

Chapter 14

Control of the Maillard Reaction during the Cooking of Food

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It was almost 100 years ago when Louis-Camille Maillard discovered the reaction between amino acids and sugars that was subsequently named after him. However, it was another 40 years before its contribution to food flavor was appreciated. Since then many hundreds of compounds derived from the Maillard reaction have been identified in cooked foods. Studies of model Maillard systems have provided understanding of the pathways involved in formation of these compounds. However, model systems never deliver all the sensory characteristics of cooked foods and model systems are much more susceptible to small variation in reaction conditions. In a food the complex mixture of sugar and amino acid precursors, and the presence of structural components and other reactive compounds, provide control of the Maillard reaction so that consistent and characteristic flavor is delivered in that food. This paper reviews some of the interactions that occur in real foods during cooking and thereby provide natural control of Maillard flavor in food.

Introduction

The reaction known as the Maillard reaction, which occurs when reducing sugars are heated with amino acids, peptides and other amino compounds, has been widely studied in food science and, more recently, has been of increasing interest in medicine. It was named after the French chemist Louis-Camille Maillard (1878-1936). He discovered the reaction when he heated glucose with glycine during

investigations of the use of polyols as dehydrating agents during the synthesis of peptides (1). He noted the formation of orange and brown colors and showed that the reaction was common to all reducing sugars and amino acids. The work was published in a few papers in the early part of the twentieth century, the first in 1912. Little or no interest was shown in the reaction for another 40 years until brown colorations were noticed in dried foods, such as milk powder. Initially described as non-enzymatic browning, the term “Maillard Reaction” was adopted in the early 1950s. The reaction also provided an explanation for the formation of the flavors associated with cooked foods. In recent years the physiological significance of the reaction has been recognized in relation to *in vivo* glycation of proteins and the link to diabetic complications, cardiovascular and other diseases (2, 3). The possibility of mutagenic compounds being formed in the Maillard reaction has also been recognized and particular attention has been directed towards heterocyclic aromatic amines in grilled meat (4) and acrylamide (2-propenamide) in fried and oven-cooked potato and cereal products (5, 6).

The first aroma compounds derived from the Maillard reaction to be identified in a food were 2-furanmethanethiol and several alkylpyrazines found in coffee in 1927 by Reichstein and Staudinger in a remarkable piece of analytical chemistry using classical separation and identification techniques (7). It was not until the 1960s, and the availability of gas chromatography and mass spectrometry, that significant numbers of aroma compounds were identified in foods.

The discovery of the reaction is rightly attributed to L.-C. Maillard, however, the unraveling of the complex chemistry was the outstanding contribution of the American carbohydrate chemist, John Hodge, who worked at the USDA laboratories in Illinois. In 1953 Hodge drew up a scheme to explain the essential steps leading to the formation of melanoidin pigments (8) and to the formation of aroma compounds (9). It is noteworthy that some 50 years later, the Hodge scheme still provides the basis for our understanding of the reaction.

Stages in the Maillard Reaction

The scheme devised by Hodge divides the Maillard reaction into three stages. A simplified version of the basic scheme, illustrating flavor formation, is shown in Figure 1. The reaction is initiated by the condensation of the carbonyl group of a reducing sugar with an amino compound, producing a Schiff base. Acid-catalyzed rearrangement gives a 1,2-enaminol, which is in equilibrium with its keto tautomer, an N-substituted 1-amino-2-deoxyketose, known as an Amadori rearrangement product. Ketosugars, such as fructose, give the Heyns rearrangement product by related pathways. The Maillard reaction has been the subject of many mechanistic studies, usually through investigations of single amino acid and sugar systems. It has been extensively reviewed, e.g. (2, 3, 10).

The Amadori and Heyns rearrangement products are unstable above ambient temperature. They undergo deamination, dehydration, and fragmentation, giving rise to a mixture of sugar dehydration and fragmentation products containing one or more carbonyl groups, as well as furfurals, furanones and pyranones (Figure 1). These carbonyl compounds react with free amino acids through

