Handbook of Molecular Gastronomy
Scientific Foundations, Educational Practices, and Culinary Applications
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Publication details
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Published online on: 09 Jun 2021

Accessed on: 10 Oct 2023

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Browning: The Glycation and Maillard Reactions – Major Non-Enzymatic Browning Reactions in Food

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Glycation is the most general internationally accepted term for addition of a sugar to another biomolecule. In particular, glycation of proteins by reducing sugars is considered the first step in the “Maillard reaction”, a central group of chemical reactions that occurs when food turns brown in cooking and is involved in formation of flavour compounds and new textures. For some 60 years, food chemists and other scientists have been working to elucidate the mechanisms involved when glycation reaction products form, and further, to interpret the impact of the glycation reaction on the quality of the food and to assess the physiological consequences related to the ingestion of such neoformed compounds. When specific glycation reaction products such as acrylamide are revealed as potentially harmful to human health, mitigation strategies should be developed, both at home and in commercial production, to reduce the risk of exposure. On the other hand, the chemical pathways of beneficial glycation products, such as melanoidins, must be promoted to ensure their optimum content in food. The most difficult task of all in food chemistry is to strike a balance between the formation of desirable and undesirable glycation reaction products.

Today, most of the foods that we eat are thermally processed either during cooking at home, in restaurants or in the course of more or less complex processes in the food industry. The heat treatments applied to fresh foods such as meat and eggs, and to mixtures of raw ingredients such as flour, butter, milk and sugar, induce thousands of chemical reactions between molecules.

These are responsible for the formation of a diverse range of sensory-active compounds, which usually enhance the sensory qualities of food (Cerny, 2008). The new odorant and taste compounds formed during cooking are usually derived from glycation reactions, which were first discovered by Emil Fischer and particularly thoroughly investigated by Louis-Camille Maillard (1912). They play a crucial role not only in the synthesis of odorant and taste compounds but also in the formation of colours, from yellow to brown, in cooked food. Another complex combination of chemical reactions that leads to the browning of food is caramelisation (Kroh, 1994). These two reactions, the Maillard reaction and caramelisation, are sometimes considered to be one and the same, which is probably because: (1) they can result in the formation of the same compounds, such as hydroxymethylfurfural (HMF), (2) they often take place in parallel during cooking and (3) they lead to the formation of the same brown colour. However, the main difference between caramelisation and the Maillard reaction is that the former needs only simple saccharides such as sucrose, glucose or fructose, whereas the latter requires both reducing sugars and amino groups from proteins, which react together to form the so-called Maillard reaction products (MRPs). Compared with caramelisation, which needs high temperatures, the Maillard reaction can start at low temperatures (around 30 °C) (Tessier, 2010).

Initially, research on the Maillard reaction focused on the discovery of its complex chemical pathways (Hodge, 1953), with the major goals of controlling the formation of key odorants in foods and producing a full range of synthetic flavourings for the food industry (Belitz and Grosch, 1999). However, since the discovery of the potential relationship between the intake of MRPs other than the aroma compounds and potential health effects (Tessier and Niquet, 2007; Delgado-Andrade and Fogliano, 2018) questions related to the toxicity of some MRPs and other neoformed molecules have been gaining increasing attention recently. The discovery of the formation of acrylamide by glycation reactions in certain foods such as coffee and French fries (Mottram et al., 2002; Tareke et al., 2002) has also attracted the attention of health scientists and public health authorities.

In this chapter, a brief presentation of the three main chemical steps of the Maillard reaction will be followed by a focus on the browning of butter during cooking and on the formation of acrylamide in a selection of foods, particularly starchy foods like bread and potatoes, and roasted plant ingredients like coffee and cocoa beans. Finally, possible beneficial or harmful health effects associated with the consumption of food high in MRPs will also be discussed.

The Basic Chemical Pathways of the Maillard Reaction

The reaction between simple sugars and amino groups from amino acids was first observed in 1884 by Emil Fischer, before Maillard explored the reaction between reducing sugars and...
amino acids (Maillard, 1912), but it was not chemically described for another 40 years. John E. Hodge (1953) was the first to propose a general scheme of the Maillard reaction, and his scheme remains the most accurate reference for all scientists in this field.

