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REVIEW ARTICLE

Maillard conjugates and their potential in food and nutritional industries: A review

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Abstract

Maillard reaction (MR) is a cascade of complex interactions between reducing sugars and amine groups in food processing and storage. It produces a variety of volatile compound, nonenzymatic intermediates, and high molecular weight melanoidin contributing improved aroma, color, flavor, and antioxidant properties to the final food products. When uncontrolled, it can produce some harmful derivatives such as acrylamide, heterocyclic amine, advanced glycation end Products (AGEs), and other substances that can be detrimental to human health leading to cancer and chronic diseases. Herein, we reviewed the MR leading to different MRPs and factors affecting the MR and MRPs, their application in food model systems, their biological activities, and the formation mechanism and effective inhibition methods of common harmful MRPs. The updated overview can be useful to explore the rational use of MR, which can ameliorate its positive biological features with reduced adverse effects.

KEYWORDS
acrylamide, AGEs, bioactive compound, biological activity, Maillard reaction, safety control

1 | INTRODUCTION

The Maillard reaction (MR) is considered as one of the most frequent natural nonenzymatic browning reactions (Jaeger, Janositz, & Knorr, 2010) forming the covalent bonds during heating of food products containing carbohydrates (reducing sugars) and protein/peptides (amino acids and proteins) (Spotti et al., 2019). It can modify the food qualities by affecting the stability, flavor, aroma, color, and nutritional value (Hwang, Kim, Woo, Lee, & Jeong, 2011). Tracing back to historical account, the French chemist L. C. Maillard in 1912 reported the reaction between glucose and glycine that led to the formation of brown-black pigments (melanoidin) during heating process (Maillard, 1912; O'Brien & Morrissey, 1989) and later in 1953 it was named as MR (Hodge, 1953). MR is the condensation reaction between the free amino group of amino acid/peptide/protein, and the carbonyl group of reducing sugars (Yilmaz & Toledo, 2005) mainly refers to aldehydes, ketones, carbonyl reducing sugars, and amino acids, peptides, proteins between free amino nitrogen compound, which produce a large number of Maillard reaction products (MRPs), such as (Cho, Lee, Jun, Roh, & Kim, 2010) highly active and ultraviolet absorption and complex melanoidin (Helou, Jacolot, Niquet-Léridon, Gadonna-Widehem, & Tessier, 2016). In addition to producing melanoidin, the reaction also produces reductive ketones, aldehydes, and heterocyclic compound, which mainly contribute color and flavor to the final food (Kato, 2002).

Abbreviations: ACE, angiotensin converting enzyme; AGEs, advanced glycation end products; ARPs, Amadori rearrangement products; CML, carboxymethyl lysine; FL, fructoselysine; GI, glycemic index; HRPs, Heyns rearrangement products; MR, Maillard reaction; MRPs, Maillard reaction products; STI, soybean trypsin inhibitor

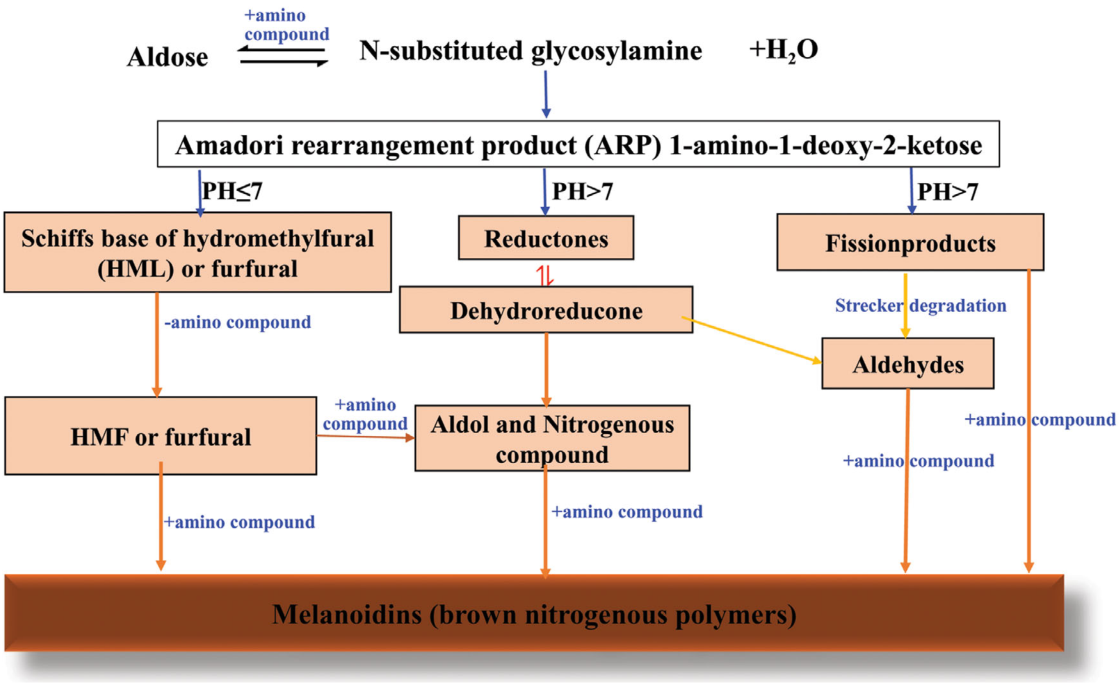

FIGURE 1 Schematic diagram of Maillard reaction with detailed account of different phases