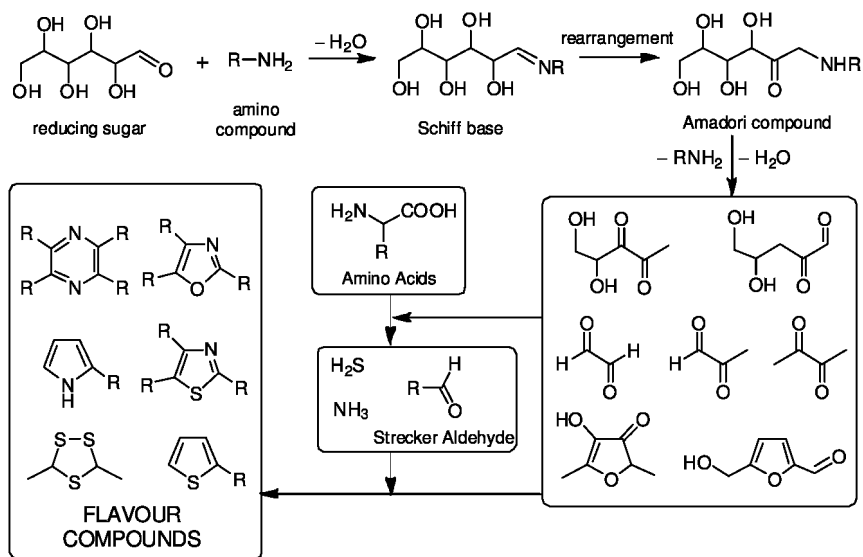


Figure 1. The essential steps of the Maillard reaction leading to the formation of aroma compounds.

Strecker degradation, in which the amino acid is deaminated and decarboxylated, to yield the corresponding Strecker aldehyde. The aldehydes, other carbonyls, furfurals, and furanones obtained from the sugar may contribute to flavor characteristics associated with the Maillard reaction. However, they are also important intermediates for the formation of other aroma compounds.

The products of the initial and intermediate stages of the Maillard reaction are colorless or pale yellow and Hodge attributed color formation to the final stage of the reaction, where condensation between carbonyls (especially aldehydes) and amines occurs to give high molecular mass, colored products known as melanoidins. These have been shown to contain heterocyclic ring systems, such as pyrroles, pyridines, and imidazoles, but their detailed structures are unknown.

The final stage of the Maillard reaction is of great importance for flavor formation when carbonyl compounds react with each other and with amino compounds and amino acid degradation products, such as hydrogen sulfide and ammonia. It is these interactions that lead to the formation of flavor compounds, including important heterocyclics, such as pyrazines, pyrroles, furans, oxazoles, thiazoles and thiophenes.

Study of Maillard Reaction in Model Systems

One of the earliest reports of the Maillard reaction between sugars and amino acids being used for the generation of flavor was the patent of Morton, Akroyd and May in 1960 which used cysteine and ribose to produce meat-like aromas (11). Many patents and papers followed, many with the aim of producing flavorings for the food industry that had improved savory and roast characteristics (12). The development of some such flavorings is discussed in another chapter

in this book (13). During the next three decades, many novel aroma compounds were identified in cooked foods and, in an attempt to determine their formation pathways, model reactions were carried out between individual amino acids and reducing sugars. Recently we compiled a list of volatile compounds that had been identified in Maillard model systems in 38 papers published between 1985 and 2002 (J.S. Elmore and D.S. Mottram, unpublished). Fifteen amino acids and seven sugars were used in these papers yielding a total of 621 volatile compounds (Table I). This list is not fully inclusive and other relevant papers appeared before and after this period. However, it illustrates the breadth of the research area and the large number of compounds that could contribute to aroma. Many of the compounds are heterocyclic and those containing nitrogen or sulfur have low odor threshold values; consequently only trace quantities are needed to contribute odor characteristics. This is particularly notable for sulfur-containing compounds.

One of the principal routes by which nitrogen is introduced into aroma molecules during the Maillard reaction is via the Strecker reaction (Figure 2). In the deamination of the amino acid by a dicarbonyl compound, an amino ketone is formed, which is relatively unstable and further reacts to give pyrazines, oxazoles and thiazoles, many of which contribute to roasted aromas in foods. Free ammonia may also be released from amino acids, and hydrolysis of cysteine gives rise to ammonia as well as hydrogen sulfide.

Sulfur-containing heterocyclic compounds, such as thiophenes, thiazoles, trithiolanes, thianes, thienothiophenes, and furanthiols and disulfides, play major roles in determining the characteristic aromas of cooked foods. Many of these compounds have extremely low odor threshold values and so make significant contributions to aroma at the part per billion ($\mu\text{g/kg}$) level or lower. Hydrogen sulfide is a key intermediate in the formation of many heterocyclic sulfur compounds. Figure 3 summarizes the reactions between hydrogen sulfide and other simple intermediates formed in the Maillard reaction.

