



Formation of polychlorinated naphthalenes during the heating of cooking oil in the presence of high amounts of sucralose

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ABSTRACT

Sucralose, an artificial sweetener, is being used in increasingly large amounts in foodstuffs and beverages worldwide. Information pertaining to its ability to participate in chlorination reactions during cooking and generate toxic compounds, however, is scarce. In this study, the formation and distribution of polychlorinated naphthalenes (PCNs), which are a group of highly toxic polychlorinated aromatic compounds, in oil heated in the presence of sucralose was investigated. The concentrations of the PCNs present in the cooking oils and oil fumes generated during the heating process were determined by isotope dilution according to a HRGC/HRMS method. The results suggested that the heating of cooking oil in the presence of sucralose promoted the formation of toxic PCNs. Although PCNs were detected in the oil fumes, no PCNs were found in the heated oils. The total concentrations of the PCNs found in peanut and olive oil fumes were 490 and 240 $\mu\text{g g}^{-1}$, respectively. The degree of chlorination for the PCNs was calculated to be 5.3 for both the peanut and olive oil fumes. To quantify the newly produced PCNs, sucralose used in the experiments were about 2 or 3 orders of magnitude higher than in reality. PCNs were not detected with real proportions under the current experimental conditions.

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1. Introduction

There have been growing concerns about polychlorinated naphthalenes (PCNs) because of their structural similarities to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Bidleman, Helm, Braune, & Gabrielsen, 2010; Domingo, 2004). The toxicity of PCNs is also similar to that of PCDD/Fs, and is measured using relative potency factors (RPFs) or toxic equivalency factors (TEFs) (Noma, Yamamoto, & Sakai, 2004; Puzyn, Falandysz, Jones, & Giesy, 2007). Some studies reported that, in samples from some locations, the proportion of PCNs was relatively high among dioxin-like compounds (Bidleman et al., 2010; Domingo, 2004). In Korea, PCNs in human serum samples accounted for 26.8% of the total toxic equivalents (TEQs) of PCDD/Fs, polychlorinated biphenyls (PCBs) and PCNs (Park, Kang, Baek, & Chang, 2010). PCNs have recently been proposed for listing under the Stockholm Convention (Stockholm Convention, 2012).

Human exposure to PCNs and related compounds occurs mainly through food intake (Domingo, 2004; Li, Wu, Zhang, & Zhao, 2007). Cooking is an important process in food preparation and could

affect the content of toxic compounds in foodstuffs. Recently, Domingo (2011) summarized published studies on the influence of cooking on the concentrations of toxic metals and organic contaminants in foodstuffs. Generally, cooking tended to reduce the concentrations of organic contaminants in food because fat is released during heating. Yet, cooking processes could promote the formation of polycyclic aromatic hydrocarbons (PAHs) (Domingo, 2011). Although the generation of PAHs in cooking processes has been intensively studied (Alomirah et al., 2011; Chen & Chen, 2001; Chiang, Wu, & Ko, 1999; Chiang et al., 1997; Farhadian, Jinap, Abas, & Sakar, 2010; Purcaro, Navas, Guardiola, Conte, & Moret, 2006), investigations on the release of polychlorinated aromatic compounds during cooking, such as PCNs, are scarce. PAHs are condensed aromatics which could be chlorinated in this process. Although it is possible for chlorinated anthracenes and other aromatics to be produced, PCNs were investigated in the current study because of their impact on human health and their simple condensed aromatic backbone, i.e. naphthalene.

PAHs can be formed through the grilling and smoking of food (Alomirah et al., 2011; Farhadian et al., 2010) or from heated cooking oils (Chen & Chen, 2001; Chiang et al., 1999, 1997; Purcaro et al., 2006). The formation of PCNs may take place through the chlorination of naphthalene or as a consequence of *de novo* synthesis from PAHs (Jansson, Fick, & Marklund, 2008; Weber et al.,

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2001). A variety of different types of chlorine-containing compounds can be found in foodstuffs, and in food additives and flavorings, that could participate in the formation of PCNs during cooking.

Sucralose (1,6-Dichloro-1,6-dideoxy- β -D-fructofuranosyl-4-chloro-4-deoxy- α -D-galactopyranoside) is an artificial sweetener and has been declared safe by public health authorities worldwide, including the Food and Drug Administration (FDA) (Grotz & Munro, 2009). Sucralose is being used in increasingly large amounts as a sugar substitute in a broad range of foods and beverages, including products baked at high temperatures. In a recent report, however, sucralose was found not to be stable under high temperatures. Using thermoanalytical techniques, Bannach, Almeida, Lacerda, Schnitzler, and Ionashiro (2009) found that the thermal decomposition of sucralose occurred at 119 °C with the liberation of constitutional water and hydrogen chloride. Rahn and Yaylayan (2010) also reported the thermal degradation of sucralose and found that it was able to chlorinate glycerol to generate toxic chloropropanols at 250 °C. Thus, it has been speculated that PCNs could be formed during cooking because of the generation of PAHs and the presence of chlorine-containing compounds in cooking processes, although the formation of PCNs during cooking has not yet been reported.

In the current study, a simulated cooking system was set up to confirm and investigate the formation and distribution of PCNs during cooking. The concentrations and distributions of dioxin-like PCBs (dl-PCBs) and PCDD/Fs formed together with PCNs were investigated to evaluate the relative importance of these polychlorinated aromatic compounds.

