

The Significance of Pyrazine Formation in Flavor Generation during the Maillard Reaction

-Review-

Seung Seok Yoo

Bioproducts Research Center, Yonsei University, Seoul 120-749, Korea

Abstract

The chemistry background of the Maillard reaction focused on pyrazines and factors affecting the reaction products were reviewed. The Maillard reaction, also called a non-enzymatic browning reaction, is quite complex and generates numerous reaction products. In processed foods, it is generally accepted as a key reaction to produce flavor components. Specially, pyrazines possess an important impact character on the roasted foods with other heterocyclic compounds. The Maillard reaction is initiated by condensation between reducing sugar and amino group, and *N*-glycosylamines are produced via Schiff base with dehydration of water. After the rearrangement of the *N*-glycosylamines, they follow transformation into deoxyhexosones which are re-active intermediates. Degradation and fragmentation are facilitated by rearranged compounds. By condensation, pyrazine, one of the final Maillard products, is generated as a relatively stable form to provide specific aromas. During the processes of the reaction, chemical or physical environmental parameters affect the formation of the products.

Key words: Maillard reaction, pyrazines, heterocyclic compound, flavor

INTRODUCTION

The Maillard reaction is a non-enzymatic browning reaction, and generally considered as a key reaction for the formation of flavors in processed foods as well as lipid oxidation. Much interest has been focused on the Maillard reaction from the flavor chemistry point of view over past decade. Food aromas are primarily generated either by enzymatic and/or microbiological processes or by thermal treatment. Most processed foods usually produce their characteristic flavors through the Maillard reaction(1). The principal reaction steps involved in the Maillard reaction have fairly well described by Hodge(2), and the scheme of the reaction is generalized. Although the mechanism of the Maillard reaction is quite complex, it is generally known that the process is initiated by the condensation reaction between an amine and a reducing sugar (3).

Heterocyclic compounds such as pyrazines, pyrroles, pyridines, thiazoles and oxazoles have an important impact on the flavor of many foods, and are specially generated by a series of these reactions(4). Pyrazines are considered to be fairly representative of the flavor of roasted foods, among these heterocyclic compounds, even though relatively few of the pyrazines are character-impact flavor compounds. They commonly possess the sensory pro-

perties of roasted, toasted, and nutty character(5-7).

Numerous studies have subsequently been reported on the formation of pyrazines through the Maillard reaction by reacting single amino acid with an equal mole of sugar in simple model systems(8-10). However, since real food systems consist of mixtures of different amino acids and sugars with complex environment, the study of pyrazine formation through the Maillard reaction based on various environmental factors have generated a great deal of interest.

The main objective of the study is to review the chemistry background of the Maillard reaction, and also scrutinize the factors affecting the pyrazine formation via Maillard reaction.

CHEMISTRY OF THE MAILLARD REACTION

The mechanism of the Maillard reaction could be briefly summarized as follows(11). Initially, *N*-glycosylamines are produced via the Schiff base from the addition of amino compounds into sugars with dehydration of water. It is followed by the rearrangement to form Amadori and Heyns products. These rearranged intermediates undergo either dehydration reaction to form furfurals or reductones, or fragmentation to produce dicarbonyl compounds by retro-aldolization reaction. These fission products such as diacetyl, acetol, and pyruvaldehyde trans-

form to further fragmented products by the Strecker degradation. From the interaction of an additional amino compound with either furfural or dehydroreductone or fission product or Strecker aldehyde, heterocyclic aroma compounds are generated besides flavorless melanoidins with a high molecular weight. The scheme of the principle reaction is generalized in Fig. 1.

To clearly understand the series of complex Maillard reaction, each stage of the reaction will be discussed separately. The proposed pathways of the Maillard reaction can be tied together and divided into three major stages: the initial, intermediate, and final stage.

Initial stage

A condensation reaction occurs between a carbonyl group of a reducing sugar and an amino group from a free amino acid, peptide, or protein(12,13). This reaction is initiated by a nucleophilic attack of the nitrogen in an amino group which gives an unshared pair of electrons to the electrophilic carbon of the carbonyl group(14). Because the amine group acts as a nucleophile, the behavior of the attack depends on the pH of the environment, and enhances at more basic pH regions. In an acidic condition, the amino group will not attack the electrophilic carbonyl carbon due to the protonated form of the amino group.

The condensation reaction is considered to involve the opening of the cyclic form of the sugar, and the addition of the amine to the carbonyl group as well as the subse-

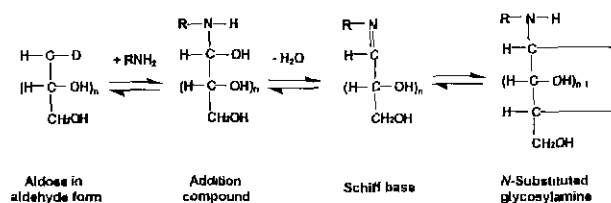


Fig. 2. Formation of *N*-substituted glycosylamine.

quent elimination of a molecule of water to produce a Schiff base(11,15). The formation of the Schiff base is dependent on the form of sugar present as well as the amount of that sugar because the Maillard reaction can only proceed if the sugar is in the open chain form as a result of mutarotation. This intermediate then cyclizes to give the corresponding *N*-substituted glycosylamine, and rapidly equilibrates with the cyclic isomer(Fig. 2).

