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Formation and reduction of carcinogenic furan in various model systems containing food additives

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ABSTRACT

The aim of this study was to analyse and reduce furan in various model systems. Furan model systems consisting of monosaccharides (0.5 M glucose and ribose), amino acids (0.5 M alanine and serine) and/or 1.0 M ascorbic acid were heated at 121 °C for 25 min. The effects of food additives (each 0.1 M) such as metal ions (iron sulphate, magnesium sulphate, zinc sulphate and calcium sulphate), antioxidants (BHT and BHA), and sodium sulphite on the formation of furan were measured. The level of furan formed in the model systems was 6.8–527.3 ng/ml. The level of furan in the model systems of glucose/serine and glucose/alanine increased 7–674% when food additives were added. In contrast, the level of furan decreased by 18–51% in the Maillard reaction model systems that included ribose and alanine/serine with food additives except zinc sulphate.

1. Introduction

Furan occurs in various processed foods (Maga, 1979) and there is concern about its potential carcinogenic effects in humans (Bononi & Tateo, 2009). Furan is a heterocyclic organic compound, which is a colourless liquid, highly volatile, and is flammable with a low boiling point of 31 °C (NTP, 1993; Owczarek-Fendor et al., 2010). Furan contributes to flavour in foods and is classified as a possible human carcinogen (Group 2B) by the International Agency for Research Cancer (International Agency for Research on Cancer, 1995). The occurrence of furan has received attention internationally, as processed foods are usually produced by thermal treatment (Nie et al., 2013). As there are limited data on furan in processed foods, more research is needed on the reducing furan formation during food processing based on furan formation mechanisms (Limacher, Kerler, Davidek, Schmalzried, & Blank, 2008).

Many precursors exist for furan to form (Limacher et al., 2008). The mechanisms of furan formation include four pathways: (1) the Maillard reaction consisting of carbohydrates and amino acids, (2) decomposition of ascorbic acid, (3) thermal oxidation of polyunsaturated fatty acids and carotenoids, and (4) thermal degradation of carbohydrates (Maga, 1979; Nie et al., 2013). Among them, the decomposition of ascorbic acid and the Maillard reaction are believed to be the major routes for furan formation. Ascorbic acid is particularly prone to degradation during food processing because of its high susceptibility to oxidation in the presence of oxygen and metal ions (Gilguem & Birlouez-Aragon, 2005). The level of furan in the Maillard reaction depends on the types of sugars, amino acids and the reaction conditions such as pH, temperature, and heating time. Pentose is more reactive in the Maillard reaction than hexose and disaccharides (Lamberts, Rombouts, & Delcour, 2008). Many studies have been performed to investigate furan formation in simple aqueous model systems containing one or more precursors dissolved in buffer (Owczarek-Fendor et al., 2011).

The participation of metal ions and antioxidants in furan model systems has been studied (Delgrado-Andrade, Seiquer, Nieto, & Navarro, 2004; Morales, Fernández-Fraguas, & Jiménez-Pérez, 2005; Owczarek-Fendor et al., 2011; Sarria & Vaquero, 2001, 2006; Seiquer, Valverda, Delgrado-Andrade, & Navarro, 2000; Whitelaw & Weaver, 1989). Antioxidants potentially inhibit furan formation (pathway 3), because they are well-known scavengers of free radicals formed during polyunsaturated fatty acid oxidation. Antioxidants, such as tocopherol acetate and butyl hydroxyanisole (BHA), reduce furan formation from a polyunsaturated fatty acid model system by up to 70% (Owczarek-Fendor et al., 2011). In contrast, another study showed increased furan formation from a linoleic acid model system with the addition of butyl hydroxytoluene (BHT) (Mark, Pollien, Lindinger, Blank & Mark, 2006). The presence of metal ions in the Maillard reaction affects the rate of formation of Maillard reaction products (Birlouez-Arragon, Moreaux, Nicolas, & Ducanze, 1997; Cottier & Descotes, 1991; Hayase, Shibuya, Sato, & Yamamoto, 1996; Rendleman & Inglett, 1990). However, the mechanism of metal incorporation into the Maillard reaction is

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not clearly understood (Ramonaityté, Kersiené, Adams, Tehrani, & Kimpe, 2009). In addition, the effect of metal ions on the formation of furan has not been reported. Although a significant amount of work has been performed to investigate the role of antioxidants and metal ions in furan model systems (pathway 3: from polyunsaturated fatty acids), no reports have investigated the effect of various food additives in furan model systems (pathway 1: ascorbic acid, 2: Maillard reaction consisting of glucose, ribose, alanine, and serine).

The cost of furan analysis in the small and medium-sized food companies is high and analytical instrumentation is insufficient; thus, it is essential to find an index of furan formation. In a previous study, the relationship between Maillard reaction products and absorbance was identified. According to that study, the brown colour produced by the Maillard reaction can be used as an indicator of the Maillard reaction stage and its possible link to antioxidant capacity (Vhangani & Wyk, 2013). Therefore, the purpose of this study was to investigate the effect of various food additives such as metal ions (iron sulphate, magnesium sulphate, calcium sulphate and zinc sulphate), sodium sulphite, and antioxidants (BHT, BHA) on the formation of furan using furan model systems (pathways 1 and 2) consisting of carbohydrates (glucose and ribose), amino acids (serine and alanine), and ascorbic acid. In addition, the relationships between the colour of the aqueous model systems and furan concentration were determined to investigate an index of furan formation.

