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Effects of certain polyphenols and extracts on furans and acrylamide formation in model system, and total furans during storage

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ABSTRACT

Using a glucose–glycine and asparagine–fructose system as a Maillard reaction model, the effects of seven polyphenols and solid phase extracts of three plants on the formation of furans and acrylamide were investigated. The polyphenols and extracts were used in biscuit formulation and acrylamide formation was observed. They were used for the storage of the glycine–glucose model system at three different temperatures. The addition of some of the extracts and polyphenols significantly decreased furan formation to different extents. All phenolic compounds and plant extracts decreased in the range of 30.8–85% in the model system except for oleuropein, and all of them decreased in the range of 10.3–19.2% in biscuit. Total furan formation was inhibited by caffeic acid, punicalagin, epicatechin, ECE and PPE during storage. This study evaluated and found the inhibitory effect on the formation of furans and acrylamide in Maillard reactions by the use of some plant extracts and polyphenols.

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1. Introduction

Foodstuffs are mixtures of certain compounds such as amino acids, lipids, carbohydrates, vitamins and minerals. Complex chemical reactions occur as a result of heat treatments such as cooking, pasteurisation and sterilisation. These reactions may cause a reduction in nutritional value and the formation of toxic chemicals. The Maillard reaction, which refers to the interaction between the free amine groups of amino acids/proteins and the carbonyl group of sugars/carbohydrates has an important role in the formation of toxic compounds (Lee & Shibamoto, 2002; Martins, Jongen, & Van Boekel, 2001). Some products of the Maillard reaction, such as heterocyclic aromatic amines and acrylamide, are mutagenic/carcinogenic or neurotoxic. Also, certain melanoidins have negative effects on the structure of DNA and collagen, Alzheimer disease, diabetes and cardiovascular complications (Somoza, 2005; Zhu, Cai, Keb, & Corkea, 2009). However, some studies report the positive effects of some melanoidins: for their curing action on intestinal flora, antioxidant activity, and preservative and antimutagenic activities (Valls-Belles et al., 2004). Furthermore, at the end of the Maillard reaction the volatile aromatic compounds form specific flavor and odour components which contribute directly to the attractiveness of products. Consequently, the Maillard reaction has both desirable and undesirable effects on products (Martins et al., 2001). Hence, researchers should optimise the formation of these components.

Reactive oxygen species (ROS) are known as oxygen derived free radicals may act as initiators of degenerative events, such as the damaging of DNA and mutation, kinds of cancer, aging and heart diseases. Many plant polyphenols have been identified as potential antioxidant, antimutagenic and anticarcinogenic agents (Negi, Jayaprakasha, & Jena, 2003; Zhu et al., 2009). Moreover certain polyphenols can inhibit/reduce the formation of carcinogenic/mutagenic heterocyclic aromatic amines and potential carcinogenic/neurotoxic acrylamides (Monti et al., 2001; Napolitano, Morales, Sacchi, & Fogliano, 2008).

This study aimed to prevent the formation of acrylamide and furan compounds using previously untried phenolic compounds and plant extracts. The effects of seven polyphenols (epicatechin, chlorogenic acid, caffeic acid, oleuropein, tyrosol, ellagic acid and punicalagin) and three plants extracts (olive mill waste water (OMWW), European cranberry bush juice (ECJ) and pomegranate peel) on the formation of certain furans (furfural (F), acetylfuran (AF) and 2-furancarboxaldehyde, 5-methyl-(5-MF)) and acrylamide were investigated. For the first time in this study, solid phase extraction (SPE) was applied to OMWW and ECJ for partial purification and enrichment of their polyphenols. The effects of all polyphenols and plant extracts on total furans in the glycine–glucose model system during storage at three different temperatures were monitored.

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2. Material and methods

2.1. Reagents and materials

Oleuropein, ellagic acid, tyrosol and asparagine were obtained from ABCR GmbH & Co. Methanol, HCl, ethyl acetate, acetone, epicatechin, caffeic acid, glycine, glucose, fructose, acrylamide and chlorogenic acids were obtained from Sigma or Merck. Pectinex® ULTRA SP-L commercial enzyme preparation was obtained from Novozymes A/S. Standard punicalagin was obtained from the food research laboratory of Ege University. Adsorbent for use in medium pressure liquid chromatography (MPLC) was procured from LiChroprep RP-18 (15–25 μm). The glass column for MPLC ($4.9087\ cm^2 \times 40$ cm) was obtained from Biochemfluidics.

2.2. Apparatus

The extracts were prepared with an extraction shaker (Simsek Laborteknik, Turkey), an ultrasonic bath (Bandelin Sonorex, Germany) and a magnetic stirrer (Heidolph MR Hei-Standard, Germany). Ultra pure water was provided by Millipore-Simplicity 185-USA. Centrifugation was performed by a Hettich-Universal 320 centrifuge (Hettich, Germany).

Preparative analysis was performed on an Agilent 1100 series MPLC system using a 5 ml injection loop (Rheodyne, USA), glass column ($4.9087\ cm^2 \times 40$ cm, RP-18) and a Diode Array Detector (DAD). Chromatographic analysis was carried out on a Shimadzu (Japan) Prominence HPLC system with a C18 column (15×4.6 mm, 5 μm), a SIL-20A HT auto sampler and UV detector. Freeze drying was performed by a Labconco (USA) freeze dryer.