By the Amadori rearrangement, *N*-substituted glycosylamine from an aldose is then converted to the 1-amino-1-deoxy-2-ketose called Amadori products under acid-catalization. When a ketose is involved instead of an aldose sugar, a ketosylamine is formed that undergoes the Heyns rearrangement to form a 2-amino-2-deoxy-1-aldose which is called Heyns products(1,16). These products are colorless and non-volatile compounds which have been isolated from sugar-amine model systems as well as from natural products including roasted meat, green tea, black tea, tomato powder, and apricots(3).

These two rearrangements are followed similar transformation except the type of reducing sugar. *N*-Substituted aldosylamine is protonated and equilibrated with the protonated Schiff base. Deprotonation occurs at carbon-2 of the protonated Schiff base to the formation of the enol form, which tautomerizes to the Amadori products. On the other hand, *N*-substituted ketosylamine is protonated at oxygen of carbon-6, which equilibrated with the protonated Schiff base. Through the tautomerization, the intermediate is converted to Heyns products. The mechanisms of the formation of Amadori and Heyns intermediates proposed by Vermin and Parkanyi(4) are shown in Fig. 3.

Amadori or Heyns intermediates are still thermally unstable although these rearranged products are more stable rather than the original *N*-substituted glycosylamines (15,17). Therefore, they undergo further reactions such as deamination and dehydration to give numerous degradation products. The products of the initial stage do not contribute to the food aromas directly, however, the rearranged intermediates are very important precursors of flavor compounds(11,15).

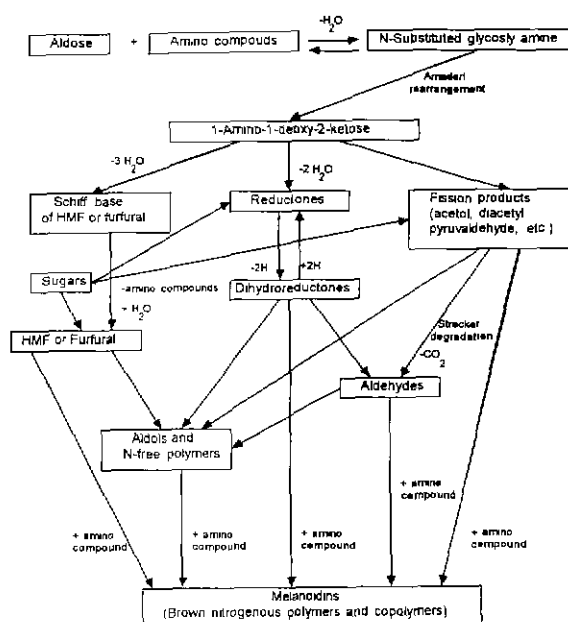


Fig. 1. General scheme of the Maillard reaction.

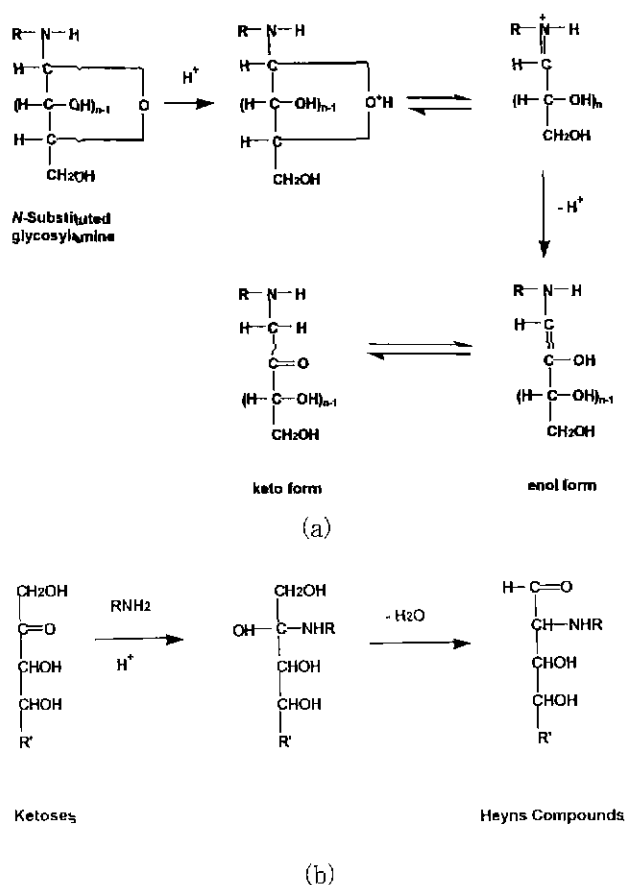


Fig. 3. The formation of a) Amadori and b) Heyns intermediates from glycosylamines.

