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Investigations on the effect of antioxidant type and concentration and model system matrix on acrylamide formation in model Maillard reaction systems

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ABSTRACT

The formation of acrylamide in model Maillard reaction systems containing phenolic compounds was examined, with regards to phenolic type, concentration, and model system matrix. In dry glyoxal/asparagine waxy maize starch (WMS) systems, 9 out of 10 examined phenolics demonstrated an inhibiting effect, with the most significant reductions (55–60%) observed for caffeoylquinic acids. In WMS glucose/asparagine systems, examination of three different concentrations (0.1, 0.5 and 1 μmol/g WMS) suggested a 'minimum effective concentration' for epicatechin and caffeic acid, whilst addition of caffeoylquinic acids resulted in dose-dependent acrylamide reduction (25–75%). The discordant results of further studies utilising different matrices (dry and wet-to-dry) indicated that, apart from the nature and chemical reactivity, the matrix and the physical state of the reactants might be important for acrylamide formation.

1. Introduction

The formation of acrylamide, a heat-induced toxicant in certain carbohydrate rich foods has been the subject of ongoing worldwide research activities. Various aspects of acrylamide formation in foods have been studied, including the extent of human exposure and assessment of health risks, chemistry, occurrence and formation mechanisms in foods and possible mitigation strategies (Mottram, Wedzicha, & Dodson, 2002; Stadler et al., 2002; Zyzak et al., 2003). Suggested effective ways for the reduction of acrylamide in foodstuffs include modification of raw materials or product formulation (Claus, Mongili, Weisz, Schieber, & Carle, 2008), change of pH and heat-processing parameters (Bråthen & Knutsen, 2005) and process technology interventions (Rufián-Henares, Delgado-Andrade, & Morales, 2006). Research on the use of exogenous additives, such as acids, amino acids, hydrogen carbonates, proteins or antioxidants suggested that they could also be an effective means of acrylamide mitigation (Amrein, Schönbächler, Escher, & Amadò, 2004; Zhang, Ying, & Zhang, 2008). The use of such additives is, however, conditional: the selected additives should not be regarded as toxic, addition levels should comply with corresponding criteria of food or chemical additives and addition should not affect the food's sensory characteristics.

Antioxidants, particularly phenolics, and antioxidant-rich extracts, are amongst the additives studied as potential acrylamide formation inhibitors. However, studies in model and various food systems indicated that the use of pure phenolic antioxidants or antioxidant extracts had an ambiguous effect on acrylamide formation; it was reported by Vattem and Shetty (2003) that oregano phenolic antioxidants stimulated the formation of acrylamide whilst cranberry extracts did not cause any effect when added to fried potato slices. Antioxidants from bamboo leaves have been reported to reduce acrylamide formation in a concentration-dependent manner, when incorporated in thermally processed potato models (Zhang, Chen, Zhang, Wu, & Zhang, 2006) and cookies (Li et al., 2012), whilst a strong correlation between the concentration of ortho-diphenolic compounds in virgin olive oil and the reduction of acrylamide in fried crisps was also reported (Napolitano, Morales, Sacchi, & Fogliano, 2008). Ismial, Ali, Askar, and Samy (2013) reported acrylamide reduction in potato chips for ferulic, protocatechuic, caffeic and gallic acids and catechin (30–98%). Addition of 1% rosemary extract led to a significant reduction of the acrylamide content in wheat buns (Hedegaard, Granby, Frandsen, Thygesen, & Skibsted, 2008), whilst a slight decrease in acrylamide levels was observed when 0.5% green tea extract was added in a crispbread model system (Capuano et al.,

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2009). Ou et al. (2010) reported that whilst the examined antioxidants [*tert*-butyl hydroquinone (TBHQ), butylated hydroxy anisole (BHA), butylated hydroxytoluene (BHT), ferulic acid, epigallocatechin gallate (EGCG) and vitamin C] did not affect acrylamide in asparagine–glucose model systems, their corresponding oxidation products were able to directly affect acrylamide and its precursor, asparagine.

Antioxidants have been traditionally used in the food industry in order to prevent product quality deterioration, as well as for maintaining nutritional value by controlling or retarding oxidation. They have also been studied extensively for their health-promoting properties (Crozier, Jaganath, & Clifford, 2009) which has been partly attributed to their ability to scavenge reactive oxygen species (ROS), thus inhibiting the formation of advanced glycation end-products (AGEs). For example, flavan-3-ols from green tea were found to scavenge methylglyoxal (MGO) under simulated physiological conditions (Lo et al., 2006) whereas procyanidins from cinnamon were shown to inhibit protein glycation (Peng et al., 2008). The reactivity of electron-rich phenols towards electrophilic carbonyls was also observed in food systems; condensation reactions between polyphenols and carbonyls, leading to the formation of various phenolic oligomers, polymers and adducts, have been examined in connection to reduced astringency and colour development in wine during ageing (Pissarra, Mateus, Rivas-Gonzalo, Santos Buelga, & Freitas, 2003).

On the basis of the reported formation of antioxidant-sugar fragment adducts in model systems, it was hypothesised that, in Maillard reaction systems, phenolic antioxidants may react with sugar fragments and/or reactive carbonyl compounds, form adducts through electrophilic aromatic substitution reactions and thus inhibit acrylamide formation. Significant reductions in Maillard reaction products in model systems with added epicatechin and hydroxycinnamic acids were attributed to similar trapping reactions between phenolics and reactive carbonyl intermediates (Jiang, Chiaro, Maddali, Prabhu, & Peterson, 2009; Lo et al., 2006; Totlani & Peterson, 2006).

