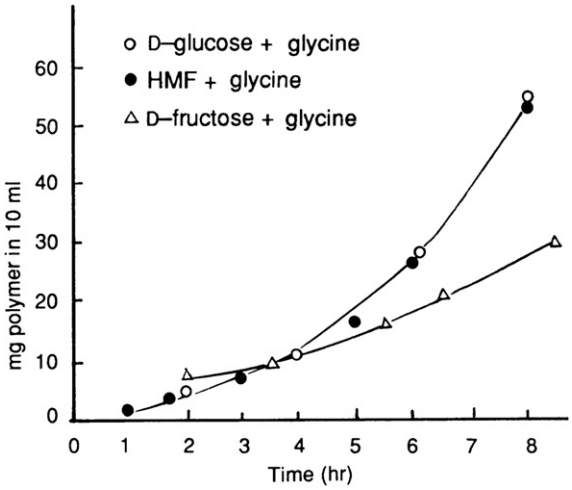



**FIGURE 6.8 Yields of non-dialyzable polymers as a function of time using glycine as the amino acid.** HMF: hydroxymethylfurfural. *(Reprinted with permission from Feather and Nelson, 1984. Copyright © by the American Chemical Society.)*

D-[1-1$^3$C] glucose, L-[1-1$^3$C]alanine, and L-[2-1$^3$C]alanine (90 atom%). Polymers prepared with the C1-labeled carbon atom in L-alanine had lower activity compared to the C2-labeled amino acid. This could be due to its degradation to volatile aldehydes, suggesting a more direct role for the Strecker degradation in the Maillard reaction as proposed by Holtermand (1966) (Section III, B). Earlier work by Olsson *et al.* (1982) found that the aldehyde NMR spectrum was similar to that of an analogous Amadori compound. Based on this study and other NMR spectra, it appeared that the non-dialyzable polymer was formed by dehydration and polymerization of an Amadori compound, as suggested previously by Olsson *et al.* (1982).

Benzing-Purdie *et al.* (1985) examined the effect of temperature on the structure of the melanoidins formed in model systems composed of D-xylose and glycine. In the presence of equimolar amounts of the reactants, an increase in temperature (22, 68, and 100°C) was accompanied by an increase in the aromatic nature of both the low- and high-molecular-weight melanoidin products. These researchers also noted considerable differences in the nature of the melanoidins produced at 22°C compared to those formed at the higher temperatures, with different types of aliphatic carbons and fewer unsaturated carbons.

The non-dialyzable melanoidins produced from glucose–glucose systems heated at 95°C at pH 6.8 were examined by Kato *et al.* (1985). These melanoidins were composed of saturated aliphatic carbons together with smaller amounts of aromatic carbons. Milic (1987) examined the kinetics of melanoidin formation between D-glucose and 2-, 3-, and 4-aminobutanoic acid isomers using cross-polarization–magic angle spinning $^{13}$C-nuclear

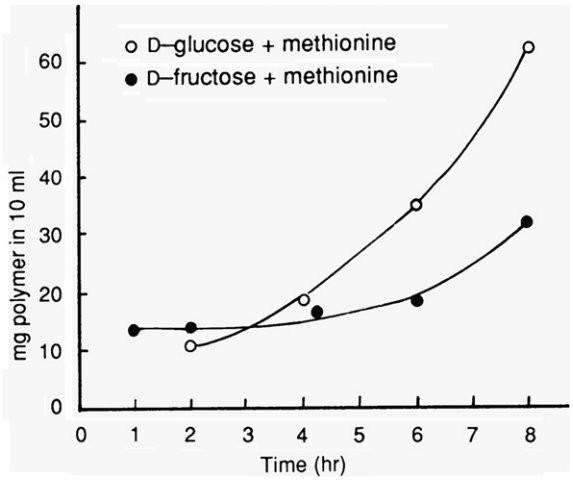



**FIGURE 6.9 Yields of non-dialyzable polymers as a function of time using methionine as the amino acid** *(Feather and Nelson, 1984).*

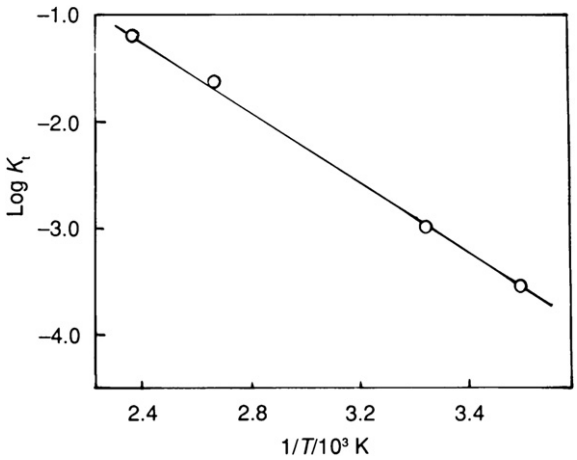
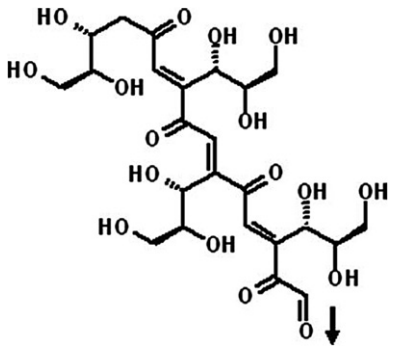



**FIGURE 6.10** **Temperature dependence of the approximate rate constant $K_t$ for the D(+)-glucose–2-aminobutanoic acid model system** *(Milic, 1987).*

magnetic resonance (CP-MAS $^{13}$C-NMR) spectroscopy. The systems were heated in sealed quartz test-tubes at 313, 343, and 371 K for $1.0 \times 10^5$ to $3.60 \times 10^5$ seconds under alkaline conditions (pH 9.0) and the brown melanoidins were eluted on an ion-exchange Permutit ES resin with 5% NaCl. The purified melanoidins were then concentrated, dialyzed, and dried under vacuum before analysis by CP-MAS $^{13}$C-NMR. Based on the CP-MAS spectra, an increase in unsaturation and/or aromaticity was observed at 100 and/or 180 ppm with increasing temperature and time, which leveled off when both glucose and aminobutanoic acid were depleted. Milic (1987) calculated the order of reaction of melanoidin formation, assuming that aromaticity, measured by CP-MAS $^{13}$C-NMR spectroscopy, corresponded to the rate of browning temperature (K). The amount of amino acid ($A_0$) (peak area at 180 ppm) was plotted against the reaction temperature at a constant time of $2.34 \times 10$ seconds and the straight line obtained showed that melanoidin formation followed first order kinetics (Figure 6.10).