MR is mainly comprised of three main stages (Figure 1), early, intermediate, and final stage (Boekel., 2001). At the beginning, reaction is initiated by the formation of covalent bond through condensation of reducing sugars with a free amino group to produce an unstable Schiff base, which undergoes the cyclization process to form a low stable condensation products: Amadori rearrangement products (ARPs) or Heyns rearrangement products (HRPs) based on the sugars type. At the beginning of intermediate stage, the ARPs and probably HRPs are degraded based on the initial pH value (Sumaya-Martinez, Thomas, Linard, Binet, & Guerard, 2005). At pH ≤ 7.0, ARPs mainly undergo 1,2-enolization pathway and form hydroxymethyl furfural compound. At pH > 7.0, formation of reductone, such as 4-hydroxy-5-methyl, 2,3-dihydrofuran-3-one, and fission products like acetol, diacetyl, and pyruvaldehyde from ARPs is dominant (Kchaou, Benbettaieb, Jridi, Nasri, & Debeaufort, 2019). These highly reactive intermediates continue to participate in further reactions to form low molecular weight colored products and melanoidin. The fragmentation of ARPs, Schiff base, and sugars leads to the formation of more reactive dicarbonyl compound with amino acids to form acetaldehyde and l-aminoketone through Strecker degradation reaction (De Oliveira, Coimbra, de Oliveira, Zuñiga, & Rojas, 2014). Toward the final stage, aldol and aldehyde-amine condensations of reductone and fission products as well as Strecker degradation products lead to the formation of brown nitrogenous polymers, melanoidin (Peng, Ma, Chen, & Wang, 2011). MR can impart unique flavor and color to food; therefore, it has become a hot spot in food research and is closely related to modern food industrial development (Khan, Jo, & Tariq, 2015). As compared to early stages, the final and advanced stages of MR give rise to more complex and versatile compound with unknown structure, chemical, and mechanical particulars (Chen, Lv, Muhammad, Guo, & Liu, 2019). Therefore, it is necessary to control the advanced stages of MR to minimize the harmful effects. Among the overall MRPs, early compound and melanoidin are of particular interest and are endowed with functional attributes, which can be utilized in food industry for the improvement of texture and flavors of many food products (Silván, Assar, Srey, Castillo, & Ames, 2011). For example, the antioxidation of food has always been an intriguing research subject at national and international platforms (Consoli et al., 2018). Antioxidants widely used in the food industry may have some adverse effects on human health, so the search for a new type of antioxidants is of great importance to the food industry (Sanderson, 1972). The MR provides a new way to find and apply natural antioxidants, because MRPs produced by the MR are a class of natural substances produced during food processing and storage, which can be considered natural and healthy (Muñoz, Hernández, Tolosa, Burillo, & Olalla-Herrera, 2020). MRPs contain melanin-like reductant and a series of volatile nitrogen-containing heterocyclic compound (Osada, & Shibamoto, 2006).

However, the MR not only produces complex products including melanoidin, reductone, and heterocyclic compound, but also forms some substances that are harmful to human health (Cui, Duhoranimana, Karangwa, Jia, & Zhang, 2018). MRPs such as high carboxymethyl lysine (CML) have been reported to promote diabetes and cardiovascular diseases, and acrylamide are produced by the MR as standard carcinogen (Wei et al., 2019a). At the same time, studies have found that people who consume a lot of processed food products develop insulin resistance and metabolic syndrome compared to those who eat vegetables and low-processed food (Sun, Zhao, Cui, Zhao, & Yang, 2010). In other words, changes in MR during food processing may also be an important factor in the development of disease (Cui et al., 2019). Studies have shown that MR may also contribute to a number of diseases, such as Alzheimer's disease and diabetes (De Oliveira

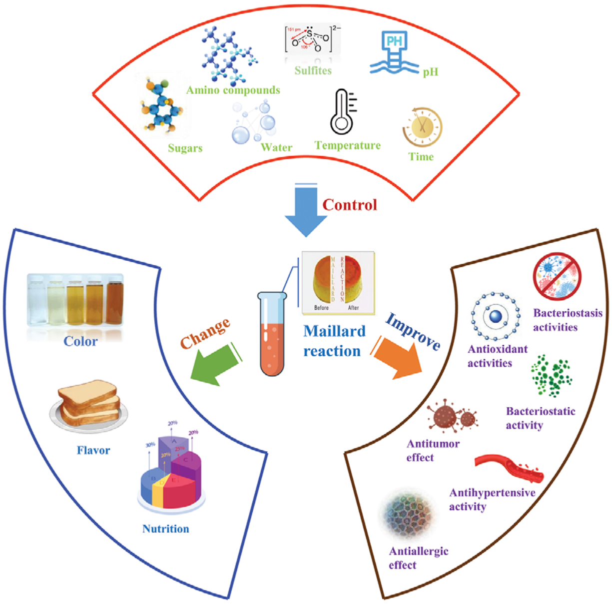

FIGURE 2 The scientific content and the areas of interests included for MR and its improvement

et al., 2014). At present, the physiological activity and health care function of MRPs have attracted much attention in the world. More and more research results showed that MR is closely related to human life activities. In the past decade, research on MR has been very active, and there have been some innovations, such as immobilized enzyme technology to obtain MRPs with better flavor (Wei, Thakur, Liu, Zhang, & Wei, 2018). Microwave treatment has been used to improve the properties of MRPs and reduce the loss of nutrients (Chandrasekaran, Ramanathan, & Basak, 2013). Some studies have also mentioned the production of natural preservatives through MR (Kanatt, Chander, & Sharma, 2008).

Today, despite the better understanding of the MR after nearly a century of research, it is still difficult to understand the complex steps and intermediates associated with the MR (Wei, Ni, Thakur, Liao, & Wei, 2020). In addition, it has a broad industrial application prospect especially in the food industry, which is closely related to human nutrition and safety. Based on the above facts, the reaction principle and influencing factors of MR were summarized in the current review, and the applications of MR in food flavor and health improvements were also analyzed (Cui et al., 2018). It is believed that MR can make greater contribution to food and medicine industries with the increasing development of related research and with the deepening of MR understanding. The scientific content and the overall view of the article are presented in Figure 2.

