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Review

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Control of Maillard Reactions in Foods: Strategies and Chemical Mechanisms

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ABSTRACT: Maillard reactions lead to changes in food color, organoleptic properties, protein functionality, and protein digestibility. Numerous different strategies for controlling Maillard reactions in foods have been attempted during the past decades. In this paper, recent advances in strategies for controlling the Maillard reaction and subsequent downstream reaction products in food systems are critically reviewed. The underlying mechanisms at play are presented, strengths and weaknesses of each strategy are discussed, and reasonable reaction mechanisms are proposed to reinforce the evaluations. The review includes strategies involving addition of functional ingredients, such as plant polyphenols and vitamins, as well as enzymes. The resulting trapping or modification of Maillard targets, reactive intermediates, and advanced glycation endproducts (AGEs) are presented with their potential unwanted side effects. Finally, recent advances in processing for control of Maillard reactions are discussed.

KEYWORDS: *Maillard, protein glycation, plant polyphenols, α-dicarbonyls, protein modifications, advanced glycation endproducts, food*

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INTRODUCTION TO MAILLARD REACTIONS IN FOODS

Maillard reactions are initiated by a condensation of amino groups on protein, peptides, and amino acids with carbonyl groups on reducing sugars, resulting in Schiff base formation and rearrangement to Amadori or Heyns products.[1,2] These molecules are fragmented or modified to reactive α-dicarbonyl species capable of facile reaction with additional nucleophiles such as other amines, guanidines, and thiols. These intermediates may undergo Strecker degradation by condensation with free amino acids, forming imines, which then fragment to form Strecker aldehydes. Further downstream reactions include formation of advanced glycation endproducts (AGEs), such as *N*-ε-(carboxymethyl)lysine (CML), *N*-ε-(carboxyethyl)lysine (CEL), pyrraline, methylglyoxal−lysine dimer (MOLD), glyoxal−lysine dimer (GOLD), and pentosidine, which are all modifications formed on Lys residues. MOLD, GOLD, and pentosidine are cross-linked compounds derived from two Lys residues (MOLD and GOLD) or from one Lys and one Arg residue (pentosidine). Arg can also be modified to methylglyoxal-derived hydroimidazolinone isomers (MG-H_n). Other reactive Maillard reaction intermediates include furfural, 5-(hydroxymethyl)furfural (HMF), reductones, and acrylamide. Eventually, large polymeric compounds, melanoidins, are formed, which causes browning.[2] Altogether, these lead to major compositional, structural, and functional changes to food components, including proteins, amino acids, and sugars,[3] and have potentially significant implications for food color, taste, protein functionality, and digestibility of foods.[3,4]

In food science, these reactions are named nonenzymatic browning reactions or Maillard reactions after Louis-Camille Maillard, who discovered the reaction in 1912.[5] In health and medical sciences, this process is known as protein glycation or glycoxidation. Several excellent reviews describing Maillard reactions in detail have been published.[2,6,7] As a consequence, this review will give only a brief introduction to Maillard reactions and instead provides a critical evaluation of recent advances in strategies for controlling the Maillard reaction and subsequent downstream reactions and products in food systems. Our approach is to present the underlying chemical mechanisms at play, to discuss strengths and weaknesses of each control strategy, and to propose reasonable reaction mechanisms to reinforce our evaluations. Development of efficient strategies for control of Maillard reactions in foods requires an understanding of reaction mechanisms and how reaction conditions affect Maillard reactions. Various strategies for controlling Maillard reactions have been investigated over the years. In Figure 1 the different reactants or intermediates that have been modified for control of Maillard reactions are highlighted; these include modification of reducing sugars, amino groups, Amadori products, α-dicarbonyl groups, and Strecker aldehydes. Environmental conditions also affect the rate and extent of Maillard reactions, and some of the most important factors are briefly described below.

Impact of Maillard Reactions on Food Product Quality. Maillard reactions affect multiple food quality parameters, including organoleptic properties, color, and protein functionality. Unique aroma profiles are developed dependent on temperature−time profiles used during food processing as reviewed by Ames.[8] In some cases, Maillard reactions contribute to desired changes such as generation of delicate flavors, whereas in other cases undesired quality

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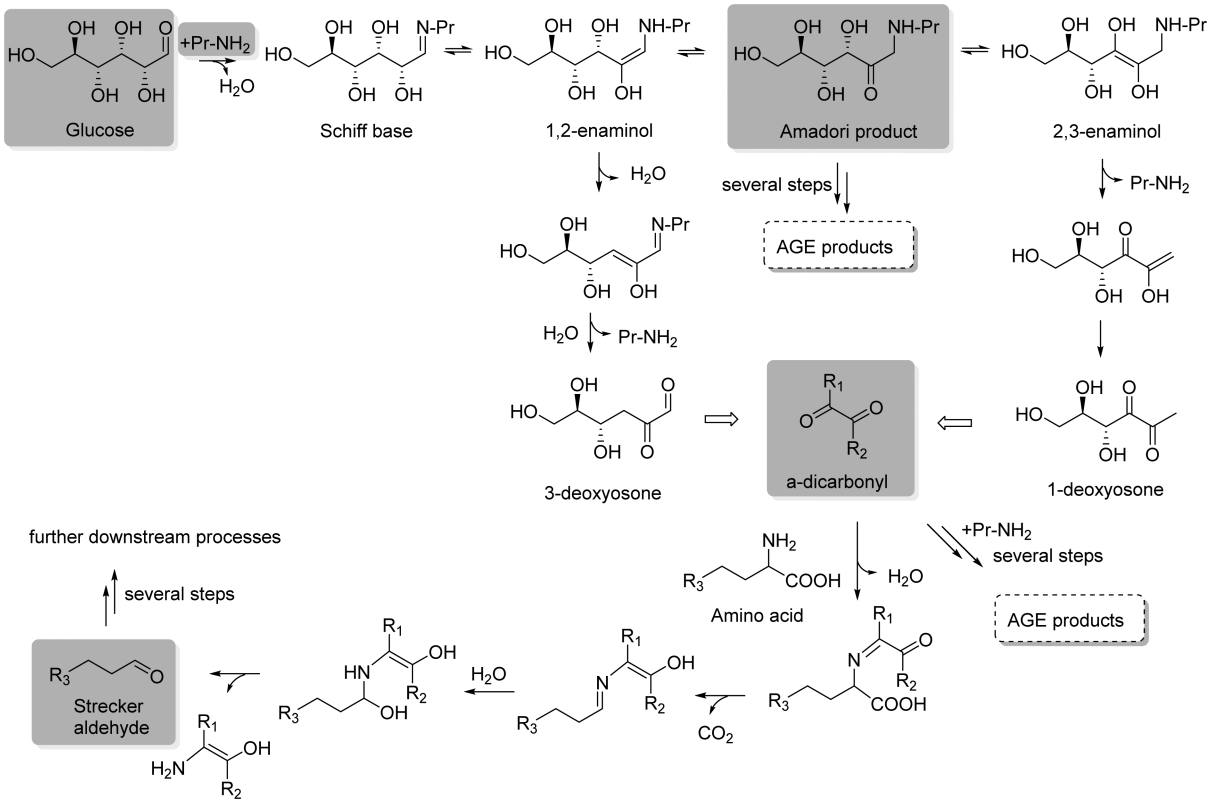

Figure 1. Simplified scheme of the Maillard reaction of a reducing sugar (glucose; an aldose) and a protein amine group to form a Schiff base, which can rearrange to an Amadori product (or Heyns product in the case of ketoses) via an 1,2-enaminol. The Amadori product can then undergo enolization to 1,2-enaminol or 2,3-enaminol and form deoxyosones (α-dicarbonyl compounds), which react rapidly with additional nucleophiles to form Strecker aldehydes. A number of the Maillard reaction intermediates can generate AGEs as marked in the scheme. Reactants and intermediates that have been modified to control Maillard reactions are highlighted in gray.

changes are obtained, especially if the Maillard reactions are too pronounced, producing bitter and burnt flavors. Thus, being able to control Maillard reactions during food production and storage is important from a food quality perspective.