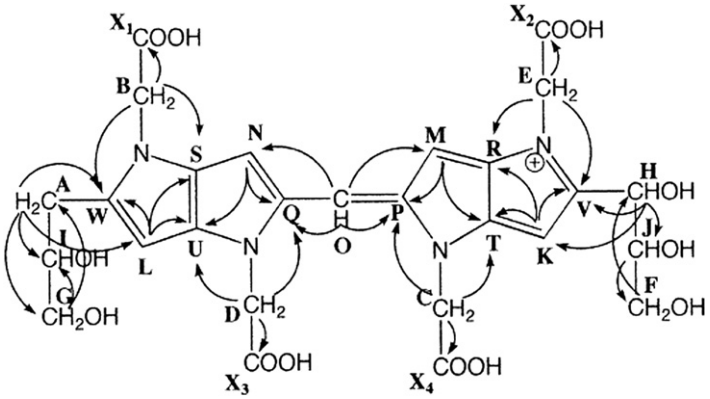
The formation of melanoidins appears to involve two separate pathways. One pathway leads to the formation of protein-based melanoidins from deoxysones, while the other is based on sugar degradation products (Kroh *et al.*, 2008). The latter reaction was shown by Hofmann (1998) to result in the formation of low-molecular-weight colored compounds with furan and pyrrolidine structures and high-molecular-weight brown compounds. α-Dicarbonyls were recently shown by Kroh *et al.* (2008) to be key intermediates in the formation of the carbohydrate-based melanoidins. These include the long-chain dicarbonyls, 1,3-deoxyosone and 1,4-dideoxyosones, and the short-chain dicarbonyls, methylglyoxal and glyoxal. They proposed the following carbohydrate-based melanoidin structure resulting from the aldol condensation of α-dicarbonyl compounds (Scheme 6.11). Colored melanoidins were formed in the presence of methylglyoxal, as under alkaline conditions it forms a carbanion on the third carbon atom, which then proceeds to form colored melanoidins by aldol condensation. In the case of glyoxal a similar reaction is not possible as it is unable to form a carbanion.

Extensive studies conducted on the formation of protein-based melanoidins used a D-xylose–glycine model system. Using this model system, Hayase *et al.* (1999) isolated a Maillard reaction-1 pigment (Blue-M1) that was




**SCHEME 6.11** Proposal of a carbohydrate-based melanoidin structure *(Kroh* et al.*, 2008).*

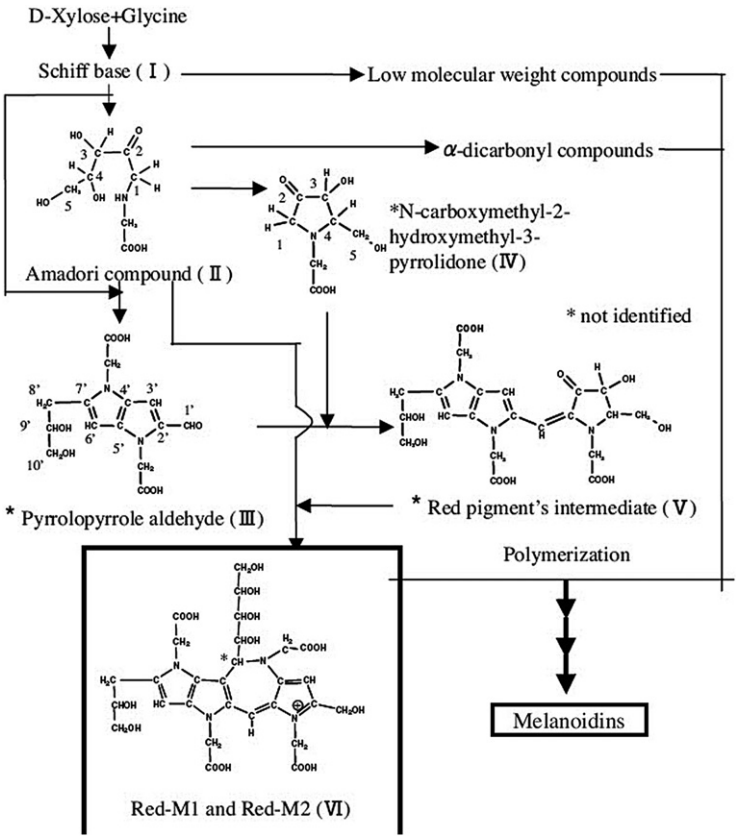
**SCHEME 6.12** Identified structure of Blue-M1 *(Hayase* et al., *1999).*

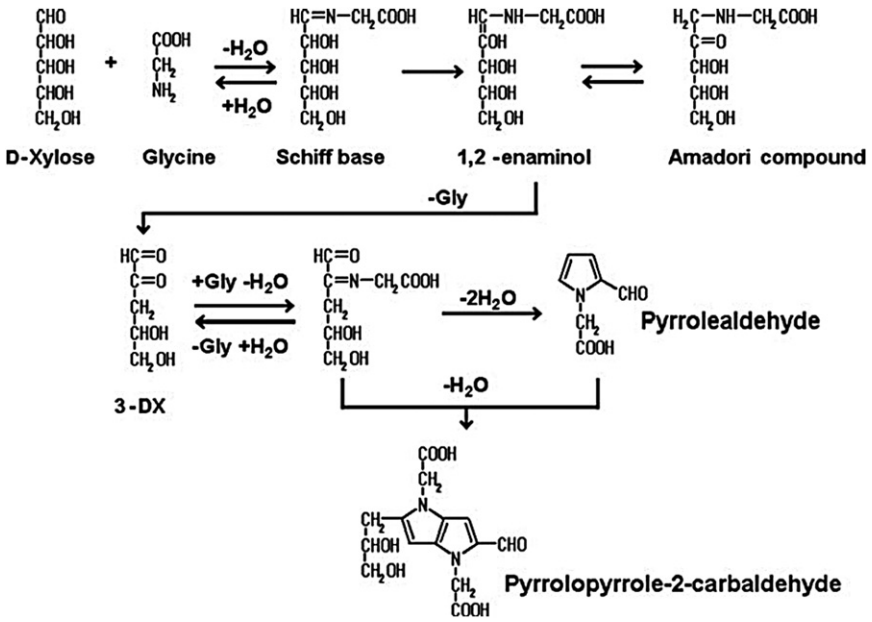


considered to be an oligomer intermediate in the formation of melanoidins. As seen in Scheme 6.12, it is made up of four molecules of D-xylose and glycine with a methine proton between two pyrrolpyrrole rings. Further work by Sasaki *et al.* (2006) identified a second blue pigment (Blue-M2) which had a higher molecular weight compound than Blue-M1 and was thought to arise from the interaction between Blue-M1 and di-D-xyuloseglycine. In addition to the blue pigments, Blue-M1 and Blue-M2, Shirahashi *et al.* (2009) recently identified several red pigments (Red-M1 and Red-M2) using the same D-xylose−glycine system. Once again, these red pigments were intermediate compounds in the formation of melanoidins. They proposed the pathway leading to the formation of melanoidins shown in Scheme 6.13.

The actual mechanism involved in the formation of melanoidins, advanced glycation end products from these intermediate pigments, was finally resolved by Hayase *et al.* (2008). Scheme 6.14 shows the formation of a Schiff base and Amadori compound from xylose and glycine, followed by the formation of 3-deoxyxylosone (3-DX). The latter

**SCHEME 6.13** Proposed formation pathway for products from the reaction of D-xylose (1 M) incubated with glycine (0.1 M) and sodium hydrogen carbonate (0.1 M) in a 60% ethanol solution (pH 8.1) *(Shirahashi* et al., *2009).*






**SCHEME 6.14** Proposed pathway for the formation of pyrrolopyrrole-2-carbaldehyde (PPA) *(Hayase* et al., *2008)*.

compound then reacts with glycine to form pyrrole-2-carbaldehyde, which then reacts with imine to form pyrrolopyrrole-2-carbaldehydes (PPA). PPA is the precursor of the blue pigment-M1, an intermediate pigment formed by decarboxylation of two molecules of PPA. The blue pigments then readily polymerize to the brown-colored melanoidins. Similar blue pigments were also detected in glucose−glycine and D-xylose−β-alanine model systems.