2 | A BRIEF OVERVIEW OF MAILLARD CONJUGATES

The production of MRPs is relatively complex and it largely depends on reaction time, temperature, pH value, solvent, etc. It is also affected by the type of sugars, amino acids, and proteins involved in the reaction. Nowadays, more focus is given on the factors affecting the MRPs (the final products of glycosylation and melanoidin). The final product of glycation is first identified as the final MRPs during food cooking (Hartog, Voors, Bakker, Smit, & Veldhuisen, 2014). It is the first formation of Schiff base of reducing sugars and amino groups of proteins, and the Schiff base is reorganized into stable Amadori products, which are the stable substances produced by the continued reaction of the Amadori products. The main difficulty in structure analysis of glycosylation end products is that many products are produced during the reaction and it is difficult to isolate a single glycosylation end product (Du, Huang, Wang, & Xiao, 2018). At present, protein cross-linking products of various glycosylation end products have been isolated such as Pentosidin (Sell, & Monnir,1989), CML (Ahmed, Thorpe, & Baynes, 1986), and Pyrralin (Miyata, & Monnier, 1992). Their accumulation in the body is reported to increase with age and these products are considerably related to the occurrence of various diseases. The recent research has shown that glycosylation end products in the human body not only induce diabetes, but also cause kidney and heart failure (Wang & Ismail, 2012). Melanoidin refers to a brown substance formed in the late MR between carbohydrates (generally sugars) and nitrogen-containing compound with free amino groups (such as amino acids, peptides, proteins), which is widely found in food and drinks (Chandra, Bharagava, & Rai, 2008). At present, researchers could not fully understand the mechanism of food color formation, and the structure of melanoidin also lacks comprehensive data (Fu, Wang, Wang, Ni, & Wang, 2018). There are mainly three views on the structure of melanoid molecules. It was proposed that melanoid compound is mainly composed of pyrrole or furan of repeating units, and eventually forms MRPs through condensation reaction (Tressl, Wondrak, Krüger, & Rewicki, 1998). It has also been suggested that low molecular weight chromatin groups are formed from high molecular weight colored substances by cross-linking the epsilon-NH_2 or arginine of lysine with proteins. Previous study suggested that it was mainly formed by the sugar degradation products in the first stage of MR through Aldol condensation polymerization (Cämmerer & Kroh, 1995). Previous studies have shown that melanoid compound are closely related to food processing and human health (antioxidation, antimutagenesis, and elimination of reactive oxygen species) (Pastoriza, & Rufián-Henares, 2014; Shen, Chen, & Li, 2018). Posttranslational modifications in proteins are defined as "covalent processing events that change the properties of a protein by proteolytic cleavage or by adding a modifying group to one or more amino acids." Knowing and analyzing these modifications of food proteins represents a challenge to understand their technological and biological function. One of the technologies for the formation of posttranslational modifications in food proteins is nonenzymatic glycation, also known as glycation via MR or simply glycation (Cao & Mezzenga, 2019; Manzano-Román & Fuentes, 2020). These glycated proteins possess the improved bioactivity and functionalities to extend the benefits of native protein. However, during the MR progression, different intermediary compound is formed, which lead to the formation of amino acid derivatives (AGEs) with toxic effects on protein (Ahmed, Mirshekar-Syahkal, Kennish, Karachalias, & Thornalley, 2010). To comprehend the complexity of MR, the advanced products formations need to be controlled in the food systems and products with added value. These modifications offer enough validations for the incorporation of byproducts of the animal-based food industry and possible use of glycoproteins as a food ingredient (Nooshkam, Varidi, & Verma, 2020).

3 | FACTORS AFFECTING MR AND MRPS

MR is an exceedingly intricate reaction, which is affected by numbers of factors. The influence of each factor on MR is as follows.

3.1 | Amino acid type

The rate of MR is different for different types of amino acid type. The reaction rate is the highest for amine, followed by amino acid, and the lowest for protein (Cerny & Davidek, 2003). Different amino acids such as leucine, isoleucine, and glucose produce different flavors in MR (Ambigaipalan, Al-Khalifa, & Shahidi, 2015). Tyrosine, serine, and alanine produce caramel aroma under the same conditions (Nie et al., 2019; Wei, Ni, Thakur, Liao, & Wei, 2020). Proline reacts with Maillard to produce a toasty aroma. Therefore, different food is endowed with different flavors when heated (Griffith & Hammond, 1989).

3.2 | Sugars

Reducing sugars are essential substrates for MR, and different types of reducing sugars participate in MR at different rates due to their different structures (Liu et al., 2012).The reactivity of reducing sugars in MR is as follows: monosaccharide > disaccharide, five-carbon sugar > six-carbon sugar, and aldehyde compound > keto-based compound (Guo, Tian, & Small, 2010).

3.3 | PH value

Since the different stages of the MR are catalyzed by different acids and bases, MR is affected by pH value (Toldrá, Aristoy, Mora, & Reig, 2012). A previous study revealed that when the pH was in the range of 3 to 9, the rate of browning reaction increased with the increase of pH (Han et al., 2018). When pH $\leq$ 3, the browning reaction degree was slightly lowered, which was further decreased with the lowering of pH. The authors suggested that it may be due to the hydrolysis of n-glucosamine, the precursor of Maillard's characteristic flavor under acidic conditions (Žilić, Kocadağlı, Vančetović, & Gökmen, 2016).

3.4 | Temperature and time

The MR involves a series of complex reaction steps, each of which has a different temperature sensitivity, consequently the MR is largely dependent on the reaction temperature of the system (Lan et al., 2010). A previous study revealed that with the increase in the reaction temperature, the content of reaction substrates in the system was increased, which accelerated the speed of MR (Rochat, Laumer, & Chaintreau, 2007). However, at the higher reaction temperature of the system, the reaction rate was rapidly accelerated, leading to the formation of a large number of final products, such as melanoidin, or even carcinogens (Kchaou et al., 2018). Therefore, it was inferred that the reaction temperature cannot be too high and it should not exceed 180 °C (Mottram, 1998). On the other hand, if the temperature is too low, the reaction will not only be slow, but it will also affect the formation of aromatic flavor substances, not to achieve the finished product flavor effect (Wei et al., 2019b). Reaction time is also an important factor affecting MR (Takayuki,1980). In a short reaction time, the yield of reaction products is small. With the increase of reaction time, the content of products in the system increases and the type of products also increase accordingly (Kchaou et al., 2019).

3.5 | Water and metal ions

Water as the medium in food and its content can also affect MR. It was reported that the water content in the range of 30% to 75% was conducive to MR and the reaction speed was increased with the rise in the water content in this range (Davidek, Gouezec, Devaud, & Blank, 2008). Besides, copper and iron can promote browning reaction, and it was revealed that the catalytic ability of ferric iron was greater than that of ferrous (Ramonaityte, Kersiene, Adams, Tehrani, & Kimpe, 2009).