Strecker aldehydes, formed by reactions between α-dicarbonyls and the α-amino group of amino acids (Figure 1, lower part), accumulate readily in thermally processed foods and beverages. Strecker aldehydes are important for flavor development in foods such as bread, coffee, cocoa, roasted meat, and dark beer;[9] however, they are perceived as off-flavors in other food products such as ultrahigh-temperature (UHT) processed milk and pilsner beers.[10,11] Due to their low olfactory threshold, the most important Strecker aldehydes formed in foods are 2-methylbutanal (from Ile), 3-methylbutanal (from Leu), phenylacetaldehyde (from Phe), methylpropanal (from Val), and methional (from Met).[12] Proteolysis occurs in many food products either naturally or due to processing (e.g., during tenderization of meat and mashing during beer production) and results in the release of free amino acids and increased amounts of amino groups.[13] Due to this increase in available amino groups, Strecker aldehydes and AGEs will accumulate even further in these products. A product that is particularly vulnerable to Maillard reactions and derived quality deterioration is lactose-free UHT milk.[10] This is partly due to the heat treatment and partly due to hydrolysis of lactose into glucose and galactose, which react 10 and 20 times more rapidly, respectively, with amines than lactose.[14] In addition, some lactase preparations used for lactose hydrolysis have been shown to have proteolytic side activity, which causes the release of free amino acids during storage and results in the generation of increased levels of Strecker aldehydes.[10,11,15]

The later stages of Maillard reactions include the formation of AGEs, where most of the characterized compounds are derived from modifications of Lys and/or Arg as described above. Cys-derived modifications have also been reported, such as the formation of hemithioacetal groups.[16] Further reactions deplete amino acid residues, resulting in the formation of a large group of polymerized products, known collectively as melanoidins, which cause browning, influence sensory properties, and in some cases compromise shelf life. Formation of AGEs and melanoidins can be significantly enhanced by elevated temperatures such as those employed during sterilization or UHT processing (e.g., of milk products), cooking, and roasting (e.g., of meat and cereals), and they accumulate during long-term ambient storage or during transportation overseas, when the temperature may increase to 70 °C in containers.[10,17−20]

Protein functionality in foods may also be affected by Maillard reactions, including heat stability and solubility of proteins, emulsifying properties, foaming, gelation, and textural properties. Tailoring protein modifications by Maillard reactions to achieve certain functionalities exploits induced changes in protein surface charge, hydrophobicity, tertiary structure, cross-linking, and polymerization. This requires strict control of reaction conditions and depends on the carbohydrate/protein used and extent of Maillard reactions. This field has recently been reviewed[21,22] and will thus not be covered in any detail here.

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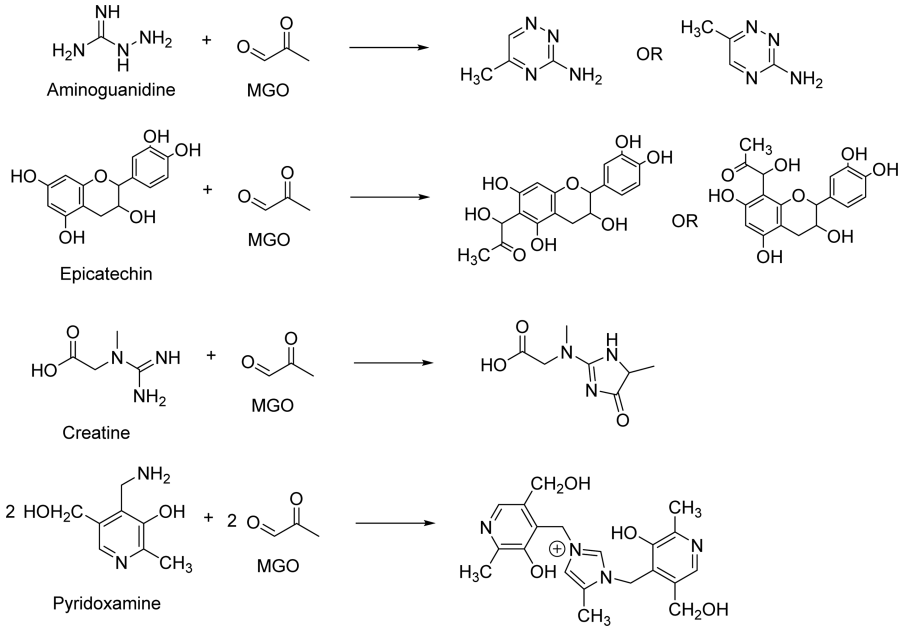

Figure 2. Examples of α-dicarbonyl trapping agents. Reactions are shown for methylglyoxal (MGO) and aminoguanidine,[57] epicatechin,[97] creatine,[82] and pyridoxamine[160] and their identified reaction products.

The rate, extent, and course of Maillard reactions are influenced by several factors including, but not limited to, type of reactants, temperature/time combinations, pH, and water activity.[8,23] As a result of this, reported activation energies range between 23 and 238 kJ/mol dependent on reaction conditions as reviewed by van Boekel.[23] The effect of pH on the rate of Maillard reactions is not so simple. The rate of the initial step of the Maillard reaction is decreased at pH values lower than the pK_a value of the amino group due to reduced nucleophilicity, but low pH increases reactivity with carbonyl groups of reducing carbohydrates and favors the formation of furfurals and acid-catalyzed sugar degradation.[24,25] The rate of Maillard reactions is maximal at intermediate water activities (0.4−0.8) due to a dual effect of water. At high water activities, the mobility of reactants will also be high, whereas at lower water activities reactants become more concentrated, which will increase the rate until a certain point when the system becomes too concentrated and limits diffusion of reactants.[23] Metal ions may also influence the rate of Maillard reactions, and this is described in more detail in the last part of this review.

Elucidating the progress of Maillard reactions in foods is complicated; the presence of multiple reactants as well as the dynamic conditions found in food matrices, processing, and storage conditions all contribute to a complex chemical landscape. For example, it has recently been shown that protein structure affects the nature of AGEs formed; Moeckel et al.[26] have shown that micellar casein−glucose solutions incubated at 100 °C for 4 h create pyrraline more quickly than nonmicellar casein−glucose solutions, whereas the opposite result was observed for CML. It is therefore necessary to quantify major Maillard reaction products formed in relevant model systems or food samples under various conditions. Their rate of formation as well as the rate of subsequent reactions must also be considered, allowing plausible reaction routes to be proposed to develop rational strategies for inhibition and control.

Impact of Maillard Reactions on Human Health. The impact of Maillard reactions on human health is a matter of great debate. Modification of Lys, an essential amino acid, by Maillard reactions is bound to result in lower nutritional value of foods.[27,28] Protein digestibility may also be lowered when proteins are modified by Maillard reactions, which has been shown in both in vitro and in vivo studies.[29−32] This may be explained by modification of enzymatic cleavage sites for intestinal proteases, which will reduce proteolysis.[33−35] On the other hand, thermal treatments are accompanied by protein unfolding and may increase digestibility by promoting the availability of cleavage sites.[35]

Apart from being formed in foods, AGEs are also formed endogenously, where they are associated with various inflammatory conditions and may contribute to the progress of renal failure,[36] diabetes,[37] chronic heart failure,[38] atherosclerosis,[39] and Alzheimer's disease.[40] However, it is unclear whether or not AGE formation in vivo is a cause or a consequence of inflammatory conditions.

The impact of *dietary* AGEs on human health is the subject of increasing scrutiny. Some studies suggest positive health effects purportedly due to the antioxidative activity of melanoidins (reviewed by Delgado-Andrade[41]). AGE formation on protein allergens has been shown to enhance T-cell immunogenicity[42] and has been proposed to be involved in the pathogenesis of food allergies.[4] Some authors have linked the ingestion of dietary AGEs to chronic diseases associated with inflammation.[43−45] However, these studies are controversial as the content of dietary AGEs was based on either estimation from a database or quantification by an immunochemical method that is no longer considered reliable,[46] and the biological role of dietary AGEs, if any, remains contentious. Some of the most important findings related to uptake and human exposure to AGEs are highlighted below. Only studies based on quantification of AGEs by chromatographic separation and detection by UV−vis/MS are included.