Intermediate stage

This stage is represented by the fragmentation of a sugar, and degradation of an amino acid or a sugar. Fig. 4 shows the proposed pathways of the decomposition of Amadori and Heyns products which lead to numerous characteristic flavor compounds or their precursors in the Maillard reaction. In either an acidic or a basic condition, the Amadori and Heyns products further react to produce 1-deoxyhexosones or 3-deoxyhexosones which are reactive intermediate compounds(3,17).

Amadori products proceed 1,2-enolization to give 1,2-enaminols in an acidic environment. By the subsequent dehydration and elimination of an amine molecule from the intermediate, 3-deoxyhexosones are formed. These α -dicarbonyl intermediates yield dehydroreductones by the loss of one molecule of water. In addition to the rearrangement from the Amadori products, 2-Amino-2-deoxy-1-aldoses(Heyns products) also give the 3-deoxyhexosones by 1,2-enolization and elimination of the amine from carbon-2, which lead to the formation of dehydroreductones. This latter compounds can lose another molecule of water and cyclize to yield either furfural from pentoses or 5-hydroxymethylfurfural(HMF) from 2-ketohexoses(11).

The rearranged intermediates undergo 2,3-enolization, in a basic condition, to give a 1-amino-2,3-enediol which eliminates the amine at C-1 to form a 1-deoxyhexosone intermediate. This dihydroreductone is in equilibrium with corresponding reductone that has strong antioxidative properties. Through the further cyclization reactions, these

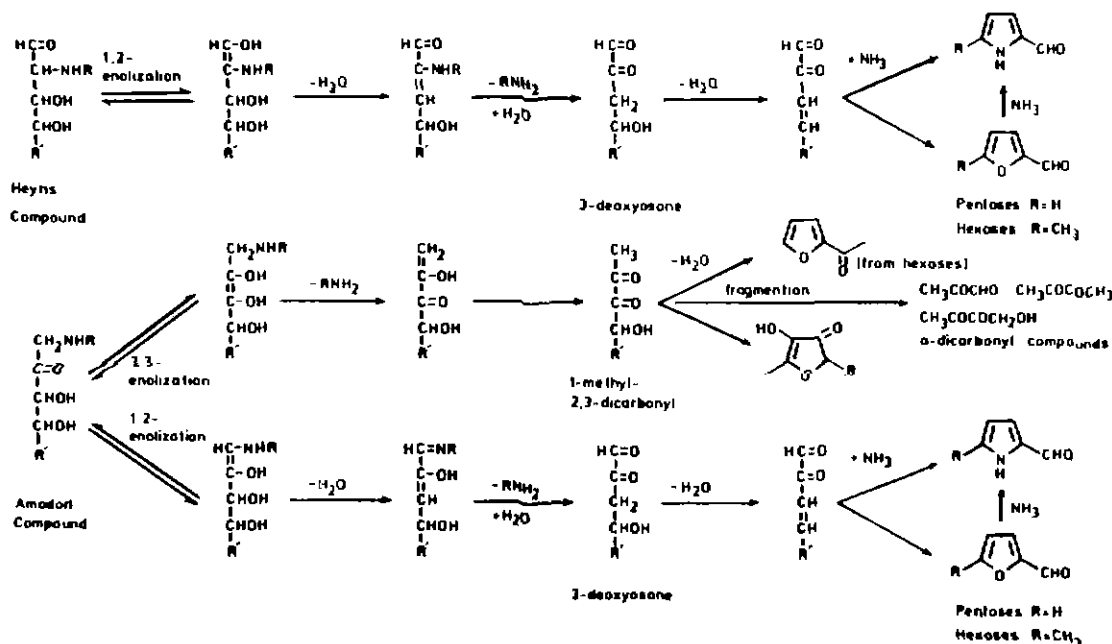


Fig. 4. Decomposition of Amadori and Heyns products.

intermediates also produce characteristic sugar degradation products such as maltol and isomaltol.

In spite of the presence of the several other intermediates, 1-deoxyhexosones and 3-deoxyhexosones are common intermediates produced as the result of catalytic and nucleophilic pathways confirmed by Yaylayan(15). These important deoxyhexosones are further fragmented into α -dicarbonyl intermediates mainly by the retro-aldolization reaction, pyruvaldehyde from 3-deoxyhexosones and diacetyl or glyoxal from 3-deoxyhexosones

Strecker degradation is also considered as another important reaction to form flavor compounds in addition to those pathways(18,19). The proposed mechanism is shown in Fig. 5. Strecker degradation involves the oxidative deamination and decarboxylation of an α -amino acid in the presence of a dicarbonyl compounds. This compound then rearranges and liberates a carbon dioxide to form an aldehyde being reduced a number of carbon, which is called the Strecker aldehyde(Table 1). The final amino carbonyl compound then reacts with another amino carbonyl, which results in the formation of a dihydropyrazine which is an unstable intermediate. By the oxidation process or other proposed pathways, this intermediate converts to heterocyclic compounds such as pyrazines(14). These compounds are very important in processed foods because of their characteristic sensory properties(20,21). Depending on the location and the kinds of substitution, these compounds possess a typical roasted, toasted, or nutty aroma character(22,23).

