Systematic Review

Bakery Product Enrichment with Phenolic Compounds as an Unexplored Strategy for the Control of the Maillard Reaction

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Abstract: The Maillard reaction (MR) is one of the main reactions that occurs during the thermal processing of food. It contributes positively to the flavor, aroma, and color of food but also produces harmful by-products, including acrylamide and advanced glycation end products (AGEs). Bakery products are major staples consumed daily by people from all walks of life and of all ages; the identification of strategies to hamper acrylamide formation in bread and bread-like products is thus crucial for public health. Several strategies have been proposed to inhibit the MR in food processing, including biochemical approaches such as the use of enzymes; innovative technologies such as ohmic heating, pulsed electric field, high pressure processing, or encapsulation of metal ions; and the chemical modification of reactants, intermediates, or products of MR. Recently, phenolic compounds have been reported to have an inhibitory effect on the formation of harmful by-products resulting from the MR. The aim of this paper is, therefore, to provide a state-of-the-art overview of the use of phenolic compounds in the formulation of bakery products to inhibit the MR. A systematic review of the most up-to-date scientific literature was thus performed. It emerged that the inhibitory action was mainly investigated in bread. Phenolic extracts and powders obtained from plant-based foods have been included in the formulation of bakery products. The effect of pure phenolic standards was also considered.

Keywords: Maillard reaction; inhibition strategies; phenolic compounds; product innovation; enriched bakery products

1. Introduction

The Maillard reaction (MR) is one of the dominant reactions that occurs during the thermal processing of food. It contributes positively to the flavor, aroma, and color of foods. However, it also produces harmful by-products, including acrylamide in starch-rich processed foods, heterocyclic amines in protein-rich cooked foods, and advanced glycation end products (AGEs) in dairy products [1].

As regards baked products, in recent years, particular attention has been paid to acrylamide as a potential health concern due to its adverse effects on human health. In fact, acrylamide is neurotoxic, cytotoxic, hepatotoxic, immunotoxic, genotoxic, and mutagenic [2]. It is also classified under Group 2A as potentially carcinogenic to humans by the International Agency for Research on Cancer [3].

Acrylamide is naturally formed in starchy food products during high-temperature cooking (above 120 °C), such as frying, baking, and grilling, but also in industrial processing [4]. Acrylamide is, therefore, commonly found in bread, biscuits, crackers, and chips. European authorities such as the European Food Safety Authority (EFSA) offer some advice to reduce the production of this harmful compound at a domestic level: e.g.,
avoid excessive burning when frying, do not keep potatoes in the fridge to avoid an increase in sugar levels, and limit the toasting of bread [4].

Several strategies have been proposed to inhibit the MR in food processing (Figure 1). Non-thermal technologies, such as the use of a pulsed electric field, have emerged as innovative approaches for controlling the MR, alongside ohmic heating, high-pressure processing, and the encapsulation of metal ions [5]. biochemical strategies such as the use of enzymes have been also applied to inhibit the MR. As an example, oxidoreductases such as glucose oxidase convert glucose to gluconic acid, which cannot react with amino acids [6]. Chemical approaches are based on (i) the removal or modification of MR reactants, such as sugars or amino acids; (ii) the trapping of intermediates of MR such as α-dicarbonyl compounds; and (iii) the trapping of MR products, namely Strecker aldehydes, advanced glycation end products (AGEs), or acrylamide. Aminoguanidine is one of the first synthetic inhibitors of the MR whose mechanism of action involves the trapping of α-dicarbonyls. Its use was abandoned due to its numerous adverse side effects [5]. The use of natural components such as phenolic compounds has also been explored. Oxidized polyphenols have been effective in inhibiting the MR since they react with amines to form benzoquinone imines or amine–quinone adducts via a Michael addition [5]. The effectiveness of phenolic compounds as MR inhibitors in foods has gained increasing consideration because they are considered natural; thus, they are more accepted as food ingredients compared with synthetic compounds. Moreover, compared with other innovative strategies, they are more user-friendly. Innovative strategies such as ohmic heating have, in fact, limited application due to their higher initial costs or the impossibility of applying them to foods containing fats and oils [7]. Some comprehensive reviews have been published on the above-mentioned strategies to inhibit the MR [5,8,9]. Bakery products are major staples consumed daily by people from all walks of life and of all ages. The identification of strategies to inhibit the MR and hamper acrylamide formation in bread and bread-like products is thus crucial for public health. Commonly bakery products are formulated with refined flours that lack phenolic compounds. The enrichment of bakery products with phenolic compounds might be welcome in view of their inhibitory effect on the MR and of their protective role against the onset of human diseases caused by oxidative stress [10]. So far, reviews on strategies to inhibit the formation of MR by-products have clarified the activity of phenolic compounds, but to the best of our knowledge, their effectiveness in the formulation of bakery products has not been reviewed.