The majority of AGEs are not transported across the intestinal epithelium, although specific AGE molecules are recognized by the peptide transporter PEPT1.[47−50] Dipeptide-

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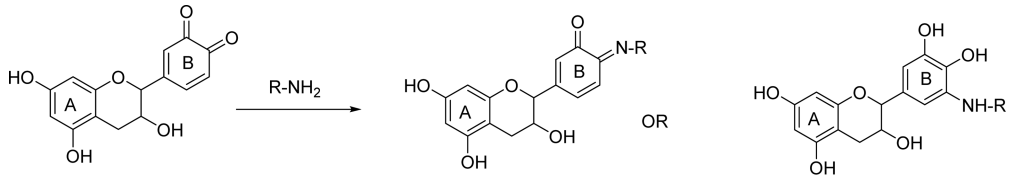

Figure 3. Blocking of amine groups by quinones through formation of benzoquinone imines or amine−quinone adducts via Michael addition.[68,72]

bound CML and pyrraline are absorbed into Caco-2 cells via the peptide transporter PEPT1 and are subsequently cleaved intracellularly followed by basolateral diffusion.[49,50] Free AGEs (CML and pyrraline) are not absorbed and transported across the intestinal epithelium of caco-2 cells.[47,48] Nevertheless, the levels of CML have been found to be up to 70-fold higher in infant formula compared to breast milk, leading to 46% higher CML levels in plasma of infants fed infant formula compared to breast milk, consistent with human exposure to CML via dietary uptake.[51] Although correlation does not prove causation, it might be postulated that the CML detected in infants is derived from dipeptide-bound CML or that the Caco-2 cell model is not representative for the immature gut wall of infants. A higher percentage of fecal excretion (22−48%) compared to urinary excretion (7−38%) in rats has been observed for CML,[52] but in vitro and in vivo studies have also shown that CML can be degraded by human gut microbiota by up to 40%, suggesting that CML can be degraded in humans and used as sources of energy, carbon, and nitrogen.[53,54] The AGE [5-(5,6-dihydro-4*H*-pyridin-3-ylidenemethyl)furanyl]-methanol, which is proposed to be formed by a condensation between HMF and 1,2-dihydropiperidine (formed from the Strecker aldehyde of lysine, 5-aminopentanal, via a cyclization), has recently been detected in bread and found to be transported across Caco-2 cell monolayers, suggesting bioavailability of this AGE.[55] The large variation in uptake patterns and mechanisms of AGEs clearly shows an urgent need for molecular characterization of the chemical composition of AGEs formed in foods to understand how AGE formation affects the nutritional composition of our diet and our health.

STRATEGIES FOR CONTROL OF MAILLARD REACTIONS BY ADDITION OF FUNCTIONAL INGREDIENTS

Many attempts have been made to find inhibitors of Maillard reactions in foods and in vivo. Aminoguanidine was one of the first pharmaceutical drugs discovered that was capable of inhibiting Maillard reaction products[56] and works by trapping α-dicarbonyls (Figure 2).[57,58] Massive adverse side effects in clinical trials resulted in abandonment of aminoguanidine,[59] and since then, the discovery of other Maillard inhibitors has been an ongoing quest. In 2005, it was shown by Totlani and Peterson[60] that epicatechin (a polyphenol compound found in plants such as green tea, grapes, and cocoa) traps α-dicarbonyls. When epicatechin was added to UHT-processed milk, it resulted in reduced off-flavor formation.[61] The effects of polyphenols from different plant sources as Maillard inhibitors have gained increasing focus in food systems because these are considered natural compounds and are therefore more accepted as food ingredients than synthetically manufactured compounds. Other naturally occurring compounds such as vitamins and amino acid and peptide derivatives have also been found to inhibit Maillard reactions by targeting reactive sites, intermediates, or products.

Targeting Reactive Sites of Maillard Reactions. Intervention of Maillard reactions by the addition of natural and synthetic chemical compounds has previously been directed toward removing one of the reactants (the amino groups or the reducing sugars) or adding sulfur-containing compounds, such as sulfur dioxide or *N*-acetylcysteine, which inhibit the reactions or create reaction products that are colorless.[8,62] Lately the focus has increasingly shifted toward trapping of α-dicarbonyl compounds, but some compounds have also been proposed to inhibit Maillard reactions through scavenging of Maillard-derived radicals, reaction with Amadori products, and trapping of specific Maillard reaction products such as Strecker aldehydes and acrylamide.

Modification of Reducing Sugars. Different reducing sugars exhibit different reactivities; pentose sugars (e.g., ribose) are more reactive than hexoses (e.g., glucose), which are more reactive than disaccharides (e.g., lactose).[34,63,64] Furthermore, the hexose galactose is more reactive than glucose due to a higher steady state concentration of the reactive open-chain form of galactose compared to glucose.[65] Fermentation of reducing sugars into nonreducing sugars by the addition of starter cultures to cheese has been shown to prevent browning.[66]

Blocking or Modification of Amines. Inhibition of Maillard has successfully been obtained by modification of amines; modification of amines on lysine residues in a whey protein isolate (WPI) by acetylation and in particular by succinylation has been shown to protect lysine from further modification during storage at 50 °C.[33] Even though the succinylation resulted in an initial loss of lysine of ca. 25% compared to native WPI, the remaining lysine concentration in the succinylated WPI was ca. 60%, whereas native WPI only had ca. 25% remaining lysine after 7 days of storage at 50 °C. As a drawback, in vitro digestibility was lowered by the succinylation.[33]

A more recent discussion on how Maillard reactions may be inhibited or modulated involves the modification of amines by oxidized polyphenols, quinones.[67−70] Quinones are readily formed in polyphenol-containing foods during processing and storage[71] and react with amines to form either benzoquinone imines or amine−quinone adducts via a Michael addition (Figure 3).[68,72,73] If the approach is to inhibit Maillard reactions by blocking amine groups in foods, it is important to consider the initial amine concentration in the food. If the inhibitor concentration (in this case the polyphenol) can only be added in low, substoichiometric, concentrations compared to the amine, then it is unlikely that the initial step of the Maillard reaction will be affected because there will still be sufficient amine groups available for reaction with reducing carbohydrates or α-dicarbonyls. It could also be questioned whether blocking of amine groups on lysine residues is a feasible strategy for healthy food products due to the unavoidable modification of

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lysine, an essential amino acid. Nevertheless, addition of polyphenols to foods will result in the formation of protein−phenol adducts, which influences protein functionality in foods,[71,74,75] and it is therefore important to understand the reaction mechanism to control the level of protein modification. The reaction product formed between quinones and amines appears to be dependent on incubation conditions of samples. In the study by Yin et al.,[68] samples were heated at 70 °C for 10 min, and both reaction products were identified by LC-MS, whereas in a study by Li et al.[73] samples were incubated at room temperature and only the amine−quinone adduct was detected by LC-MS. Downstream reactions result in a variety of additional products, including reoxidation of the amine−quinone adduct,[73] reaction with another amine group to form amine−quinone−amine adducts,[68] and formation of benzoquinone imines on both oxo groups of the B-ring.[69]

Quinones also react with thiol groups on amino acids, peptides, and proteins to form thiol−quinone adducts.[71−73] The reaction of quinones with thiols has been found to be >500,000 times faster than with amines, showing that thiols are kinetically preferred targets for quinone modification.[73] However, thiols are very prone to oxidation during processing and storage,[76−78] and in thiol-depleted food products the reaction of quinones with amines is therefore likely to take place even though the reaction is much slower. Furthermore, the concentration of thiols in foods is usually much lower than the concentration of amines (μM levels of thiols versus mM levels of amines), so if polyphenols have been dosed in higher concentration than the available thiol concentration (and the polyphenols are oxidized to quinones), modification of amines by quinones is likely to take place. For milk, the maximum dose of epicatechin has been found to be 0.1% due to the risk of generating background bitterness if dosed higher,[61] which corresponds to 3.45 mM epicatechin. This concentration of polyphenol is much higher than the thiol concentration in milk and suggests that the amine−quinone reaction is a likely reaction in milk added catechins considering the concentrations of reactants.

