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Effects of dicarbonyl trapping agents, antioxidants, and reducing agents on the formation of furan and other volatile components in canned-coffee model systems

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ABSTRACT

The formation of furan and certain volatiles related to furan formation mechanisms was studied using gas chromatography–mass spectrometry combined with solid-phase micro extraction after adding dicarbonyl trapping agents [epicatechin (EC), epigallocatechin gallate (EGCG), and catechin], water-soluble antioxidants (Trolox, caffeic acid, ferulic acid, and chlorogenic acid), fat-soluble antioxidants (α-tocopherol, BHT, and β-carotene), and reducing agents (glutathione and sodium sulfite) to canned-coffee model systems (CMS). The level of furan formation decreased significantly following the addition of EC (by 65.3%), EGCG (by 60.0%), and catechin (by 44.7%). In addition, the formation of Maillard reaction products, including furan derivatives (furfural and 5-methylfurfural), Strecker aldehyde (2-methylbutanal), pyrazines (2,6-dimethylpyrazine), and lipid oxidation products (including hexanal and 2-pentylfuran) was suppressed when any of the dicarbonyl trapping agents was added. Among the water-soluble antioxidants studied, chlorogenic acid most significantly decreased the furan level, by 67.0%, followed by ferulic acid (57.6%), Trolox (50.1%), and caffeic acid (48.2%) in the CMS. Chlorogenic acid also reduced the formation of furfural and lipid oxidation products. However, the addition of caffeic acid, ferulic acid, and chlorogenic acid decreased the generation of key coffee aroma components, such as Strecker aldehydes (2-methylpropanal and 2-methylbutanal), 5-methylfurfural, and pyrazines (2,6-dimethylpyrazine and 2-ethyl-5-methylpyrazine). Among the fat-soluble antioxidants, BHT and α-tocopherol decreased the furan level by 49.3% and 39.3%, respectively, while β-carotene increased the furan level by 34.8%. The addition of sodium sulfite and glutathione to CMS also led to considerable reductions in furan, of 64.1% and 44.9%, respectively.

1. Introduction

Furan is a heterocyclic aromatic compound with a high volatility and low boiling point (NTP, 1993). The presence of furan in foods has recently received significant attention due to it being classified as being "possibly carcinogenic to humans" (Group 2B) by the International Agency for Research on Cancer (IARC, 1995). There have been large variations in the reported levels of furan measured in various foods, such as from 1.4 μg/kg to 90 μg/kg in baby foods (Yoshida, Isagawa, Kibune, Hamano-Nagaoka, & Maitani, 2007), from 1.9 μg/kg to 210.7 μg/kg in soy sauce (Nie et al., 2013), from non-detectable to 122 μg/kg in canned fruits and vegetables (US FDA, 2004), and from 2.8 μg/kg to 194 μg/kg in canned meats (Kim, Kim, & Lee, 2010). In particular, the furan level has been found to be much higher in coffee than that in other food products (Becalski et al., 2010; Liu & Tsai, 2010). A previous study found that the use of longer roasting times and darker coffee beans tended to increase the furan level in the produced coffee (Guenther, Hoenicke, Biesterveld, Gerhard-Rieben, & Lantz, 2010). The highest furan level detected in roasted coffee beans was 3660 μg/kg) while, instant coffee and roasted ground coffee contained furan at 394 μg/kg and 1936 μg/kg, respectively (EFSA, 2011).

Furan formation in foods is known to be associated with thermal degradation of carbohydrates, amino acids, ascorbic acid, and polyunsaturated fatty acids (PUFAs) (Crews & Castle, 2007; Mariotti et al., 2012; Van Lancker, Adams, Owczarek-Fendor, De Meulenaer, & De Kimpe, 2010). Regarding its possible formation mechanism in model systems containing furan precursors, Weenen (1998) proposed that reducing hexoses can result in the generation of both 1-deoxyosone and 3-deoxyosone while pentoses can be involved in the formation of 3-deoxyosone in the presence of amino acids. According to Perez Locas and Yaylayan (2004), these reactive dicarbonyl intermediates can produce aldotetrose and 2-deoxyaldotetrose via α-dicarbonyl cleavage. Aldotetrose is subsequently converted to 3-furanone via a dehydration reaction, subsequently leading to furan, whereas 2-deoxyaldotetrose can generate furan via decarboxylation and cyclization reactions. On the other hand, oxidation of PUFAs such as linoleic acid and linolenic acid can produce 4-hydroxy-2-butenal, which