Hence, the aim of this paper is to provide a state-of-the-art overview of the use of phenolic compounds in the formulation of bakery products to inhibit the MR. To this aim, a systematic review of current scientific literature was performed, and studies on the enrichment of bakery products with phenolic compounds were retrieved and discussed.

![Figure 1. Strategies to inhibit the Maillard reaction (MR).](image-url)
2. Materials and Methods

2.1. Literature Search

As the first step in the literature search, a date range was established in the Scopus database; only studies published in the last 10 years in peer-reviewed journals were deemed eligible. The queries reported in Table 1 were used in the search. The main details of the identified studies were collated using the Mendeley software (Mendeley Desktop Version 1.19.4, Mendeley Ltd., London, UK).

**Table 1. Search strategy.**

<table>
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<tr>
<th>Search ID</th>
<th>Scopus Query</th>
<th>Documents (No.)</th>
</tr>
</thead>
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<td>78</td>
</tr>
<tr>
<td>#2</td>
<td>(TITLE-ABS-KEY (maillard AND reaction AND inhibition) AND TITLE-ABS-KEY (bakery AND products)) AND PUBYEAR &gt; 2014</td>
<td>2</td>
</tr>
<tr>
<td>#3</td>
<td>(TITLE-ABS-KEY (maillard AND reaction AND inhibition) AND TITLE-ABS-KEY (bread)) AND PUBYEAR &gt; 2014</td>
<td>5</td>
</tr>
<tr>
<td>#4</td>
<td>(TITLE-ABS-KEY (maillard AND reaction AND inhibition) AND TITLE-ABS-KEY (pasta)) AND PUBYEAR &gt; 2014</td>
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</tr>
<tr>
<td>#5</td>
<td>(TITLE-ABS-KEY (maillard AND reaction AND inhibition) AND TITLE-ABS-KEY (biscuits)) AND PUBYEAR &gt; 2014</td>
<td>4</td>
</tr>
<tr>
<td>#6</td>
<td>(TITLE-ABS-KEY (maillard AND reaction AND inhibition) AND TITLE-ABS-KEY (phenolic AND compounds)) AND PUBYEAR &gt; 2014</td>
<td>39</td>
</tr>
<tr>
<td>#7</td>
<td>(TITLE-ABS-KEY (maillard AND reaction AND inhibition) AND TITLE-ABS-KEY (flavonoids)) AND PUBYEAR &gt; 2014</td>
<td>33</td>
</tr>
<tr>
<td>#8</td>
<td>(TITLE-ABS-KEY (maillard AND reaction AND inhibition) AND TITLE-ABS-KEY (phenolic AND compounds) AND TITLE-ABS-KEY (bakery AND products)) AND PUBYEAR &gt; 2014</td>
<td>0</td>
</tr>
<tr>
<td>#9</td>
<td>(TITLE-ABS-KEY (maillard AND reaction AND inhibition) AND TITLE-ABS-KEY (phenolic AND compounds) AND TITLE-ABS-KEY (bread)) AND PUBYEAR &gt; 2014</td>
<td>3</td>
</tr>
<tr>
<td>#10</td>
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<tr>
<td>#11</td>
<td>(TITLE-ABS-KEY (acrylamide) AND TITLE-ABS-KEY (phenolic AND compounds)) AND PUBYEAR &gt; 2014</td>
<td>126</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>413</td>
</tr>
</tbody>
</table>

2.2. Study-Selection Process and Data Extraction

Studies retrieved from the literature search were screened independently by two of the authors. The following inclusion and exclusion criteria were applied: duplicates were excluded. Only studies published in English were considered. Reviews and book chapters were excluded, and only research articles were considered eligible. Titles, abstracts, and full texts were screened. Studies reporting the application of phenolic compounds as MR inhibitory agents in food matrices other than bakery products were excluded, as well as articles about (i) the effect of phenolic compounds in in vitro studies, (ii) studies on enzymatic immobilization, and (iii) phenolic compound bioaccessibility studies. Research articles reporting data on MR compound content in cereal/pseudocereal-based products enriched with phenolic compounds were included. To minimize bias, only research articles published in peer-reviewed journals were considered eligible. Conflicts and inaccuracies were solved by a third author/scientist. The study search and selection process were summarized in a Preferred Reporting Items for Systematic reviews and Meta-Analyses (PRISMA) flow diagram [11].