2.3. Purification of punicalagin

The pomegranate peel was obtained from a fruit juice processing plant located in the city of Denizli in Turkey. It was dried to constant weight at room temperature and then ground into powder. Thirty grams of the powder was put into a 100-ml flask and methanol was added up to the 100-ml level. The extraction procedure was carried out for 1 h. After filtration using Whatman 4 paper, the methanol was removed under vacuum by a rotary evaporator. Then, 15 ml distilled water was added and the solution was incubated in an ultrasonic bath for five minutes. Finally, the suspension was centrifuged at 5000 rpm for five minutes and the supernatant was filtered by using a syringe filter (0.22 μm) and separated by MPLC.

The phenolic compounds were detected at 280 nm and 360 nm by MPLC. Solvent gradients were formed by the dual pumping system by changing the ratio of solvent A [water–acetic acid (99:1, (v/v)] to solvent B (methanol). Gradient elution was performed according to the following program: Solvent B was 0% for 5 min and increased from 0% to 15% in 15 min and hold 90 min. Then, it was increased from 15% to 30% in 40 min and hold 20 min. Following, solvent B increased from 30% to 80% in 80 min. Finally, B decreased from 80% to 30% in 50 min. Hence the analysis was completed in 300 min. The flow-rate was 1.3 ml min^{-1}

The punicalagin from MPLC was analysed/confirmed by HPLC-UV. A Shimadzu Prominence LC system with a C18 column at an oven temperature of 30 °C was used for the analyses. Ultra pure water with acetic acid-1% (solvent A) and methanol (solvent B) were used as the mobile phase. Gradient elution was performed according to the following program: Solvent B was 5% for 8 min and increased from 5% to 70% in 25 min then decreased to 5% in 7 min. The analysis lasted for 45 min. Confirmation of identity was made by comparison of the retention time against the standard of punicalagin. Sample calculations were made by comparison of the peak area with that of the standard (Wennberg, Rauha, & Vuorela, 2001; Yasoubi, Barzegar, Sahari, & Azizi, 2007).

2.4. Application of Solid Phase Extraction (SPE) to olive mill waste water, pomegranate peel and European cranberry bush (Viburnum opulus L.) juice

SPE is known as on/off chromatography and has been widely used for the partial purification of polyphenols from plant extracts. In the SPE technique, depending on the characteristic of the packing material, certain groups of components are selectively isolated from a mixture. Phenolic compounds have been separated from polar compounds (sugar and organic acids) by using the SPE technique. In this context, SPE was applied to olive mill waste water, pomegranate peel and European cranberry bush (Viburnum opulus L.) juice for partial purification.

The European cranberry bush was obtained from the city of Kayseri in Turkey. The juice was obtained by mechanical pressing after applying pectinase to the pulp for depectinization at room temperature for 24 h. The mix was then centrifuged at 9000 rpm for 10 min and filtered by syringe filter (0.45 μm). Then 120 ml of filtrate was loaded, at a 2 ml min^{-1} flow rate, by syringe pump, into the column (10×200 mm) packing with RP-18 adsorbent (15–25 μm). In order to remove the organic acids and sugars, 40 ml of pure water was passed through the column at a 2 ml min^{-1} flow rate. Finally, the elution stage was performed by using 80 ml of methanol at a 2 ml min^{-1} flow rate. The collected solution was dried by rotary evaporator at 50 °C and resolved in 20 ml of methanol. To improve the precipitation of the phenolic compounds, 20 ml of acetone was added. The mix was centrifuged at 5000 rpm for 5 min. The precipitate was separated and washed in 10 ml of acetone, then centrifuged again. The resulting product was dried by using nitrogen gas and was turned into particle form.

The OMWW was obtained from an olive oil processing plant located in the city of Mersin in Turkey. OMWW was centrifuged at 9000 rpm for 10 min and frozen in a freezer at −18 °C for clarification and skimming. After that the oil on the surface was separated mechanically. All of the steps applied to European cranberry bush were carried out for the OMWW except for the depectinization procedure.

Due to the different phenolic content of pomegranate peel, the SPE technique was slightly modified. After the pomegranate peel was ground into powder, thirty grams of the powder was put into a 100-ml flask and methanol was added up to the 100-ml level. The mixture was processed in an extraction shaker for 1 h. After filtration using Whatman 4 paper, the solution was injected into the MPLC system for the reduction of sugar and organic acid concentration. Portions were collected at the beginning from the coloured output. Then, fractions were collected according to the colour and the collected fractions were concentrated by rotary evaporator and freeze-dried.

2.5. Determination of the effects of phenolic compounds and extracts on certain furan compounds formation in glycine-glucose model system

The preparation of the glycine-glucose model system was carried out according to the method of Zhu et al. (2009) with some modifications. The model systems were prepared by dissolving 3 M L-glycine (0.5 mL) and 3 M D-glucose (0.5 mL) in a phosphate buffer (0.067 M) with a pH of 6.8. Prepared powder extracts (15 mg/mL) and phenolics (0.05 M) were added to 30 mL headspace vials, and the vials were heated for 8, 15 and 60 min at 180, 140 and 100 °C respectively. After cooling, furan compounds were determined by GC–MS according to the method reported by Goldmann, Perisset, Scanlan, & Stadler (2005) and Zhu et al.

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