Targeting Intermediates of Maillard Reactions. *Trapping of α-Dicarbonyls.* α-Dicarbonyls, such as glyoxal (GO), methylglyoxal (MGO), and deoxyosones, are reactive intermediates that accelerate Maillard reactions due to their higher reactivity compared to glucose.[79−81] Many of the pharmaceuticals and food ingredients that inhibit Maillard reactions have been found to trap α-dicarbonyls, with most studies being conducted with GO and MGO. Reported trapping agents include creatine,[82] hydroxytyrosol,[83] pyridoxamine,[83−85] low molecular mass thiols such as cysteine, homocysteine, and glutathione,[85] and phenolic compounds such as flavonoids and phenylpropanoids.[60,83] It is therefore believed that α-dicarbonyl trapping is one of the major mechanisms by which these compounds inhibit accumulation of Maillard reaction products. Figure 2 shows examples of α-dicarbonyl trapping agents and identified products formed by reaction with MGO.

α-Dicarbonyls are formed through fragmentation and dehydration of Amadori or Heyns products as shown in Figure 1, but may also be formed through sugar degradation.[86] α-Dicarbonyls have been characterized in foods and, in particular, those that have been subject to heating or extended storage.[70,87−90] Large variations in the quantification of α-dicarbonyls have been reported in dairy products. Hellwig et al.[89] found concentrations of deoxyosones up to 0.1 mM concentrations, whereas MGO and GO were detected in smaller quantities in a wide range of dairy products.[89] Troise et al.[70] reported significantly higher concentrations of α-dicarbonyls: ca. 35 mM GO, ca. 7 mM MGO, and ca. 6 mM 3-deoxyglucosone in UHT milk. Kokkinodou and Peterson[90] reported concentrations in the micromolar range: ca. 40 μM GO, ca. 2.5 μM MGO, and ca. 5 μM 3-deoxyglucosone in fresh UHT milk. In the same study samples were also analyzed after storage for 30 days at 30 °C, when concentrations of GO were decreased, MGO increased, and 3-deoxyglucosone decreased compared to the concentrations determined in the fresh samples. The discrepancy between reported α-dicarbonyl values in dairy foods can be explained by different methods used for the quantification, different types of samples analyzed, processing/incubation conditions, and the reactive nature of the α-dicarbonyls.

Model studies have shown that GO is formed at a faster rate than 3-deoxyglucosone during glucose degradation at 37 °C for up to 15 days.[86] In the presence of peptides, GO and MGO react more rapidly with peptides than 3-deoxyglucosone and 3-deoxygalactosone at 37 °C for up to 12 h.[81] Taken together this suggests a fast conversion of GO (and possibly also MGO) during reaction with amine-containing compounds and a low steady-state concentration compared to other α-dicarbonyls, which may explain the low levels of GO and MGO detected in dairy foods. In another study glucose was incubated with phenylalanine at 98 °C for up to 8 h, and GO was formed at much lower concentrations than 3-deoxyglucosone.[91] In the same study it was found that the Strecker aldehyde reaction product, phenylacetaldehyde, was formed in similar levels (and even slightly higher concentrations) when phenylalanine was incubated with GO compared to 3-deoxyglucosone. These studies indicate that even though GO and MGO are generally not detected in high concentrations in dairy foods, they may influence Maillard reactions significantly, and suggest that trapping of GO and MGO in foods is important for controlling Maillard reactions.[90]

Phenolic compounds are widely dispersed in plants and include more than 8000 structures ranging from low molecular weight structures with a single aromatic ring to large and complex polyphenol polymers.[92] Many different polyphenol compounds have been shown to be efficient α-dicarbonyl trapping agents, of which mostly phenylpropanoids and flavonoids present in tea, cinnamon, rosemary, mate, and other herbal plants have been investigated as reviewed by Wu et al.[93] The highly activating hydroxyl groups present on the A-ring of the flavonoids and phenylpropanoids facilitate para- and ortho-directed electrophilic aromatic substitution,[94] and it is predominantly by this mechanism that α-dicarbonyl species are trapped. Examples of α-dicarbonyl trapping polyphenols ranging from low molecular weight phenylpropanoids to larger flavonoid structures are shown in Figure 4; their sites for dicarbonyl trapping are marked by stars.

α-Dicarbonyl trapping has also been observed for low molecular weight phenols and phenolic acids, such as gallic acid, which is found in many types of plant foods.[83,95] Synthetic phenolic compounds such as 2,4,6-trihydroxybenzoic acid, 1,3,5-trihydroxybenzene, and pyrogallol (1,2,3-trihydroxybenzene) have been found to exhibit better α-dicarbonyl trapping ability than gallic acid, showing that the amount and position of hydroxyl groups influence the α-dicarbonyl trapping efficiency.[95,96] Most of the polyphenols examined for α-dicarbonyl trapping ability are flavonoids, and the investigated compounds are listed in Table 1. All reported studies agree that the A-ring is

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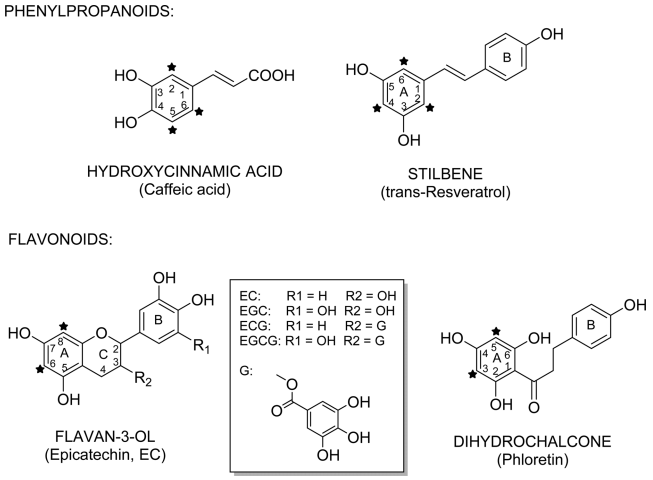

Figure 4. Examples of phenolic structures that have been found to trap α-dicarbonyls categorized into phenylpropanoids and flavonoids. α-Dicarbonyl trapping sites are marked by stars for hydroxycinnamic acids,[94] stilbenes,[161] flavan-3-ols,[97] and dihydrochalcones.[161] EC, epicatechin; EGC, epigallocatechin; ECG, epicatechin gallate; EGCG, epigallocatechin gallate.

Table 1. Flavonoids Found To Exhibit α-Dicarbonyl Trapping Ability

flavonoid	subgroup	ref
epicatechin	flavan-3-ol	60
		97
		96
epigallocatechin	flavan-3-ol	100
epicatechin gallate	flavan-3-ol	100
epigallocatechin gallate	flavan-3-ol	98
genistein	isoflavone	96
		162
		163
quercetin	flavonol	96
		164
luteolin	flavon	96
daidzein	isoflavone	96
apigenin	flavon	96
phloretin	dihydrochalcone	165
		96
phloridzin	dihydrochalcon	165
rutin	flavonol	164
theaflavin	theaflavin	100
theaflavin-monogallate	theaflavin	100
theaflavin-digallate	theaflavin	100

the active site of flavonoids contributing to their α-dicarbonyl scavenging ability.[96−98] Structural elucidation of the requirements for α-dicarbonyl trapping ability suggest that (1) meta configuration of the electron-donating groups of the benzene ring has superior reactivity to the ortho configuration, (2) the hydroxyl group at C-5 on the A-ring enhances trapping efficiency, (3) the double bond between C-2 and C-3 on the C-ring could facilitate the trapping efficiency, and (4) the number of hydroxyl groups on the B-ring does not significantly influence the trapping efficiency.[96,99]

Apart from considering α-dicarbonyl trapping efficiency, it is also necessary to consider potential unwanted side reactions caused by the chosen polyphenol, such as discoloration, background bitterness and astringency, and protein modification. These side reactions will limit the possible polyphenol concentration that can be added to food products. For example, Colahan-Sederstrom and Peterson[61] found that 0.1% epicatechin could be added to milk, whereas 0.2% resulted in undesired bitterness. Many foods are readily oxidized during production and storage, leading to oxidation of proteins, lipids, carbohydrates, vitamins, and polyphenols. For polyphenols, oxidation includes complex polymerization reactions either by polyphenols alone or by reaction with proteins to form protein−quinone adducts as described above. These polymerization reactions may cause changes in color, but are not expected to change the α-dicarbonyl trapping ability unless the polymerization is extensive and includes precipitation. The α-dicarbonyl trapping takes place on the A-ring of the flavonoid, and because the oxidation takes place on the B-ring, the α-dicarbonyl trapping is largely unaffected by oxidation of the flavonoid. In fact, theaflavins have been found to exhibit a trapping ability toward MGO superior to that of the monomer epicatechin after 1 h of incubation at 37 °C.[100] This is likely to be caused by the presence of additional α-dicarbonyl trapping sites in the dimer compared to the monomer catechin. Figure 5