## VIII. CARAMELIZATION

Caramelization is another example of non-enzymatic browning involving the degradation of sugars and generally proceeds simultaneously with the Maillard reaction (Ajandouz and Puigserver, 1999). Caramelization of sugars contributes markedly to the production of brown pigments and may lead to an overestimation of the Maillard reaction and its associated properties in foods (Ajandouz *et al.*, 2001). This was evident by the more rapid disappearance of fructose in a lysine-containing fructose solution compared to the amino acid. Caramelization of fructose accounted for 10−36% of total brown development between pH 4.0 and 7.0. When sugars are heated above their melting points they darken to a brown coloration under alkaline or acidic conditions. If this reaction is not carefully controlled it can lead to the production of unpleasant, burned, and bitter products. Consequently, it is important to control this reaction during food processing while still retaining the pleasant qualities of caramel. Caramel colors used for coloring foods vary in color from very dark brown to black, syrup-like liquids or powders. In 1987, von Smolnik classified caramel colors into four distinct groups based on differences in functional properties, as shown in Table 6.4. The different caramel colors are prepared by heating food-grade carbohydrates with ammonia, sulfite, and/or acid and alkaline reactants (Licht *et al.*, 1992a). Of these, caramel color IV accounts for approximately 70% of all caramel colors produced worldwide (Licht *et al.*, 1992b). This classification is recognized by both the Joint FAO/WHO Expert Committee on Food Additives (JECFA) and the US Food and Drug Administration definition of Caramel, Code of Federal Regulations. Caramel remains one of the most widely used coloring agents in food and pharmaceuticals.

The chemical composition of caramel is extremely complex and still poorly understood, although caramels produced from different sugars all show similarity in composition. Bryce and Greenwood (1963), using chromatographic techniques, found that pyrolysis of sucrose, glucose, and starch all produced caramels of similar composition. Heyns and Klier (1968), in a series of studies on a whole group of different monosaccharides, disaccharides, and polysaccharides, also found that the volatile products formed at high temperatures were almost identical. Studies by these and other researchers, as reviewed by Feather and Harris (1973), clearly indicated a common pathway for both the acidic and alkaline degradation of sugars. Later research identified new groups of compounds formed during this process (Popoff and Theander, 1976; Theander, 1981).

**TABLE 6.4** Classification of Caramel Colors for Food Use

| Classification | Food Use |
|---|---|
| I. Plain (alcohol) caramel | Spirits |
| II. Caustic sulfite caramel | Spirits |
| III. Ammonia caramel | Beer |
| IV. Sulfite ammonia caramel | Soft drinks |

From von Smolnik (1987).

## A. Acidic Degradation

The first step involves the stepwise conversion of D-glucose to D-fructose and D-mannose, referred to as the Lobry de Bruyn–Alberda van Eckenstein transformation (Scheme 6.15). These transformations can be mediated by organic acid catalysts over a pH range of 2.2–2.9 (Hodge and Osman, 1976). The interconversion of these sugars occurs primarily through the 1,2-enolic form and depends on the ease with which the ring opens. Since D-glucose is the most conformational stable form in both acid and alkaline media there is much less of the carbonyl (open-chain) form present in solution. This explains the presence of relatively high levels of glucose when fructose is heated at high temperatures over a pH range of 3.0–6.9, whereas only trace amounts of fructose are found when D-glucose is heated under identical conditions. Enolization takes place very slowly under acidic conditions, whereas the hydroxyl group next to the carbonyl group is rapidly removed.

The process of enolization via 1,2-enediol of sugars under acidic conditions was questioned when Ohno and Ward (1961) reported the presence of only small amounts of fructose when D-glucose was treated with 2.5% sulfuric acid, with no mention of mannose. Mawhinney *et al.* (1980) detected the presence of both fructose and mannose when D-glucose was isomerized in acidic solution. Table 6.5, taken from their data, shows that fructose levels off at around 0.8 μg, while mannose increased with reaction time. These data show the levels of sugars generated but give no information on their degradation by dehydration, which probably occurred at different

**SCHEME 6.15** The Lobry de Bruyn–Alberda van Eckenstein transformation *(Eskin* et al., *1971).*

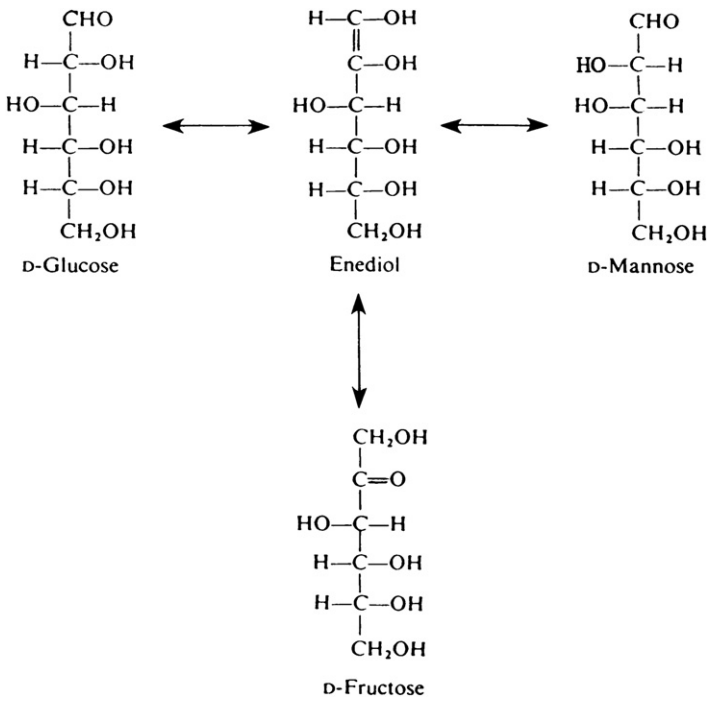
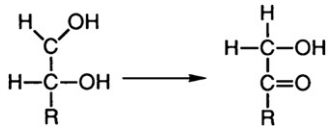


**TABLE 6.5** Yield of Sugar Obtained from 50 mg of D-Glucose after Treatment with 2.5% Sulfuric Acid at 120°C

| Reaction Time (hours) | Glucose (μg) | Mannose (μg) | Fructose (μg) |
|---|---|---|---|
| 0 | 50.0 | 0 | 0 |
| 1.0 | 46.2 | 4.7 | 0.6 |
| 2.5 | 43.6 | 10.8 | 0.8 |
| 5.0 | 39.7 | 19.1 | 0.8 |
| 7.5 | 37.1 | 27.7 | 0.9 |
| 10.0 | 35.9 | 43.8 | 0.8 |

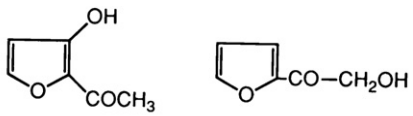
From Mawhinney *et al.* (1980).

reaction rates. The mechanism of this reaction resembled the corresponding isomerase enzyme reaction involving a C1→C2 intramolecular hydrogen transfer in which D-glucose-2-H is converted to D-fructose-1-H (Harris and Feather, 1973, 1975):