3. Results and Discussion

3.1. PRISMA Flow Diagram of the Search Strategy and Selection Process

The PRISMA flow diagram in Figure 1 shows that 413 papers were retrieved by the literature search. A total amount of 56 papers were excluded because they were duplicates. Reviews and book chapters were first removed from the list of the remaining 357 documents, which were then screened by title and abstract. A total of 249 studies were excluded at the title and/or abstract analysis because they fell beyond the scope of this systematic review. In addition, 13 papers were not accessible. Following the analysis of the full text, 83 more papers were excluded because they were not relevant to the analysis and discussion of this study. A total of 12 papers were finally selected for analysis (Figure 2).
3.2. The Maillard Reaction: An Overview

The Maillard reaction involves the condensation of carbonyl groups from reducing sugars, such as glucose or fructose, with amino groups present in amino acids, peptides, and proteins (Figure 3). This condensation initially produces imines, referred to as Schiff bases, bearing a hydrocarbyl group on the nitrogen atom. These are aldosylamines or ketosylamines when the reducing sugar involved in the reaction is an aldose or a ketose, respectively. The Schiff bases are unstable and can rearrange into more stable compounds called Amadori compounds (Figure 3) or Heyns compounds via a 1,2-enaminol [12]. Amadori compounds are N-substituted 1-amino-1-deoxyketoses, while Heyns compounds are N-substituted 2-amino-2-deoxyaldoses. Amadori and Heyns compounds are more stable than imines since they can be converted into cyclic molecular structures [13]; however, they are partially stable. They can undergo enolization to 1,2-enaminol or 2,3-enaminol; then, α-dicarbonyl compounds such as deoxyosones can form [5] (Figure 3). At pH ≤ 7, the Amadori compounds undergo 1,2-enolization, and 3-deoxyosone is generated. The cyclization and dehydration of 3-deoxyosone produces 5-hydroxymethylfurfural from hexose and furfural from pentose. When the pH is higher than 7, the Amadori compound is subjected to 2,3-enolization to form 1-deoxyosone, which can form furanones following cyclization [14,15] (Figure 4). Deoxyosones can also degrade into α-dicarbonyl compounds, such as glyoxal (GO) and methylglyoxal (MGO) [14], or react with the α-amino group of amino acids and form Strecker aldehydes (Figure 4), which impart a pleasant flavor to some foods, such as bread, coffee, cocoa and roasted meats. The production of Strecker aldehydes commonly occurs in food with higher concentrations of free amino acids and under more drastic conditions such as higher temperatures [13]. Nucleophilic and electrophilic intermediates of the MR can react via condensation reactions, and colored compounds, referred to as melanoidins, can be obtained (Figure 4). They are responsible for the brown color of processed foods, such as in bread crusts and meat [16]. In the advanced phase of the MR, dicarbonyl compounds react with the arginine and lysine residues of proteins and form AGEs (Figure 4) such as 3-deoxyglucosone, 3-deoxyglucosone lysine dimers, glyoxal, glyoxal–lysine dimers, methylglyoxal-derived hydroimidazalone, and methylglyoxal–lysine dimers [12]. AGEs are classified into three groups: (i) fluorescent crosslinking AGEs, namely crossline and pentosidine; (ii) non-fluorescent crosslinking AGEs, such as imidazolium dilsine crosslinks, and (iii) non-fluorescent non-crosslinking AGEs, including N3-carboxyethyl-lysine and N 3-carboxymethyl-lysine.
Figure 3. Simplified scheme of the formation of α-dicarbonyl compounds during the Maillard reaction.
Figure 4. Degradation of Amadori/Heyns compounds and the formation of flavor compounds, melanoidins, and AGEs. Lys: lysine; Arg: arginine; AGEs: advanced glycation end products.

The formation of melanoidins and AGEs increases due to the high temperatures reached during sterilization, cooking, and roasting. These processes result in significant changes in color and taste, as well as digestibility and protein functionality [17,18].

Describing the Maillard reaction chain in foods is challenging due to the different dynamic conditions found in various food matrices. Additionally, the presence of multiple reactants and the varied processing and storage conditions further contribute to the complexity of this chemical landscape [5].

The determination of the rate of the Maillard reaction is also difficult because it is affected by various factors, including pH, temperature, humidity, and the food matrix. For instance, an increase in pH and temperature promotes the progression of the reaction; high pH values enhance protein solubility, and temperatures higher than 55 °C induce protein denaturation, resulting in more abundant amino acid residues [2]. Variations in humidity also play an important role; low humidity levels facilitate the Maillard reaction, whereas elevated humidity dilutes the concentration of reactants, consequently decelerating the reaction kinetics [2].

3.3. Inhibition of the Maillard Reaction by Phenolic Compounds

Phenolic compounds are secondary metabolites naturally present in plants. They have at least one aromatic ring and one or more substituted hydroxyl groups [1]. Over 8000 phenolic compounds have been identified, ranging from low-molecular-weight compounds to large polyphenolic polymers. They are considered the most abundant antioxidants in the human diet and have been widely used as nutritional supplements for their associated health benefits. They are now also increasingly being studied for their potential inhibitory effects on the formation of harmful products resulting from the Maillard reaction [1]. Two mechanisms have been proposed for the inhibition of the Maillard reaction.