3.6 | Sulfites

Addition of sulfites at the initial stage of MR can effectively inhibit the browning reaction (Dalefield & Mueller, 2016). The main reason is that sulfites can condense with amino compound after additional reaction with reducing sugars, thus inhibiting the whole reaction (Gogus, Wedzicha, & Lamb, 1997). In the actual production process, MR should be controlled according to the needs of the product (Kim, Chun, Oh, Lee, & Lee, 2019). Based on the above factors, we can summarize the measures to control the degree of MR by (1) removing one of the reactants: the corresponding enzymes such as glucose invertase can be used, or calcium salts can be added to combine with amino acids to form insoluble compound; (2) lowering the inverse temperature or pH modulation to slightly acidic; (3) maintaining the low moisture content in food; (4) adding sulfites at the initial stage of the reaction (Wedzicha, Bellion, & German, 2005).

4 | APPLICATION OF MR IN FOOD INDUSTRY

The influence of MR on different categories of food is shown in Table 1.

TABLE 1 The influence of Maillard reaction (MR) on different categories of foods

Types of food	Specific type	Impact of the MR on food quality	Control condition	Reference
Cereal products	Infant cereals	Involvement of lysine in MR	Control of the storage conditions	Ramıŕez-Jiménez, Garcıá-Villanova, & Guerra-Hernández, 2004
	Infant cereals	Destruction of essential amino acids, inhibition of proteolytic and glycolytic enzymes, interaction with metal ions	Flour type	Guerra-Hernandez, Corzo, & Garcia-Villanova, 1999
	Wheat flour	Acrylamide formation during heating	Effect of sulfur addition	Elmore, Parker, Halford, Muttucumaru, & Mottram, 2008
	Long-grain rice cultivars	Browning development	Steaming temperature	Elmore et al., 2008
	Tortilla chips	Acrylamide formation during heating	Addition of calcium hydroxide	Salazar et al., 2014
	You-tiao	Acrylamide formation during frying	Frying temperature and time and dough pH	Huang, Yu, Zou, & Tilley, 2008
	Fried bread sticks	Acrylamide formation during frying	Addition of antioxidant of bamboo leaves and extract of green tea	Zhang & Zhang, 2007
	Cookies, fried tortilla chips, baked tortilla chips	Acrylamide formation during heating	Addition of amaranth flour or amaranth protein isolate	Salazar, Arámbula-Villa, Hidalgo, & Zamora, 2012
	Biscuits	Acrylamide formation during heating	Asparaginase concentration	Anese, Quarta, & Frias, 2011
	Cookies	Acrylamide formation during cooking	Effect of radio-frequency postdrying	Palazoğlu, Coşkun, Kocadağlı, & Gökmen, 2012
	Buckwheat ginger cakes	Acrylamide formation during heating	Addition of spices	Marková et al., 2012
	Gingerbread	Acrylamide formation during heating	Effect of baking agents, type of sugar, organic acid and process conditions	Amrein, Schönbächler, Escher, & Amadò, 2004
	Mixed rye bread	Acrylamide formation during heating	Addition of low pH fermented products	Bartkiene et al., 2013
	Bread	Generation of MR products during baking	Effect of grain addition in bread formulation	Serpen, Gökmen, & Mogol, 2012
	Wheat bread and bread rolls	Acrylamide formation during heat	Effect of NaCl, enzyme and cysteine addition	Claus, Mongili, Weisz, Schieber, & Carle, 2008
	Yeast-leavened bread	Acrylamide formation during heating	Fermentation time	Mustafa et al., 2009
	potato flour and semolina	Acrylamide formation during extrusion	Variation of the ratios of potato flour and semolina	Mulla, Bharadwaj, Annapure, & Singhal, 2011
	Potato crisps, French fries	Acrylamide formation during heating and frying	Addition of glycine or glutamine	Bråthen, Kita, Knutsen, & Wicklund, 2005
	Biscuits and potato chips	Acrylamide formation during heating and frying	Vacuum treatments with different conditions	Anese, Suman, & Nicoli, 2010
Potato-based products	Freeze-dried potato sample	Formation of acrylamide during heat treatment	Impact of raw material	Knutsen et al., 2009
	Potato powders	Generation of acrylamide during heating of potato powders	Composition of the raw material	Zhu, Cai, Ke, & Corke, 2010
	Potato	Generation of acrylamide during heating	Composition of the raw material	Elmore et al., 2008

(Continues)

TABLE 1 (Continued)

Types of food	Specific type	Impact of the MR on food quality	Control condition	Reference
	Potato model system	Generation of acrylamide during heating	Impact of different additives on acrylamide formation	Mestdagh, Wilde, Delporte, Peteghem, & Meulenaer, 2008
	Potato chip model	Generation of acrylamide during frying	Soaking in a taurine solution	Shin et al., 2010
	French fries and potato chips	Generation of acrylamide during frying	Effect of blanching time and temperature	Mestdagh et al., 2008
	Fried potato strips	Generation of acrylamide and browning during frying	Effect of immersing in water or solutions with additives, blanching	Pedreschi, Kaack, & Granby, 2006
	Potato chips	Generation of acrylamide during frying	Effect of radio-frequency postdrying after partial frying	Koklamaz, Palazoğlu, Kocadağlı, & Gökmen, 2014
	Sweet potato flour	Browning development during storage	Effect of peeling, drying temperature, and pretreatment	Ahmed, Akter, & Eun, 2010
	Potato flour and chips	Generation of acrylamide during heating	Effect of potato variety	Halford et al., 2012
	Potato samples	Generation of acrylamide during heating	Heating temperature and time	Rydberg et al., 2003
	Fresh and stored potatoes, dried potato products	Generation of acrylamide during heating	Immersion in asparaginase solution at various concentrations	Ciesarová, Kiss, & Boegl, 2006
	Fresh potatoes	Generation of acrylamide during heating	Addition of olive oil and oregano phenolic compounds	Kotsiou, Tasioula-Margari, Kukurová, & Ciesarová, 2010
	Potato strips	Generation of acrylamide during frying	Soaking potato strips in a solution containing vitamins	Zeng et al., 2009
	Fried potatoes	Generation of acrylamide during frying	Immersion of potatoes in solutions containing natural extracts	Morales, Jimenez, Garcia, Mendoza, & Beristain, 2014
Coffee and coffee substitutes	Coffee and coffee substitutes	Formation of acrylamide during roasting of chicory roots	Influence of the raw material	Loaëc et al., 2014
	Instant coffee	Generation of acrylamide and HMF during roasting	Influence of yeast fermentation	Akıllıoglu & Gökmen, 2014
	Coffee powder	Generation of furans during roasting	Effect of vacuum treatment	Quarta & Anese, 2012
	Coffee beans	Generation of acrylamide during roasting	Effect of roasting under vacuum	Anese et al., 2014
Dairy products	UHT milk	Reaction of lactose with protein during UHT processing	Addition of green tea flavonoids	Schamberger & Labuza, 2007
	Liquid infant milk	Reaction of lactose with protein during heat treatment and storage	Control of the storage conditions	Guerra-Hernandez, Leon Gomez, Garcia-Villanova, Corzo Sanchez, & Romera Gomez, 2002
	Powdered infant formula	Involvement of lysine in MR during spray-drying	Impact of temperature	Schmitz, Gianfrancesco, Kulozik, & Foerst, 2011
	Milk-cereal-based baby foods	Blockage of lysine + decrease in protein digestibility	Storage temperature	Bosch, Alegría, Farré, & Clemente, 2008
	Milk-based infant formulas	Involvement of essential amino acids and carbohydrates in the MR during processing and storage	MR indicators	Contreras-Calderón, Guerra-Hernández, & García-Villanova, 2009

