

Investigation of the chemical safety of microwaved popcorn in respect of acrylamide formation

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Abstract

Acrylamide, known as a toxic substance, can be formed in foods as a result of the Maillard browning reactions. The right conditions for these reactions during processing, and presence of precursors in corn kernels, leads to the uncertainty in respect of the chemical safety of popcorn. This study investigated the effect of microwave (MW) treatment of popcorn on the possibility of acrylamide formation. The instrumental determination was carried out by gas chromatography–mass spectrometry (GC–MS) using a direct injection of samples (5 µl) into the column. New scientific evidence indicating the presence of D-allose in MW popcorn were demonstrated. No acrylamide was detected in fractions of popcorn treated in MW oven for 2, 5 and 8 min. Lack of the key substance for acrylamide formation, asparagine, in the pericarp of corn kernels, was found to be the main factor of results obtained.

Keywords

Popcorn

Chemical safety

Acrylamide

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Introduction

The chemical safety of foods was defined by the Centre for Food Safety and Applied Nutrition as the absence of chemicals, ranging from intentionally used additives to unavoidable contaminants. Therefore, aspects of chemical safety of products can be divided as follows: hazardous ingredients added by unscrupulous manufacturers to improve organoleptic properties of the product; hazardous ingredients transmitted from packaging; hazardous ingredients formed through chemical reactions while processing.

A lack of scientific knowledge of the interaction between compounds in foodstuffs, as well as new scientific knowledge in respect of the effects of some additives on the human organism leads to potential risks in consuming different foodstuffs, even if produced in compliance with the HACCP-regulation and only using additives allowed by Codex Alimentarius. Products, which are credited with having potential negative effect on human health, include popcorn (Masatcioglu *et al.*, 2014). MW popcorn flavoring mixtures can include diacetyl (Lockey *et al.*, 2009; Rigler and Longo, 2010), which is credited with having several worrying properties for brain health, and lung disease (Harber *et al.*, 2006). Data about the transfer of dibutyl phthalate,

diethyl phthalate and diisobutyl phthalate from packaging into products (Sax, 2010; Bhunia *et al.*, 2013) is significant concerning popcorn sold in packages containing polyethylene terephthalate (PET). The above mentioned substances are shown to cause endocrine diseases (Sax, 2010), and found to be nephrotoxic, hepatotoxic and cardiotoxic (Singha and Li, 2011).

The process of popcorn preparation inevitably involves processing at high temperatures, which creates sufficient pressure within kernels to burst them (Byrd and Perona, 2005). That leads to the formation of Maillard reaction products, some of which are highly carcinogenic (Taylor and Linforth, 2009; Gökmen, 2015). The scientists divided the Maillard reactions between amino - acids and reducing sugars into the following stages (Nursten, 2005): Reactions of sugar-amine condensation and Amadori rearrangement; Reactions of sugar dehydration, sugar fragmentation, and amino acid degradation; and Reactions of aldol condensation, aldehyde-amine condensation, and formation of heterocyclic nitrogen compounds.

Products with yellow colour and specific flavour are formed in the second stage of the Maillard reactions (Nursten, 2005). Dark-brown pigments, melanoidins, are formed in the third stage of this

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reaction (Nursten, 2005). Among the other products of the third stage of the Maillard reactions, toxic acrylamide can be detected in foodstuffs containing asparagine and reducing sugars (Mottram *et al.*, 2002). Approximately 8% concentration of asparagine in corn kernels made acrylamide formation possible during processing (Gökmen, 2015). There is an evidence that the way the food is processed is the main factor in producing toxic products of the Maillard reactions (Zilic *et al.*, 2014). The time of MW treatment was found to be the main condition of acrylamide presence in food products (Zilic *et al.*, 2014). However, the acrylamide formation in MW popcorn has been rarely reported.

The presence of brown or black popcorn kernels in ready to eat popcorns is not allowed by food standards, and can demonstrate a violation of cooking modes. Nevertheless, there are data showing the burn element presence in ready to eat commercial samples as well as in MW popcorn (Bocharova *et al.*, 2012; Bocharova, 2014). High selectiveness and sensitivity were shown to be advantageous when using GC-MS for acrylamide determination in different foodstuffs, as demonstrated by Nemoto *et al.* (2002), Rothweiler (2003). Therefore, the main aim of this study was to investigate the possibility of acrylamide formation in MW popcorn, using GC-MS to determine acrylamide.

Material and Methods

Material and procedure of its preparation

The popcorn to be investigated was the product of 'Freshly' trademark (USA). This choice was made because popcorn originated in America, and the 'Freshly' trademark is known world-wide. Ingredients of the product include popping corn, palm oil and salt. The mentioned above popcorn in unfolded packages was placed in MW oven accordingly with MW directions on the package label. The package was exposed to full power (625 W heating power, and 2.45 MHz) for the treatment time. The treatment time was 2 min for white fraction preparation, 5 min for yellow fraction preparation, and 8 min for brown fraction preparation. These particular timing were chosen as a result of preliminary studies carried out in respect of 'colour-treatment time' correlation.

White, and yellow fractions were taken for further investigation. Dark-coloured parts of popcorn, represented mostly by the pericarp of corn kernels, were cut from the 8-min treated popcorn to prepare the brown fraction. 10 g of each milled fractions was mixed with 65 ml water-ethyl alcohol (1:1) solutions, and held at a temperature of 25°C for 30 minutes.

After filtration through the paper filters extracts were used for GC-MS investigations.

