Formation of Flavour Compounds in Food by 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.

Keywords: Maillard Reaction; Formation of Flavour Compounds; Proteins; Kinetics

I. INTRODUCTION

The Maillard reaction is one of the most common and most complex reaction that takes place mainly in foods. In 1912, a French chemist Louis-Camille Maillard (1878-1936) observed the formation of yellow-brown pigments in the reaction among sugars and amino acids, polypeptides, or proteins; and among polysaccharides and polypeptides, or proteins, in a heated solution. He began to study the condensation of amino acids by using glycerol and as a result, obtained cycloglycylglycine and pentaglycylglycine. Then, he used sugars instead of glycerol to investigate the formation of polypeptides from amino acids.**1** In the latter investigation, he found that the aldehyde group (of an aldose) had more intense effect on amino acids than the hydroxyl groups. This led to the discovery of the browning reaction, which is now more commonly known as the Maillard reaction. Two types of browning are normally observed in foods, namely enzymatic and non-enzymatic browning. Enzymatic browning is caused by oxidation of phenolic substances, such as those occurring at the cut surfaces of some fruits and vegetables. There are several types of non-enzymatic browning. One of the most popular being the reaction of carbonyl compounds, especially, reducing sugars, with compounds which contain a free amino group, such as amino acids, amines and proteins. This reaction is also known as Maillard reaction.

The Maillard reaction occurs on heating or on prolonged storage and is one of the deteriorative processes that take place in stored foods. It has also been detected in mammalian organisms.[2] The sugar component must contain a reactive carbonyl group (reducing sugar) and amino acids may be present in foods either as free or as part of a protein. Accordingly, when reducing sugars react with amino compounds, an extraordinarily complex mixtures of compounds or pigments is obtained, which are present in widely ranging amounts. Products formed are subject to large variations, depending on the reaction conditions. The Maillard reaction results in: [2,3,4,5,6,7,8,9,10,11]

1) Production of brown pigments known as melanoidins, which contain variable amounts of nitrogen, molecular weight and solubility in water. Little is known about the structure of these compounds. Most of the products are brown in colour, but may also of other colours. Browning is desired in baking and roasting, but not in foods which have a typical weak or other colour of their own.
2) Production of volatile compounds which are often potent aroma and flavour substances (premelanoidins). It is important for desired aromas and flavours to be formed during cooking, baking, roasting or frying. However, it may also generate off-flavours in foods during storage, especially in the dehydrated state, or on heat treatment for the purpose of pasteurization and sterilization, in grilled meat or fish (roasting bitter substances) and in over-heated tea or coffee.
3) Production of reductones and antioxidants which contain highly reductive properties and can, contribute to the stabilization of foods against oxidative deterioration. These compounds are believed to be able to reduce the risk of degenerative diseases.
4) Production of mutagenic compounds, which are generally produced during long time storage.

II. GENERAL OUTLINE OF 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- lycosylamine in the case of an aldosesugar 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 - amino group of lysine, because the a-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[12]. 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[16]. An alternative view on the Maillard reaction has been given by[18] who considers the initial stage as three primary 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.

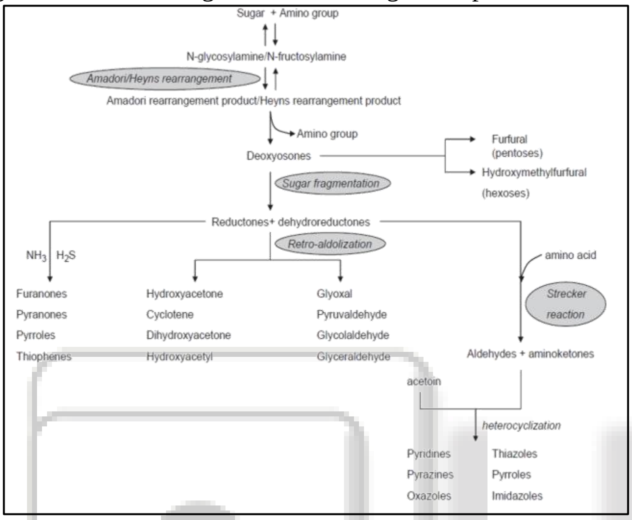

Fig. 1: Formation of flavour compound as end-product.

III. 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[15]. 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. 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[13], 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 degradation products can react with the q-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[17]; these milk-based products hardly contain free amino acids, and therefore the Maillard reaction will take place mainly via the lysine side chains.

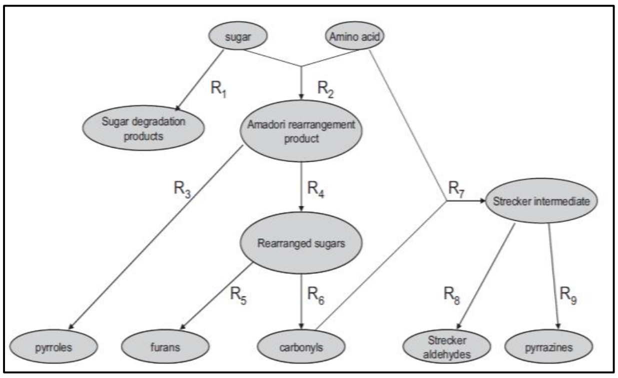

Fig. 2: Rate Determining Steps R1 to R9 describing the formation of flavour compound in Maillard Reaction.

IV. KINETICS OF 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 multi-response modelling in which many steps are analysed simultaneously, 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.[15]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).

V. 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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