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generates furan via cyclization and dehydration. In addition, Yaylayan (2006) showed that pyrolysis of amino acids such as serine, which could degrade to acetaldehyde and glycolaldehyde, produced furan by aldol condensation followed by cyclization and dehydration.

Several researches have focused on reducing furan formation in various model systems by the use of precursors. Märk, Pollien, Lindinger, Blank, and Märk (2006) explained that the addition of serine or erythrose, which are known to be precursors of furan, significantly reduced furan formation in an ascorbic acid model system, possibly due to the competitive reactions of furan precursors that can occur in complex systems. They also demonstrated that antioxidants such as α-tocopherol and sodium sulfite in PUFAs and an ascorbic acid model system reduced furan formation by 17.0% and 57.0%, respectively. Although the exact mechanism of furan formation in coffee has not been fully elucidated, the Maillard reaction and lipid oxidation could be mainly responsible for its formation in coffee (Buffo & Cardelli-Freire, 2004; Murkovic & Derler, 2006; Perez Locas & Yaylayan, 2004). It is therefore reasonable to assume that, several factors affecting the Maillard reaction and lipid oxidation can influence the formation of furan in coffee. Wang and Ho (2009) showed that flavonoids [i.e., epicatechin (EC)], which are widely distributed in plants, can act as dicarbonyl trapping agents to trap intermediate Maillard products such as sugar fragments in Maillard model systems. In addition, antioxidants such as caffeic acid and chlorogenic acid significantly inhibited the formation of furan derivatives such as furfural and 5-methylfurfural in a glycine–glucose model system by reacting with intermediate Maillard products (Oral, Dogan, & Sarioglu, 2014).

However, few studies have investigated the effects of dicarbonyl trapping agents and antioxidants on the formation of furan itself and other volatile compounds in food model systems. In particular, there has been no investigation of the effects of dicarbonyl trapping agents on the formation of furan, despite such agents affecting both the Maillard reaction and lipid oxidation, which are major pathways for furan formation in coffee. The objective of the current study was to determine the effects of dicarbonyl trapping agents, antioxidants, and reducing agents on the formation of furan and certain other volatile compounds related to furan formation mechanisms in canned-coffee model systems (CMS) and to elucidate the relationship between furan and the generation of other volatiles.

2. Materials and methods

2.1. Chemicals and reagents

In order to prepare CMS, diverse ingredients including instant coffee powder (Nestlé Taster's Choice®, Nestlé Korea, Cheongju-si, Chungcheongbuk-do, Korea), sugar (sucrose, CJ CheilJedang, Seoul, Korea), skimmed milk powder (Seoul Milk, Seoul, Korea), and soy lecithin (ES Ingredients, Gunpo-si, Gyeonggi-do, Korea) were obtained from a local market in Seoul, South Korea. HPLC grade water and methanol were purchased from J.T. Baker (J.T. Backer, Phillipsburg, NJ, USA). Furan (≥99%), (+)-catechin hydrate (≥98%), (−)-epicatechin (≥98%), epigallocatechin gallate (≥95%), glutathione (99%), sodium sulfite (98%), butylated hydroxytoluene (BHT, ≥99%), (±)-α-tocopherol (≥96%), β-carotene (≥95%), caffeic acid (3-caffeoylquinic acid, ≥98%), *trans*-ferulic acid (99%), chlorogenic acid (≥95%), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox, 98%), d_4-furan (98%), and 4-acetylpyridine (97%) were purchased from Sigma Aldrich (St. Louis, MO, USA).