2. Materials and methods

2.1. Reagents

Furan (+99%, purity), d4-furan (>99 atom % D), D (-)-ribose (Rib, ⩾99%, purity), L-serine (Ser, ⩾99%, purity), L-alanine (Ala, ⩾98%, purity), sodium sulphite (Na, ⩾98%, purity), BHA (⩾98%, purity) and BHT (⩾98%, purity) were obtained from Sigma–Aldrich Corp. (St. Louis, MO, USA). D(+)-glucose (98.0% purity), magnesium sulphate (Mg^{2+}, 99% purity), zinc sulphate (Zn^{2+}, 99% purity) and calcium sulphate (Ca^{2+}, 76% purity) were obtained from Junsei Chemical Co., Ltd. (Tokyo, Japan). Iron sulphate n-hydrate (Fe^{2+}, 60–80% purity) was purchased from Kanto Chemical Co., Inc. (Pulau Pinang, Malaysia) Water and methanol (HPLC grade) were purchased from J.T. Baker (Phillipsburg, NJ, USA).

2.2. Sample preparation for the various furan model systems

A 10 ml aqueous solution containing three models of 1.0 M ascorbic acid (model I), 0.5 M glucose and alanine/serine each (Model II), and 0.5 M ribose and alanine/serine each (Model III) and 0.1 M of each food additives such as (iron sulphate, magnesium sulphate, calcium sulphate and zinc sulphate, BHA, and BHT), and sodium sulphite were prepared in a 20 ml headspace vial (Agilent Technologies, Santa Clara, CA, USA). The vial was completely filled and closed with a silicone–PTFE septum and an aluminium seal, and heated at 121 °C for 25 min in an oven. Immediately after heating, the vials were cooled in an ice bath for 30 min.

2.3. Colour measurement of samples from the furan model systems

The colour of the reaction mixture was measured using a colour difference metre (NE 4000, Nippon Denshoku, Tokyo, Japan). The results are expressed as L^* (lightness) and b^* ($+b^*$ = yellowness, $-b^*$ = blueness) according to the methods specified in the equipment manual. The instrument was standardised with a standard white tile. Measurements were made three times for each sample, and results are expressed as mean ± standard error.

2.4. Furan analysis

2.4.1. Preparation of stock, working, and standard solutions

Stock furan and d4-furan solutions were prepared in 20 ml headspace vials by adding 1 μl of native furan or d4-furan in cold methanol weekly. Working solutions were prepared daily with 100 μl of refrigerated stock solutions and 10 ml of high performance liquid chromatography grade water. The final concentration of furan and d4-furan solutions was approximately 1.0 μg/ml for the stock solution and 0.1 μg/ml for the working solution. All stock and working solution vials were sealed with silicone–PTFE septa and aluminium seals and were stored at −18 and 4 °C until analysis, respectively.

2.4.2. Validation of furan analysis

Furan was quantified using the internal standard method. Different volumes (10–100 μl) of furan working standard solution and a constant volume (10 μl) of internal standard working solution were spiked. The following validation parameters were determined for the method used: percent recovery, linearity, limit of detection (LOD) and limit of quantification (LOQ). Recovery efficiency of furan was assessed for furan standards at 10 ng and 100 ng in water reacted at 121 °C for 25 min in an oven to test the sealed vial.

2.4.3. Headspace-solid phase microextraction (SPME) analysis

According to a previous study (Kim, Kim, & Lee, 2010), 75 μm carboxen/polydimethylsiloxane (CAR/PDMS; Supelco, Bellefonte, PA, USA) was selected to analyse furan. Before the furan analysis, the SPME fibre was conditioned in the GC injector at 300 °C for 1 h to absorb the furan. A 75 μm stainless steel needle was pushed through the septum of the vial containing the CAR/PDMS. The fibre was exposed to the headspace (1.5 cm in depth) at the optimised extraction temperature (50 °C) and extraction time (20 min). After extraction, the fibre was inserted into the injection port for desorption of the analytes (4 cm in depth). The fibre was baked for 10 min at 250 °C before the next analysis to remove residual analytes. The analysis was performed in triplicate.

2.4.4. Gas chromatography–mass spectrometry

Analyses were performed using an Agilent Technologies 6890N network gas chromatograph system coupled to an Agilent Technologies 5975 inert mass selective detector. Furan in the model systems was separated using a HP-PLOT Q fused silica capillary column (15 m × 0.32 mm I. D., 20 μm film thickness, J & W Scientific, Folsom, CA, USA). The injector port was heated to 250 °C, and the splitless injection mode was used. The GC oven temperature program was set to 50 °C (held for 5 min) and increased to 230 °C at 25 °C/min (held for 2 min). The mass spectrometer was operated in positive electron impact ionisation mode using automatic gain control with 70 eV of electron energy and selective-ion monitoring mode by recording the current following ions: m/z 68 $[M]^+$ and m/z 72 $[M]^+$ for furan and d4-furan determinations, respectively. The ions m/z 39 $[M\text{-}CHO]^+$ and m/z 42 $[M\text{-}CDO]^+$ were monitored to confirm detection of furan and d4-furan.

2.5. Statistical analysis

Furan concentration and colour parameters were analysed using IBM SPSS Statistics software ver. 22.0, (Armonk, NY, USA). The experiments were conducted in triplicate. Analysis of variance and Duncan's multiple range tests were applied. A $p < 0.05$ was considered significant.

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