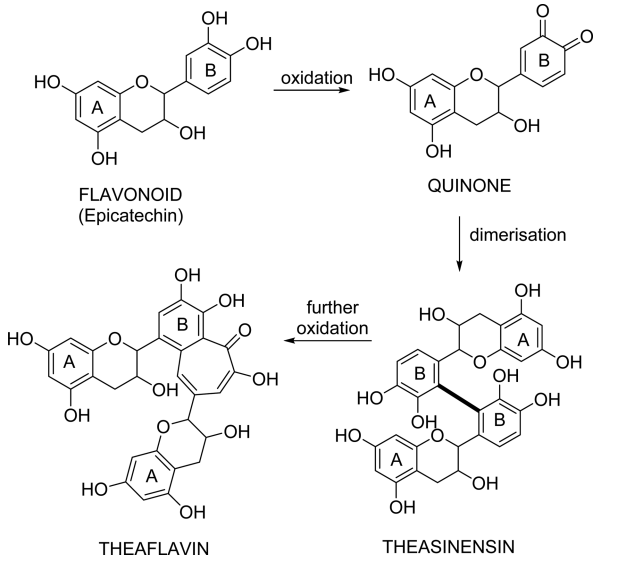

Figure 5. Simplified scheme of oxidation stages of epicatechin with formation of a quinone, dimerization into theasinensin, and further oxidation into theaflavin. The bold bond in theasinensin shows the interflavan linkage between the B-rings of each epicatechin unit (inspired by the findings of Hashimoto et al.[101]).

shows a simplified scheme of various stages of oxidation of epicatechin starting with the formation of a quinone, which dimerizes into a theasinensin compound. Further oxidation has been shown to create theaflavin compounds, for example, during the fermentation of green tea into black tea.[101] The oxidation and polymerization of tea polyphenols are far more complex than what is shown in Figure 5 and include numerous products in which catechins and/or phenolic acids, such as gallic acid, are combined in dimers and oligomers.

In wine, thiol compounds, such as cysteine and glutathione, are added to prevent browning caused by polyphenol polymerization through the formation of colorless thiol−quinone adducts.[72,102] Thiols have also been found to trap α-dicarbonyls,[85] but this approach would need to be carefully controlled in foods in terms of concentration and thiol source due to potential off-flavor formation; for example, thiol

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compounds added to beer have been shown to develop "sewer-like" off-flavors.[103] As opposed to the colorless thiol−quinone adducts, some polyphenol−protein compounds have been reported to create other types of huge discoloration problems. Chlorogenic acid−protein-derived compounds are dark green species formed in cookies baked with sunflower meal,[104] and amine−quinone adducts are red species,[73] which may also cause discoloration of food products. Adducts formed between unoxidized (+)-catechin and glyoxylic acid, an oxidation product from tartaric acid that is found in wine, have also been shown to contribute to color changes (Figure 6).[105]

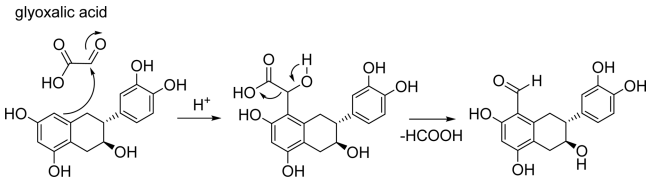

Figure 6. Reaction between glyoxalic acid and (+)-catechin leading to the formation of a glyoxalic acid−catechin adduct.[105]

Accumulation of these UV-active products, the structures of which were elucidated by comprehensive NMR spectroscopic analysis, was found to correlate with an increase in brown color of the reaction mixture and a decrease in the presence of (+)-catechin, suggesting that compounds of this type play a role in the development of color in polyphenol-containing foods. Finally, quinones may also generate Strecker aldehydes by reaction with amino acids due to their α-dicarbonyl structure, which has been shown in aqueous model systems and wine, and may influence flavor.[106,107]

To control Maillard reactions in foods without creating any deleterious side effects, it is necessary to consider the possible concentration of inhibitor that can be added to foods as well as the kinetics of the reactions. For efficient inhibition of Maillard reactions, the inhibitor added to foods will have to compete with the reaction rate of the reaction that it should inhibit. For example, if the major reaction to inhibit is the reaction between α-dicarbonyl and lysine, the inhibitor would have to react more rapidly with the α-dicarbonyl than the rate between lysine and α-dicarbonyl.

Scavenging of Maillard-Derived Radicals by Polyphenols. Maillard reactions also generate stable radicals, which has been characterized in model systems[108−110] and foods.[111,112] In model systems, the radical has been identified as a pyrazinium radical cation,[109] which may be formed by reaction of an amine with either α-dicarbonyls or carbohydrates,[110] and its formation is accompanied by the development of browning.[109]

Addition of catechins [epigallocatechin gallate and (+)-catechin] to a model system generating pyrazinium radicals resulted in increased radical signal intensities as detected by electron paramagnetic resonance (EPR) spectroscopy at concentration ratios up to 10:1 (GO/catechin). Higher concentration ratios of catechins to GO decreased the radical signal.[110] It was concluded that catechins influence the formation of pyrazinium radicals, but it was not possible to determine if catechins catalyzed or quenched pyrazinium radical generation. Other Maillard-derived radicals have been detected by use of spin traps, but the identity of the radicals was not characterized.[68,113,114] Nevertheless, these studies showed that flavonoids[68,114] and 4-methylcatechol[113] inhibited radical formation. In the study by Bin et al.,[110] 4-methylcatechol had no effect on the generation of pyrazinium radicals, which suggests that the radicals detected by spin trapping react differently from the pyrazinium radical.

Action of Pyridoxamine on Amadori Products. The preceding section highlighted the potential of vitamin B6 complex molecules as AGE scavengers in foods. As illustrated in Figure 2, a mechanism that may be of interest to food scientists is exploiting the pyridoxamine component in vitamin B6 and its capacity to act as a carbonyl-trapping nucleophile by virtue of the methylamino moiety present in the 4-position of the pyridine ring. Although not yet investigated in any depth in food matrices, model studies have revealed that pyridoxamine will form adducts with Amadori products.[115] A series of model Amadori products were synthesized and subjected to pyridoxamine. Although the formation of the corresponding Schiff base is reversible, via base-catalyzed hydrolysis of the imine, reducing conditions employing sodium cyanoborohydride were utilized to convert the initially formed Schiff base to the corresponding secondary amine, allowing full characterization of this stable product (Figure 7). In the same study a second beneficial

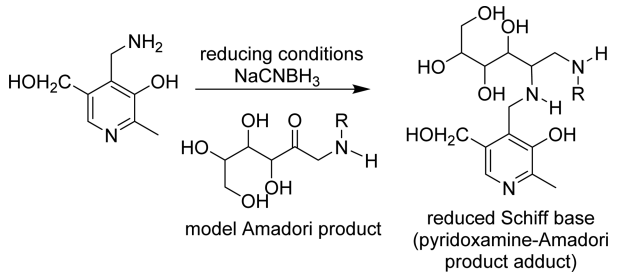

Figure 7. Trapping of Amadori product by pyridoxamine.[115]

characteristic of pyridoxamine was observed, namely, its capacity for chelating metal ions. The presence of metal ions can catalyze autoxidation of Amadori products, thereby facilitating further downstream reactions. Chelation of metal ions thus inhibits post-Amadori reactions. We suggest that systematic investigation of vitamin B6 components in food systems could reveal an attractive strategy for the control of both early and late Maillard reaction product formation.

Targeting Maillard Reaction Products. Pharmaceutical AGE inhibitors (trap intermediates) and AGE breakers (trap products) have been investigated for therapeutic treatment of diseases associated with AGE formation (reviewed by Rahbar and Figarola[116]). Although these pharmaceuticals are not specifically relevant for foods, mechanistic understanding of Maillard inhibition can be abstracted from this research and applied to food components exhibiting similar chemical function. For example, aminoguanidine (the first α-dicarbonyl trapping drug discovered) bears binding sites similar to those of the food ingredient creatine (see Figure 2).

