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Suppression of the formation of furan by antioxidants during UV-C light treatment of sugar solutions and apple cider

Gaofei Hu[a,b], Huaizhi Liu[a], Yan Zhu[a], Marta Hernandez[a], Tatiana Koutchma[a], Suqin Shao[a,*]

[a] Guelph Research and Development Centre, Agriculture and Agri-Food Canada, Guelph, ON, Canada
[b] School of Science, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

Furan, which has been identified as a carcinogenic risk for humans, can be induced in different foods by UV-C light. In this study, we hypothesized that furan was produced by a UV light-induced free radical mechanism and antioxidants could suppress its formation. Our results demonstrated that, by adding antioxidants, such as butylated hydroxyl toluene, ascorbic acid or gallic acid, to simulated juice or apple cider during UV-C treatment, amounts of furan were significantly reduced. For example, the concentration of furan produced in apple cider by UV-C at 9.0 J/cm^2 was 636 ppb but was less than 20 ppb with 0.25 ppm butylated hydroxyl toluene present, less than 3 ppb with 0.5% (w/v) ascorbic acid, and less than 1.0 ppb with 0.5% (w/v) gallic acid. These findings confirmed that antioxidants can be used as a safe and simple mitigation measure to control furan production in fruit drinks exposed to UV-light.

1. Introduction

Furan (C_4H_4O) is a five-membered heterocyclic organic compound with four carbon atoms and one oxygen. It is used by chemical industries and has been found in some foods, especially those that had undergone heat treatment, such as, canned and jarred products (Bakhiya & Appel, 2010). Animal experiments have demonstrated liver toxicity in rats and indicated effect in humans including carcinogenicity (Hamberger, Kellert, Schauer, Dekant, & Mally, 2010). The International Agency for Research on Cancer (IARC) has classified furan as a possible carcinogen for humans (IARC, 1995). Therefore the presence of furan in food poses a potential health concern for humans.

A variety of food components can lead to the formation of furan during thermal treatment including sugars, amino acids, ascorbic acids and unsaturated fatty acids (Becalski & Seaman, 2005; Limacher, Kerler, Davidek, Schmalzried, & Blank, 2008). Two pathways for furan, from sugars and amino acids, proposed by Limacher, Kerler, Conde-Petit, and Blank (2007) are: (i) splitting of C1 and/or C2 units from the intact hexoses; (ii) recombination of reactive fragments that might originate from both sugars and amino acids (Limacher, et al., 2007). The involvement of free radicals has been indicated in the formation pathway from ascorbic acid and unsaturated fatty acids to furan (Shen et al., 2017).

In addition to thermal processing, which can induce furan formation in food, non-thermal UV-light treatment also leads to the formation of furan in various foods such as juices and sugar solutions (Bule et al., 2010; Fan & Geveke, 2007). Bule et al. (2010) demonstrated that fructose was the main constituent in fruit juices responsible for furan formation during UV-C light treatment (Bule et al., 2010), although the formation mechanism has not yet been identified. It is known that UV-C light can induce photochemical reactions in a food system (Spikes, 1981). UV-C light at 253.7 nm has a radiant energy of 112.8 kcal/Einstein. Thus, it is theoretically possible for 253.7 nm light to affect O–H, C–C, C–H, C-N, H-N, and S-S bonds if it is absorbed (Spikes, 1981), leading to the formation of free radicals. Free radicals are unstable and very reactive, and can result in different oxidized products. Potentially, furan is one of the free radical products that can be formed in aqueous solutions after exposure to UV irradiation. As UV-light is used by the juice industry to reduce microbial contamination, e.g. CiderSure 3500 UV unit (FPE Inc., Macedon, N.Y., U.S.A.), it is imperative that mitigation measures are developed to control furan production in UV-treated food products.

Antioxidants, which are able to scavenge free radicals, can be used to terminate free radical chain reactions. Many molecules, synthetic

* Corresponding author at: 93 Stone Road West, Guelph, ON N1G 5C9, Canada.
E-mail address: suqin.shao@agr.gc.ca (S. Shao).

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and naturally-occurring, have been identified as effective, e.g., ascorbic acid, tocopherols, butylated hydroxyanisole (BHA), butylated hydroxyl toluene (BHT), phenolic compounds and flavonoids.

In this study, the aim was to examine the effect of antioxidants on furan formation in sugar solutions and apple cider during UV treatment. Ascorbic acid (AA), gallic acid (GA) and BHT were chosen because their antioxidant activities are well established.

2. Materials and methods

2.1. Reagents and materials

Furan (≥99%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). All the sugars including D-fructose, D-glucose, sucrose, and D-maltose, as well as DL-malic acid, L-ascorbic acid, gallic acid and butylated hydroxyl toluene were also obtained from Sigma-Aldrich (St. Louis, MO, USA). Water was purified using a Barnstead Nanopure purification system (Thermo Scientific, Dubuque, USA). Stock solutions of furan were prepared by adding around 12 μL of the standard via a syringe through the septum of a 15-mL headspace vial (Supelco) containing 10 mL of HPLC grade methanol (Caledon Laboratories Ltd., Georgetown, Canada). The septum was replaced subsequently with a new one. The increase in weight was measured to determine the exact concentration of furan (at 1000 mg/L level). The stock solution was stored at 4 °C for not more than two weeks.

Fresh apple cider was obtained from a local farm market (without addition of AA and pasteurization) and stored at −20 °C prior to use. The sugar solutions (5% (w/v) each) were prepared in water or 0.25% malic acid and contained: fructose (F), glucose (G), sucrose (S), maltose (M), and a mixture of fructose, glucose and sucrose (5% each) in 0.25% malic acid denoted as FGSM. The pH of the sugar solutions was 6.8 or, with malic acid, 4.0.