3.3.1. Blocking or Modification of Amines

One of the strategies to inhibit the Maillard reaction concerns the activity toward MR reactive sites, such as amino groups. It is possible to modify amines using oxidized
polyphenols, i.e., quinones. The formation of quinones occurs easily during the processing and storage of foods containing polyphenols. Quinones can react with amines, forming benzoquinone imines or amine–quinone adducts through nucleophilic addition [5]. The specific reaction product formed depends on the incubation conditions of the samples in terms of time and temperature. If the samples are incubated at room temperature, only the amine–quinone adduct is detected. If they are heated to 70 °C for 10 min, both reaction products are formed [5]. Further reactions can take place with these products. Reoxidation of the amine–quinone adduct can occur, or a reaction can occur with another amino group, leading to the formation of an amine–quinone–amine adduct. To understand the feasibility of this strategy, it is important to consider the initial concentration of amines in the food matrix. If the polyphenol, i.e., the inhibitor, is present at low concentrations compared with amines, it becomes difficult to block or slow down the Maillard reaction because amino groups can react with reducing sugars or with α-dicarbonyls [5]. Another aspect to consider is to evaluate whether this strategy is feasible even in cases where the amino groups of lysine residues are involved. In fact, a modification of lysine, an essential amino acid, would lead to a reduction in the nutritional value of the food matrix.

In addition, quinones can also act with thiol groups present on amino acids, peptides, and proteins to form thiol–quinone adducts. The reaction with thiols is favored because it is much faster than the reaction with amines. But usually in foods, the concentration of thiols is much lower than that of amines, and for this reason, it is easier for quinones to modify amines [5].

3.3.2. Trapping or Elimination of Intermediates of Maillard Reactions

Phenolic compounds can be used as trapping agents for α-dicarbonyls, such as glyoxal, methylglyoxal, and deoxyosones, which are produced during the fragmentation and dehydration of Amadori or Heyns products [5]. In particular, flavonoids and phenylpropanoids found in tea, cinnamon, rosemary, and other herbaceous plants have been studied [19]. It has been observed that even low-molecular-weight phenolic acids such as gallic acid can trap α-dicarbonyls [5]. Trapping is possible due to the presence of hydroxyl groups that react with the reactive carbonyl compounds, forming adducts through electrophilic aromatic-substitution reactions; this allows the progression of the Maillard reaction to be inhibited. The effectiveness of trapping depends on the number and position of hydroxyl groups present in the phenolic compound [20].

3.4. Antiglycative Activity of Phenolic Compounds

Phenolic compounds have been reported to have antiglycative activity [12]. Several mechanisms are responsible for this effect, and the various phenolic compounds occurring in plant foods influence the AGE production in different ways. The main antiglycation mechanisms are the decrease in free radical production and the inhibition of carbonyl compound formation.

In the early stage of the MR, large amounts of free radicals are produced. Thanks to their ability to inhibit reactive oxygen species, phenolic compounds can thus reduce or prevent the formation of AGEs.

AGEs are also produced because of the reaction between carbonyl compounds, mainly methylglyoxal, and amino acids. Hence, decreasing the production of reactive carbonyl groups or trapping them can inhibit the glycation function. The methylglyoxal-trapping activity of phenolic acids, flavonoids, and stilbenes has been well documented in the scientific literature [21–23].

The production of AGEs is also associated with transition-metal ions. Phenolic compounds have the ability to carry out metal chelation [24]. Hence, they are effective in preventing AGE formation through the chelation of metal ions and the suppression of free radicals catalyzed by metals.
3.5. Use of Phenolic Compounds to Inhibit or Block the Maillard Reaction in Bakery Products

Evidence showed that the enrichment of bakery products to inhibit the formation of harmful compounds following the MR can be carried out by adding phenolic compounds, in the form of purified extracts or as a powder/meal, to the food formulation (Table 2). The inhibitory action was mostly studied in bread and biscuit formulations.

Table 2. Inhibitory activity of Maillard reaction products by specific sources of phenolic compounds.