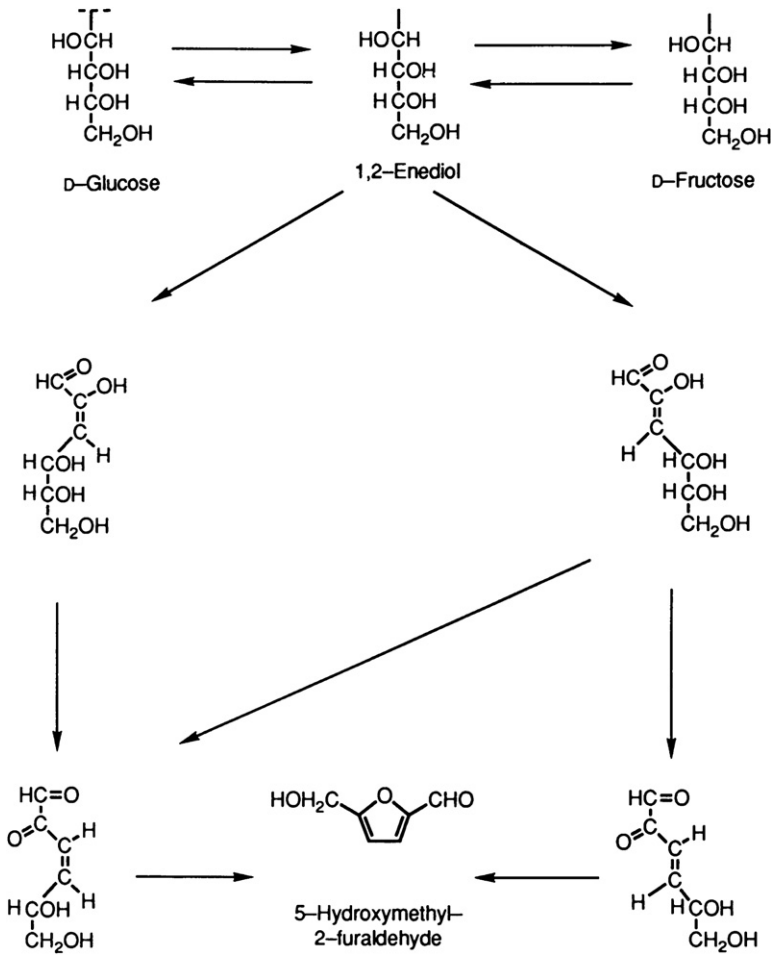
Continued heating results in the dehydration of sugars, leading to the formation of hydroxymethylfurfural, levulinic acid, and humin. This process is initiated by the removal of a hydroxyl group from the 1,2-enediol form located in the α position to the carbonyl group. The initial product, a dicarbonyl, undergoes further degradation. The postulated intermediates in this reaction were thought to be 3-deoxyaldos-2-ene,3-deoxyosulose, and osulos-3-ene (Isbell, 1944; Wolfrom *et al.*, 1948). These compounds were isolated by Anet (1962) during the acidic degradation of fructose. If the initial sugar was a pentose, the final product was 2-furaldehyde. For example, D-xylose yielded approximately 93% 2-furaldehyde, although the yields from other pentoses were much lower. The dehydration rate of D-glucose was reported to be approximately one-fortieth of that observed for D-fructose, with considerably lower product yields (Kuster and Van der Bean, 1977). The mechanism of sugar dehydration from 1,2-enol to 5-(hydroxymethyl-2-furaldehyde) originally described by Anet (1964) has since been modified. This resulted from work by Feather *et al.* (1972) using isotope exchange in which D-xylose in tritiated water was found to be converted to 2-furaldehyde. By monitoring the proportion and amount of isotope converted into 2-furaldehyde they established the existence of an aldose−ketose 1,2-enediol equilibrium as incorporation at C1 of the sugar corresponded to the α-carbon of the 2-furaldehyde. Formation of 3-deoxyglyculose as an intermediate, however, should result in isotope incorporation at the C3 position in the furan ring. The absence of any isotope exchange eliminated any 1,2-enediol equilibrium during the reaction, thus making 1,2-enediol the rate-limiting step. It also eliminated 3-deoxyglyculose as an intermediate and supported the reaction sequence shown in Scheme 6.16.

Isomaltol and 2-(hydroxyacetyl)furan are formed during the acid treatment of D-fructose, suggesting that 2,3-enediol is the precursor:



Isomaltol 2-Hydroxyacetyl furan

Their formation involved removal of a hydroxyl at C4 and C1 followed by dehydration of the furanone ring. Using tritium-labeled D-glucose, D-fructose, and D-mannose, Harris and Feather (1975) found that D-fructose underwent acid-catalyzed dehydration and degradation at a much faster rate than the aldose sugars. Among the major products detected were 5-(hydroxymethyl)-2-furaldehyde, 2-(hydroxyacetyl)furan, and levulinic acid. The




**SCHEME 6.16** Mechanism of sugar dehydration from 1,2-enediol to 5-hydroxymethyl-2-furaldehyde. *(Adapted from Feather and Harris, 1973.)*

difference in rates of degradation explained, in part, why the levels of fructose observed by Mawhinney *et al.* (1980) remained low and constant during the isomerization of acidified D-glucose. Kuster and Temmink (1977) investigated the influence of pH and weak acid anions on the dehydration of D-fructose but were unable to detect 5-hydroxymethyl-2-furaldehyde (HMF) formation from D-fructose at pH $> 3.9$, while at pH $> 2.7$ no levulinic acid was formed. Isomerization of D-fructose to D-glucose was observed at pH above 4.5. It was apparent that the formation of HMF by dehydration of D-fructose and rehydration of HMF to levulinic and formic acids were catalyzed by acids, the latter requiring greater acidity. The formation of HME, one of the major caramelization products produced over a pH range of 6.0−6.7, is presumably a precursor of the pigment. In addition to HMF, a minor product, 2-(2-hydroxyacetyl)furan, also appeared to be formed by 2,3-enolization instead of 1,2-enolization of D-fructose.

The pyrolysis of sucrose was reported by Johnson *et al.* (1969) to produce maltol. The formation of maltol and isomaltol, together with ethyl lactate, furfural, 3-hydroxypropionic acid, 5-hydroxymethylfurfural, levulinic acid, and 2-furoic acid, was later detected by Ito (1977) when an aqueous solution of sucrose at pH 2.3 was heated to 120°C. The initial step in the acid-catalyzed browning of sucrose is hydrolytic cleavage with release of the constituent monosaccharides. Several studies have shown that this can occur in freeze-dried sucrose systems at 37°C, where the monolayer of absorbed water is involved in the hydrolysis (Karel and Labuza, 1968; Schoebel *et al.*, 1969). Flink (1983) monitored the development of non-enzymatic browning in sucrose-bound systems during freeze-drying and storage at room temperature. Hydrolysis of sucrose to glucose and fructose occurred following the primary sublimation stage of drying. The increased production of HMF, measured by monitoring absorbance at 280 nm, was evident at the end of the primary freeze-drying process. Storage of the freeze-dried samples over an $a_w$ range of 0−0.40 showed a reduction in absorbance in the presence of increased levels of water due to the slowing down of the

reaction. The reduction in weight at $a_w$ of 0 was a clear indication that water can be produced in the browning reaction. Following production of HMF, a brown color developed which was monitored at 400 nm. The browning reaction was attributed to the increase in hydrogen ion concentration taking place with passage of ice interface during freeze-drying. Increase in temperature was accompanied by a rapid hydrolysis of sucrose to glucose and fructose in which fructose rapidly underwent dehydration. This study explained the stability of products during freeze-drying and the storage needs of high-acid foods containing sugar, such as fruit juices.