Gas chromatography-mass spectrometry (GC-MS) study procedure

The GC-MS studies were conducted at the special department of Criminal Research Centre (Ukraine). The research was carried out using electronic scale AXISANG200C and gas chromatograph Agilent 6890 N/5975 Inert GC/MS System with mass-selecting detector 5975 Inert MSD and with autosampler 7683 B AutoInjector. The samples were tested in compliance with standard procedure for detecting trace amounts of substances, as applied by Bayerman (1987). The chemically pure dichloromethane of Merck' firm was used for the extraction process. The extraction process lasted 5 minutes, and during this time the system was continually stirred. The volume of samples for extraction process was 4 ml each. The volume of dichloromethane was 2 ml. The organic layer was separated, and then dried using sodium sulphate; after that it was injected into CG-MS. Operating conditions of chromatographic mass-spectrometric complex were: open-tubular column HP-1MS, length 30 m, diameter 0.25 mm, phase 0.25 μm , flow rate 1.0 ml/min, helium carrier gas, autoinjector, split ratio was from 50:1 to splitless regime (for trace pollutant testing); vaporizing device temperature 280°C; thermostat: initial temperature 40°C, exposure time 5 minutes, heating 15°C/min, final temperature 150°C, exposure time 10 minutes; inlet pressure 6.83psi, ionization by electron impact, ionization energy 70 eV, ion source temperature 230°C, quadrupole temperature 150°C; sample volumes 5 μl ; scanning speed was 7 scans per second (weight 20-300 amu). The samples were tested for acrylamide.

Results and Discussion

Acrylamide determination

The results of the identification of white, yellow, and brown fractions of popcorn, are presented in Table 1. Acrylamide, at a level of sensitivity of the method used, was not detected in any samples (Table 1). Such results are in accordance with the reference data showing that formation of acrylamide is a function of many factors, such as a sort of raw materials, extrusion conditions, CO₂ presence (Masatcioglu *et al.*, 2014; Zilic *et al.*, 2014). The absence of acrylamide in brown fraction of popcorn can be explained by the fact that this fraction is represented mainly by the pericarp of corn kernel. Such part of corn is rich in fibres but limited in amino acids, asparagine in

Table 1. GC-MS data research of extracts of different fractions of popcorn

| Substance | Fraction of popcorn | | |
|--|---------------------|--------|-------|
| | White | Yellow | Brown |
| D-allose | + | + | + |
| 1,6-anhydro-beta-D-glucopyranose (Levoglucozan) | + | - | - |
| Guanosine | + | + | - |
| Galactose | + | - | - |
| 2-propylfuran | - | + | + |
| Pyrazole-4-carboxaldehyde | - | + | + |
| Pyrrolo [1,2-a]-pyrazine-1,4-dione | - | + | + |
| Acrylamide | - | - | - |

particular (Inglett and Munck, 2012). The absence of the factor mentioned above is significant because the pericarp constitutes up to 7% of all the grain (Taylor and Linforth, 2009). Therefore, the absence of key participants for acrylamide formation should be the most likely explanation of data obtained. Absence of acrylamide in yellow fraction should be explained by the fact that 5 min time of MW treatment was not enough for formation of acrylamide in asparagine containing part of corn kernel. Results obtained showed that MW popcorn is chemically safe in respect of acrylamide formation.

Transformation of substances in popcorn during MW treatment

Reference data demonstrated that the main elements of the pericarp of corn kernels are cellulose, and pentosans (Inglett and Munck, 2012). Data of Table 1 showed presence of products of cellulose degradation, such as levoglucosan, in the white sample, but no levoglucosane was found in other samples. Data obtained correlates well with reference data, which represented levoglucosan as the first product of cellulose degradation at high temperature (Rogovina *et al.*, 2010). This product is destroyed by further heat treatment with formation of low-molecular substances (Rogovina *et al.*, 2010).

The monosaccharides in endosperms of corn, such as glucose, fructose, galactose, ribose, and mannose, presence of which was demonstrated by the authors (Inglett and Munck, 2012), are the main sources for the first stage of the Maillard reactions. The galactose determined in the white fraction of popcorn (Table 1), was not found in coloured ones (Table 1), where products of the second and the third stages of the Maillard reactions are present. That can be explained by the complete conversion of this reducing monosaccharide in the first stage of the Maillard reactions.

Monosaccharide D-allose was first identified in all samples (Table 1). Therefore, D-allose did not take part in the Maillard reactions, which could be explained by the possibility for this aldohexose of being in its hemiacetal form. Results obtained demonstrated that D-allose can take part in formation of flavour of ready to eat popcorn. Guanosine was found in white, and yellow fractions (Table 1). This substance consists of purine base, guanine, and reducing monosaccharide, ribose. There was no guanosine found in brown fraction (Table 1). Therefore, 5 min time of MW treatment was not enough for degradation of this substance. Obtained results showed products of the Maillard reactions, such as 2-propylfuran; pyrazole-4-carboxaldehyde; pyrrolo [1,2-a]-pyrazine-1,4-dione in both yellow and brown fractions of popcorn (Table 1). These data are in accordance with possibility of pyrazines, furans, and pyrroles formation as results of the Maillard reactions in popcorn (Yu and Chi-Tang, 2012).

Conclusion

Limit in asparagine amino acid in the pericarp of corn kernels incorporated with short heating time, resulted in no acrylamide formation in MW popcorn. The effect of different methods of popcorn preparation on acrylamide formation is an ongoing investigation. Monosaccharide D-allose was first identified in MW popcorn. Results showed that D-allose did not take part in the Maillard reactions. This could be explained by this monosaccharide being in its hemiacetal form. Further study of this phenomenon is needed to improve the theory of interaction between food components during processing.

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