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TBHQ and peanut skin inhibit accumulation of PAHs and oxygenated PAHs in peanuts during frying

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ABSTRACT

The effects of tert-butylhydroquinone (TBHQ) and peanut skins on the concentrations of polycyclic aromatic hydrocarbons (PAHs) and oxygenated PAHs (OPAHs) in fried peanuts were investigated. Sixteen PAHs and five OPAHs were quantified using gas chromatography-mass spectrometry (GC-MS). Addition of TBHQ to the frying oil reduced the total PAH and total OPAH concentrations by up to 71.75% and 74.80%, respectively. After frying, average PAH and OPAH levels were respectively 22.63% and 79.22% lower in peanuts with skins versus those without skins. The concentration of benzo[*a*]anthracene (BaA) was significantly correlated with that of benzo[*a*]anthracene-7,12-dine (BaAQ) in the fried peanuts. These results may be helpful for production of good quality fried peanuts with a low PAH content, as well as providing guidance for reducing PAHs in other fried foods.

1. Introduction

Peanuts are a common foodstuff all over the world. Annual production was approximately 34.4 billion kg in 2014. China is the largest producer, contributing 45% of the world's peanuts (Arya, Salve, & Chauhan, 2016). Consumption of peanuts and peanut products here has reached 6.5 billion kg per year, which translates as 4.7 kg of peanuts for each Chinese citizen.

Fried peanuts, a very common peanut product, are widely consumed around the world, especially in Asian countries. The literature contains many studies on the effects of various frying parameters, such as temperature, time, frying oils and antioxidants, on the chemical stability, consumer acceptance and shelf-life of fried peanuts (Miyagi & Ogaki, 2014; Olmedo, Asensio, Nepote, Mestrallet, & Grosso, 2009). Although their unique flavor, appearance and texture make fried peanuts highly palatable and generally acceptable, harmful compounds are formed during frying. For example, acrylamide and heterocyclic aromatic amines have been detected in fried food (Jinap, Iqbal, Talib, & Hasnol, 2016; Vinci, Mestdagh & Menulenaer, 2012). PAHs have been found in non-fried peanuts and peanut oils (Wennrich, Popp, & Zeibig, 2002; Wu & Yu, 2012), but their levels in fried peanuts have not, as yet, been investigated. PAHs are well-known carcinogenic, mutagenic and tumor-promoting compounds, and they have been found in high concentrations in a number of fried foods. Perelló, Martí-Cid, Castell, Llobet, and Domingo (2009) reported that PAH concentrations in fried pork loin, potato, chicken and lamb were 21.45, 28.69, 14.96 and 16.91 μg/kg, respectively.

The oxidized products of PAHs, known as oxygenated PAHs (OPAHs), are also highly toxic, and can sometimes exceed the toxicity of the parent PAH. Studies have found that OPAHs can cause severe adverse biological effects such as allergic inflammation and disruption of vascular tone (Cheng et al., 2012). Our recent studies have revealed high OPAH concentrations in vegetable oils (Hua, Zhao, Wu, & Li, 2016) and fried dough (Li, Wu, Zeng, Wang, & Yu, 2016). These findings highlight the need for investigations into OPAH levels in other fried foods.

The concern caused by the high levels of toxic PAHs in foodstuffs has directed researchers towards interventions that reduce PAH production, ingestion or remove them from the food (Fasano,

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Yebra-Pimentel, Martínez-Carballo, & Simal-Gándara, 2016; Pérez-Gregorio, García-Falcón, Martínez-Carballo, & Simal-Gándara, 2010; Yebra-Pimentel, Fernández-González, Martínez-Carballo, & Simal-Gándara, 2014). Several studies have examined measures to reduce PAHs in the food or oil, such as adjusting cooking parameters (Rose et al., 2015), using appropriate charcoal filters (Essumang, Dodoo, & Adjei, 2014) and bleaching (Hua et al., 2016). Furthermore, the addition of spices, beer marinades and pickle sauces have all been found to inhibit PAH formation (Janoszka, 2011; Viegas, Yebra-Pimentel, Martínez-Carballo, Simal-Gandara, & Ferreira, 2014).

However, to the best of our knowledge, the effect of antioxidant additives on PAH levels in fried foods remains unknown. In the current study, we investigated the ability of the most prevalent synthetic antioxidant in edible oils, TBHQ, to inhibit PAH production during frying. We also considered the antioxidants occurring naturally in the food itself and chose the skin of the peanut as an experimental factor. The skin makes up 3.5%–4.5% of the total weight of the peanut kernel and has a high concentration of natural polyphenols (90–149 mg/g of dry skin), including flavonoids, proanthocyanidins, isoflavones and phenolic acids (Zhao, Chen, & Du, 2012). These polyphenols exhibit high antioxidant activities (Chukwumah, Walker, & Verghese, 2009). Although the peanut's red skin adds a lot of nutritional value along with various other beneficial effects, they tend to be removed during processing owing to their unpopular taste. In China, fried peanut products with and without skins are available in markets. It would be useful to know if the skin is beneficial in terms of its ability to inhibit formation of harmful PAHs.

In this study, we examined the effects of retaining the skins on peanuts and adding TBHQ into the frying oil (Soybean) on the levels of PAHs and OPAHs in fried peanuts.