Trapping of Strecker Aldehydes. As illustrated previously, the A-ring of the flavonoids, due to the activating phenolic hydroxyl groups, is an effective nucleophile bearing two potential trapping sites for electrophiles. We have already shown that flavonoids will readily form adducts with α-dicarbonyls. This is also the case for other aldehydes, such as acetaldehyde,[117−119] which is formed during oxidation of alcoholic beverages, furfurals,[105] secondary lipid oxidation products,[120] and those formed from Strecker degradation. One important example of this mechanism is the trapping of the Strecker degradation product, phenylacetaldehyde, by

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epigallocatechin gallate.[121] Model systems comprising glucose, phenylalanine, and creatinine were heated in the presence or absence of epigallocatechin gallate. The Strecker degradation product phenylacetaldehyde was found in models lacking epigallocatechin gallate, but formation was inhibited by >80% in models containing epigallocatechin gallate in a molar ratio of 0.25:1 to phenylalanine. This finding is of importance for the food industry because phenylacetaldehyde is a key intermediate of 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine, a mutagenic heterocycle found in foods.

Trapping of Acrylamide. Acrylamide began to receive attention as a potentially toxic Maillard reaction product in the early 2000s.[122,123] The α,β-unsaturated enone motif in acrylamide acts as a potent Michael acceptor, which results in facile reactions with nucleophiles such as the thiol group of protein-bound Cys, glutathione, and protein amino groups, in particular ε-NH_2 in Lys and the imidazole group in His. Acrylamide is orally bioavailable, and increased accumulation of hemoglobin−acrylamide adducts has been found in the plasma of humans and animals exposed to acrylamide. However, liver glutathione does provide an effective level of acrylamide removal, via glutathione *S*-transferase catalyzed conjugation.[124] Nevertheless, mitigating the formation of acrylamide in foods has been a major topic for food researchers. Acrylamide can be formed from the reaction of a reducing sugar or early Maillard reaction products (*N*-glycosides) with Met, Gln, or Cys, but the key component for its facile reaction is Asn.[122] For example, fried potatoes contain the highest levels of acrylamide found in foods, which is affected not only by processing but also by cultivar type, farming systems, and fertilization.[125] Unsurprisingly, the levels of free Asn in potato, as well as glucose, are significant for the formation of acrylamide under frying conditions.

The formation and subsequent reduction of acrylamide in foods has naturally been the subject of much scientific study, resulting in several reviews. Zhang and Zhang's paper[126] is an excellent example, covering the mechanistic aspects of the formation of acrylamide both in model studies and in foods and strategies for mitigating its formation. However, since this review was published, new findings have come to light, which will be highlighted in this section.

Vitamins such as nicotinic acid (niacin), pyridoxamine, pyridoxine, and pyridoxal (vitamin B6 complex molecules) have been shown to lower levels of acrylamide generated in model Asn−glucose systems.[127] Furthermore, pyridoxal and niacin were found to inhibit accumulation of acrylamide in fried potatoes.[128] The acrylamide−niacin adduct was subsequently characterized by NMR spectroscopy as 1-propanamide-3-carboxypyridinium, the conjugate addition product generated via nucleophilic attack of the ring nitrogen toward the enone motif in acrylamide (Figure 8) and presumably pyridoxal, pyridoxamine, and pyridoxine trap acrylamide by the same mechanism. The researchers also found that incubation of niacin with acrylamide under physiological conditions resulted in acrylamide trapping. Niacin thus exhibits potential to scavenge acrylamide from a wide variety of food systems as well as preventing in vivo accumulation.

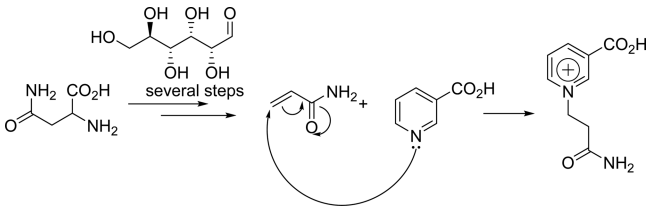

Figure 8. Trapping of acrylamide by niacin.[128]

Although the formation of acrylamide in foods is undesired, the Maillard reaction can be an important source of flavor and aroma, and thus strategies for selective mitigation of the formation of acrylamide while allowing the formation of sensorially important flavor and aroma components is particularly attractive and is discussed in a recent review.[129] Asparaginase (L-asparagine aminohydrolase, EC 3.5.1.1) catalyzes the hydrolysis of Asn into Asp and ammonia. When applied to Asn and reducing sugar-containing foods that are subsequently processed at high temperature, asparaginase has been shown to significantly reduce the levels of acrylamide formed.[130] With regard to the use of asparaginase in this manner, it is important to consider both the amount of Asn present in a given foodstuff and also the residence time of the enzyme in the food matrix preprocessing.

■ ENZYMATIC STRATEGIES FOR INHIBITION OF MAILLARD REACTIONS

Enzymes are commonly used in food and ingredient processing and are often a preferred strategy for food producers because they offer a "clean label" solution. Enzymes are usually inactivated in the final processing steps (e.g., during pasteurization) and are therefore not required to be labeled as an ingredient. Multiple enzymes have been utilized in efforts to ameliorate the onset of Maillard reactions in foods, such as asparaginase, which we have discussed in the preceding section. The following section will highlight recent developments in the use of enzymatic intervention against the Maillard reaction, downstream products thereof, and AGE generation.

Fructosamine Oxidase. Oxoreductases will catalyze the oxidation of reducing sugars to the corresponding lactones, which in aqueous media hydrolyze to acids.[131] Although this mechanism does lead to a decrease in the abundance of reducing sugar and has been presented as an effective method for controlling browning in some food products,[130,132] the redox process ultimately leads to the generation of hydrogen peroxide, which may subsequently result in further undesired protein modification and lipid peroxidation.

Enzymatic deglycation of Amadori products has emerged from the discipline of biotechnology as a strategy for limiting protein modification and is the subject of previously published reviews.[133−135] Of the enzymes that can be employed in protein repair, fructosamine oxidase (Faox), which catalyzes the oxidative deglycation of Amadori products, has attracted attention as a possible strategy for limiting Maillard reactions in foods (Figure 9).[136] Recombinant enzymes Faox I and Faox II isolated from *Aspergillus* sp. were added to commercial low-lactose milk and β-lactoglobulin−glucose model systems, which were subsequently stored for 17 days at 37 °C. CML and protein-bound HMF levels were found to be lower in all enzyme-treated samples and were particularly reduced in low-lactose milk.

These preliminary results were confirmed in lactose hydrolyzed milk stored at 37 °C for 12 days.[137] Protein-bound furosine, CML, and total (free and bound) Amadori product were found to be lower in Faox-treated milk during the time course. Interestingly, losses of Lys were similar for both Faox-treated and untreated milks. Although sensitivity of the

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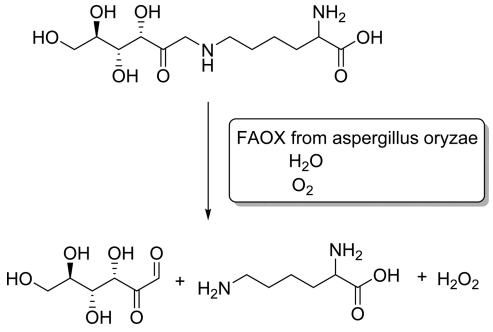

Figure 9. Oxidative deglycation of the Amadori product of lysine and glucose with generation of glucosone, lysine, and hydrogen peroxide.

analytical method used may influence the interpretation of this result, we postulate that this may partly be explained by the mechanism of enzymatic deglycation; the oxidative deglycation catalyzed by the Faox enzyme results in the generation of glucosone, hydrogen peroxide, and an amino acid. Glucosone, an α-dicarbonyl, in the presence of trace amounts of metal ion and hydrogen peroxide may lead to further undesired protein modification[138] and associated quality deterioration (Figure 10). Thus, the action of Faox may introduce other types of Lys modifications simultaneously to the deglycation and hereby explain the similar levels of Lys observed in the Faox-treated and untreated milks. It is therefore proposed that further research into the implications of this reaction pathway upon food quality is conducted before Faox enzymes are considered for use in food applications.