Final stage

The aldol condensation and the polymerization are main processes for each fragmented compounds or each reactive intermediates in the final stage of the Maillard reaction(24). It is described and divided into three categories the transformation pathways of the intermediates into final products by Weir(5). Dehydration and degradation reactions are predominantly involved in these proposed mechanisms, and amino compounds are commonly required to generate the final products.

FACTORS AFFECTING THE PYRAZINE FORMATION

The study of the factors to affect the formation of the products from the Maillard reaction focused on pyrazines have been extensively reported. These factors include chemical and physical parameters and can be categorized

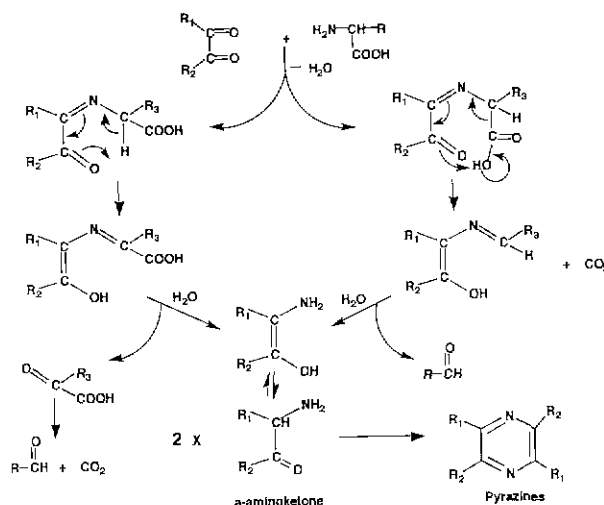


Fig. 5. Proposed mechanism of Strecker degradation from dicarbonyls and amino acids.

Table 1. Volatile Strecker aldehydes from the Reaction of α -amino acids and α -dicarbonyl compounds

Amino acids	Strecker aldehydes
Glycine	Formaldehyde
α -Alanine	Acetaldehyde
α -Aminobutyric	Propionaldehyde
Valine	Isobutyraldehyde
Leucine	Isovaleraldehyde
Isoleucine	2-methylbutanal
Serine	Glycolaldehyde
Threonine	Lactaldehyde
Methionine	Methional
S-methylmethionine	Acrolein
Cysteine	Acet or 2-Mercaptoacetaldehyde
Phenylglycine	Benzaldehyde
Phenylalanine	2-Phenylethanal
Tyrosine	2-(<i>p</i> -hydroxyphenyl)-ethanal

as i) composition of the system which includes amino acids, sugars, and reaction medium, ii) moisture content or water activity, iii) processing conditions including reaction time and temperature, and iv) other factors such as pH(acid-base effect), and reactant ratio.

System composition

The role of amino acids has thoroughly examined because they are not only one of the major reactants for initiating the Maillard reaction, but also required for the formation of pyrazine compounds(25). In the backbone of the structure of the pyrazines, nitrogen atom can only come from amino compound or free ammonia.

To the formation of the Maillard products including pyrazines, the type and the reactivity of amino acids should be importantly considered. Most of the amino groups in

amino acids are primary amines but proline and hydroxyproline are particularly secondary amines. They react with carbonyls differently compared to the reaction manner of other primary amino compounds. Tressl(26,27) studied the characteristics of reaction particularly during the Strecker degradation stage, and showed the differences in products affecting the flavor development. Specific bi-cyclic and tri-cyclic hetero compounds were produced from either proline or hydroxyproline by the results of their study. This is due to the presence of the acid group around the secondary amine portion of the molecule. The reactivity as well as the amount of amino acids also affect the generation of pyrazines. The reactivity of the amino acids are changed by the functional group of the α -carbon atom reported(28). Piloty and Baltes explained every amino acid possesses its own reaction rate in the Strecker degradation although the common structure of the amino acids is identical. It is demonstrated that arginine, histidine, glycine, and lysine are relatively reactive. Threonine, serine, phenylalanine, and β -alanine possess average reactivities while the reactivities of amino acids not mentioned here are comparatively low. The reactivities of the amino acids can be generally described as both basic and hydroxy amino acids have strong reactivity while the reactivity of the acidic and non-polar amino acids is weak.

