

Research review paper

Formation of flavour compounds in the Maillard reaction

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Abstract

This paper discusses the importance of the Maillard reaction for food quality and focuses on flavour compound formation. The most important classes of Maillard flavour compounds are indicated and it is shown where they are formed in the Maillard reaction. Some emphasis is given on the kinetics of formation of flavour compounds. It is concluded that the essential elements for predicting the formation of flavour compounds in the Maillard reaction are now established but much more work needs to be done on specific effects such as the amino acid type, the pH, water content and interactions in the food matrix. It is also concluded that most work is done on free amino acids but hardly anything on peptides and proteins, which could generate peptide- or protein-specific flavour compounds.

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1. Introduction

The Maillard reaction is of utmost importance for quality of foods, more in particular for heated foods. It induces browning of foods, has an effect on nutritive value, can have toxicological implications (such as the formation of acrylamide), can produce antiox-

idative components and it has also a large effect on flavour. The present article discusses the Maillard reaction in general, and then focuses on the formation of flavour compounds, with an emphasis on kinetics. The goal of this paper is to indicate to what extent certain pathways can be promoted or inhibited, so that technologists have a tool to stimulate formation of desired flavour compounds and prevent or inhibit that of undesired compounds (flavours or otherwise).

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2. Outline of the Maillard reaction

The Maillard reaction is usually divided into three stages. The initial stage starts with a condensation between an amino group and a reducing sugar, leading to an *N*-glycosylamine in the case of an aldose sugar that rearranges into the so-called Amadori product (or Heyns product if the reducing sugar is a ketose). The intermediate stage starts from the Amadori/Heyns product, leading to sugar fragmentation products and release of the amino group. The final stage leads to all kinds of dehydration, fragmentation, cyclization and polymerisation reactions in which amino groups participate again. Especially in relation to flavour formation, the so-called Strecker degradation is of utmost importance, in which amino acids are degraded by dicarbonyls formed in the Maillard reaction, leading to deamination and decarboxylation of the amino acid. It should also be mentioned that sugar degradation reactions in the absence of amino groups (caramelisation) lead to similar products, but in the Maillard reaction, the amino group acts as a catalyst, so that the Maillard reaction results in a faster reaction and higher amounts of very reactive intermediate products. The various possible reaction

paths taking place depend strongly on temperature, pH and nature of the reactants (i.e., type of sugar, type of amino acid, or protein). A general overview is given in Fig. 1. It should be noted that in the case of proteins or peptides the reactive amino group is the ϵ -amino group of lysine, because the α -amino groups are tied up in the peptide bond and are not available for the Maillard reaction nor the Strecker reaction. This results in a different behaviour of amino acids compared to proteins and peptides. In the case of proteins, the Maillard reaction often leads to crosslink formation, while brown pigments are for a large part covalently attached to proteins (Brands et al., 2002).

The general scheme of the Maillard reaction, more or less summarized in Fig. 1, is under debate. For instance, the central role of Amadori/Heyns products given in most schemes is not undisputed. It may be that these products are just relatively stable intermediates but not essential for the progress of the Maillard reaction. Deoxyosones on the other hand are considered as essential intermediates (e.g., Weenen, 1998; Martins and van Boekel, 2005). An alternative view on the Maillard reaction has been given by Yaylayan (1997) who considers the initial stage as three primary