<table>
<thead>
<tr>
<th>Bakery Product Category</th>
<th>Phenolic Compound Source</th>
<th>Inclusion Form</th>
<th>MR Inhibition Markers</th>
<th>Effect on the MR Inhibition Marker</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bread</td>
<td>common buckwheat seeds</td>
<td>extract</td>
<td>acrylamide</td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>common buckwheat sprouts</td>
<td>extract</td>
<td>acrylamide</td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>grapeseed</td>
<td>extract</td>
<td>acrylamide</td>
<td>↓</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>green tea</td>
<td>extract</td>
<td>acrylamide</td>
<td>∼/↑</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>green tea</td>
<td>extract</td>
<td>acrylamide</td>
<td>↑</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>sorghum bran</td>
<td>extract</td>
<td>acrylamide</td>
<td>↓</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>Tartary buckwheat seeds</td>
<td>extract</td>
<td>acrylamide</td>
<td>↓</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>Tartary buckwheat sprouts</td>
<td>extract</td>
<td>acrylamide</td>
<td>↓</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>wholegrain white, brown, wild, red, and black rice</td>
<td>GF flour</td>
<td>3-DG</td>
<td>highest (brown rice) lowest (white and black rice)</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>yellow and purple corn</td>
<td>GF flour</td>
<td>fluorescent intermediate compounds</td>
<td>↓</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>roasted and raw buckwheat</td>
<td>GF flour</td>
<td>free fluorescent AGEs</td>
<td>highest (brown rice) lowest (purple corn)</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>wholegrain white, brown, wild, red, and black rice</td>
<td>GF flour</td>
<td>furosine</td>
<td>↓</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>yellow and purple corn</td>
<td>GF flour</td>
<td>furosine</td>
<td>highest (wild rice) lowest (yellow corn)</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>roasted and raw buckwheat</td>
<td>GF flour</td>
<td>methylglyoxal</td>
<td>highest (white and brown rice) lowest (wild rice, purple corn)</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>wholegrain white, brown, wild, red, and black rice</td>
<td>GF flour</td>
<td>Nε-(carboxymethyl)lysine</td>
<td>highest (wild rice) lowest (yellow corn)</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>yellow and purple corn</td>
<td>GF flour</td>
<td>Nε-(carboxymethyl)lysine</td>
<td>↓ (all concentrations) highest (0.1%) lowest (2%)</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
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<td>GF flour</td>
<td>Nε-(carboxymethyl)lysine</td>
<td>↑</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>date seed</td>
<td>powder</td>
<td>acrylamide</td>
<td>↓</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>EGCG from green tea</td>
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<td>acrylamide</td>
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<tr>
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<td>acrylamide</td>
<td>↓ (all concentrations) highest (0.1%) lowest (2%)</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>caffeine</td>
<td>pure standard</td>
<td>acrylamide</td>
<td>↓ (all concentrations) highest (0.1%) lowest (2%)</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>caffeic acid</td>
<td>pure standard</td>
<td>Nε-(carboxymethyl)lysine</td>
<td>↑</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>ferulic acid</td>
<td>pure standard</td>
<td>acrylamide</td>
<td>↓ (all concentrations) highest (1%) lowest (0.1%)</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>gallic acid</td>
<td>pure standard</td>
<td>acrylamide</td>
<td>↓ (all concentrations) highest (0.1%, 0.5%) lowest (2%)</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>quercetin</td>
<td>pure standard</td>
<td>acrylamide</td>
<td>↓ (0.1%)</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>quercetin</td>
<td>pure standard</td>
<td>Nε-(carboxymethyl)lysine</td>
<td>highest (0.1%) lowest (2%)</td>
<td>[34]</td>
</tr>
<tr>
<td>Biscuits</td>
<td>olive-leaf extract</td>
<td>extract</td>
<td>free fluorescent AGEs</td>
<td>↓</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>fennel and black cumin seeds</td>
<td>powder</td>
<td>acrylamide</td>
<td>↓</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>lotus seedpod oligomeric procyanidins</td>
<td>powder</td>
<td>AGEs</td>
<td>↓</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>gallic acid</td>
<td>pure standard</td>
<td>3-DG</td>
<td>↓</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>hydroxytyrosol</td>
<td>pure standard</td>
<td>3-DG</td>
<td>↑</td>
<td>[35]</td>
</tr>
</tbody>
</table>
hydroxytyrosol ▼ [35]
quercetin ▼ [35]
EGCG: (−)-epigallocatechin gallate; ▼: decrease in the concentration of the MR inhibition marker; ↑: increase in the concentration of the MR inhibition marker; =: non-significantly different MR inhibition-marker concentration; 3-DG: 3-deoxyglucosone.

3.5.1. Bread

Extracts from cereals and pseudocereals (e.g., sorghum, buckwheat, pigmented rice, corn, etc.) and extracts from plant-origin foods (e.g., grapeseed, tea, etc.) have been successfully used to inhibit the formation of Maillard reaction products (MRPs) in bread. Chen et al. investigated the inhibitory potential of sorghum bran extract (SBE), grape-seed extract (GSE), and green-tea extract (GTE) against acrylamide formation in bread [26]. The three phenolic extracts were especially rich in flavonols but were also a good source of anthocyanins and proanthocyanidins, flavones, and flavanols. The enrichment of bread with SBE was the most successful; supplementation with SBE at 0.5, 1.0, and 1.5% allowed for a reduction in the acrylamide content of 53, 61, and 70%, respectively, compared with the control [26]. On the other hand, enrichment with the GSE at 0.5, 1.0, and 1.5% resulted in a decrease in acrylamide concentration equal to 22, 48, and 60%, respectively. The addition of GTE to the bread formulation was not equally promising; enrichment at 0.5 and 1.0% resulted in a non-significantly different content of acrylamide in bread compared with the control [26]. It was speculated that the more effective action of phenolic extracts from sorghum bran and grape seeds against acrylamide formation was due to the phenolic profile of the two extracts compared with that of the green-tea extract.