2. Material and methods

2.1. Materials

Hexane, dichloromethane and acetone were purchased in pesticide grade from J. T. Baker (Phillipsburg, NJ, USA). Sucralose (purity >98%, HPLC grade) was purchased from Sigma–Aldrich, Inc. (St. Louis, MO, USA). Sodium chloride (purity >99.8%, GR grade) was purchased from Sinapharm Chemical Reagent Co., Ltd (Shanghai, China). ^{13}C -labeled standards of the PCNs were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA) and ^{13}C -labeled standards of PCDD/Fs and PCBs were purchased from the Wellington Laboratories Inc. (Guelph, ON, Canada). Peanut oil and extra virgin olive oil were purchased from a supermarket in Beijing, China.

2.2. Cooking process and sampling

A schematic representation of the stainless steel system used in the current study has been provided elsewhere by Dong, Wu, Liu, Zhang, and Zheng (2011). In each experiment, 50 g of cooking oil (peanut oil or olive oil) and 5 g of sucralose or sodium chloride were poured into a stainless steel bowl. Sucralose is hydrophilic and consequently insoluble in the oil. Thus, the raw materials were mixed carefully with a glass rod to make the sucralose suspension in the oil as homogeneous as possible. The mixtures were heated on an electric stove for 15 min, reaching a temperature of 200 ± 5 °C or 245 ± 5 °C. The temperatures of the mixtures and the oil fumes generated during the heating process were recorded using a thermo sensor. An air pump, with an air flow rate of $1.5 \text{ m}^3 \text{ h}^{-1}$ was turned on during the heating process and left running for an additional 10 min during the cooling phase to trap any oil fumes. Approximately 20 g of XAD-2 resin (Supelco, Bellefonte, PA, USA) was used in each sample to absorb the oil fumes generated during the heating process. The XAD-2 resin was pre-extracted with

a solvent mixture of dichloromethane and hexane (1:1, v/v) for approximately 48 h, stored in dichloromethane, and dried under N_2 prior to use.

2.3. Chemical analysis

The tetra- to octachloro-CN congeners were analyzed by isotope dilution high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS). Prior to extraction, 1 ng of each of the ^{13}C -labeled internal standards (CN 27, 42, 52, 67, 73 and 75) was added to the samples. The oil fumes absorbed in the XAD-2 resin were Soxhlet extracted with a solvent mixture of acetone and hexane (1:1, v/v) for about 24 h. The concentrated fume extracts, as well as the oil samples taken before and after heating, were cleaned up according to the following procedures. First, a gel permeation chromatography (GPC) column, packed with Boibeads SX-3 (Bio-Rad Laboratories, Inc., Hercules, CA, USA), was used to remove the high molecular weight interfering compounds. After loading, the extracts were eluted with 160 mL of a mixture of dichloromethane and hexane (1:1, v/v). The first 60 mL of the eluent was discarded and the following 100 mL was collected and concentrated for further purification. The concentrated extracts were then subjected to a further round of purification on an acid silica gel column packed with (from bottom to top) 5 g of acidic silica gel (44%, w/w), 5 g of acidic silica gel (22%, w/w), and 1–2 cm of anhydrous sodium sulfate. The third column was a multilayer silica gel column packed with (from bottom to top) 1 g of activated silica gel, 2 g of AgNO_3 silica gel (10%, w/w), 1 g of activated silica gel, 4 g of basic silica gel (33%, w/w), 1 g of activated silica gel, 8 g of acidic silica gel (44%, w/w), and 1–2 cm of anhydrous sodium sulfate. Finally, a basic alumina column was employed to obtain the PCN fraction. Prior to injection, the concentrated extracts were spiked with a ^{13}C -labeled standard (CN 64) for quantification of recovery.

Analyses of PCNs were conducted on a gas chromatograph (GC) coupled with a DFS mass spectrometer (Thermo Fisher Scientific, Hudson, NH, USA) with a resolution of approximately 10,000 using an electron impact (EI) source (45 eV), in selected ion monitoring (SIM) mode. A DB-5 capillary column (60 m \times 0.25 mm i.d. \times 0.25 μm , J&W) was used for the separation of the PCN congeners with the following GC oven program. Following an 80 °C hold period for 2 min the temperature was increased at a rate of $20 \text{ }^\circ\text{C min}^{-1}$ to 180 °C (1 min), then at the rate of $2.5 \text{ }^\circ\text{C min}^{-1}$ to 280 °C, and finally at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to 290 °C (5 min). The injector and the interface temperatures were set to 260 and 290 °C, respectively. The carrier gas flow of helium was held at 1 mL min^{-1} . A sample size of 1 μL was injected in the split-less mode. Peaks corresponding to the individual PCN congeners were identified on the basis of their retention times relative to those of internal standards as well as on their ion ratios. Analyses of the 17 toxic PCDD/F and 12 dl-PCB congeners were carried out according to the US EPA Methods 1613 and 1668A, respectively. Sample extraction, cleanup and instrument analysis of the PCDD/Fs and dl-PCBs were conducted according to the methods of Wu, Dong, Liu, Zhang, and Zheng (2011) and Dong et al. (2011).

2.4. Quality assurance and control

All experiments were run at least in duplicate. The relative percent difference (RPD) of the concentrations of the target compounds measured for duplicate experiments was within 25%. The recoveries of the ^{13}C -labeled standards (CN 27, 42, 52, 67, 73 and 75) of the PCNs were in the range of 35–100%. In the samples of the oil fumes, the recoveries were all greater than 51%. In the oil samples, however, the recovery of CN 27 was much lower than that of the other five internal standards, which reached a value 35% as its

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