Initial Phase

In food matrices, the initial step in the reaction corresponds to the formation of imine intermediates (also known as Schiff bases or N-substituted-glycosylamines) between reducing sugars such as glucose or fructose and free amino acids or protein-bound amines. The unstable imines can then regenerate the initial substrates (i.e., sugar and amine), generate dicarbonyl compounds through oxidative reaction (e.g., glucosone), or rearrange themselves into stable Amadori and Heyns products (Ruﬁan-Henares and Pastoriza, 2016). The two types of early Maillard products are formed from aldoses (e.g., glucose) and ketoses (e.g., fructose), respectively. They represent the first stable MRPs that can be detected and thus quantified in foods. Neither the Amadori nor the Heyns compounds absorb wavelengths of visible light. Therefore, in the early step of the Maillard reaction, no browning can be observed on the food.

The main early product found in food is fructoselysine (FL), which is an amino-deoxy-ketose formed from the nucleophilic attack of the ε-amino group of lysine (an essential amino acid) on a molecule of glucose. The FL is either found on dietary proteins or as a free Maillard product when the reaction occurs on free lysine.

Different studies indicate that 1 L of UHT milk contains between 130 and 600 mg FL (Henle, 2003; Erbersdobler and Faist, 2001). Due to the difference in the intensity of the heat treatment, pasteurised milk always contains less FL than sterilised milk (also known as UHT milk). The concentration of FL is usually proportional to the heat load as long as the heat treatment of food is moderate. When the thermal processing is more intense, such as in baking or roasting, the degradation of FL may become more intense than its formation, and therefore an apparent decrease of FL can be observed over the cooking time. Overall, the daily intake of FL has been estimated at around 100 mg per day when a Western diet is consumed (Tessier and Birlouez, 2012).

Propagation Phase

The propagation phase of the Maillard reaction, also called the intermediate stage, is a cascade of parallel chemical reactions that lead to the formation of thousands of compounds, some of which are more or less stable (Figure 13.1). Depending on the physicochemical conditions of the food matrices (pH, water activity, temperature, etc.), different intermediate molecules will be formed after the rearrangement of the Amadori or Heyns products (Ruﬁan-Henares and Pastoriza, 2016). For instance, fission reactive products such as glyoxal, methylglyoxal and other carbonyls will react with amino groups to generate more stable compounds, including odorants (e.g., pyridines, pyrazines and imidazoles) and browning products. Some of the stable products formed during the propagation phase are UV active, exhibit the typical brown colour of the Maillard reaction, have fluorescent properties and can be classified as flavour compounds.

Among the stable products formed during the propagation phase, some of them, such as Nε-carboxymethyllysine (CML), glucosepane, pentosidine and pyrraline, were discovered almost at the same time in human tissues and in foods. It must be noted that the Maillard reaction also occurs at 37 °C in the human body (Tessier, 2010). In this case, the reaction is called “glycation” and the products formed are named the AGEs, or advanced glycation end products (Henning and Glomb, 2016). Thus, AGEs and MRPs may define the same molecules, and it is simply the case that biologists and physicians use the term AGEs whereas food chemists use the term MRPs.

In physiological conditions, CML, pentosidine and other AGEs are the most advanced products that can be found in living organisms, and it can be said that they “finish” the reaction. In food, the situation is quite different, especially when the duration of the treatment is long and the temperature level is high (e.g., roasting, baking, frying or grilling). In such cases, the final compounds are called “melanoidins”.