Phenolic extracts of common buckwheat (Fagopyrum esculentum Moench) and Tartary buckwheat (Fagopyrum tataricum Gaertn.) have been also applied in breadmaking [25]. In detail, phenolic extracts from Tartary buckwheat seeds, Tartary buckwheat sprouts, common buckwheat seeds, and common buckwheat sprouts were added to bread formulations, and it emerged that the acrylamide content was reduced by 23.5, 27.3, 17.0, and 16.7%, respectively [25]. However, only the extracts obtained from Tartary buckwheat determined a significant decrease compared with the control. A significant positive correlation between the reduction in the acrylamide content and the total phenolic compound content and antioxidative activity of the extracts was also observed. In this study, it was also found that the enrichment did not affect negatively the organoleptic properties of bread; rather, it improved the color characteristics [25].

The effect of the inclusion of flours from different cereals on the formation of furosine, free fluorescent AGEs, deoxyglucosone (3-DG), methylglyoxal (MGO), and N ε-(carboxymethyl)lysine in the crust and crumb of model breads has also been investigated [28]. N ε-carboxymethyl-lysine (CML) and N ε-carboxyethyl-lysine (CEL) are both AGEs. Wholegrain white, brown, wild, red, and black rice flour and yellow and purple corn flour were added to the bread formulations. Pigmented grains and wholegrains are, in fact, known to be raw materials very rich in phytochemicals [38–41]. The furosine content was generally higher in the crust than in the crumb, except for bread made from brown-rice flour, which showed no significant statistical difference between the furosine concentration in the crust and in the crumb [28]. As regards bread crust, the furosine concentration was highest in wild rice and lowest in yellow corn bread (Table 2). The levels of free fluorescent AGEs were highest in the crust of bread formulated with brown-rice flour and lowest in purple-corn-flour-formulated bread. It was speculated that the lowest concentration of free fluorescent AGEs might be due to several aspects. First, purple corn flour showed low levels of cysteine and methionine, whose thiol groups are converted to thiol radicals, which can react with C–H bonds in peptides and proteins, thus generating carbon-centered radicals that are responsible for protein degradation. Purple corn flour is also rich in flavonoids, and the high levels of flavonoids may prevent free-fluorescent-AGE formation because any tetrahydroxyl and hexahydroxyl groups in their structures can protect against the oxidation of free thiol groups in proteins via the formation of
monothiol, dithiol, and trithiol adducts. Finally, some phenolic acids contained in purple corn flour (i.e., ferulic, p-coumaric, malvidin) and the total phenolic compound content correlated negatively with free fluorescent AGEs, indicating that they might show anti-glycative behavior. The concentration of 3-DG ranged from 376.65 mg/kg crust in the GF bread formulated with brown rice to 38.3 mg/kg crust in the white-rice-flour-formulated bread. Methylglyoxal formation was highest in white and brown rice and lowest in wild rice and purple corn. It was observed that some phenolic compounds, such as sinapic acid, syringic acid, and malvidin, correlated negatively with MGO formation. The concentration of CML ranged from 228.23 mg/kg crust in the yellow-corn-flour-formulated bread to 626.34 mg/kg crust in the wild-rice-flour-formulated bread (Table 2). Positive correlations between the level of CML and individual phenolic compounds, such as sinapic acid, syringic acid, and malvidin, were found. However, it was observed that the phenolic compounds present in gluten-free (GF) bread formulated with the different flours were effective against the formation of Amadori products in the early MR stage and of the fluorescent compounds in the advanced stage but were not effective against the inhibition of CML formation.

Rózanska et al. investigated the formation of some MRPs (i.e., furosine, fluorescent intermediate compounds, and CML) in GF bread formulated with roasted and raw buckwheat flour [24]. It was observed that the levels of furosine were significantly reduced (about 91%) in roasted-buckwheat bread compared with raw-buckwheat bread. Negative correlations were found between the furosine content and the concentrations of p-coumaric, gallic, ferulic, vanillic, and syringic acids, and catechin and rutin, indicating that these phenolic compounds might be involved in the protein protection [29]. The concentration of fluorescent intermediate compounds were also increased by about 38% in the crust of roasted-buckwheat bread, while the level of CML level increased by about 21% in roasted-buckwheat crust [29].