(Continues)

TABLE 1 (Continued)

Types of food	Specific type	Impact of the MR on food quality	Control condition	Reference
Fruits and vegetables	Apple juice	Development of nonenzymatic browning during storage	Influence of the raw material	Burdurlu & Karadeniz, 2003
	Orange juice	Development of nonenzymatic browning during storage	Application of electro-reduction and electro-oxidation treatment	Fustier, St-Germain, Lamarche, & Mondor, 2011
	Citrus juice	Development of nonenzymatic browning during storage	L-ascorbic acid amount	Roig, Bello, Rivera, & Kennedy, 1999
	Grape juice	Development of nonenzymatic browning during processing and storage	Addition of glutathione	Wu, 2014
	Dried strawberries	Degradation of vitamin C	Impact of drying conditions	Gamboa-Santos et al., 2014
	Banana fritters	Formation of acrylamide during frying	Effect of maturity stage	Daniali, Jinap, Hanifah, & Hajeb, 2013
	Ripe olive	Formation of acrylamide during sterilization treatment	Addition of salts, amino acids, antioxidants	Casado, Sánchez, & Montaño, 2010
Meat products	Chicken and duck breast	Generation of HAs during cooking	Comparison of various cooking methods	Liao, Wang, Xu, & Zhou, 2010
	Fried chicken meat product	Generation of HAs during frying	Addition of green tea extract	Haskaraca, Demirok, Kolsarıcı, Öz, & Özsaraç, 2014
	Fried chicken	Generation of acrylamide during frying	Effect of flour type	Barutcu, Sahin, & Sumnu, 2009
	Beef and chicken meatballs	Generation of HAs during cooking	Addition of pomegranate seed extract in the formulation of meatballs	Keşkekoğlu, & Üren, 2014
	Meat products	Generation of HAs during cooking	Effect of the type of meat	Puangsombat, Gadgil, Houser, Hunt, & Smith, 2012
	Meat flavor model system	Generation of HAs during cooking	Effect of temperature, time, precursors	Bordas, Moyano, Puignou, & Galceran, 2004
	Pan-fried beef	Generation of HAs during cooking	Effect of the marinating time	Quelhas et al., 2010
	Meat and gravy samples	Generation of HAs during cooking	Addition of onion and garlic	Janoszka, 2010
	Pan-fried bacon	Generation of HAs during frying	Impact of pan-frying temperature and time	Gibis, Kruwinnus, & Weiss, 2015
	Fried beef patties	Generation of HAs during cooking	Addition of grape seed extract and rosemary extract in marinades	Gibis & Weiss, 2012
Fish and fish products	Grass carp	Generation of HAs during frying	Impact of the frying temperature and the number of frying cycles	Wang et al., 2015

4.1 | MR and food color

MRs give rise to a certain dark brown-black color to different varieties of food such as bread, coffee, black tea, beer, pastries, and soy sauce (Geng et al., 2019). However, the flavor substances generated mostly from food nutrients such as sugars, protein, fat, and nucleic acids, and vitamins in the process of storage and processing of MR are unfavorable from technological and nutritional perspectives (Ma, Zhao, & Chi, 2019). In addition, as a result of browning, white products become discolored and light products become dark, which to some extent affect the sensory quality of some products (such as milk and dairy products) (Bosch, Alegría, Farré, & Clemente, 2007).

4.2 | MR and food flavor

MR plays an important role in the formation of food flavor characteristics such as color, aroma, and taste (Zhao et al., 2019). By controlling the raw materials, temperature, and processing methods, a variety of substances with different flavor and aroma can be prepared (He et al.,

TABLE 2 Aroma compounds generated during the MR in different kinds of foods and food products

Classification of compounds	Related flavor	Food	References
Pyrazine	Saute, roast, bake, roast, nutty	Baked goods, coffee, meat, popcorn	Xu, Oruna-Concha, & Elmore, 2016
Pyrimidine	Grass taste, bitter taste, baked taste, biscuit taste	Barley, barley malt and other grain products	Weenen, 1998
Aldehyde	Pungent, spicy, cocoa, fruity	Fruit, onions, meat, roasted peanuts	Ma et al, 2010
Thiophene	Roast, grass,	Canned beef, broth	Burin, Marchand, de Revel, & Bordignon-Luiz, 2013
Ketones	Caramel, onion	Caramel, onion	Wang et al., 2018
Furan, furan ketone	Sweet, fruity, toasted, spicy, caramel	Coffee	Srivastava et al., 2018
Thiazole	Roast meat taste	Stewed beef, baked potato	Yu, Tan, & Wang, 2012
Pyrrole	Grain taste	Cereal, coffee	Solina, Johnson, & Whitfield, 2007