Termination Phase

The termination phase in food occurs during prolonged heating and at temperatures usually above 100 °C. In such conditions, the water content and activity are usually low, at least at the surface of the food matrices (e.g., the high dehydration of the bread crust, the roasting of coffee), and the intermediate MRPs undergo interactions between themselves and other compounds to promote the formation of brown polymers named melanoidins (Wang et al., 2011) (Figure 13.1). Although the term “melanoidins” was very likely created more than a century ago by Schmiedeberg (1897) and used by Maillard to define the end products of his chemical reaction (1912), no precise chemical structure for them has been fully characterised so far. The complexity of isolating and solubilising them makes their identification and quantification difficult, if not impossible (Helou et al., 2016). What is known so far is that their structures vary greatly depending on the composition of the raw ingredients and the processing of the foodstuff (Martins and van Boekel, 2003). For instance, the chemical structures of melanoidins found in coffee are considerably different from those in cereal-based products. Even in a single food type, such as bread, a complex variety of melanoidins can be observed.

At least four hypotheses have been proposed concerning the formation of melanoidins: (1) a polymerisation of furan and pyrrole units (Tressl et al., 1998); (2) a polymerisation of sugar degradation products formed during the Maillard reaction and linked by amino compounds (Cämmerer et al., 2002); (3) a protein skeleton cross-linked by carbohydrate-derived structures (Hofmann, 1998) or MRPs (Hofmann et al., 1999); and (4) ketal and acetal linkages between phenolic compounds, hydroxyl acids and sugars (Moreira et al., 2017).

Overall, melanoidins can be defined as high-molecular-weight nitrogen-containing brown-coloured pseudo-polymers (Wang et al., 2011).
Yield of Different Maillard Reaction Products

The yield of formation of the different MRPs at each stage of the reaction has been estimated through different tests with model systems for the Maillard reaction (e.g., the reaction between sugars and amino acids in test tubes) and more importantly, through the analysis of a variety of food products over recent decades (Cerny, 2008). Depending on the food products, 1% to 10% of the initial reactants, both amino acids and sugars, can be transformed into Amadori or Heyns products, 0.1% to 1% are modified into stable AGEs such as CML, deoxyglucosone and other reactive intermediate compounds, 0.01% to 0.1% lead to the formation of fragmentation products such as glyoxal, and, lastly, odorant compounds represent less than 0.1% of the initial reactants.

The yield of formation for the most chemically reactive, most thermodynamically unstable or most volatile MRPs may have been underestimated, since they do not accumulate over time in food matrices but either react with other compounds or are partly eliminated in the atmosphere.

What Is behind the Browning of Butter?

Traditional butter contains fat (81% w/w), proteins (0.85%), sugars (0.06%) and water (16%). We are all familiar with the fact that the colour of butter changes from yellow to brown when it is heated. One might believe that the formation of a brown colour is due to lipid peroxidation, but our data indicate that the oxidation of fat from butter is always very low and cannot explain the browning after heating (Niquet-Léridon et al., 2015). The absence of browning in clarified butter (100% fat) indicates that the fatty acid residues present in the triglycerides of butter are stable even at temperatures above 150 °C. The high proportion of saturated fatty acid residues and low proportion of unsaturated fatty acid residues in butter account for this stability.

The lack of browning in heated clarified butter also suggests that proteins and saccharides, alone or together, are the key players of the browning reaction. In order to confirm the involvement of the Maillard reaction in the process of browning, CML and HMF, two markers of this reaction, have been quantified in raw and cooked butter. No detectable HMF and only traces of CML were found in raw butter, but they significantly increased in cooked butter, indicating that the Maillard reaction is responsible for the brown colour of butter.

FIGURE 13.1 Schematic representation of the three phases of the Maillard reaction.
found in raw butter. But after an exaggerated heat treatment of butter (25 min at 150 °C), CML and HMF were found in significant amounts (2 to 3 µg/g and 51 to 58 µg/g, respectively). CML and HMF were not detected in either raw or heated clarified butter. While CML is indeed a unique marker of the Maillard reaction, HMF is not fully specific for this reaction and can also be a marker of caramelisation. This implies that caramelisation, in addition to the Maillard reaction, is a potential agent in the formation of browning in cooked butter.