However, when examining the effect of phenolics on acrylamide, positive, negative or no effects were reported, highlighting the antioxidants' ambiguous role on acrylamide formation (Bassama, Brat, Bohuon, Boulanger, & Günata, 2010; Ou et al., 2010; Zhang et al., 2008; Zhu, Cai, Ke, & Corke, 2009). These studies differed greatly on many experimental parameters, in that a diverse range of antioxidants has been examined (i.e., flavan-3-ols, hydroxycinnamates), in different concentrations and purity states (chemically pure or part of antioxidant-rich plant extracts) and in different model and food systems (Maillard reaction mixtures, cereal- and potato-based systems). Therefore, it may be suggested that variability in experimental parameters may explain the conflicting observations regarding their efficacy as acrylamide inhibitors.

On the basis of previous reports suggesting carbonyl trapping as an effective means of acrylamide reduction, the objectives of this study were (a) to examine the effect of different antioxidants on acrylamide in a model system with glyoxal, a key reactive dicarbonyl implicated in acrylamide formation, (b) to compare asparagine–antioxidant–glyoxal interactions with those of asparagine–glucose–antioxidant systems and (c) to evaluate the impact of the matrix on the effect of antioxidants on acrylamide in different model systems.

2. Materials and methods

2.1. Materials and chemicals

Asparagine, D-(+)-glucose, glyoxal (40% aqueous solution), ethyl acetate, bromine, potassium bromide, hydrobromic acid (48% aqueous solution), sodium sulphate, sodium thiosulfphte, (−)-epicatechin, caffeic acid, ferulic acid and epicatechin gallate were purchased from Sigma–Aldrich (Poole, Dorset, UK) and were ⩾98% pure. 3-Caffeoylquinic acid (chlorogenic acid, 93.67%), 4-caffeoylquinic acid (cryptochlorogenic acid, 84.3%), 5-caffeoylquinic acid (neochlorogenic acid, 98.8%), 3,4-dicaffeoylquinic acid (isochlorogenic acid B, 86.3%), 3,5-dicaffeoylquinic acid (isochlorogenic acid A, 85.3%) and 4,5-dicaffeoylquinic acid (isochlorogenic acid C, 98.8%), were provided by Nestlé (Orbe, Switzerland). Waxy maize starch (WMS) was obtained from Roquette S.p.a (Cassano Spinola, Italy).

2.2. Model system preparation and heating

Three different model systems, waxy maize starch (WMS), wet-to-dry (WTD) and dry (freeze-dried, FD) were used in this study. The choice of model systems was based on simulating the Maillard reaction in the presence or absence of matrix (WMS) at the surface of products during the last stages of baking, while WTD systems were set up to simulate the total effect of baking, taking into consideration water evaporation but in the absence of matrix effects. WMS systems consisted of a solid matrix, resulting from freeze-drying a 5% WMS slurry containing the reactants. In particular, WMS model systems were prepared using a suspension of WMS in deionised water (5%, 2.5 g/50 mL) with added reactants in aqueous solutions (25 μmol/g WMS for asparagine, glucose or glyoxal and 0.1, 0.5 or 1.0 μmol/g WMS for each of the phenolic compounds tested). The suspension was then gelatinised in a shaking water bath set at 90 °C for 5 min, cooled rapidly in an ice bath and aliquots (5 g) of the resulting homogenous slurry were transferred to 20 mL SPME vials (Chromacol Ltd., Welwyn Garden City, UK). The samples were frozen at −18 °C before being freeze-dried for 72 h to a final moisture of 0.2% (Koutsidis et al., 2008). WTD and FD model systems were prepared by adding aliquots of aqueous solutions containing the reactants (2 mL total volume), in SPME vials. The FD samples were then sealed, frozen (−18 °C) and subsequently freeze-dried for 48 h while the WTD (liquid solutions) were heated immediately after preparation. All samples were prepared in triplicate. Dry systems (WMS and FD) were sealed using metal caps with 1.5 mm silicone/PTFE septa whilst liquid model systems (WTD) remained unsealed throughout the heating process to allow for water evaporation. All samples were heated accurately at 160 °C using a Julabo heating tank (Julabo, Seelbach, Germany) containing Rhodorsil (47 V 20) heat transfer fluid (VWR, Lutterworth, UK). A Julabo ME circulator provided accurate and consistent temperature control within the heat transfer fluid (±1 °C). Following heating, model systems were rapidly cooled by submersion in an ice bath for 5 min.

2.3. Acrylamide extraction and analysis

All samples were prepared for acrylamide analysis using a direct extraction–bromination approach (Koutsidis et al., 2008). The brominating reagent (1 L) was prepared with potassium bromide (400 g), hydrobromic acid (20 mL), saturated bromine solution (320 mL) and deionised water.

For the WMS samples, the matrix was pulverised, aliquots (0.1–0.2 g) were accurately weighed, 720 ng (300 μL) of internal standard (1,2,3-^{13}C-acrylamide, 2400 ng/mL) and 5 mL of brominating reagent were added and the samples were stirred for 1 h and then left to brominate overnight. For the FD and WTD samples, internal standard (300 μL) and 3 mL of brominating reagent were directly added in the sample vial, mixed vigorously and left overnight to brominate. Each sample was then neutralised with 3–4 drops of sodium thiosulphate (1 M) and extracted twice with 4 mL of ethyl acetate. The combined organic phase was collected and subsequently evaporated over granular anhydrous sodium sulphate in a TECHNE sample concentrator coupled to a