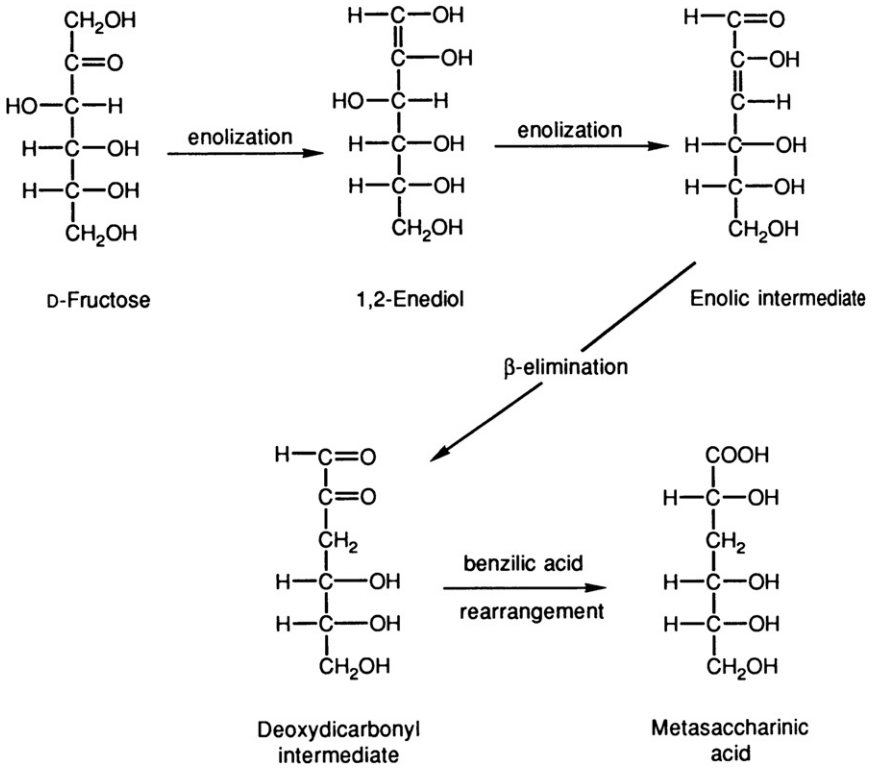
## B. Alkaline Degradation

The initial reaction in the degradation of sugars under alkaline conditions follows the Lobry de Bruyn–Alberda van Eckenstein transformation via the 1,2- and 2,3-enediol. As discussed previously, enolization is a general reaction for carbonyl compounds with an α-hydrogen atom. Alkalis are much more effective catalysts than acids for the enolization of sugars (Pigman and Anet, 1972). Under mild alkaline conditions the series of reactions shown in Scheme 6.17 takes place. Under strong alkaline conditions, continuous enolization progresses along the carbon chain, resulting in a complex mixture of cleavage products including saccharinic acids. The formation of metasaccharinic acid is detailed in Scheme 6.17.

A particular feature of the alkaline degradation of hexoses is the extensive fragmentation which occurs, resulting in the production of 2- and 4-carbon fragments, including saccharinic acids, lactic acid, and 2,4-dihydroxybutyric acid (Harris, 1972; Feather and Harris, 1973). The recombination of some of these fragments accounts for the formation of a variety of compounds, including 2,4-dihydroxybutyric acid (Harris, 1972). A detailed discussion of fragmentation and recombination reactions of sugars under alkaline conditions is covered by Feather and Harris (1973).

## C. Aromatic Compounds

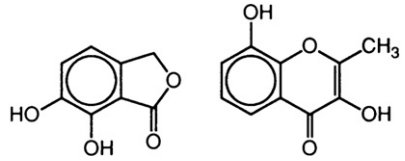
A number of cyclic compounds were isolated among the products formed when aqueous solutions of D-glucose and D-fructose were heated to 160°C at pH 4.5. While these compounds were similar for both hexoses, the yields were




**SCHEME 6.17** Alkaline degradation. *(Adapted from Feather and Harris, 1973.)*

much lower in the case of D-glucose. The major compound formed was hydroxymethylfurfural, although a large number of phenolic compounds were also produced.

The predominant phenol detected during the acid degradation of hexoses was isobenzene furanone, whereas chromone alginetin was the major product formed from pentoses and hexuronic acids (Theander, 1981):




Isobenzene furanone Alginetin

This difference in specificity was not evident, however, when sugars were degraded under alkaline conditions. Forsskahl *et al.* (1976) noted a similarity in the pattern of phenolics formed under alkaline or neutral conditions. The compounds identified included a number of cyclic enols and phenols. The low yields obtained for these compounds reflected their instability under alkaline conditions. The formation of cyclopentones was reported earlier by Shaw *et al.* (1968) from the alkaline treatment of D-fructose. These compounds were isolated among the aroma components of roasted coffee by Gianturco *et al.* (1963) and had a strong caramel-like odor. The only common phenolic compounds identified from either the acid or alkaline treatments of glucose were catechol, 4-methyl-1,2-benzene diol, and 3,4-dihydroxy benzaldehyde (Popoff and Theander, 1976).

The development of color is extremely complex and involves a series of polymerization reactions. Theander (1981) reported that reductic acid and catechols were much more active color producers than furfurals.

### D. Difructose Anhydrides: A Caramelization Tracer

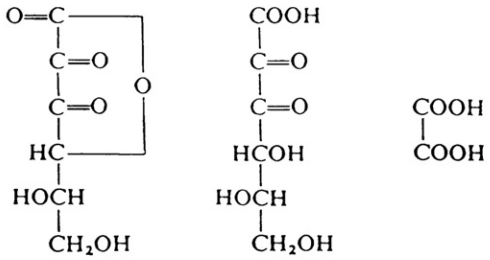
The condensation of two fructose molecules via caramelization was reported to occur during the heating of sugars or food products rich in sugars, leading to the formation of a major non-volatile fraction containing difructose anhydrides (Defaye *et al.*, 2000). Difructose anhydrides, which are pseudodisaccharides, were first reported by Tschiersky and Baltes (1989), with later structural studies by Defaye and Garcia Fernandez (1994, 1995). They are monitored as a tracer for caramelization in food and food additives as caramels, chicory, and dehydrated foods (Defaye *et al.*, 2000). Montilla *et al.* (2006) reported that difructrose anhydrides could be used as an indicator of coffee quality as well as to test the authenticity of honey.

## IX. ASCORBIC ACID OXIDATION

The browning of citrus juices and concentrates also involves Maillard-type reactions between amino acids and sugars present in citrus products. This was confirmed by Clegg (1969), who demonstrated improved color stability of lemon juice following the removal of amino nitrogen by cation-exchange resins. A patent was subsequently registered by Huffman in 1974 based on improved flavor stability when orange concentrate was treated with cation-exchange resins. The acceleration of browning by the addition of amino acids to model systems containing citrus confirmed their role in browning (Curl, 1949; Joslyn, 1957; Clegg, 1964). A review of citrus browning by Handwerk and Coleman (1988) suggested that the Maillard reaction was initiated in citrus juice by the formation of hexosamines from amino acids and sugars. The involvement of ascorbic and dehydroascorbic acids occurred at a later stage in this process via the formation of α-dicarbonyls, similar to that formed during the degradation of sugars. A recent paper by Schulz *et al.* (2007) used electrospray ionization mass spectrometry to simultaneously detect α-dicarbonyls formed from the thermal treatment of L-ascorbic acid. The compounds identified were glyoxal, methyl glyoxal, diacetyl, 3-deoxy-L-pentosone, and L-threosone. This section will focus on the degradation of ascorbic acid in citrus products in addition to their role, together with amino compounds, in the browning of dehydrated cabbage.

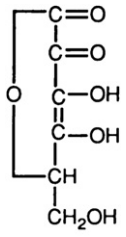
Ascorbic acid plays a central role in the browning of citrus juices and concentrates, for example, lemon and grapefruit. The reaction of ascorbic acid in fruit juices and concentrates is very much dependent on pH, as the browning process is inversely proportional to pH over a range of 2.0−3.5 (Braverman, 1963). Juices with a higher pH are much less susceptible to browning, for example, orange juice at a pH of 3.4. Below pH 4.0, browning is due primarily to decomposition of ascorbic acid to furfural (Huelin, 1953; Huelin *et al.*, 1971).