CML and HMF are currently under investigation for their potential deleterious effects on health (Tessier et al., 2016; Murkovic and Pichler, 2006). However, a reasonable daily intake of cooked butter (20 g) would correspond to approximately 1% and 6% of the total exposure to CML and HMF, respectively, when foods commonly consumed are taken into account. A recent study also showed that the concentration of volatile α-dicarbonyl compounds found in cooked butter was much lower than that in heated beef fat, margarine and safflower oil (Jiang et al., 2013). Based on current scientific knowledge, we can conclude that there is no evidence that heated butter is potentially toxic and, therefore, that it is, in fact, perfectly suitable for cooking.

Acrylamide, the Dark Side of Glycation

Acrylamide is a colourless and odourless amide (CH$_2$CHCONH$_2$) of low molecular weight, 71.08 g/mol. In 1994, it was classified by the International Agency for Research on Cancer (IARC) as probably carcinogenic to humans (Group 2A), and its status has remained unchanged. The IARC originally stated that acrylamide was not known to occur as a natural product and that it was chemically produced for various industrial practices such as water treatment (IARC, 1994). Exposure to it was believed for that reason to be essentially occupational (and related to smoking) until the discovery by Tareke and her colleagues in 2002 that acrylamide is present in heated foods (Tareke et al., 2002). This was rapidly confirmed by other groups who found acrylamide in grilled, baked, fried and toasted foods but not in raw or boiled foods (Ahn et al., 2002).

Several mechanisms may be involved in the formation of acrylamide during the cooking process, but the predominant reaction is the Maillard reaction (Mottram et al., 2002). It is, in fact, the glycation between asparagine in its free form (not protein-bound) and reducing sugars or dicarbonyl compounds that leads to acrylamide forming at temperatures usually higher than 120 °C and where the water content is low (Figure 13.2). Free asparagine is a natural constituent of many plant-derived foods, but it is hardly found in animal-derived foods. Consequently, acrylamide is found, in significant amounts, mainly in plant-based foods such as cereals, potatoes, chicory and coffee beans, where the raw materials contain its two precursors, asparagine and reducing sugars, and when the foods are processed at high temperatures.

After more than a decade of investigation by public and private scientific organisations, the European Food Safety Authority...
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Concluding Remarks and Perspectives

The glycation reactions are key reactions that influence not only the sensory quality of cooked food but also its nutritional quality. They can, though, be harmful to health when high temperatures are used in cooking. People who cook, whether chefs, those in the food industry or people at home, are fortunately, however, in control of the Maillard process to the extent that they have evidence of the process when the food turns brown. As long as they are aware of the potential dangers of cooking at high temperatures, they are fully able to strike a balance between making the food taste good and putting health at risk.

However, the recent discovery of acrylamide in food, together with the potential physiopathological role of other MRPs, has raised new questions about the safety of foods cooked at high temperatures and brought new concerns for consumers already aware of the problems.

There are conflicting opinions about the ultimate effects of MRPs on human health. Some studies show that MRPs contribute to the development of non-communicable and age-related pathologies (Cai et al., 2008; Cai et al., 2014; Grossin et al., 2015). In this state, the MRPs are referred to as “glycotoxins”. Another study indicates that CML, a major Maillard product, accumulates in the body over time (Tessier et al., 2015). However, there are voices challenging the conclusions drawn from these and similar studies because of the methods underlying the evidence on which these conclusions are based (Delgado-Andrade and Fogliano, 2018). The fact that experiments used in some of those studies are animal-rather than human-based is one important argument. There are other concerns in terms of the methodology of the experiments, chiefly about the specificity and the accuracy of the dietary exposure to glycotoxins and other MRPs.

As well as MRPs being detrimental to human health, certain MRPs, such as melanoidins, are potentially beneficial for human health. Taking all this into account, it is the overall composition of the diet, in addition to isolated molecules or ingredients, that must be focused on in future studies.

Until the toxic effects of some MRPs have been conclusively refuted or confirmed, the best recommendation is to use a variety of cooking methods (e.g., boiling, blanching, steaming, poaching, simmering, searing, braising, roasting and grilling) as well as eating a variety of foods. Our message is not “Cook Less to Age Better” but “Cook Better to Age Better”.

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