There is also evidence of MRP inhibition in bread enriched with phenolic compounds obtained from tea. For instance, (−)-epigallocatechin gallate (EGCG) was extracted from green tea, and the obtained powder was used in white-bread formulations at different concentrations: 3.3, 6.6, and 9.9 g·kg\(^{-1}\) [31]. Quantitation of the acrylamide content showed that the level was reduced by 30.2, 34.3, and 37.4%, respectively, compared with the control [31]. A non-linear relationship between the concentration of EGCG fortification and the acrylamide reduction in the crust of the bread was observed. EGCG may have acted as an antioxidant during baking by scavenging the free radicals; however, more studies are required to understand the chemical pathways and inhibition mechanisms.

The potential of green-tea extract to inhibit acrylamide formation in rye bread has also been tested [27]. The effect of the phenolic extract addition (0.1% and 0.5% on a flour basis) was investigated in combination with other factors, such as the dough preparation method (direct and indirect) and baking temperature (230 and 260 °C). The addition of the green-tea extract did not affect the acrylamide content in bread prepared from sour-dough, which was higher in this type of bread than in the others. It is likely that the extract had a negative effect on starter cultures by reducing free asparaginase or had a synergistic action with other compounds involved in acrylamide formation [27].

The antiglycoxidative properties of the polyphenol-enriched fraction (PEF) from decaffeinated-tea dust powder have also been explored [32]. In that study, the quantity of water used in the bread formulation was replaced by PEF. Different substitutions were experimented with 30, 50, and 70 g per 100 g of flour. Experiments showed that the inclusion of the PEF in the bread formulations prevented AGE formation in the glycoxidation model systems. In detail, the PEF fraction allowed for the production of bread with higher antioxidative activity and total phenolic content, a lower amount of harmful compounds, and better sensorial quality [32].

Date-seed powder has also been used to enrich pita bread, and the effect of the formulation at different percentages (5, 10, 15, 20%) on acrylamide content was evaluated in Platat et al. [30]. Whatever the degree of date-seed powder enrichment, the level of
acrylamide was significantly lower than that in whole-wheat pita bread; the reduction ranged from 50% to 80%, with the 5% addition being the most effective. The inhibitory effect might be related to the fact that the powder is very rich in flavonoids; however, non-linear behavior between the date-seed powder and acrylamide content was found. The highest inhibitory action was, in fact, observed for pita bread enriched at 5% with date-seed powder, and the lowest was found in pita with a 20% addition. Although the reasons for this trend are not fully understood, it is possible that the increase in fat content resulted in a higher proportion of carbonyl groups that were likely to react with amino acids and, consequently, release acrylamide.

Since the mechanisms beyond the inhibitory effect of the addition of phenolic extracts or powders rich in phenolic compounds still remain unclear, because of the chemical diversity of polyphenols and the complexity of their composition in plant foods, the effect of pure phenolic compounds was taken into consideration [33]. Mildner-Szkudlarz et al. added pure standards of gallic acid, ferulic acid, caffeic acid, (+)-catechin, and quercetin to a bread model at different concentrations (0.1%, 0.5%, 1.0%, and 2.0%, w/w) and investigated their effect in inhibiting acrylamide formation [33]. (+)-Catechin, ferulic acid, gallic acid, and caffeic acid exhibited an inhibitory effect on acrylamide formation at all concentrations, while the addition of quercetin reduced acrylamide content only at the lowest concentration (0.1%). This result might be linked to the fact that in some cases, such as for catechol compounds, high concentrations of phenolic compounds generate hydrogen peroxide, which is actually involved in the formation pathway of acrylamide [33]. Comparing the effects of the different concentrations for each phenolic compound on acrylamide formation, it emerged that gallic acid was most effective when added at 2.0%, ferulic acid at 1.0 and 2.0%, caffeic acid at 2.0%, and (+)-catechin at 0.1% [33].

The effect of the same pure standards (i.e., (+)-catechin, quercetin, gallic acid, ferulic acid, and caffeic acid) on the CML formed by Maillard reaction was also investigated [34]. Inclusion of the phenolic compounds in the bread formulation showed that the rates of CML-formation inhibition ranged from 0.01% to 87.56% in bread crust; this inhibitory effect was dependent on the phenolic compound concentration, but not in a linear manner. Except for ferulic acid, the strongest inhibitory activity of each phenolic compound was exerted at the lowest concentration (0.1%) [34].

3.5.2. Biscuits

The effect of phenolic compounds as inhibitory agents of MRPs was also investigated in biscuits. These were added in the form of powders, extracts, and pure standards. Al-Ansi et al. investigated the effect of fennel (Foeniculum vulgare L.) and black cumin seeds (Nigella sativa L.), also known as Nigella or black seeds, on the acrylamide content in conventionally and microwave-cooked biscuits [36]. The two ingredients were included in the form of a powder in different amounts: 2, 4, and 6%. The highest content of acrylamide was found in conventionally baked biscuits; however, it was observed that the addition of fennel and Nigella had a positive effect on these biscuits. Fennel addition decreased acrylamide levels in conventionally baked biscuits and resulted in a concentration of acrylamide equal to the minimum limit of quantitation in microwave-baked biscuits. As a matter of fact, fennel addition at 2, 4, and 6% diminished the acrylamide content by 38, 61, and 78%, respectively [30]. The addition of Nigella also had a positive effect on the acrylamide content. The decrease was about 60% in conventionally baked biscuits (355.2 vs. 138.6 µg/kg) and 68% (306.9 vs. 97.8 µg/kg) in microwave-baked biscuits [36].