Meat has higher levels of cysteine, the principal sulfur-containing amino acid, than most other foods and, consequently, sulfur compounds are major contributors to meat aroma. In particular, furans and thiophenes with a thiol group in the 3-position, possess strong meat-like aromas and exceptionally low odor threshold values (14) and a number of such compounds have been isolated in the volatiles of cooked meat, including 2-methyl-3-furanthiol and the corresponding disulfide, bis-(2-methyl-3-furanyl) disulfide (15, 16). Disulfides and thiols containing a furan ring have also been found among the volatiles of coffee; however, in coffee those containing the 2-furylmethyl moiety are more abundant than compounds with the 2-methyl-3-furyl moiety (17).

Maillard Reaction in Foods

Studies of the Maillard reaction between individual amino acids and sugars have provided a wealth of understanding on the pathways for formation of aroma compounds and have provided considerable insight into the range of compounds that are produced in the reaction. However, real foods are much more complex and data provided by the models do not reflect the aroma profiles generated in

real foods. The free amino acids in foods comprise mixtures of all the common occurring amino acids, in different proportions in the different foods. Similarly, they contain several different sugars. In some high carbohydrate foods such as cereals, sugars may be present in excess compared with free amino acids but in proteinaceous foods, such as meat, the amino acids are in excess over the sugars. Thus competition can occur between amino acids for available sugar or between sugars for available amino acids. Hence, the aroma profile in a food is unlikely to be a simple summation of the profile produced by the reactions of individual precursors. The aroma compounds produced in the Maillard reaction are derived from the interaction of different intermediates and, in a food, these are provided by reactions of mixtures of amino acids and sugars; thus many different interactions will be possible. As a consequence, it is very difficult to predict the course of a Maillard reaction in a food or provide external means of controlling the reaction pathways. However, it is interesting to reflect how much the food composition and structure control the reaction. Each food is very clearly recognizable from the aroma produced during cooking under wide ranges of conditions.

Other reactions occurring during cooking may also provide intermediates for the later stages of the Maillard reactions. Many lipid degradation products contain carbonyl groups and these are able to react alongside sugar-derived carbonyls in the later stages of the Maillard reaction (18).

Competition between Maillard Precursors

The discovery, in 2002, that acrylamide was generated in heated cereal and potato products, led to an upsurge of interest in the Maillard reaction. It was quickly established that the essential precursor for acrylamide was asparagine (6) and the pathway by which it is formed involved the formation of a Schiff base from the asparagine and a reducing sugar, and its subsequent decarboxylation, rearrangement and fragmentation, via a mechanism related to Strecker degradation (19). However, this reaction on its own cannot predict the rate of formation of acrylamide in a heated food. At elevated temperatures, acrylamide will react with amino and sulfhydryl groups and this needs to be taken into account in predicting yields (20, 21). In foods, other Maillard reactions will take place alongside that of asparagine. These could influence the formation of acrylamide by competing with asparagine for available sugars and, when sugars are limiting, reducing the amount of asparagine reacting. Conversely, the Maillard reaction will provide carbonyls from the breakdown of sugar and these could react with asparagine to give acrylamide and, thence, increase acrylamide yields. The different Maillard reaction pathways that may contribute to acrylamide formation are shown in Figure 4.

Some recent data from our laboratory illustrates the roles that other amino acids play in determining the amount of acrylamide formed in heated potato and cereals. Through changing the agronomic conditions, in particular sulfate content of the soil, for different varieties of wheat and potato, we obtained material that had a wide range of asparagine levels (22, 23). In wheat, sugars were in considerable excess compared with the free amino acids and in the heated wheat flour very good correlation between asparagine content and acrylamide formation was found,

Table I. Maillard model systems reported in literature between 1985 and 2002, showing reactants used and numbers of volatile compounds produced

<i>Sugars</i>	<i>Amino acids</i>	<i>Numbers of volatile compounds</i>
glucose	glycine	Pyrazines 59
fructose	isoleucine	Pyrroles 104
ribose	lysine	Pyridines 40
ribose phosphate	serine	other N-compounds 20
rhamnose	phenylalanine	Thiophenes 67
arabinose	proline	Thiazoles 40
sucrose	hydroxyproline	other S-compounds 102
	cysteine	Furans 90
	methionine	Oxazoles 6
	glutathione	other O-compounds 83
	threonine	Aromatic hydrocarbons 10
	aspartic acid	TOTAL 621
	asparagine	
	glutamine	
	γ -aminobutyric acid	