The sugar-amino acid model systems were used to demonstrate the reactivity of amino acids(29). The amount of pyrazines was measured and compared. Higher amount of pyrazines was produced when asparagine was reacted with glucose instead of aspartic acid. The result could be explained that the effect is due to the total ammonia concentration in the reaction medium released from each amino acid. Some amino acids have more than one reactive nitrogen in the molecule which participated in the Maillard reaction. However, it is not necessary all the constituent nitrogen of each amino acid should be reactive, because α -amino group of the amino acids is more reactive than others. The effect of the nitrogen source on pyrazine formation was also investigated by reacting glucose and several type of bases(30). Wong and Bernhard concluded the distribution of pyrazines strongly depended on the nature of the each nitrogen source.

The type and the amount of sugar affect the Maillard reaction since sugar is also one of the initial reactants as well as amino compounds. Different type of sugar owns different reactivity based on the rate of ring opens to the

reducible form, because only a open-chain form of the sugar can condensate with amines in the initial step of the Maillard reaction(31). In most reducing sugars, an open-chain form rapidly equilibrates with its closed-chain form of the α and β isomers by mutarotation, and the reactivity of the sugar strongly depends on the rate of mutarotation. It is reported pentoses are more reactive than hexoses, and disaccharides are less reactive rather than either of the monosaccharides. Among the hexoses, D-galactose has the highest ring open rate and highest browning rate, followed by D-mannose, D-glucose, and D-fructose(32). Non reducing sugars such as sucrose can not involve in the Maillard reaction, however, at high temperatures, the glycosidic bond of the sucrose is hydrolyzed to release its monosaccharides and the reactions could proceed in the normal way. The amount of available reducing sugar also affects the rate of the Maillard reaction. In general, the rate of browning reaction increased as glucose level increased due to the closer proximity of glucose to the reactant amino groups. It is suggested that increased proximity overcome the greater diffusion barrier caused by the higher viscosity associated with increased glucose levels.

To elucidate the influence of each sugar on the generation of roast aromas, the total yield and distribution of pyrazine formation were examined(33,34). When asparagine was reacted with either glucose, fructose, sucrose or arabinose, the alkylpyrazine yields were higher with fructose than with glucose, and the ratio of dimethylpyrazine to methylpyrazine was much higher. The higher yields could be due to the fact that fructose forms carbon fragmentation units more readily than glucose. Sucrose also produced good yields of alkylpyrazine compounds, although less than either glucose or fructose. While a 5-carbon sugar must yield one 2-carbon fragment for each 3-carbon unit upon fragmentation, it might be expected more methylpyrazine from a pentose and more dimethylpyrazine from a hexose(34,35).

Moisture content

Water generally acts as both a solvent and a reactant so that it is considered as an important factor in chemical reactions. In the Maillard reaction, water can play as both a positive and a negative role in a number of steps. As a negative effect, water is known to retard several steps in the Maillard reaction. Since the elimination of water is required in either the condensation step between a re-

ducing sugar and an amine in the initial stage of the Maillard reaction, or the dehydration steps in the degradation processes, the excessive amount of water present in the reaction system is likely to inhibit these steps(36). According to the study of the role of water in both dry and aqueous system, rearrangement of *N*-glycosylamine is less dependent on the presence of water.

In general, the optimal moisture content for the formation of pyrazines is at intermediate moisture level(37, and 38). The effect of water on the products from the Maillard reaction seems to depend on a balance between the formation of ketoseamino acid and their decomposition. The former reaction is favored by a low moisture content, while the latter favored by a higher moisture content. The influence of water on the Maillard reaction is also explained as follows. The increase of water content to an optimal amount helps to locate the active groups of reactants close to each other, however, excessive amount of water content in turns inhibits the reaction by diluting the concentration of those reactants, or reducing the possibility of reacting each other. Moisture content also provided a significant effect on the sensory character of aroma compound.

The formation of pyrazines was investigated with an aspect of water activity(*A_w*). Through the kinetic study of pyrazine formation at *A_w* ranging from 0.32 to 0.84, it is found that pyrazine and 2-methylpyrazine production appeared to a maximum at *A_w* of 0.75. In the previous study by Hartman, the sensory results indicated that the higher *A_w* systems gave more boiled aroma, while the lower *A_w* systems provided more roasted aroma character(37,39).

With respect to the Maillard reaction, water can retard the rate of the initial glycosylamine reaction in which water was a product. This effect, known as product inhibition, reported that the maximum yield of the Maillard reaction was at a water activity of 0.7 and that no reaction occurred when it was less than 0.2. At low water activity, water was tightly bound to surface polar sites by chemisorption and was generally unavailable for reaction and solution(40).

Processing conditions

The formation of the Maillard products can varied with the food composition and the range of the temperature which is processed. The Maillard reaction does not require high temperatures and proceeds even room temperature or below of it(41). However, the rate of the Ma-

illard reaction is markedly increased with temperature, and the formation of flavor compounds generally occurs at the temperatures associated with cooking or roasting.