The degradation of ascorbic acid was investigated by Herrmann and Andrae (1963), who identified 17 decomposition products, including dehydroascorbic acid and 2,3-diketogulonic and oxalic acids:



Dehydroascorbic acid | 2,3-Diketogulonic acid | Oxalic acid

Otsuka *et al.* (1986) identified a degradation product of 2,3-diketogulonic acid by preparative HPLC. The structure of this compound appeared to be the 3,4-enediol form of 2,3-diketogulono-δ-lactone. It was extremely unstable and developed intense brown coloration under mild temperature conditions. These researchers considered 3,4-enediol to be important in the browning of ascorbic acid:

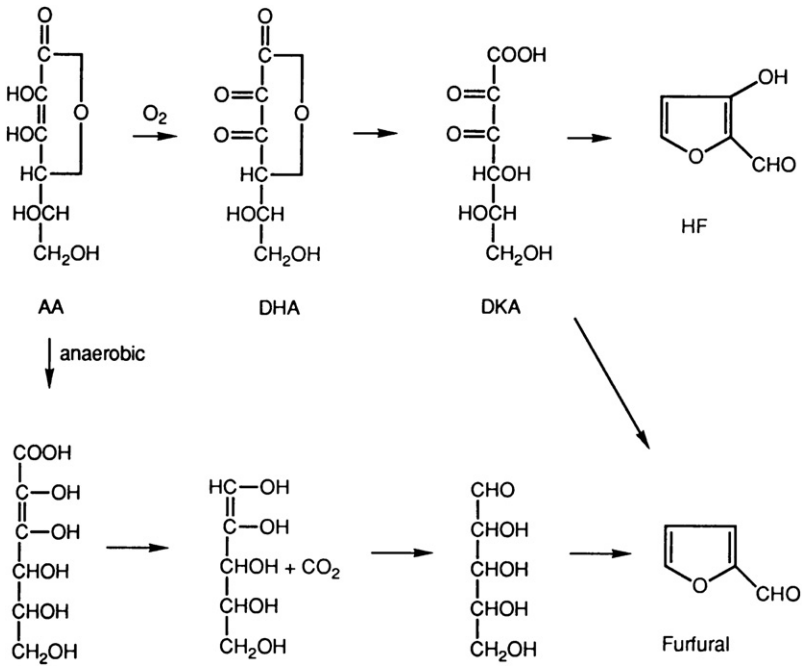


3, 4 Enediol

Ascorbic acid degradation can occur under both aerobic and anaerobic conditions. While the level of air in juice is kept as low as possible by the use of vacuum deaeration and live steam injection, there is still some dissolved oxygen in the juice (0.05%) (Nagy, 1980). Only after the oxygen has been used does anaerobic degradation of vitamin C occur, but at a much slower rate. Tatum *et al.* (1967) reported degradation products of ascorbic acid, half of which were identical to the non-enzymatic browning products found in dehydrated orange and grapefruit powders, that is, instant juices. The aerobic and anaerobic degradation of ascorbic acid is outlined in Scheme 6.18 (Bauernfriend and Pinkert, 1970). The dependency of vitamin C degradation on headspace oxygen was recognized by Bauernfriend (1953). Kefford (1959) reported that the oxidative degradation of ascorbic acid in canned, pasteurized juice occurred during the first few days until the free oxygen was utilized (Nagy and Smoot, 1977). Following this, anaerobic breakdown of ascorbic acid proceeds, but at a tenth of the rate. Improved stability of vitamin C was found in juice sold in tin cans compared to enamel-lined cans as a result of oxygen reacting with the tin and competing with ascorbic acid (Riester *et al.*, 1945). A recent study on lemon juice concentrate by Mazin *et al.* (2007) found that an increase in concentration and temperature increased the rate of degradation of ascorbic acid. In addition, they developed a direct equation that estimated the shelf-life of stored lemon juice based on a first order loss of ascorbic acid at any specified temperature and degradation ratio.

The browning of citrus juices, as discussed earlier, is not due solely to ascorbic acid. Amino acids are also involved via the Maillard reaction, depending on the pH of the juice and basicity of the amine. This is illustrated by the fact that the main degradation product of juices with pH below 4.0 is furfural (Huelin, 1953; Huelin *et al.*, 1971). At pH above 4.0 this pathway is inoperative and explains the discoloration of dehydrated vegetables, which also involves ascorbic acid. Ranganna and Setty (1968) found that the discoloration of dehydrated cabbage was due to Strecker degradation between ascorbic acid and amino acid. This was facilitated by interactions between the oxidized products of ascorbic acid, dehydroascorbic or 2,3-diketogulonic acids, and amino acids during the final stages of the drying process.

The formation of pyrazines from ascorbic acid and amino acids was reported under dry-roasting conditions (Adams and De Kimpe, 2009). The reaction between L-ascorbic acid and L-threonine/L-serine resulted mainly in the formation of pyrazines. The alkylpyrazines formed were 2-methylpyrazine, 2,5-diethylpyraine, 2-ethylpyrazine,




**SCHEME 6.18** Possible vitamin C (ascorbic acid) degradation pathways. AA: ascorbic acid; DHA: dehydroascorbic acid; DKA: diketogulonic acid; HF: hydroxyfurfural *(Nagy, 1980)*.

2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, 3-ethyl-2,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, and 3,5-diethyl-2-methylpyrazine (Yu and Zhang, 2010).

## X. ANTIOXIDANT ACTIVITY OF NON-ENZYMATIC BROWNING PRODUCTS

The ability of MRPs to retard the development of rancidity has been reported by a number of researchers (Griffith and Johnson, 1957; Anderson *et al.*, 1963; Kato, 1973; Yamaguchi and Fujimaki, 1974; Lingnert, 1980). Most studies, including recent ones, have focused on the *in vitro* antioxidant effects of brown MRPs or melanoidins in model systems (Jing and Kitts, 2000; Morales and Jimenez-Perez, 2004; Hayase *et al.*, 2006; Gu *et al.*, 2009, 2010; Rao *et al.*, 2011). Antioxidant effects of melanoidins have also been reported in beer (Morales and Jimenes-Perez, 2004), roasted cocoa (Summa *et al.*, 2008), bread crusts (Michalska *et al.*, 2008), vinegar (Tagliazucchi *et al.*, 2010a), honey (Brudzynski and Miotto, 2011), and wine (Lopez de Lerma *et al.*, 2010). The antioxidant protective effects of melanoidins were attributed, in part, to their ability to chelate metals (Verzelloni *et al.*, 2010), while the anionic nature of melanoidins enabled them to chelate transition metals (Daglia *et al.*, 2008; Rufian-Henares and de la Cueva, 2009; Tagliazucchi *et al.*, 2010b). Cosovic *et al.* (2010) proposed that the nitrogen atoms in melanoidins may chelate Cu. In addition to chelating metal ions, the ability of melanoidins to scavenge free radicals appears to be another mechanism explaining their antioxidant properties. A strong linear relationship was reported between the color intensity of the melanoidin fraction and their ability to scavenge such free radicals as peroxyl (Gomez-Ruiz *et al.*, 2008) and 2,2′-azobis-2-methyl-propanimidamine, dichloride (AAH) (Brudzynski and Miotto, 2011). This is shown in Figure 6.11 by the linear relationship between browning (as expressed as $a_{420}$) and the ability of melanoidins to scavenge peroxyl radicals, expressed as $R_{inh}$ (Morales and Jimenez-Perez, 2004). Some studies were unable to find any linear correlation between radical-scavenging activity and browning (Morales and Jimenez-Perez, 2004; Morales, 2005). However, this was attributed to the complex nature of the components in melanoidins, as well as the assay methods used to measure radical-scavenging activity (Wang *et al.*, 2011).