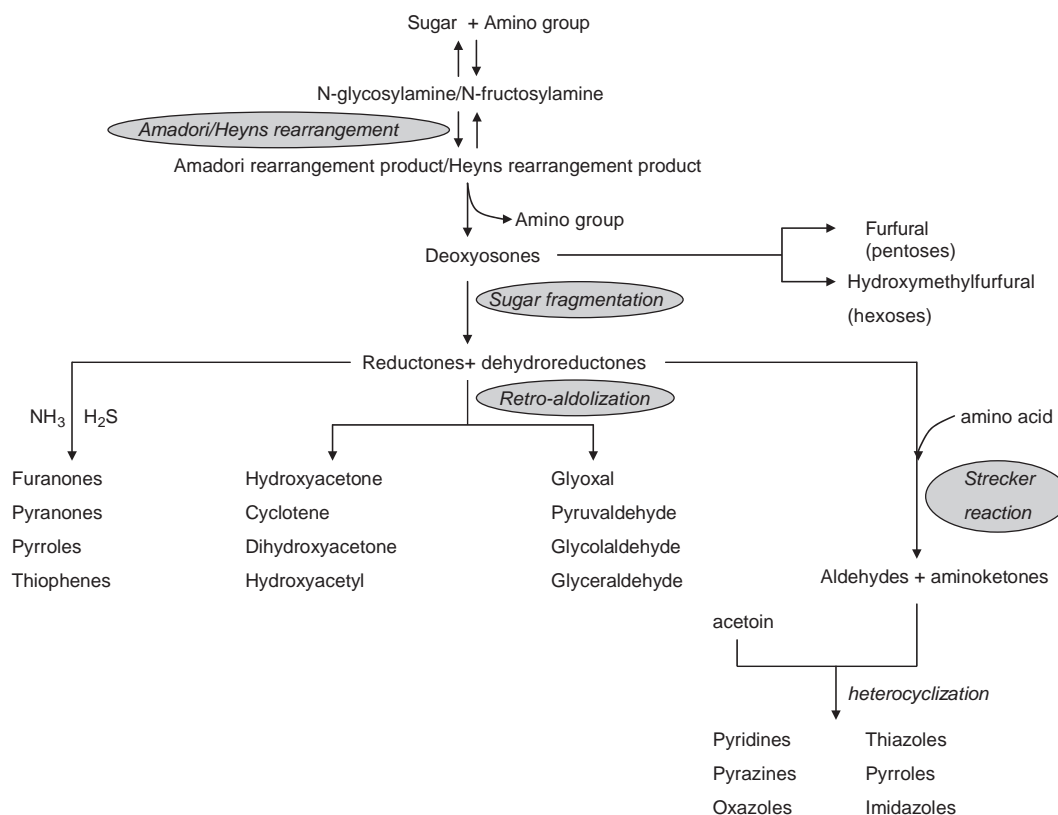


Fig. 1. General overview of the Maillard reaction showing flavour compounds as end products (after Ho, 1996).

Table 1
Overview of some classes of Maillard-derived flavour compounds

Compound class	Associated flavour/aroma	Food examples	Remarks
Pyrazines	Cooked, roasted, toasted, baked cereals	Heated foods in general	
Alkylpyrazines	Nutty, roasted	Coffee	
Alkylpyridines	Green, bitter, astringent, burnt	Coffee, barley, malt	Generally regarded as unpleasant
Acylpyridines	Cracker-like	Cereal products	
Pyrroles	Cereal-like	Cereals, coffee	
Furans, furanones, pyranones	Sweet, burnt, pungent, caramel-like	Heated foods in general	
Oxazoles	Green, nutty, sweet	Cocoa, coffee, meat	
Thiofenes	Meaty	Heated meat	Typical for heated meat, formed from ribose and cysteine

fragmentation pools arising from sugars, amino acids and Amadori/Heyns products. The Maillard reaction then propagates by interactions between the different pools to generate low and high molecular weight end products.

3. Formation of flavour compounds in the Maillard reaction

Flavour compound formation in the Maillard reaction depends on (1) the type of sugars and amino acids involved, and (2) on reaction temperature, time, pH and water content (Jousse et al., 2002). In general, the first factor mentioned determines the type of flavour compounds formed, while the second factor influences the kinetics. Some examples of the first factor are that meat-related flavour compounds are mainly sulphur-containing compounds, derived from cysteine and ribose (coming from nucleotides), while the amino acid proline gives rise to typical bread, rice and popcorn flavours.

Many Strecker aldehydes themselves are important for food flavour, but also all kinds of reaction products derived from them. Table 1 gives an overview of some important classes, while Fig. 1 indicates where they are formed in the Maillard reaction.