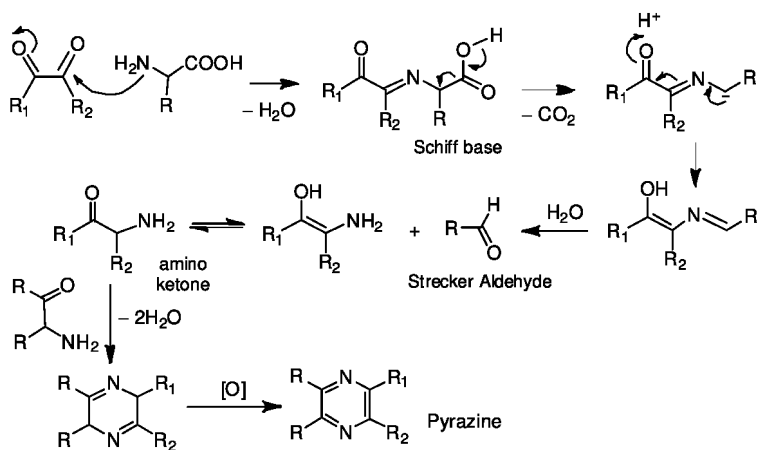


Figure 2. Strecker degradation of amino acids and formation of alkylpyrazines.

indicating that acrylamide could be predicted from the asparagine level in the flour. However, in potato these were not correlated ($n=18$; $r^2=0.23$). Sugars are not usually in excess in potatoes, which will affect the asparagine–acrylamide correlation, but acrylamide was not correlated with sugar levels either ($r^2=0.42$). However, when the ratio of asparagine to total free amino acids was plotted against acrylamide, a good correlation was obtained ($r^2=0.83$). This shows that when attempting to predict the quantities of Maillard reaction products formed in heated foods, it is necessary to consider all the Maillard precursors and not just those directly related to the products of interest.

The diagram illustrates the Maillard reaction pathway. It starts with a reducing sugar (R-CHOH-CHO) reacting with asparagine (H₂N-CH(COOH)-CH₂-CONH₂) in a dehydration step (-H₂O) to form a Schiff base (R-CHOH-CH=N-CH(COOH)-CH₂-CONH₂). This Schiff base then undergoes further dehydration to form an Amadori compound from asparagine (R-C(=O)-CH₂-NH-CH(COOH)-CH₂-CONH₂). The Amadori compound can follow two main pathways: 1) Dehydration to a Schiff base from ASN + Carbonyl (R-C(=O)-CH=N-CH(COOH)-CH₂-CONH₂), which then loses CO₂ to form an intermediate (R-CHOH-CH=N-CH=CH-CONH₂) and finally an acrylamide (R-CH=CH-CONH₂). 2) Conversion to DEOXYOSONES (Dicarbonyls, Hydroxycarbonyls, Furanones, Pyranones). A general reaction at the bottom shows a reducing sugar reacting with another amino acid (H₂N-CH(COOH)-Z) to form an Amadori compound (R-C(=O)-CH₂-NH-CH(COOH)-Z).

reducing sugar + asparagine $\xrightarrow{-H_2O}$ Schiff Base \rightarrow Amadori compound from asparagine

Amadori compound from asparagine \rightarrow DEOXYOSONES
Dicarbonyls
Hydroxycarbonyls
[Furanones]
[Pyranones]

Amadori compound from asparagine \rightarrow Schiff base from ASN + Carbonyl $\xrightarrow{-CO_2}$ Intermediate \rightarrow acrylamide

reducing sugar + other amino acid $\xrightarrow{-H_2O}$ Schiff Base \rightarrow Amadori compound

Kinetic modeling has been used to predict rates of formation of components of the Maillard reaction, as a function of temperature, pH, water activity/content, and chemical reactivity (24). A few papers have reported applications to predict acrylamide formation in heated foods (21, 25), although there have been many more papers just examining the kinetics of asparagine-sugar model systems. However, the latter do not often provide predictions for acrylamide in real foods. The application of kinetic modeling to the Maillard reaction for color and flavor are discussed in several other papers in this book (26–28).