2019). For example, ribose reacts with cysteine and glutathione to produce roast pork flavor and roast beef flavor, respectively (Chiang, Eyres, Silcock, Hardacre, & Parker, 2019). After the use of same reactants reacting at different temperatures, they produce different flavors. For example, glucose and valine react at 100 °C to 150 °C and 180 °C to produce the flavor of toast and the flavor of chocolate, respectively (Wang & Ho, 2008). The reaction of xylose and yeast hydrolyzed protein at 90 °C and 160 °C produced biscuit flavor and sauce flavor, respectively (Danehy, 1986). Different processing methods can affect the aroma of the same food. For instance, boiled potatoes can produce 125 kinds of aroma, and when baked can produce 250 kinds of aroma (Sun et al., 2018). The MR can be used in the production of salty flavors and some flavoring substrates (Meng et al., 2020). At present, these salty flavor essences have been widely used in frozen food, canned food, instant noodles, sausage and salty body idle food, and other food processing and seasoning (Al Loman & Ju, 2017). However, the compounds formed in the MR are not all favorable, and some compounds such as alkyl pyrimidines and pyrrole are generally considered to have an unpleasant taste (Mazumder, Hongsprabhas, & Thottiam Vasudevan, 2019). Therefore, reaction conditions should be properly controlled during food processing to make the reaction go in the favorable direction according to the consumer demand (Shang et al., 2020). The main flavor substances formed by MR are shown in Table 2.

4.3 | MR and food nutrition

MR may cause an unnecessary decrease in the nutritional value of some food mainly including amino acid and mineral loss (Robert, Labat-Robert, & Robert, 2010). MR is the main consumption of amino acids and sugars in food raw materials. Amino acids suffer loss due to the formation of pigment complex and the destruction in Strecker degradation, and the pigment complex cannot be hydrolyzed in the digestive tract, which reduces the biological titer of proteins (Sung, Chang, Chou, & Hsiao, 2018). The results showed that the essential amino acids, such as lysine were most easily lost in the browning reaction, thus reducing the nutritional value of food. Decreased bioavailability of minerals has been reported after the MR, which may be caused by the formation of metal complexes between metal elements and MRPs (Delgado-Andrade, Seiquer, & Navarro, 2008).

5 | BIOLOGICAL ACTIVITY OF MR PRODUCTS

5.1 | Antioxidant and mutation resistance activities of MRPs

First, due to the high reactivity of intermediates and the occurrence of complex polymerization and dehydration, brown melanoidin is formed (Brudzynski & Miotto, 2011). The antioxidant mechanism of MRPs is shown in Figure 3. There are three main types of melanoidin (Rufian-Henares & Morales, 2007). The antioxidant properties of MRPs are prime due to the following three substances such as melanoidin (composed of furan or pyrrole repeating units), melanoid (condensation of alcohols and aldehydes), and protein-based melanoidin (cross-linking proteins with low molecular weight coloring compound) (Eichner, 1980). Melanoidin has the activity of removing hydroxyl groups, which is mainly caused by the chelation of high molecular weight chelates containing hydroxyl groups in melanoidin. Melanoidin class compound is mainly formed in the later stage of MR, and it has many functional properties such as antioxidant, antibacterial, and antihypertensive activities (Rufián-Henares, Morales, 2007).

5.1.1 | Reductone

When MR is in its initial stage, reducing sugars and amino acids react to produce unstable amino-reducing ketones, which participate in a series of reactions to form brown substances, leading to the browning of food (Troise, Wiltafsky, Fogliano, & Vitaglione, 2018). The reduced ketones in MRPs are used for reduction and chelation, which have antioxidant effects. Previous researchers reported that the characteristics and antioxidant properties of ultrafiltration MRPs obtained by the reaction of casein and glucose, and the MRPs of high polymer quality showed the highest reduction capacity and metal chelating activity (Song et al., 2016). Reductive ketones in MRPs break free radical chain

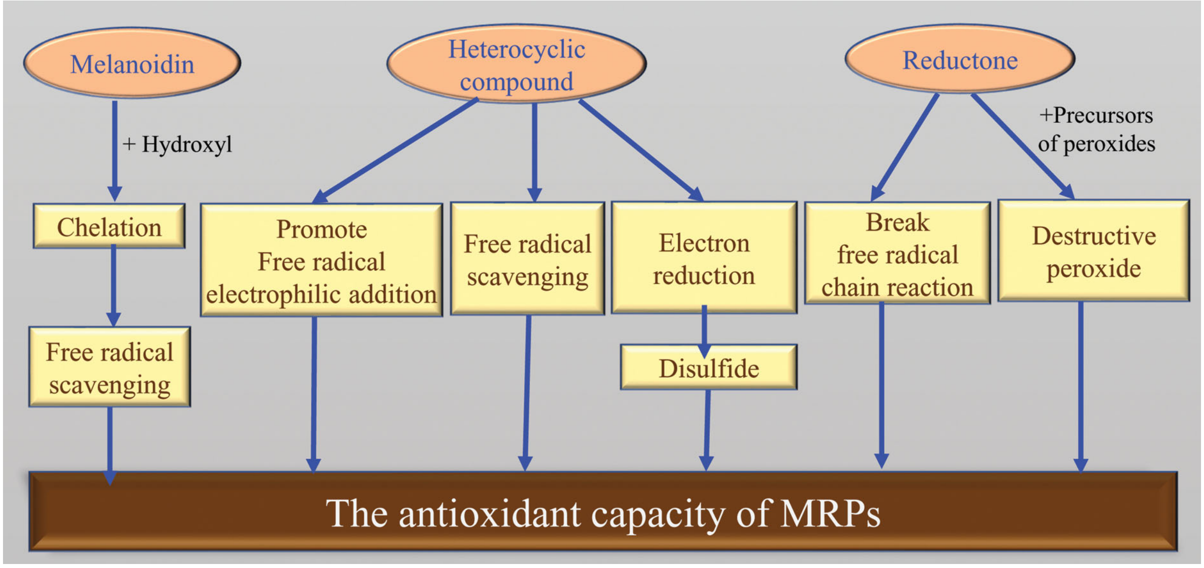

FIGURE 3 Antioxidation mechanism of Maillard reaction products

reactions by providing hydrogen atoms (Osada & Shibamoto, 2006). Reduced ketones can react with some precursors of peroxides to prevent the formation of peroxides, thus achieving the purpose of antioxidation. The antioxidant capacity of MRPs increases with the increase of reaction time (Xiong et al., 2020), while the reduction capacity is the opposite, which indicates that the antioxidant capacity is not entirely dependent on the reduction capacity, but is related to other factors, such as the ability to provide hydrogen, the ability to chelate metal ions, and the ability to remove reactive oxygen species (Wang, Zhang, Wang, Wang, & Liu, 2019).