It should be noted that most of the research on the formation of Maillard-based flavour compounds is on mixtures of sugar and free amino acids, and hardly on sugar–protein or sugar–peptide mixtures. In 1992, Izzo and Ho wrote: ‘the roles in aroma generation of amino acids bound in proteins and peptides have not been studied to an appreciable extent’. Thirteen years later this is still the case. With peptides and proteins, and in the absence of free amino acids, the Strecker reaction cannot take place, and this has consequences for flavour generation. According to Izzo and Ho (1992), peptide-specific flavour compounds may be formed in the Maillard reaction. In principle, free amino acids may be generated during heating from proteins or peptides if hydrolysis occurs, but this will be limited during normal heat treatments of foods. What remains is that sugar

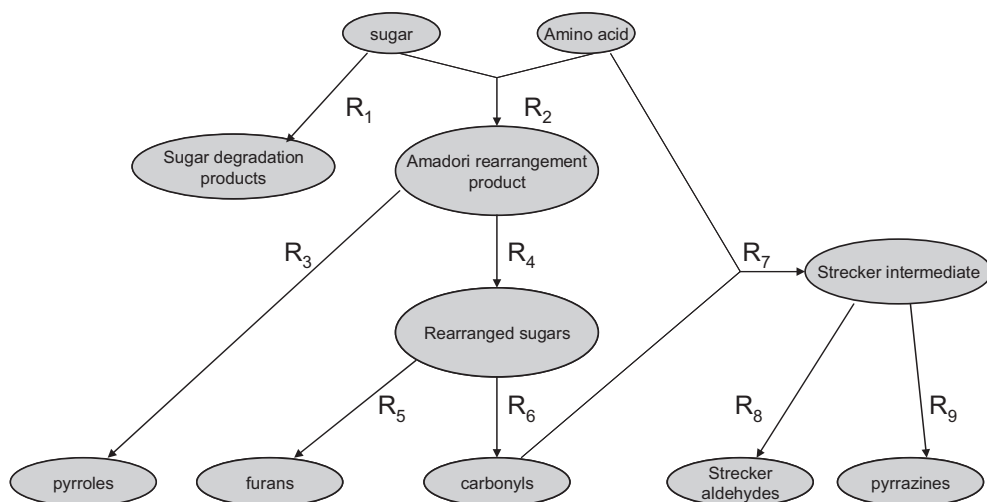


Fig. 2. Kinetic model with essential rate-determining steps R1–R9 describing the formation of the most important Maillard reaction flavour compounds (based on Jousse et al., 2002).

degradation products can react with the ϵ -amino groups of lysine residues, but also with other amino acid side chains, such as arginine and tryptophan. It is also known that the Maillard reaction in milk-based products leads to undesired flavour compounds (Morr and Ha, 1991); these milk-based products hardly contain free amino acids, and therefore the Maillard reaction will take place mainly via the lysine side chains.

4. Kinetics of the Maillard reaction

The kinetics of the Maillard reaction is very complicated due to the many reaction paths and effect of processing conditions. The traditional approach of applying simple kinetics (zero-, first-, or second-order behaviour) is not very helpful because it pertains to only one single step. Rather, kinetic modelling can be done in a more fruitful way via multiresponse modelling in which many steps are analysed simultaneously (e.g., Martins and van Boekel, 2005), be it that this kind of work has focused until now on browning reactions rather than on flavour compound formation. An interesting approach can be found in Jousse et al. (2002) who focused on kinetics of flavour compound formation. They were able to derive a more or less generic model based on a compilation of literature sources. The kinetic model resembles the scheme in Fig. 1, but is simplified and considers 9 essential rate-determining steps for the formation of flavour compounds. It is shown in Fig. 2.

In order to be able to apply such models to practical situations, an even more comprehensive model is needed, because the Maillard reaction does not only lead to flavour compounds but also to coloured compounds and other interesting compounds such as acrylamide, the formation of which should be minimized, obviously. So, it seems that a coupling of the various models that are now published in literature is a next step in

developing a tool for product and process design. With such a tool, it should be possible to predict the formation of desired flavour and coloured compounds, as well as that of undesired compounds (which could also be flavour compounds).

5. Conclusion

The formation of flavour compounds in the Maillard reaction is very complicated. The general chemical pathways leading to classes of compounds are more or less known, but it is still unknown how reaction pathways can be directed in a desired way. Also, most of the papers published on this topic are using model systems rather than real foods. The effects of the food matrix, including effects of pH, water content, specific catalysis, are still largely unknown.

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