2.2. Sample preparation for CMS

CMS were prepared by using instant coffee powder, sugar, skimmed milk powder, and soy lecithin. Each coffee ingredient was mixed with water (HPLC grade) in falcon tubes (high-clarity polypropylene conical tube, Franklin Lakes, NJ, USA) according to a coffee formula of Nestle with a modification: instant coffee powder (10%), sugar (10%), skimmed milk powder (3%), and soy lecithin (0.1%) (http://www.ecplaza.net/nescafe-canned-extra-rich–everything/TH——/1.html). Dicarbonyl trapping agents such as catechin, EC, and epigallocatechin gallate (EGCG), antioxidants including water-soluble antioxidants (Trolox, caffeic acid, ferulic acid, and chlorogenic acid) and fat-soluble antioxidants (BHT and α-tocopherol), and reducing agents such as glutathione and sodium sulfite were added in CMS at a final concentration of 5 mM, respectively. The mixture was then homogenized for 1 min using a homogenizer (T-10 basic Ultra-Turrax, IKA, Konigswinter, Germany). After that, the sample (1 mL) was transferred into a 1.2 mL ampoule vial (Wheaton, Millville, NJ, USA). The vial was then flame-sealed and immediately cooled in an ice water bath before heating at 120 °C for 10 min in a mineral oil bath (Fisher Scientific, Fair Lawn, NJ, USA) to simulate the sterilization condition of coffee processing. After cooling in the ice water bath for 30 min, the sample was spiked with 50 μL of d_4-furan (1150 μg/L in methanol) and 50 μL of 4-acetylpyridine (92 μg/mL in methanol) to obtain the final concentrations of 50 μg/L and 4 μg/mL, respectively, in a 10 mL vial (headspace screw top clear vial, Agilent Technologies, Waldbronn, Germany). All samples were prepared in triplicate to analyze furan and other volatiles in CMS.

2.3. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analysis was performed using a 7890A series gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with a HP-PLOT Q fused silica capillary column (15 m length × 0.32 mm ID, 20 μm film thickness, J&W Scientific, Folsom, CA, USA) and an CTC-PAL auto-sampler (GC sampler 80, Agilent Technologies), and a 5975C mass selective detector (MSD) (Agilent technologies) equipped with the HP-PLOT Q fused silica capillary column (15 m length × 0.32 mm ID, 20 μm film thickness, J&W Scientific, Folsom, CA, USA). The carrier gas was helium at a constant flow rate of 1.7 mL/min. The oven temperature was initially held at 50 °C for 5 min, raised to 120 °C at 10 °C/min and to 230 °C at 4 °C/min, and then held at 230 °C for 20 min. Both inlet and detector transfer line temperatures were 250 °C and the splitless injection mode was used. The MS was operated in the electron ionization (EI) ion source mode at 70 eV and a scanning range of 35–350 amu. Also, selected ion monitoring (SIM) was used for the determination of furan and d_4-furan. For quantification, m/z (mass/charge) 68 and 72 were used for furan and d_4-furan, respectively, and for qualification, m/z 39/68 and 42/72 were compared for furan and d_4-furan, respectively.

2.4. Automated solid-phase micro extraction (SPME)

The automated solid-phase micro extraction (SPME) method was used to extract furan and other volatile components in CMS. For adsorption of furan and other volatile components, a carboxen/polydimethylsiloxane fiber (CAR/PDMS, 85 μm, Supelco, Bellefonte, PA, USA) was used. The vial was kept at 50 °C with agitation at 250 rpm for 10 min to obtain an equilibrium state. The SPME fiber was exposed into the headspace of the vial for 20 min before desorption in the GC injection port at 250 °C for 5 min. All experiments were conducted in triplicate.

2.5. Identification and quantification of furan and other components

Furan and other volatile components were positively identified by comparing both their mass spectral data and retention times with those of authentic standard compounds. When each authentic standard was not available, volatile compounds were tentatively identified using on-computer library (Wiley 7n.L) mass spectral databases (Hewlett-Packard Co., Palo Alto, CA, USA, 1995). Furan and other volatile