The SPME device and carboxen/polydimethylsiloxane (CAR/PDMS) fused silica fibres (75 μm) were supplied by Supelco (Bellafonte, PA, USA). All the extraction fibres were conditioned according to the manufacturer's instructions prior to use. Headspace glass vials (15 mL) with open top screw-caps (phenolic) and septa (PTFE/silicone) were also purchased from Supelco (Bellafonte, PA, USA).

2.2. UV light (UV-C) treatment of sugar solutions and apple cider

UV-C light treatment was performed by using a model R-52G Mineralight lamp (UVP, Upland, CA, USA) at 253.7 nm. The sugar solutions and apple ciders were exposed to UV-C radiation in a quartz demountable cuvette with an inner thickness of 2.0 mm, i.e. UV-C light path length was 2 mm (model 20ES2, Precision Cell Inc., Farmingdale, NY, USA). Each sample (~750 μL) was transferred to the quartz cuvette (filled up) containing a mini-magnetic stirrer bar (with PTFE coating), the cuvette was sealed carefully using a demountable quartz lid to avoid the generation of bubbles. All samples were stored in the fridge (4 °C) prior to treatment. During UV-C treatment, the quartz cuvette was set directly beneath the UV lamp and on a stirring plate within a marked area, and the sample was stirred constantly to achieve even exposure. A schematic diagram of the experimental setup for UV-C treatment is shown in Fig. 1. The distance between the UV lamp and the cuvette can be adjusted according to the required UV-C intensity, which was measured using a digital ILT1700 radiometer (International Light Technologies, MA, USA). In the present study, the distance was fixed at 8.0 cm to attain 5.0 mW/cm^2. UV-C fluences (0.3, 1.5, 2.4, 3.0, 6.0 and 9.0 J/cm^2) were achieved by setting the exposure time to 1, 5, 8, 10, 20 and 30 min, respectively.

2.3. Suppression of furan formation by antioxidants during UV-C treatment

Different amounts of BHT, GA and AA were added to the sugar solutions or apple cider separately before UV-C treatment, and vortexed for one minute at room temperature to ensure they had dissolved fully. The final concentrations of BHT were 0.01, 0.03, 0.1, 0.25, 0.5 and 1 ppm; the final concentration of GA and AA were 0.01, 0.03, 0.1, 0.5 and 1% (W/V). The antioxidant sugar solutions and supplemented apple ciders were subjected to UV light treatment as described above.

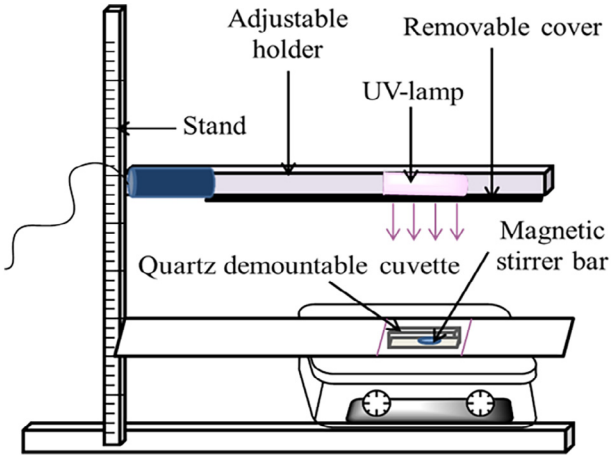

Fig. 1. Schematic diagram of experimental setup for UV-C treatment of sample.

2.4. Determination of furan concentration in UV-C treated sugar solutions and apple cider

After the UV-light treatment, furan concentrations in all the samples were determined using an established headspace solid phase microextraction and gas chromatography – flame ionization detection (HS-SPME/GC-FID) method we have reported previously (Hu, Zhu, Hernandez, Koutchma, & Shao, 2016). In brief, the HS-SPME was carried out as follows: Samples (5 mL sugar solutions or 5 mL diluted apple cider [1:4]) were transferred into a glass vial (15 mL, 21 × 70 mm) containing a magnetic stirrer bar and 15% (w/v) NaCl. The vial was sealed and incubated at 32 °C for 10 min before a SPME fibre (75 μm CAR-PDMS) was inserted into the headspace (10 mL of headspace was used, $V_h/V_s = 2$) for 20 min. Samples were stirred (600 rpm) continuously throughout.

Furan was analyzed by introducing the SPME fibre into the injection port of an Agilent 6890N GC system equipped with a flame ionisation detector (FID) and an SPB-1 column (length = 30 m, i.d. = 0.25 mm, stationary film thickness = 0.25 μm, Supelco, MA, USA). Hydrogen (99.999%, Air Liquide, Bramalea, ON, Canada) was used as carrier gas. The oven temperature was 35 °C for 5 min and increased to 140 °C at a rate of 10 °C/min, and then to 240 °C at a rate of 50 °C/min before being held at this temperature for 4 min. The injection port temperature was 250 °C. Identification of furan was achieved by spiking samples with standards and comparison of the retention time with the standard. Quantification of furan in the sample was based on the calibration curve obtained from the standard solutions: $y = 1.135x + 0.965$, in which y is the concentration of furan in the sample and x is the peak area, x ranges between 1.02 ng/mL to 102 ng/mL (Hu, et al., 2016).

2.5. Statistical analysis

Each analysis was repeated independently at least three times and the results are presented as mean values. Data were analyzed by standard analysis of variance (ANOVA) followed by least squares difference (LSD) to compare the mean values at P-value = 0.05, using Statistix® software (V2.0, Analytical Software, Tallahasse, FL).