Using a coffee MRP model system, made up of arabinose and serine (C), Liu and Kitts (2011) showed the Maillard reaction to be the main contributor to the antioxidant activity in roasted coffee beans (RC). The formation of MRPs in roasted coffee beans, non-roasted coffee beans (NRC), and the arabinose−serine model system (C) was measured by fluorescence, ultraviolet−visible spectra and tristimulus Hunterlab measurements. The relative antioxidant activities of RC, NRC, and C were monitored by the oxygen radical absorbance capacity and Trolox equivalent antioxidant capacity methods and reducing power (Rp), while total chlorogenic acid content was

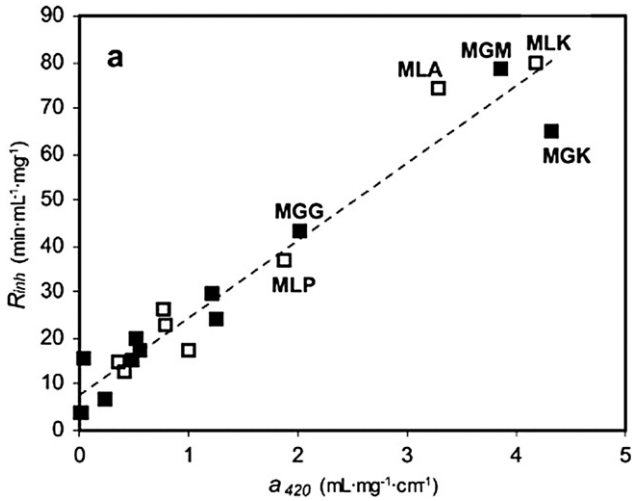



**FIGURE 6.11 Relationship between peroxyl radical scavenging activity of melanoidins, expressed as $R_{inh}$, and browning (expressed as $a_{420}$), for glucose melanoidins (■) and lactose melanoidins (□).** The dotted line shows the linear regression for melanoidins from model systems *(Morales and Jimenez-Perez, 2004).*

determined in RC and NRC extracts. The ultraviolet absorption (250−700 nm) spectrum for RC was similar to the model MRP extracts (C) but quite different from NRC (Figure 6.12). The NRC spectrum, however, was similar to the chlorogenic acid standard but its absence in RC confirmed its almost complete destruction during the roasting process (Budryn *et al.*, 2009). While the fluorescent spectrum for RC was similar to the control (C), no fluorescence was observed in the NRC extract, owing to the absence of a Maillard reaction and the lack of formation of MRPs. The high antioxidant activity associated with the NRC extract was attributed to the natural phenolics, which were substantially lost in the roasted sample. Consequently, any significant antioxidant activity in RC was attributed primarily to the MRPs formed during the roasting of the coffee beans and their similarity to the MRPs produced in the model system.

## XI. INHIBITION OF NON-ENZYMATIC BROWNING

A major concern of food technologists is to control or minimize non-enzymatic browning reactions in food processing. The particular method used must be adapted to each food product. Various methods have been proposed for controlling these reactions.

### A. Temperature

An increase in temperature or time of heat treatment accelerates the rate of these reactions (Labuza and Baisier, 1992). Thus, lowering the temperature during processing and storage can lengthen the lag phase, that is, the period needed for the formation of brown-colored products. Most foods will not brown below −10°C during normal storage (Nursten, 2005).

### B. Moisture Content

The dependency of browning reactions on moisture content provides a convenient method for control. A reduction in moisture content in solid food products by dehydration reduces the mobility of reactive components (Loncin *et al.*, 1968; Eichner and Karel, 1972; Labuza and Saltmarch, 1981; Fox *et al.*, 1983). However, the rate of browning often exhibits a maximum with a moisture content of 5−30%, so that partial dehydration may make browning worse rather than better (Nursten, 2005). In the case of solutions, an increase in water activity will diminish the reaction velocity. Not only does this dilute the effect of the reactants but water also represents the first reaction product of the condensation step in the Maillard browning reaction. This is illustrated in Figure 6.13, where the browning rates of an avicel−glucose−glycine system were low at both high and low $a_w$ (McWeeny, 1973).

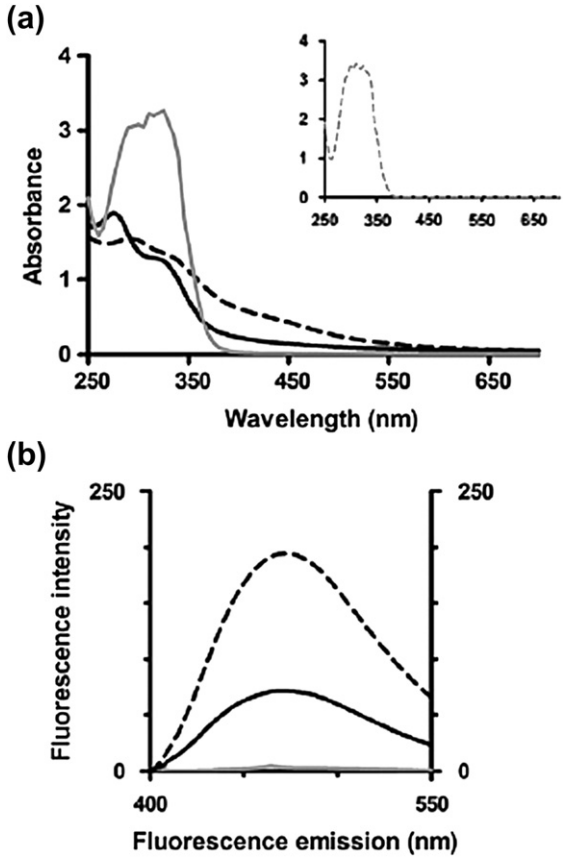



**FIGURE 6.12 (A) Ultraviolet (UV) visible spectra and (B) Fluorescence emission spectra of coffee and model Maillard reaction products (MRPs).** The UV spectra of 0.1 mg/ml chlorogenic acid (CGA) are also shown (dashed line; A insert). Samples were diluted to 0.5 mg/ml with distilled deionized water before UV spectrum measurement and diluted to 0.25 mg/ml with milli-Q water before fluorescence spectrum measurement. Non-roasted coffee beans (NRC) (solid gray line); roasted coffee beans (RC1) (solid black line); model Maillard reaction product (MRP-1) (dashed line). The spectra patterns of RC1 and RC2 are similar, so only the spectra of RC1 are shown in the figure *(Liu and Kitts, 2011)*.

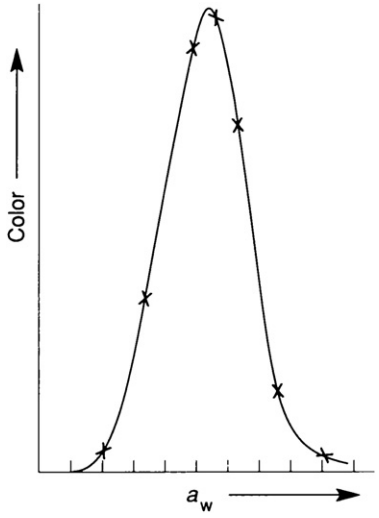



**FIGURE 6.13 Browning of avicel–glucose–glycine as affected by water activity ($a_w$) after 8 days at 38°C** *(McWeeney, 1973).*

## C. pH

The Maillard reaction is generally favored under more alkaline conditions, so lowering the pH provides a useful method of control (Fox *et al.*, 1983; Nursten, 2005). This method has been used in the production of dried egg powder in which acid is added prior to the dehydration process to lower the pH. The pH is restored by the addition of sodium bicarbonate to the reconstituted egg.