Interaction between the Maillard Reaction and Lipids

The Maillard reaction is just one group of reactions occurring during the cooking of foods that contributes to flavor. Other food components, such as thiamin, tocopherol and carotenoids, can degrade and provide taste and flavor compounds. However, autoxidation of lipids provides the largest source of compounds with flavor potential.

The major class of lipid autoxidation products are saturated and unsaturated aldehydes. The presence of reactive carbonyls in these compounds provides additional intermediates for the Maillard reaction thus giving the potential of modifying the overall profile of Maillard compounds and/or forming other aroma compounds. In heated model systems containing ribose and cysteine, it was demonstrated that the addition of phospholipid gave compounds formed by the interaction of lipid autoxidation products with intermediates of the Maillard reaction (29, 30). Compounds that arise from the interaction of lipid with the Maillard reaction have also been found in the volatiles of cooked foods (18). These compounds include O-, N- or S-heterocycles containing long *n*-alkyl substituents. The *n*-alkyl groups are derived from aliphatic aldehydes obtained from lipid oxidation, while amino acids are the source of the nitrogen and sulfur.

Meat volatiles have been found to contain the largest number of such compounds (31). Heterocyclic compounds with long *n*-alkyl substituents found in cooked meat include 2-pentylpyridine, and 2-alkylthiophenes, 2-alkyl-(2*H*)-thiapyrans, 2-alkylthiazoles and 2-alkylthiazolines with *n*-alkyl substituents containing between 2 and 15 carbons (Figure 5).

In studies on the polyunsaturated fatty acid (PUFA) composition of lamb and beef, it was observed that meat from animals fed sources of PUFA gave meat with higher PUFA levels (32, 33). This meat was more prone to lipid autoxidation during cooking, resulting in higher concentrations of lipid-derived aldehydes. The cooked meat with higher PUFA also contained higher levels of alkylthiophenes, alkylthiapyrans, alkylthiazoles and alkylthiazolines, confirming that the lipid-derived aldehydes interacted with Maillard intermediates. Some alkylimidazoles and alkylloxazolines were also identified tentatively but their identities were not confirmed (J.S. Elmore, unpublished). The pathway to the alkylthiophenes and alkylthiapyrans was believed to be the reaction of hydrogen sulfide with dienals. To explain formation of alkylthiazoles and alkylthiazolines, it was suggested that dicarbonyls, ammonia and hydrogen sulfide, from the Maillard reaction, reacted with alkanals derived from lipid autoxidation.

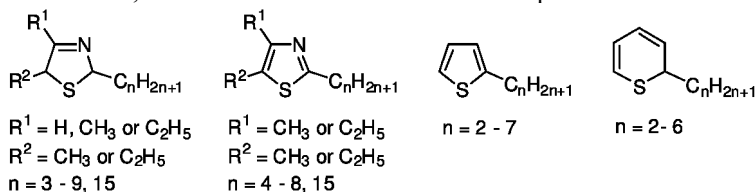


Figure 5. Thiazolines, thiazoles, thiophenes and thiapyrans found in cooked meats resulting from the interaction of lipid-derived aldehydes with the Maillard reaction.

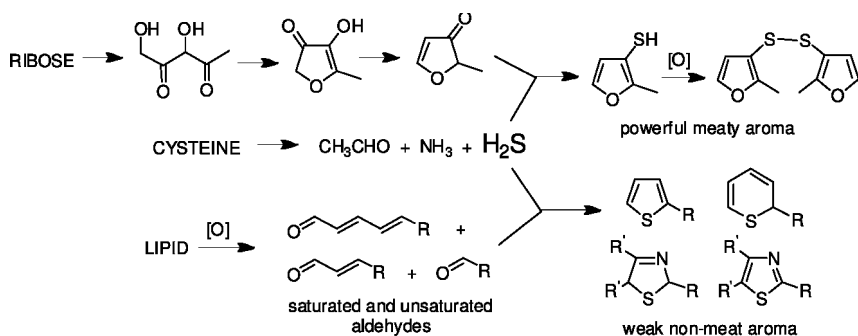


Figure 6. Competition between lipid derived aldehydes and Maillard-derived furanones for available hydrogen sulfide in thermal generation of meat flavor.