Fructosamine Kinase. An alternative approach to furnishing deglycation of Amadori products is through the use of fructosamine kinase. In this case, the deglycation step is not oxidative; rather, the fructosamine kinase catalyzes a phosphorylation of the hydroxyl group that is positioned next to the carbonyl in the Amadori product. This phosphorylated intermediate subsequently undergoes deglycation, regenerating the protein amino moiety, 3-deoxyglucosone, and phosphate. This approach has resulted in lowering Amadori product accumulation in bacteria,[133] but it remains to be seen how applicable this is to food systems. In particular, the presence of 3-deoxyglucosone may result in further protein modification or accumulation of HMF.

Carbohydrate Oxidases. Volatile thiols are a source of off-flavor in UHT-treated milk. The reaction of Maillard-derived α-dicarbonyls with Met followed by subsequent Strecker degradation leads to the formation of methional, which in turn can undergo cleavage yielding 2-propenal and methanethiol, a major source of off-flavor in newly produced UHT milk (Figure 11, lower reaction).[139] Treatment of the milk with

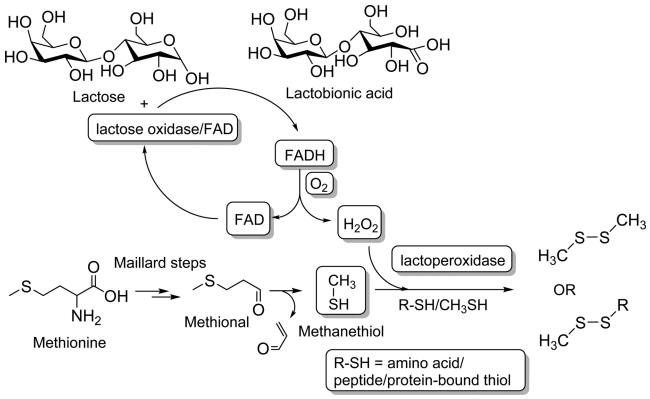

Figure 11. Proposed mechanism for the oxidation of free thiol in UHT milk via treatment with lactose oxidase by stimulation of residual lactoperoxidase in the milk. FAD, flavin adenine dinucleotide.

oxoreductase enzymes such as lactose oxidase either pre- or post-heating, reduces the presence of free thiol in UHT milk and causes a significant reduction in the intensity of thiol-derived sensory descriptors associated with UHT milk off-flavor.[140] Lactose oxidase in the presence of redox cofactor flavin adenine dinucleotide (FAD) catalyzes the oxidation of lactose into lactobionic acid while FAD is concomitantly reduced to FADH. FADH subsequently oxidizes to FAD, regenerating the catalytic system, and oxygen is reduced to hydrogen peroxide (Figure 11, upper reaction). Hydrogen peroxide, in the presence of either metal ions or the milk lactoperoxidase system, which retains some residual activity in pasteurized milk,[141] will result in the oxidation of free thiols to disulfides, thereby minimizing thiol derived off-flavor. Although this may well reduce one source of off-flavor, Maillard reactions as such is not expected to be affected, and indeed unless the generation of hydrogen peroxide is very carefully controlled, for example, through the use of catalase, undesired oxidative protein and lipid modifications may take place. Despite these apparent issues, hexose oxidase is now approved for use as a flavor stabilizer in UHT and sterilized milk in Canada (http://www.hc-sc.gc.ca/fn-an/consult/hexose-oxydase/hexose-oxydase-eng.php).

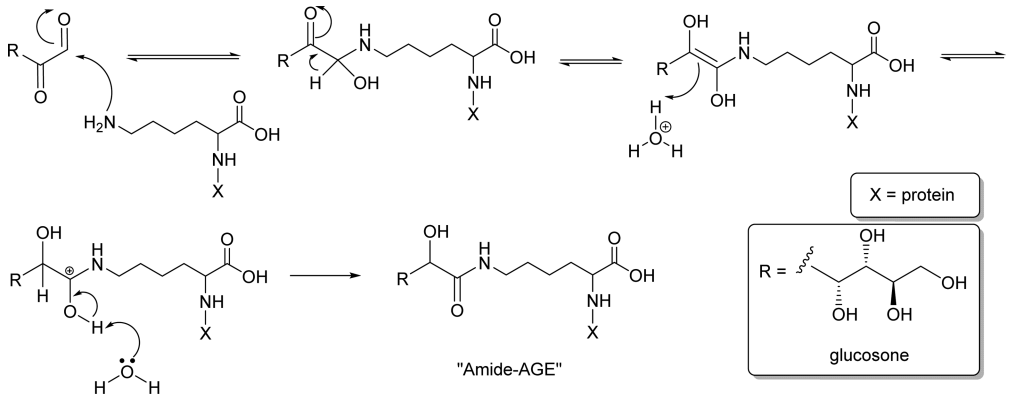

Figure 10. Protein modification by α-dicarbonyl leading to "amide-AGE" (adapted from Henning et al.[138]).

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Related enzymes glucose and hexose oxidases have also seen use as methods of controlling Maillard-derived browning in foods. Mechanistically, their action is comparable to that of lactose oxidase, albeit with differing substrate specificities. Glucose oxidase[131] in tandem with catalase has been used to minimize browning during the production of dried egg white through removal of glucose.[142,143] Hexose oxidase has been used to mitigate browning in potato,[132] which may also lead to a reduced accumulation of acrylamide and uncontrolled browning of pizza mozzarella.[130]

EMERGING STRATEGIES FOR INHIBITION OF MAILLARD REACTIONS BY ALTERNATIVE PROCESSING

The use of nonthermal technologies such as pulsed electrical field technology to control the Maillard reaction in food processing was last reviewed in 2010.[144] In this section we will summarize the potential of emerging processing technologies for controlling Maillard reactions in food and subsequently focus on more recent advances in this discipline, specifically developments using tandem high-temperature–high-pressure and encapsulation technologies to control Maillard reactions in foods.

Ohmic Heating. Ohmic or Joule heating exploits the electrical resistance of the food matrix to convert electricity into heat,[145] providing extremely uniform heating throughout a given food because thermal conductivity is not a limiting factor. This allows short-time–high-temperature thermal processing that circumvents localized overheating and thus a potential to control or minimize Maillard reactions. Because ohmic heating occurs evenly throughout a food, surface Maillard reactions are minimized, and the absence of physical surfaces such as those present in heat exchangers also allows a higher level of control of thermally driven modifications. For example, wall overheating resulting in protein deposits on conventional plate heat exchanger UHT processing can be limited by using ohmic heating.[146] Ohmic heating was also shown to inactivate peroxidase in pea after a shorter processing time compared to hot water sterilization, which also resulted in limiting nonenzymatic browning.[147]

Pulsed Electrical Fields (PEF). PEF processing relies on cell membrane permeability to render microbial cells inactive through the application of short (μs–ms) pulses of high (kV cm^{-1}) electrical fields. PEF does show some promise in reducing undesired heat-derived modifications or chemical change in foods. In particular, PEF has been shown to inhibit the formation of HMF in some fruit juices[148] compared to thermal processing, although the effectiveness of the process varied greatly depending upon fruit type as well as pulse frequency, width, and polarity. PEF-treated orange juice was shown to contain lower levels of HMF directly after processing and reduced browning over a 6 week storage period compared to a thermally pasteurized juice.[149] However, the differences in HMF levels observed initially were found to decrease during storage. PEF clearly shows some potential as an alternative to thermal processing for controlling Maillard reactions in foods, where this is undesired, although there appears to be some variation in results. Perhaps the most promising use of PEF is as an adjunct process step in tandem with methodologies that result in the removal of one or more of the reactive partners of the Maillard reaction. For example, PEF treatment of potatoes resulted in increased diffusion of glucose and infusion of glucose oxidase, thereby reducing levels of one of the partners in the Maillard reaction. This occurs via improved mass transfer as a consequence of increased membrane permeability via pore generation in the potato cells and resulted in a 65% total reduction of glucose.[144]

High-Pressure Processing (HPP). The effects of HPP upon the Maillard reaction and related downstream reactions are complicated, and it would be incorrect to suggest that HPP, although nonthermal, is an effective tool for minimizing undesired chemical changes in foods. A recent review[150] provides an excellent systematic overview of the complex effects of HPP on the Maillard reaction pathway, and as a consequence, this section will focus on recent new findings, wherein tandem high-pressure and high-temperature processing and their effects on Maillard chemistry in skim milk and whey protein–sugar solutions have been investigated.