5.1.2 | Volatile heterocyclic compounds

The MR of volatile heterocyclic compound not only produces substances with antioxidant activities such as melanoidin and reduced ketone, but also produces volatile heterocyclic MRPs, which impart food flavor and antioxidant properties (Nooshkam, Varidi, & Bashash, 2019). These substances are mainly heterocyclic compounds containing oxygen, nitrogen, and sulfur, including oxy hetero cyclic furans, aza cyclic pyrazines, thiophene, and thiazole containing sulfur heterocyclic thiophene (Osada & Shibamoto, 2006). MRPs containing pyrazines, pyrrole, and furans can be obtained purposefully by selecting different kinds of amino acids and sugars to react at different temperatures and times (Burin, Marchand, de Revel, & Bordignon-Luiz, 2013). MRPs also have a considerable ability to resist mutation with a good correlation between antioxidant activity and reducing power. Researchers often use different amino acids–sugars combination study of MRPs (Yen, Tsai, & Lii, 1992). In one study, three kinds of monosaccharide (fructose, glucose, and xylose) and four kinds of amino acid (tryptophan, arginine, glycine, and lysine) were used for the preparation of MRPs. Through the Ames test of rat microglobulin, MRPs resistant ability of five kinds of mutation factors was observed. It was found that xylose-tryptophan could strongly suppress the three-mutagen mutagenesis except aflatoxin B1, thus MRPs for mutagenic factors may show the opposite of biological properties (Xu, Huang, Xu, Liu, & Xiao, 2019). In addition, the selection of the system model has different effects on the antimutation performance of MRPs. It was found that MRPs generated in the glucose–glycine alcohol solution model had a stronger inhibitory effect on the mutagens 4-nitroquinoline-N-oxide than those obtained from aqueous solution mode (Ko et al., 2018). The melanoidin is often produced in the later MR stage, and its structure is complex and molecular weight is relatively large (Zhang et al., 2018). Studies have shown that the reductivity of melanoidin may be related to the antimutation ability of MRPs to some extent, and this macromolecular substance has the capability of scavenging free radicals and inactivating enzyme activity inhibition (Hayase, Hirashima, Okamoto, & Kato, 1989).

5.2 | Antiproliferation effect of MRPs

Melanoidin has been reported to exert significant antiproliferation effects in heated potato fiber, monosodium glutamate, soy sauce, and coffee. However, melanoidin is similar to the fiber behavior of colonic microorganisms, so it is often believed that its antiproliferation and anticancer properties are mainly derived from microbial fermentation metabolites (Ludwig, Clifford, Lean, Ashihara, & Crozier, 2014). The antiproliferative activity of different carbonyl–amino model systems differ from each other. In one study, the effect of sugars (fructose and glucose) and 20 amino acids in the model system of various biological activity of MRPs was evaluated (Hwang et al., 2012). It was revealed that glucose MRPs showed stronger antiproliferative activity than fructose MRPs. In another study, the ethyl acetate component of MRPs was identified with an antiproliferative composition of 2, 4-double (of hydroxy phenyl)-2-butene aldehyde (HPB242), which has a good inhibitory effect on the proliferation of all six types of cancer cells (Hwang et al., 2012).

5.3 | Bacteriostatic activity of MR

Bacteriostatic preservatives present an indispensable link in food processing and preservation industry. At present, the food industry commonly uses synthetic antimicrobial agents; therefore, there is need to develop safe and effective natural bacteriostatic agent, and some of the MRPs have been proved to have good antibacterial ability with an obvious effect on the improvement of the natural antiseptic function properties (Zhao, Yuan, Zhang, & Yang, 2018). Studies have shown that indoles, furans, imidazole, and other derivatives in MRPs have antibacterial activities (Trang et al., 2009). In addition, *in vivo* studies of water-soluble melanosomes have confirmed that they are resistant to pathogenic enterobacteriaceae through their cell membranes destruction mechanism (Huang, Wang, Song, Zhang, & Liu, 2017). In another study, it was found that MRPs prepared by glucose and chitosan oligosaccharide had higher antibacterial activity and fresh-keeping effect (Sun et al., 2017). Similarly, chitosan derivatives prepared by monosaccharide (glucose) by MR had better antibacterial performance (Ming et al., 2012). Studies on the antibacterial activity of MRPs were limited to protein peptides with certain antibacterial activity, exogenous sugars or protein–polysaccharide complexes (such as polylysine and glucan complex) as the reaction precursors, which were enhanced by MR modification. Recent studies have reported that part of the antibacterial activity of MRPs can be attributed to dicarbonyl compound (such as glyoxal and acetone aldehyde), and the exploration of its antibacterial mechanism has become a hot research topic (Hrynets, Bhattacherjee, Ndagijimana, Hincapie Martinez, & Betti, 2016).