The odors of thiazolines and thiazoles with 2-*n*-alkyl substitution were described as slightly fatty, but they did not have low odor threshold values. Thiazolines and thiazoles with 2-methyl or 2-acetyl substituents possess thresholds in the low $\mu\text{g}/\text{kg}$ range, but it appears that the larger molecules with long alkyl substituents are not such potent odorants. Similarly, the aromas of the alkylthiapyrans and alkylthiophenes were weak, suggesting that it is unlikely that any of these compounds contribute directly to cooked meat aroma. However, their presence in the meat confirms that lipid–Maillard interactions do take place during the cooking of meat. Such interactions will modify the profile of aroma compounds produced by the Maillard reaction and thus indirectly affect the aroma. Hydrogen sulfide is a key component in the formation of meat-like aroma compounds, such as furanthiols and disulfides. The aldehydes that are produced in meat during cooking will compete with the furanone precursors of these S-containing furans for available hydrogen sulfide (Figure 6). This results in only low concentrations of the potent S-containing furans in meat.

While this might suggest that lipids prevent the production of desirable aroma, in practice only very low concentrations are required to give meaty aroma and it is hypothesized that, through competition for hydrogen sulfide, lipid maintains these compounds at an optimum level in cooked meat. In systems where high levels are found, e.g. reaction mixtures of cysteine and ribose, the aromas can be overpoweringly sulfurous. This is an example of how, in real foods, flavor generation in the Maillard reaction is controlled by other meat components.

Interaction between Maillard Reaction Products and Protein

The importance of compounds such as bis(2-methyl-3-furyl) disulfide and bis(2-furfuryl) disulfide and their corresponding thiols in heated flavors, especially meat and coffee, has been discussed above. It has been found that these compounds will interact with protein, providing another mechanism by which their concentration in meat and other proteinaceous food is controlled. When these two disulfides were added to a meat system (minced beef) and to ovalbumin, a significant proportion of the disulfides were broken down to corresponding thiols (2-methyl-3-furanthiol and 2-furanmethanethiol, respectively) and some

were lost completely (34, 35). In addition, small amounts of mixed disulfides, and 2-methyl-3-furyl methyl disulfide and 2-furfuryl methyl disulfide were formed in the meat system. An aqueous blank, which was used as a control, showed no breakdown of the disulfides. Furthermore, it was observed that very little change was seen when the disulfides were added to casein, which does not contain free sulfhydryl groups. In proteins, redox reactions involving interchange of sulfhydryl and disulfide groups within the protein or with external thiol groups are well known (36) and such interaction between the furan disulfides and protein sulfhydryl groups provides a clear explanation for their loss in meat systems. As well as having implications for the control of these Maillard reaction products in foods during cooking, this observation is also important in their application in food flavorings.

Other disulfides, including dialkyl disulfides were shown to interact with proteins in a similar way, resulting in large decreases in concentration when they were heated with protein (37). This raises other questions about interactions in food between volatiles and food components. Alliacious vegetables, such as onions and garlic, contain large quantities of di- and tri-sulfides, and these would be expected to interact with protein if heated with a proteinaceous food. Meat is often cooked with onions and changes to the aroma profile are very noticeable. Analysis of the volatiles of onion heated with and without meat showed very large differences in the profiles (Figure 7), with extensive loss of di- and tri-sulfides when meat was present, due to binding to the meat protein (38). Although, in this work no evidence of reaction between the Maillard-derived disulfides and onion di- and tri-sulfides was found, this is an interesting area of research which may, in the future, identify novel compounds from such interactions.