For appreciable pyrazine formation, temperature above 100°C was required(42). Pyrazine formation increased as the temperature of aqueous reaction solutions, however, pyrazines were detected even in the solutions reacted at 50°C. A recent study on the effect of reaction temperature and on the formation of roast aromas has shown that the formation of pyrazines dominated, especially, at higher temperatures, which is the result of the higher formation of α -aminoketones by the Strecker degradation of amino acids with α -dicarbonyl compounds(43,44).

The reaction time, likewise temperature, is an important factor to control the extent of the Maillard reaction. In general, at a given temperature, the formation of brown pigments increased with the reaction time, and the production of pyrazine compounds also increased rapidly as the length of heating period. It is investigated the production of pyrazine compounds at 120°C increased rapidly as the length of the heating period was increased up to 24hr, and the ratio of dimethylpyrazine to methylpyrazine produced continued to increase although methylpyrazine was the major product in the early stage of the reaction. Reineccius(45) also mentioned that processing time most obviously influences flavor by influencing the amount of each flavor constituent which is present, and thus flavor balance. The sensory properties of pyrazines to affect roast aromas are shown in Table 2 with a wide range of sensations.

The yields of pyrazines and brown pigments increased

Table 2. Sensory Properties of typical alkylpyrazines

Pyrazines	Odor descriptions
Methyl	Green, nutty, roasted, sweet
Ethyl	Buttery, nutty, sweet, green
2,3-Dimethyl	Meaty, nutty
2,5-Dimethyl	Strong nutty, musty, meaty roasted
2,6-Dimethyl	Green nutty
2-Ethyl-3-methyl	Fragrant, floral, earthy, raw, nut-like
2-Ethyl-5-methyl	Raw green, sickly, fruity, coffee
2-Ethyl-6-methyl	Mild roasted, raw green, fruity, coffee
Trimethyl	Musty, nutty, sweet, caramel, potato-like
Tetramethyl	Walnuts, green
2,5-Dimethyl-3-ethyl	Roasted, nutty, earthy, walnuts, baked potato-like
2,6-Diethyl	Steam cooked

with the temperature and time, but the optimal processing conditions will be varied or determined on the reaction systems which are chosen.

Others

The Maillard reaction as well as the formation of pyrazines is effectively controlled by the pH of the reaction system(16,45). Generally, the rate of the formation of the Maillard products and pyrazines are accelerated by increasing pH. The yield of methylpyrazine and dimethylpyrazine were dramatically increased when base was incorporated into the media(46). It could be explained that changing the pH of the reaction system influenced both the reactivity of the amino group of the amino acid toward the carbonyl of sugar, and the rearrangement and fragmentation of sugar itself. At low pH, the carbonyl-amino condensation to the Schiff base is slowed because of the loss of the basic amino groups. The effect of pH on the flavor character and strength was also evaluated. Besides the effect of pH as well as that of composition of the system including amino acids and sugars, moisture contents, processing conditions, other factors such as lipid, reactant ratio, and medium were also investigated by a number of groups as factors affecting the formation of pyrazines through the Maillard reaction(47-49).

SUMMARY

The mechanism of the pyrazine formation during the Maillard reaction and environmental factors affecting the reaction products were thoroughly reviewed. The Maillard reaction which generates numerous characteristic reaction products provides important meaning to the flavor industries. Pyrazines frequently generating the roast aromas are mainly formed by Strecker degradation after condensation and rearrangement of the precursors. The pyrazine formation is affected by different reaction factors during processing. The specific Maillard products, pyrazines, which are heterocyclic compounds, could be finely regulated and controlled by understanding the chemistry background of the each steps and factors which ruling the reaction products.