5.4 | Antiallergic effect of MRPs

Allergic reactions, especially when the immune system attacks normal body tissues and organs, can cause certain harm to human health. It was reported that ribose MR was optimized by response surface method to enhance the antiallergic effect of fish proteolytic substance, and it was found that MRPs of fish proteolytic substance at ribose concentration of 28.36% and reaction time of 38.09 min at pH 8.26 had obvious antiallergic effect on β-hexosamine and histamine (Yang et al., 2015). In another study, maltopentose was combined with α-lactoalbumin to reduce the antigenicity of α-lactoalbumin (Enomoto et al., 2009). This chemical modification method is often used to weaken the antigenicity of proteins, so as to avoid the bitter taste caused by proteolysis to form peptides and the cooking taste is formed by direct heating to destroy the protein structure. Heating a soybean trypsin inhibitor (STI) and sugars mixture in a 120 °C oven, the Maillard products of glucose, lactose, and maltose with STI reduced the antigenicity of STI by 60% to 80% compared to that of the control group without adding sugars (Zhong, Tan, & Langrish, 2018). Starch was less effective than glucose, lactose, and maltose. When glucose and STI were heated for 10 min, the antiallergic effect of glucose and STI was generated (Zhong et al., 2018). With the extension of heating time, the darker the browning of Maillard products, the antiallergic effect of the products remained unchanged.

5.5 | Antihypertensive activity

Some experts found that melanin, MRPs could effectively inhibit the ACE activity and thus reduce blood pressure (Mesías & Delgado-Andrade, 2017). It was also found that the *in vitro* inhibitory activity of ACE was related to the structure of melanin-like compound extracted by MR in the glucose–amino acid aqueous solution system (100 °C, 24 hr, pH 7). This provides a theoretical basis for the development of MRP-related health food for cardiovascular disease prevention.

5.6 | Antitumor effect

There have been studies that showed that MRPs have inhibitory effects on cancer cells. MRPs obtained from heated food as an antitumor agent have been shown to inhibit the growth of gastric cancer cells by blocking the cell cycle and apoptosis (Marko et al., 2003). This suggests that the MRPs may affect the growth of human tumor cells and make a contribution to the anticancerous compound.

5.7 | Regulation of immune metabolism and intestinal flora by MRPs

A large number of studies have shown that MRPs are related to the immune system. The conformational epitome of MRPs is recognized by pattern recognition (PRRs) on the surface of human immune cells, and signals are transmitted to the nucleus, whereupon the nuclear factor kappa-b (NF-kB) is activated (Simões, Miguel, & Correia, 2018). The immune system is involved in cell response to external stimuli and makes extracellular responses (Muscat, Pelka, Jörg, Weigle, & Pischetsrieder, 2010). MRP$_S$ and AGEs are absorbed by the gut and reach mucosal tissues to encounter a local immune system, and this exposure leads to immune activation that has local effects in the gut, including inducing tissue damage, inflammation, and immune responses (T-cell activation and Ig A antibody production). AGEs affect the immune system at three levels: by the changes in signaling pathways that occur after AGEs interact with their receptors; by changing signaling pathways, AGEs induce or inhibit the production of certain cytokines, hormones, and free radicals; due to the AGEs effect and the enhancement of pro-oxidative activity, protein modification in target tissues leads to functional abnormalities (Mališauskas et al., 2003). The intestinal health is in close relationship with human health fructose base lysine (N epsilon-fructoselysine, FL) as Amadori products has antipeptic properties. In one study, FL was used by the human gut microbes for *in vitro* fermentation (Hellwig et al., 2015). After 4 hr, FL was completely decomposed, which suggested that the human gut microbes may use FL as a carbon source or nitrogen source of growth metabolism. It was also found that melanoidin is not easy to digest, so it can be fermented by intestinal microflora, further expanding the application scope of MRPs in health (Pérez-Burillo et al., 2018).

5.8 | Control of MR in food systems: Strategies and chemical mechanisms

Despite the fact that different MRPs led to the modifications of food properties, protein functionality, and digestibility, several negative aspects of the glycated peptides cannot be ignored (Zhang et al., 2019). Besides, browning derived from the MR affects the sensory quality of food and ultimately leads to the lower acceptability of consumers. Previous studies have reported that addition of cysteine to MR system can inhibit the brown color formation and lead to light-colored Maillard flavor-enhancing peptides (Eric et al., 2013). Another study revealed that these peptides are generated after the interaction of cysteine and amadori compound and inhibition of dicarbonyl compound (Zhai et al., 2019). A recent study reported the use of glucosamine, a highly reactive amino sugars for the generation of light-colored Maillard flavor-enhancing peptides (Fu et al., 2019). It is imperative to control processing conditions, inhibit the MR progression, and detection of early and intermediate MRPs. Therefore, numerous measures have been applied for controlling the MR and subsequent downstream reaction products in food during the past decades (Ghaderi & Monajjemzadeh, 2019). Previous studies suggested different strategies including addition of functional ingredients (vitamins and plant polyphenols), targeting reactive sites and intermediates of MR, modification of reducing sugars, blocking or modification of amines, trapping of α-dicarbonyls, strecker aldehydes, and acrylamide, and scavenging of Maillard-derived radicals by polyphenols, action of pyridoxamine on amadori products. Besides, enzymatic and alternative processing methods have also been applied for tailoring the extent of the MR and related conjugates (Martínez Herrera, Sánchez-Chino, Corzo-Ríos, Dávila-Ortiz, & Jiménez Martínez, 2019).

6 | CONCLUSION

To improve the flavor development during food processing and storage, increasing attention has been paid to the unique molecular structures and formation mechanisms of MRPs. This review demonstrates that MRPs also possess diverse bioactivities, such as antioxidant, antibacterial, antihypertensive, anti-inflammatory, and bifidogenic properties. However, more *in vivo* studies are required for subsequent understanding of structure–function relationship of MRPs as functional food ingredients. Past studies have also highlighted their potential negative effects, therefore, novel monitoring and controlling automated strategies must be applied to obtain early compound and melanoidin besides a significantly low quantity of AGEs via employing AGEs inhibitors. Through recent interventions, the technological functionality of food proteins as delivery vehicles has been enhanced through MR between reducing sugars and proteins to protect many food-derived bioactive compound and increase their bioavailability in food and pharmaceutical industries. The safety assessment of the MRPs and their stability in the GI tract can be the next research target of pharmaceutical researchers. This review was aimed to accumulate the updated knowledge of series of parallel intricate reaction stages with the positive (food industry) and negative (detrimental to our health) modulations mediated by MR during the food processing and flavor development.

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ETHICAL GUIDELINES

Ethics approval was not required for this research.

CONFLICT OF INTEREST

There is no conflict of interest to declare.

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