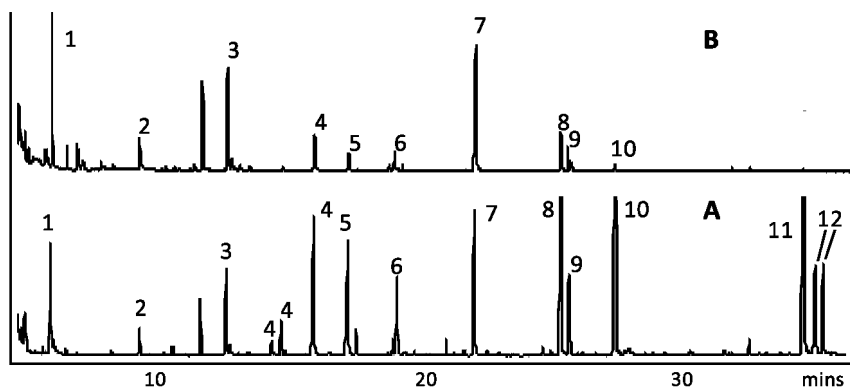


Figure 7. GC-MS analysis of volatiles from onion: A heated without meat; B heated with meat. 1. 1-propanethiol, 2. dimethyl disulfide, 3. 2-methyl-2-pentenal, 4. dimethylthiophenes, 5. methyl propyl disulfide, 6. dimethyl trisulfide, 7. dichlorobenzene (IS), 8. dipropyl disulfide, 9. 1-propenyl propyl disulfide, 10. methyl propyl trisulfide, 11. dipropyl trisulfide, 12. (E/Z)-1-propenyl propyl trisulfides

Conclusions

For over 60 years the Maillard reaction has been of considerable academic and technological interest to food scientists. Through studies of reactions between individual amino acids and sugars a significant knowledge has been acquired of the products of the reaction, their pathways of formation and their contribution to quality aspects of heated foods, especially flavor. Foods are more complex than model systems since they contain mixtures of many free amino acids and sugars, as well as structural food components and other components that react during cooking. The profile of aroma compounds in a heated food depends on the interaction between Maillard intermediates derived from sugars and amino acids, and these intermediates depend on the relative composition of free amino acids and sugars in the food. In addition compounds derived from lipid oxidation, and other food components, participate in these interactions and help to provide natural control for the Maillard reaction so that recognizable characteristic flavor for a particular food is delivered consistently over wide ranges of cooking conditions.

References

1. Maillard, L. C. *Compt. Rend.* **1912**, *154*, 66–68.
2. Ledl, F.; Schleicher, E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 565–706.
3. Nursten, H. E. *The Maillard Reaction*; Royal Society of Chemistry: Cambridge, U.K., 2005.
4. Negishi, C.; Wakabayashi, M.; Tsuda, M.; Sato, S.; Sigimura, T.; Saito, H.; Maeda, M.; Jagerstad, M. *Mutat. Res. Lett.* **1984**, *140*, 55–59.
5. Tareke, E.; Rydberg, P.; Karlsson, P.; Eriksson, S.; Törnqvist, M. *J. Agric. Food Chem.* **2002**, *50*, 4998–5006.
6. Mottram, D. S.; Wedzicha, B. L.; Dodson, A. T. *Nature* **2002**, *419*, 448–449.
7. Reichstein, T.; Staudinger, H. *Perfum. Essent. Oil Rec.* **1955**, *46*, 86–88.
8. Hodge, J. E. *J. Agric. Food Chem.* **1953**, *1*, 928–943.
9. Hodge, J. E. In *Chemistry and Physiology of Flavors*; Schultz, H. W., Day, E. A., Libbey, L. M., Eds.; AVI Publishing: Westport, CT, 1967; pp 465–491.
10. Mottram, D. S. In *Flavours and Fragrances: Chemistry, Bioprocessing and Sustainability*; Berger, R. G., Ed.; Springer-Verlag: Berlin, 2007; pp 269–284.
11. Morton, I. D.; Akroyd, P.; May, C. G. Flavoring Substances and Their Preparation. British Patent 836694, 1960.
12. MacLeod, G. M.; Seyyedain-Ardebili, M. *Crit. Rev. Food Sci. Nutr.* **1981**, *14*, 309–437.
13. Baines, D. A.; Bishara, S.; Parker, J. K.; Mottram, D. S. In *Controlling Maillard Pathways To Generate Flavors*; Mottram, D. S., Taylor, A. J., Eds.; ACS Symposium Series 1042; American Chemical Society: Washington, DC, 2010.
14. Evers, W. J.; Heinsohn, H. H.; Mayers, B. J.; Sanderson, A. In *Phenolic, Sulfur and Nitrogen Compounds in Food Flavors*; Charalambous, G., Katz, I., Eds.; ACS Symposium Series 26; American Chemical Society: Washington, DC, 1976; pp 184–193.