REFERENCES

- Whitfield, F. B. : Volatiles from interactions of Maillard reactions and lipid. *Crit. Rev. Food Sci. Nutr.*, **31**, 1(1992)
- Hodge, J. E. . Dehydrated Foods: Chemistry of browning reactions in model systems. *J. Agric. Food Chem.*, **1**, 928 (1953)
- Nursten, H. E. : 5th International symposium on the Maillard reaction. *Trns. Food Sci. Techn.*, **5**, 53(1994)
- Vernin, G. and Parkanyi, C. : Mechanisms of formation of heterocyclic compounds in Maillard and pyrolysis reactions. In *"The chemistry of heterocyclic flavouring and aroma compounds"* Vernin, G(ed.), Ellis Horwood Publishers. London, p.151(1982)
- Weir, G. S. D. : Hydrolysis of proteins as a precursor for flavor. In *"Protein hydrolysate as flavorings"* Weir, G. S. D.(ed.), Wiley. New York, p.175(1989)
- Maga, J. A. . Pyrazine update. *Food Rev. Int.*, **8**, 479(1992)
- Maga, J. A. : Pyrazines in Foods: An Update. *CRC Crit. Rev. Food Sci. Nutr.*, **16**, 1(1982)
- Arnoldi, A., Arnoldi, C., Baldi, O. and Griffini, A. . Flavor components in the Maillard reaction of different amino acids with fructose in cocoa-butter-water. Qualitative and quantitative analysis of pyrazines. *J. Food Sci.*, **36**, 988 (1988)
- Baltes, W. and Mevissen, L. : Model reactions on roast aroma formation. VI. Volatile reaction products from the reaction of phenylalanine with glucose during cooking and roasting. *Z. Lebensm. Unters. Forsch.*, **187**, 209(1988)
- Hwang, H. I., Hartman, T. G. and Ho, C.-T. : Relative reactivities of amino acids in pyrazine formation. *J. Agric. Food Chem.*, **43**, 179(1995)
- Ledl, F. : Chemical pathways of the Maillard reaction. In *"The Maillard reaction advances in life sciences"* Academic Press, New York, p.19(1990)
- Huang, T. C., Bruechert, L. J. and Ho, C. T. : Kinetics of pyraizne formation in amino-glucose systems. *J. Food Sci.*, **54**, 1611(1990)
- Oh, Y. C., Shu, C. K. and Ho, C. T. : Formation of novel 2(1H)-pyrazinones as peptide specific Maillard reaction products. *J. Agric. Food Chem.*, **40**, 118(1992)
- Hayashi, T. and Namiki, M. . On the mechanism of free radical formation during browning reaction of sugars and amino compounds. *Agric. Biol. Chem.*, **45**, 933(1981)
- Yaylayan, V. A. : Chemistry of Amadori rearrangement products; analysis, synthesis, kinetics, reactions, and spectroscopic properties. *Crit. Rev. Food Sci. Nutr.*, **34**, 321 (1994)
- Leahy, M. M. and Reineccius, G. A. : Kinetics of the formation of alkylpyrazines, Effect of pH and water activity. In *"Thermal generation of aromas"* Parliment, T. H., McGorin, R. J. and Ho, C. T (eds.), ACS Symposium Series 409, American Chemical Society, Washington, DC, p.196 (1989)
- Peyron, L. : Recent techniques in the analysis of Heterocyclic aroma compounds in food. In *"Chemistry of heterocyclic compounds in flavors and aromas"* Vernin, G.(ed.), Ellis Horwood Ltd., Chichester. p.262(1982)
- Rizzi, G. R. : A mechanistic study of alkylpyrazine formation in model systems. *J. Agric. Food Chem.*, **20**, 1081 (1972)
- Shigematsu, H., Kurata, T., Kato, H. and Fujimaki, M. : Volatile compounds formed on roasting DL- α -alanine with