Based on these findings, it can be speculated that besides the positive effect of the cooking method (microwave cooking minimizes acrylamide formation due to the temperatures being lower than 120 ºC), the high antioxidative activity of the two additives positively affects the inhibition of acrylamide. Antioxidative compounds are effective in reducing the acrylamide formation because of the following: (i) carbonyl trapping, (ii) the reduction in sugar degradation through Maillard reaction processes, and (iii) radical-
scavenging activities [36]. In addition, some flavonoids can decrease acrylamide formation because of the number of phenolic hydroxyl groups [42].

The effect of lotus-seedpod oligomeric procyanidins on the inhibition of AGE formation in tough biscuits was also investigated [37]. It emerged that the formation of fluorescent AGEs was significantly inhibited by this enrichment. It is possible that the phenolic compounds had antiglycative activity that was attributable to the capture of dicarbonyl compounds and antioxidative activity by scavenging free radicals and metal-ion chelation.

Biscuits were also formulated by adding pure standards of single phenolic compounds (i.e., hydroxytyrosol, quercetin, and gallic acid) and an olive-leaf extract at different concentrations up to 0.75% (w/w) of the total solid content [35]. Following the addition of hydroxytyrosol (HT), a significant reduction in the 3-DG content of biscuits, compared with the control, was observed. The increase in HT enrichment resulted in a higher reduction in 3-DG content. When the dough was formulated with 6.15 and 12.31 mg HT/g, 3-DG formation was reduced by 37.9% and 41.6%, respectively. On the contrary, the addition of gallic acid resulted in an increase in the 3-DG content. As regards the formation of free Maillard-derived fluorescent compounds, the addition of quercetin was the most effective against the formation of this class of compounds (64.9% inhibition), followed by HT addition, which exerted an inhibitory activity of 28.8%. The biscuits enriched with gallic acid, or the extract of olive leaves showed an inhibitory activity of below 10%; the free-fluorescent-AGE concentration was not statistically different to that in the control sample. However, similar antiglycative activity for pentosidine was observed for the biscuits enriched with the olive-leaf extract. It was speculated that other structures contained in the extract may have contributed synergistically to the antiglycative activity.

4. Strengths, Limitations, and Practical Implications of the Study

To the best of our knowledge, no reviews are currently available about the use of phenolic compounds for the control of the MR in bakery products. The main strength of this study relies also on its methodological approach. A systematic examination of primary studies was performed. The search criteria and keywords used in sourcing the studies were specific and predefined before starting the review, as well as the inclusion and exclusion criteria for selecting the primary studies. This approach enabled the limiting of bias that can occur in narrative reviews that may lack thoroughness and rigor.

Thanks to its rigorous approach, a systematic review is also reproducible, and its replicability helps establish a greater degree of confidence in the obtained results. Hence, this study offers a trustworthy overview of the use and efficacy of phenolic compounds in controlling the Maillard reaction. It also helps uncover areas in which more research is needed.

In particular, the study findings can have practical implications. The investigation of the inhibitory effect of pure phenolic standards on MRPs suggests, for instance, that more studies should be designed to investigate mechanisms beyond the inhibitory effect of adding phenolics. The review also pointed out that the intrinsic properties of the food matrix, such as the pH, were not taken into consideration in the evaluation of the inhibitory action of phenolics. This finding should be considered in future research.

Possible limitations of this review include the analysis of the role of phenolic compounds for the control of the MR only in bakery products. It could be interesting to also investigate the effect of phenolic compounds on the pathways of the MR and product formation in other food matrices, such as in UHT-processed bovine milk during thermal processing and storage.

5. Conclusions

This study highlights that the enrichment of bakery products with phenolic compounds represents a valuable strategy to reduce the formation of harmful MR products. So far, the inhibitory action has been mainly investigated in bread, but some studies also investigated the effect in biscuits. Phenolic extracts and powders obtained from plant-based foods have been included in the formulation of bakery products. The effect of pure phenolic standards was also considered to exclude synergistic activity by extract and
powder components other than phenolics. The inhibitory action was mainly studied with regard to acrylamide and AGE content. Further studies are nevertheless needed to understand the effect of the mechanisms activated by the diverse sources of phenolic compounds on the formation of acrylamide and the other products of the MR.

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