15. Gasser, U.; Grosch, W. *Z. Lebensm. Unters. Forsch.* **1988**, *186*, 489–494.
16. Mottram, D. S. *Food Chem.* **1998**, *62*, 415–424.
17. Flament, I. In *Volatile Compounds in Foods and Beverages*; Maarse, H., Ed.; Marcel Dekker: New York, 1991; pp 617–669.
18. Whitfield, F. B. *Crit. Rev. Food Sci. Nutr.* **1992**, *31*, 1–58.
19. Zyzak, D. V.; Sanders, R. A.; Stojanovic, M.; Tallmadge, D. H.; Eberhart, B. L.; Ewald, D. K.; Gruber, D. C.; Morsch, T. R.; Strothers, M. A.; Rizzi, G. P.; Villagran, M. D. *J. Agric. Food Chem.* **2003**, *51*, 4782–4787.
20. Knol, J. J.; Van Loon, W. A. M.; Linssen, J. P. H.; Ruck, A. L.; Van Boekel, M.; Voragen, A. G. J. *J. Agric. Food Chem.* **2005**, *53*, 6133–6139.
21. Wedzicha, B. L.; Mottram, D. S.; Elmore, J. S.; Koutsidis, G.; Dodson, A. T. In *Chemistry and Safety of Acrylamide in Food*; Friedman, M., Mottram, D. S., Eds.; Springer: New York, 2005; pp 235–253.
22. Elmore, J. S.; Mottram, D. S.; Muttucumar, N.; Dodson, A. T.; Parry, M. A. J.; Halford, N. G. *J. Agric. Food Chem.* **2007**, *55*, 5363–5366.
23. Muttucumar, N.; Halford, N. G.; Elmore, J. S.; Dodson, A. T.; Parry, M.; Shewry, P. R.; Mottram, D. S. *J. Agric. Food Chem.* **2006**, *54*, 8951–8955.
24. van Boekel, M. A. J. S. *Kinetic Modeling of Reactions in Foods*; CRC/Taylor & Francis: Boca Raton, FL, 2009.
25. Knol, J. J.; Viklund, G. A. I.; Linssen, J. P. H.; Sjöholm, I. M.; Skog, K. I.; van Boekel, M. *Food Chem.* **2009**, *113*, 103–109.
26. Wedzicha, B. L.; Mottram, D. S. In *Controlling Maillard Pathways To Generate Flavors*; Mottram, D. S., Taylor, A. J., Eds.; ACS Symposium Series 1042; American Chemical Society: Washington, DC, 2010.
27. van Boekel, M. A. J. S. In *Controlling Maillard Pathways To Generate Flavors*; Mottram, D. S., Taylor, A. J., Eds.; ACS Symposium Series 1042; American Chemical Society: Washington, DC, 2010.
28. Balagiannis, D. P.; Howard, J.; Parker, J. K.; Desforges, N.; Mottram, D. S. In *Controlling Maillard Pathways To Generate Flavors*; Mottram, D. S., Taylor, A. J., Eds.; ACS Symposium Series 1042; American Chemical Society: Washington, DC, 2010.
29. Whitfield, F. B.; Mottram, D. S.; Brock, S.; Puckey, D. J.; Salter, L. J. *J. Sci. Food Agric.* **1988**, *42*, 261–272.
30. Farmer, L. J.; Mottram, D. S. *J. Sci. Food Agric.* **1990**, *53*, 505–525.
31. Mottram, D. S.; Elmore, J. S. In *Heteroatomic Aroma Compounds*; Reineccius, G. A., Reineccius, T., Eds.; ACS Symposium Series 826; American Chemical Society: Washington, DC, 2002; pp 101–109.
32. Elmore, J. S.; Mottram, D. S.; Enser, M.; Wood, J. D. *J. Agric. Food Chem.* **1997**, *45*, 3603–3607.
33. Elmore, J. S.; Mottram, D. S.; Enser, M. B.; Wood, J. D. *J. Agric. Food Chem.* **1999**, *47*, 1619–1625.
34. Mottram, D. S.; Szauman-Szumski, C.; Dodson, A. *J. Agric. Food Chem.* **1996**, *44*, 2349–2351.
35. Mottram, D. S.; Nobrega, I. C. C. In *Flavor Release*; Roberts, D. D., Taylor, A. J., Eds.; ACS Symposium Series 763; American Chemical Society: Washington, DC, 2000; pp 274–281.

36. Jocelyn, P. C. *Biochemistry of the SH Group*; Academic Press: London, 1972; p 404.
37. Adams, R. L.; Mottram, D. S.; Parker, J. K. *J. Agric. Food Chem.* **2001**, *49*, 4333–4336.
38. Friend, A. M. The Interaction of Sulphur-Containing Aroma Compounds from Allium Vegetables with Meat Protein. Ph.D. Thesis, University of Reading, 2004.