- D-glucose. *Agric. Biol. Chem.*, **36**, 1631(1972)
20. Tressl, R. : Formation of flavor components in roasted coffee. In "Thermal generation of aromas" Parliment, T. H., McGorin, R. J. and Ho, C.-T.(eds.), ACS Symposium Series 409, American Chemistry Society, Washington, DC, p.285(1989)
 21. Vercellotti, J. R., Crippen, K. L., Lovegren, N. V. and Sanders, T. H. . Defining roasted peanut flavor quality. Part I. Correlation of GC volatiles with roast color as an estimate of quality. In "Food science and human nutrition" Vercellotti, J. R.(ed.), Academic Press, London, p.298(1992)
 22. Fors, S. M. and Olofsson, B. K. : Alkylpyrazines volatiles formed in the Maillard reaction. I. Determination of odor detection thresholds and odor intensity functions by dynamic olfactometry. *Chemical Senses*, **10**, 287(1985)
 23. Masuda, H. and Mihara, S. : Olfactive properties of alkylpyrazines and 3-substitute-2-alkylpyrazines. *J. Agric. Food Chem.*, **36**, 584(1988)
 24. De Rijke, D., Van Dort, J. M. and Boelens, H. : Shigematsu variation of the Maillard reaction. In "Flavor '81" Schreier, P.(ed.), Walter de Gruyter, Berlin, p.256(1981)
 25. Tressl, R. : Formation of 2,3-dihydro-1H-pyrrolizines as proline specific Maillard products. *J. Agric. Food Chem.*, **33**, 919(1985)
 26. Tressl, R. : Formation of 2-(1-pyrrolidinyl)-2-cyclopentenones and cyclopent(b)azepin-8(1H)-ones as proline specific Maillard products. *J. Agric. food Chem.*, **33**, 1132(1985)
 27. Tressl, R. : Formation of pyrroles and tetrahydroindolizin-6-ones as hydroxyproline-specific Maillard products from glucose and rhamnose. *J. Agric. food Chem.*, **33**, 1137(1985)
 28. Piloty, M. and Baltes, W. : Investigations on the reaction of amino acids with α -dicarbonyl compounds. I. Reactivity of amino acids in the reaction with α -dicarbonyl compounds. *Z. Lebensm. Unters. Forsch.*, **168**, 368(1979)
 29. Baltes, W. : Roast aroma formation—the role of amino acids during the Maillard reaction. In "The Maillard reaction advances in life sciences" Academic Press, New York, p.43(1990)
 30. Wong, J. M. and Bernhard, R. A. : Effect of nitrogen source on pyrazine formation. *J. Agric. Food Chem.*, **36**, 123(1988)
 31. Nedvideck, W., Ledl, F. and Fisher, P. : Detection of 5-hydroxymethyl-2-methyl-3(2H)-furanone and of α -dicarbonyl compounds in reaction mixtures of hexoses and pentoses with different amines. *Z. Lebensm. Unters. Forsch.*, **194**, 222(1992)
 32. Hodge, J. E. and Osman, E. : Carbohydrates. In "Principles of food science. Part I. Food chemistry." Fennema, O. (ed.). Marcel Dekker Inc., Princeton, p.41(1976)
 33. Koehler, P. E. and Odell, G. V. A. : Factors affecting formation of pyrazine compounds in sugar-amine reactions. *J. Agric. Food Chem.*, **18**, 895(1970)
 34. Baltes, W., Kunert-Kirchhoff, J. and Reese, G. : Model reactions on generation of thermal aroma compounds. In "Thermal generation of aromas" Parliment, T. H., McGorin, R. J. and Ho, C.-T.(eds.), ACS Symposium Series 409, American Chemistry Society, Washington, DC, p.143(1989)
 35. Reese, G. and Baltes, W. : Model reactions on roast aroma formation. XI. Heating of serine with selected sugars and sugar degradation products in an autoclave. *Z. Lebensm. Unters. Forsch.*, **194**, 417(1992)
 36. Zhang, J. : Thermal deamidation of proteins in a restricted water environment. *J. Agric. Food Chem.*, **41**, 1840(1993)
 37. Labuza, T. P., Tannenbaum, S. R. and Karel, M. : Water content and stability of low-moisture and intermediate-moisture level foods. *Food Technol.*, **24**, 543(1970)
 38. Hartman, G. J., Scheide, J. D. and Ho, C.-T. : Effect of water activity on the major volatiles produced in a model system approximating cooked meat. *J. Food Sci.*, **49**, 607(1984)
 39. Eichner, K. and Karel, M. : The influence of water content and water activity on the sugar-amino browning reaction in model systems under various conditions. *J. Agric. Food Chem.*, **20**, 218(1972)
 40. Hartman, G. J., Scheide, J. D. and Ho, C.-T. : Formation of volatile compounds from the reaction of leucine and D-glucose in propylene glycol. *Perf. Flav.*, **8**, 81(1984)
 41. Rizzi, G. R. : Formation of pyrazines from acylain precursors under mild conditions. *J. Agric. Food Chem.*, **36**, 349(1988)
 42. Shibamoto, T. and Bernhard, R. A. . Effect of time, temperature and reactant ratio on pyrazine formation in model systems. *J. Agric. food Chem.*, **24**, 847(1976)
 43. Kunert-Kirchhoff, J. and Baltes, W. : Model reactions on roast aroma formation. VII. Specific products of phenylalanine after cooking L-phenylalanine with D-glucose in a laboratory autoclave. *Z. Lebensm. Unters. Forsch.*, **190**, 9(1990)
 44. Baltes, W. and Bochmann, G. : Model reactions on roast aroma formation. I. Reaction of serine and threonine with sucrose under the conditions of coffee roasting and identification of new coffee aroma compounds. *J. Agric. Food Chem.*, **35**, 340(1987)
 45. Reineccius, G. A. : The influence of Maillard reactions on the sensory properties of foods. In "The Maillard reaction advances in life sciences" Academic Press, New York, p.157(1990)
 46. Shu, C.-K. and Ho, C.-T. : Effect of pH on the volatile formation from the reaction between cysteine and 2,5-dimethyl-4-hydroxy-3(2H)-furanone. *J. Agric. Food Chem.*, **36**, 801(1988)
 47. Huang, T.-C., Bruechert, L. J., Hartman, T. G., Rosen, R. T. and Ho, C.-T. : Effect of lipids and carbohydrates on thermal generation of volatiles from commercial Zein. *J. Agric. Food Chem.*, **35**, 985(1988)
 48. Arnoldi, A., Arnoldi, C., Baldi, O. and Ghuzzoni, A. : Effect of lipids in the Maillard reaction. In "The Maillard reaction advances in life sciences" Academic Press, New York, p.133(1990)
 49. Ho, C.-T. : Contribution of lipids to the formation of heterocyclic compounds in model systems. In "Thermal generation of aromas" Parliment, T. H., McGorin, R. J. and Ho, C.-T.(eds.), ACS Symposium Series 409, American Chemistry Society, Washington, DC, p.105(1989)

(Received November 1, 1997)