## D. Gas Packing

Gas packing excludes oxygen by packing under an inert gas. This reduces the formation of lipid oxidation products capable of interacting with amino acids. The exclusion of oxygen is thought to affect those reactions involved in the browning process and not the initial carbonylamino reaction step.

## E. Biochemical Agents

Removal or conversion of one of the reactants in the sugar–amino acid interactions forms the basis of the biochemical method. For instance, in the commercial production of egg white, glucose is removed by yeast fermentation prior to drying. The direct application of enzymes such as glucose oxidase and catalase mediates the conversion of glucose to gluconic acid, which is no longer capable of combining with amino acids. This enzyme has been used for many years to remove glucose from egg before spray-drying (Lightbody and Fevold, 1948). Glucose oxidase has the additional advantage of removing any residual oxygen and is used to reduce headspace oxygen during the production of bottled products.

## F. Chemical Inhibitors

A variety of chemical inhibitors has been used to limit browning during the production and storage of a number of different food products. The most widely used are sulfur dioxide and sulfites, although thiols, calcium salts, and aspartic and glutamic acids have also been studied. The use of thiols as inhibitors is limited because of their unpleasant properties.

### *1. Sulfur Dioxide/Sulfites*

Sulfur dioxide is unique in its ability to inhibit the Maillard reaction and can be applied as a gas or in solution as sulfite or bisulfite. Sulfur dioxide is not only capable of partially bleaching chromophores that have already formed but also inhibits color formation at the beginning of the reaction (McWeeny, 1984). The mechanism involves the binding of sulfur dioxide/sulfite with glucose to form hydroxy-sulfonate and other compounds from which sulfur dioxide/sulfite can be reversibly released. This results in the blocking of the carbonyl group of the sugar, rendering it unavailable for interaction in the typical Maillard reaction. As the reaction proceeds, sulfur dioxide/sulfite becomes irreversibly bound. This permits monitoring of the progress of browning by measuring the amount of sulfur dioxide or sulfite in the bound or free form. For example, color development for a glucose–glycine model system was not observed by McWeeny (1969) until all the free sulfite was depleted, while the ratio of bound to free sulfite increased as the reaction proceeded (Figure 6.14).

Inhibition of non-enzymatic browning by sulfite appears to involve the formation of stable sulfonates. In the case of ascorbic acid browning, 3-deoxy-4-sulfopentulose is formed with the corresponding 6-carbon compound, 6-deoxy-4-sulfohexulose, for the sulfited inhibition of the Maillard reaction (Knowles, 1971; Wedzicha and McWeeny, 1974a, b). Wedzicha and McWeeny (1975) monitored the formation of several organic sulfonates from sulfited foods. These compounds possess a dicarbonyl group, which makes them particularly reactive and at elevated temperatures can lead to the formation of sulfur compounds with other food components. McWeeny (1984) pointed out that future research on the role of sulfur dioxide and sulfites in inhibiting the Maillard reaction should focus on the nature of those precursors with which they react. In addition, further information is needed on the effect of time, temperature, pressure, pH, and additives on the quantitative and qualitative formation of compounds formed in foods to which sulfur dioxide or sulfite has been added. This work is particularly important in light of the current trend towards limiting intake of sulfur dioxide and sulfites in foods.

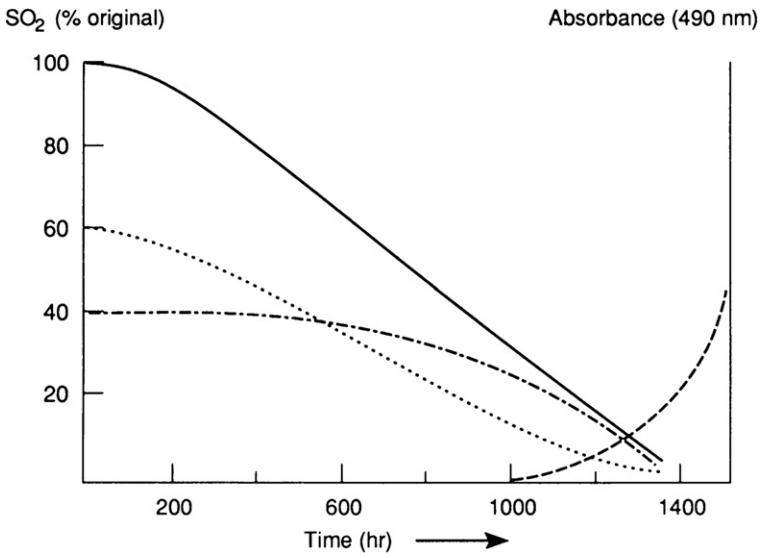



**FIGURE 6.14 Color production and loss of sulfur dioxide ($SO_2$) from glucose–glycine–$SO_2$ during incubation at 55°C.** (● ● ●) free $SO_2$; (● – ● –) bound $SO_2$; (– –) total $SO_2$; (—) absorbance at 490 nm (McWeeny, 1969). *(Copyright © by the Institute of Food Technologists.)*

### 2. Aspartic and Glutamic Acids

A study by Nafisi and Markakis (1983) indicated the potential of aspartic and glutamic acids for inhibiting the Maillard browning reaction. Using model systems containing lysine–glucose/lysine–fructose (pH 8.0, 60°C for 58 hours), these researchers found that L-aspartic acid or L-glutamic acid decreased the rate of browning, as seen in Table 6.6. Dipping specially prepared potato chips into either aspartic or glutamic acid solutions before frying was accompanied by less darkening as measured by Hunter *L* values. This corresponded to a mean value of 38.4 for the untreated potato chips compared to 46.4 and 43.7 for the potato chips dipped in aspartic and glutamic acids, respectively.

While the various chemical inhibitors discussed can, with varying degrees of success, limit the progress of browning, the nutritional value of the food could still be reduced. For instance, the initial stage of the Maillard reaction, the carbonylamino step, could still render the amino acids unavailable without any visible browning during this stage. It is extremely difficult to ensure that this step is prevented.

**TABLE 6.6 Hunter *L* Values of Control and Treated Potato Chips[a]**

| Replicate | Control | Dipped in Aspartic Acid | Dipped in Glutamic Acid |
|---|---|---|---|
| 1 | 39.0[b] | 47.6 | 44.2 |
| 2 | 38.3 | 44.6 | 44.7 |
| 3 | 38.2 | 45.3 | 43.0 |
| 4 | 39.0 | 47.0 | 43.0 |
| 5 | 37.9 | 46.8 | 43.7 |
| 6 | 36.7 | 46.6 | 43.9 |
| 7 | 39.5 | 47.2 | 43.6 |
| Mean | $38.4 \pm 0.57$[c] | $46.4 \pm 1.00$ | $43.7 \pm 0.57$ |

[a] *The treatment consisted of freeze-drying potato slices and dipping them in 0.04 M aspartic or glutamic acid before frying.*
[b] *Each* L *value is the average of three readings obtained by rotating the sample at 120° angles.*
[c] *The differences between control and treated samples are significant at the 99% probability level. The difference between treated samples is not significant.*
Reproduced from Nafisi and Markarkis (1983).

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