2. Materials and methods

2.1. Materials and reagents

Sound, mature kernels of peanuts as cultivars of (*Arachis hypogaea* L. var. *vulgaris* Harz) Baisha 1016 (named P1) and (*Arachis hypogaea* L. var. *fatigiata*) Puxi 11 (named P2) were obtained from Haoxiong Food Co. Ltd. (Shanghai, China). Before processing, each peanut was carefully inspected and bruised or damaged kernels were discarded. To study the effect of peanut skins on the levels of PAHs and OPAHs, the peanuts were randomly divided into two groups, whole unpeeled peanuts and those with their outer skins peeled off.

Soybean oil (Liangyou Co. Ltd., Shanghai, China) was used for frying. For half the samples, TBHQ was added into the soybean oil at 60 mg/kg before frying begun.

All solvents used during extraction and chromatographic analysis in this study were of high-performance liquid chromatography (HPLC) grade. Methanol, *n*-hexane, dichloromethane, acetone and acetonitrile were obtained from CNW Technologies GmbH (Darmstadt, Germany). Water was purified with a Milli-Q water purification system (Millipore, Milford, CT, USA). Standard and stock solutions were stored at −80 °C in the dark to prevent photodegradation and volatilization. The standard PAH mixture consisted of naphthalene (Na), acenaphthylene (Ap), acenaphthene (Ac), fluorene (F), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*c,d*]pyrene (Ip), dibenzo[*a,h*]anthracene (DBahA) and benzo[*ghi*]perylene (BghiP) in 1 mL dichloromethane (AccuStandard, New Haven, CT, USA). 9-Fluorenone (9FO) and anthracene-9, 10-dione (ATQ) were bought from Dr. Ehrenstorfer Gmbh (Augsburg, Germany). Benzo[*a*]anthracene-7, 12-dione (BaAQ) was supplied by AccuStandard. Benzanthrone (BZA) and 9, 10-dihydrobenzo[*a*]pyren-7(8H)-one (BaPO) were obtained from Chiron (Trondheim, Norway). Standard stock solutions were prepared by weighing neat OPAH crystals and dissolving them in dichloromethane. Eight calibration solutions were prepared from the stock solutions and the concentration of each PAH ranged from 5 to 600 ng/mL. The calibration solutions were prepared prior to each analysis using the stock solutions kept at −20 °C. C18 solid phase extraction (SPE) cartridges (2 g, 12 mL) and Florisil SPE cartridges (1 g, 6 mL) were purchased from Supelco Inc. (Bellefonte, PA, USA).

2.2. Preparation of fried peanuts

Frying was conducted by placing peanuts in a 5.5 L electric fryer (Verly, Guangzhou, China) at 170 °C. Every 10 min, 100 g of peanuts was fried using 4 L of soybean oil for 4 min and collected every 4 h for analysis. The frying oil kept frying batches of peanuts for as long as 12 h.

2.3. Extraction and clean-up procedure

The extraction and clean-up procedure followed that in a previous study (Li, Wu, Wang, & Akoh, 2016). Fried peanuts (100 g) of were ground and then vacuum-dried (DZF-6020; Yiheng Technology Co. Ltd., Shanghai, China) at 60 °C for 2 h. Dried homogeneous samples were extracted three times with 350 mL of *n*-hexane in an ultrasound bath for 1 h. The resulting extract was evaporated nearly to dryness using a rotary evaporator (N-1100; EYELA, Japan) at 40 °C. The oil samples were then placed in a sealed glass vessel and stored in the dark at 4 °C.

For the SPE clean-up, 2.5 g of the oil sample were diluted in 10 mL of acetonitrile/acetone (3:2, v/v), then shaken for 30 s, ultrasonicated for 5 min and finally, centrifuged for 5 min at 2311 × *g*. The upper liquid was collected and evaporated under a stream of nitrogen at 35 °C. The extraction procedure was repeated three times to give a mixed residue weighing 200–800 mg. The oil residue was extracted again with 2 mL acetonitrile/acetone (3:2, v/v), agitated and centrifuged as above three more times, and the top layer was transferred to an activated ENVI-18 SPE cartridge. A 5 mL aliquot of acetonitrile/acetone (3:2, v/v) was eluted through the cartridge. All of the collected eluate was evaporated to 50 mg under nitrogen flow and the residue was then dissolved in 1 mL of *n*-hexane. The solution was then transferred to a Florisil SPE cartridge activated with dichloromethane and *n*-hexane. Another 5 mL of *n*-hexane and 5 mL of *n*-hexane/dichloromethane (95:5, v/v) were eluted through the cartridge respectively and discarded. The parent and oxygenated PAHs were then eluted using 5 mL of *n*-hexane/dichloromethane (1:2, v/v) and subjected to a nitrogen flow reduced the volume to about 1 mL. At this point, 0.5 mL of methylbenzene was added and the evaporation was continued until a final volume of 20 μL was reached. The residue was diluted with dichloromethane to give a total volume of 250 μL and the mixture was then subjected to GC-MS analysis.

2.4. GC-MS analysis of PAHs and OPAHs

Analytical detection of parent and oxygenated PAHs was performed in a gas chromatography-mass spectrometer (7890A-5975C; Agilent, Santa Clara, CA, USA). Chromatographic resolution was achieved using splitless injection (injector volume, 1 μL; injector temperature, 300 °C) with a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm; Agilent) and the carrier gas (helium,