Color change and proteolysis of reconstituted skim milk subjected to either high-pressure thermal processing (HPTP) or thermal processing were studied by Devi et al.[151] Both color change and proteolysis were shown to increase with both temperature and pressure. Consumption of free amino groups, as determined by derivatization with *o*-phthaldialdehyde, was shown to be accelerated by temperature, indicating that the rate of Maillard reactions is higher than proteolysis. However, increasing pressure at a constant temperature apparently inhibited Maillard reactions. This result mirrors previous work,[152] which reported an inhibited loss of free amino groups in a bovine serum albumin (BSA)–glucose model at pH 9 subject to HPTP, indicating that the early stages of the Maillard reaction may be inhibited by the use of HPTP when compared to high-temperature processing only. Herein there are several mechanistic details to consider, which are discussed in depth in Martinez-Monteagudo amd Saldana.[150] It has been shown that high pressure favors the open form of reducing sugars such as glucose, a consequence of the smaller molar volume occupied by the ring-opened form of the sugar. This would suggest that high pressure would result in higher availability of the reactive form of a reducing sugar and thus promote Maillard reactions. However, because loss of protein amino groups was limited upon increasing pressure, this would not appear to be the case. The authors postulate that the activation volumes (ΔV^*) for the subsequent step, that is, formation of the Schiff base, may be positive, which would account for this process being unfavored under high pressure. This condition will of course change for reactive partners other than BSA and glucose, because, for example, a Lys- or Arg-containing peptide, which may also be expected to act as a nucleophile toward a reducing sugar, will exhibit a different activation volume than a whole protein. In the case of the study by Devi et al.,[151] the authors refrain from proposing a mechanistic explanation for their findings, which is understandable considering the complexity of the system under investigation. The theme of elucidating the combined effects of high pressure and thermal processing on Maillard chemistry in milk-like matrices was continued in a study by Ruiz et al.,[153] who investigated the effect of high-pressure–high-temperature processing (HPHT) (123 °C, 700 MPa) on whey protein–sugar solutions at pH 6, 7, and 9. Browning as measured by UV absorbance at 420 nm was found to be significantly lower for whey protein–glucose solutions subject to HPHT rather than high temperature (HT) at both pH 7 and 9, indicating some inhibition of Maillard reactions, in agreement with previous results. Accumulation of furosine, CML, and CEL was found to be lower in HPHT-treated whey protein–glucose solutions at all pH values, again supporting

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previous results that although high temperatures and pressure may furnish protein unfolding, Maillard reactions is inhibited. Intriguingly, at pH 7 whey protein−glucose and trehalose solutions subject to HPHT treatment exhibited smaller particle sizes compared to thermally treated solutions, in contrast to previous studies.[154] Furthermore, at pH 9 no difference in particle size between HPHT and HT was observed, again in contrast to previous work.[152] Clearly the nature of the reacting partners and the ΔV^* of the individual steps in the Maillard pathway as well as protein unfolding kinetics and subsequent changes to surface chemistry will influence these results. Further mechanistic studies addressing the effect of HPHT on glycation of individual food proteins are therefore needed. Conceptually, however, the use of HPHT may form part of a useful strategy for food processing, as well as unfolding of food proteins, such as β-lactoglobulin, thereby altering protein surface chemistry, functionality, and in vivo behavior, without subjecting the protein to undesired Maillard-derived modifications.

Encapsulation of Metal Ions. The presence of metal ions in foods can both promote and inhibit the formation of Maillard reaction products, and therefore understanding the mechanisms by which given Maillard reaction pathways are affected by metal ions is of crucial importance. For instance, in Asn−glucose models, Ca^{2+} has been shown to inhibit the formation of acrylamide while levels of HMF and furfural were simultaneously increased.[155] The relationship between NaCl concentration and acrylamide formation is a more complex case. Levine and Ryan[156] found that acrylamide accumulation was decreased in model dough with increasing NaCl concentration. However, this was not entirely in agreement with earlier work wherein acrylamide formation was increasingly inhibited in systems containing 1−2% (w/w) NaCl but formation was promoted at NaCl concentrations >2% (w/w),[157] a trend that was also observed by Gökmen and Senyuva.[155] HMF accumulation in cookie models[158] was found to be promoted by the presence of NaCl in a concentration-dependent manner. Mechanistically, this is attributed to the Lewis acid behavior of Na^+ toward sucrose promoting cleavage of the disaccharide, yielding glucose and fructofuranosyl cation and subsequently HMF (Figure 12).

Encapsulation of NaCl was found to reduce the levels of HMF in cookies without significantly altering their sensory properties, indicating the potential of this strategy for reducing levels of this reactive aldehyde in processed foods.[159] It is worth noting that the mechanism of formation of HMF from sucrose, a nonreducing sugar, is, strictly speaking, not a Maillard pathway. However, because the presence of reactive intermediates 3-deoxyglucosone and 3,4-dideoxyglucosone as well as fructose itself can result in unwanted protein modification, the findings from this study remain relevant as an attractive strategy for limiting intermediate to late Maillard reaction product formation in foods.

PERSPECTIVES

The complexity of the Maillard reaction and subsequent downstream reactions in food matrices is well-known. It is apparent from the work reviewed herein that there is in all likelihood not one "silver bullet" that will completely inhibit or allow control of this reaction pathway, although the combination of high pressure and high temperature, processing costs notwithstanding, appears to be very promising. We have illustrated examples of effective Maillard reaction inhibition that

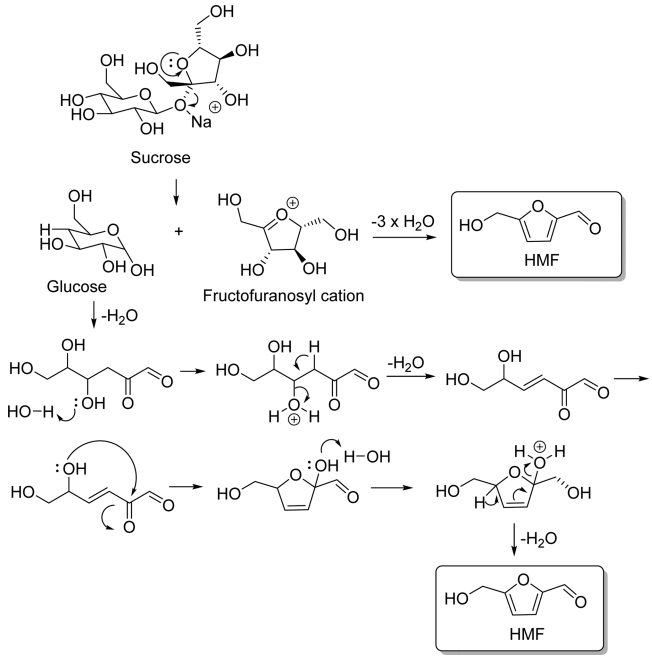

Figure 12. Promotion of the formation of 5-hydroxymethylfurfural (HMF) by the presence of NaCl.[159]

may regardless lead to undesired protein modification as well as highly effective methods for trapping reactive carbonyl species, which certainly limit protein modification and accumulation of volatile off-flavors, but simultaneously affect other organoleptic properties of food. We would recommend that when strategies for tailoring the extent of the Maillard reaction and accumulation of Maillard reaction products in foods are developed, the Maillard reaction is approached as a series of discrete chemical reactions; how processing and storage conditions will affect these reactions and what overall effect this will have on a given food product must be evaluated.

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The authors declare no competing financial interest.

ABBREVIATIONS USED

AGE, advanced glycation endproduct; BSA, bovine serum albumin; CML, *N*-ε-(carboxymethyl)lysine; CEL, *N*-ε-(carboxyethyl)lysine; GO, glyoxal; HMF, hydroxymethylfurfural; HPP, high-pressure processing; HPHT, high-pressure−high-temperature processing; HPTP, high-pressure thermal processing; HT, high temperature; MGO, methylglyoxal; PEF, pulsed electrical fields; UHT, ultrahigh temperature; WPI, whey protein isolate

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