Chemosphere 208 (2018) 352–357

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Carcinogenic and neurotoxic risks of acrylamide consumed through caffeinated beverages among the lebanese population

Ghada El-Zakhem Naous [a], Areej Merhi [a], Martine I. Abboud [b], Mohamad Mroueh [c], Robin I. Taleb [a, *]

[a] *School of Arts and Sciences, Department of Natural Sciences, Lebanese American University, Byblos, Lebanon*
[b] *Department of Chemistry, University of Oxford, Oxford, UK*
[c] *School of Pharmacy, Department of Pharmaceutical Sciences, Lebanese American University, Byblos Lebanon*

HIGHLIGHTS

- High acrylamide levels in caffeinated beverages sold in the Lebanese market.
- Acrylamide level in caffeinated beverages is 29,176 μg/kg sample.
- Consumption of acrylamide from caffeinated products is carcinogenic and neurotoxic.
- WHO should set acrylamide levels in caffeinated products to 7000 μg/kg sample.

ARTICLE INFO

Article history:
Received 18 April 2018
Accepted 29 May 2018

Handling Editor: A. Gies

Keywords:
Caffeinated beverages
Lebanese coffee
Espresso
American coffee
Acrylamide
Carcinogenic
Neurotoxic
Gas chromatography mass spectrometry

ABSTRACT

The present study aims to quantify acrylamide in caffeinated beverages including American coffee, Lebanese coffee, espresso, instant coffee and hot chocolate, and to determine their carcinogenic and neurotoxic risks. A survey was carried for this purpose whereby 78% of the Lebanese population was found to consume at least one type of caffeinated beverages. Gas Chromatography Mass Spectrometry analysis revealed that the average acrylamide level in caffeinated beverages is 29,176 μg/kg sample. The daily consumption of acrylamide from Lebanese coffee (10.9 μg/kg-bw/day), hot chocolate (1.2 μg/kg-bw/day) and Espresso (7.4 μg/kg-bw/day) was found to be higher than the risk intake for carcinogenicity and neurotoxicity as set by World Health Organization (WHO; 0.3–2 μg/kg-bw/day) at both the mean (average consumers) and high (high consumers) dietary exposures. On the other hand, American coffee (0.37 μg/kg-bw/day) was shown to pose no carcinogenic or neurotoxic risks among the Lebanese community for consumers with a mean dietary exposure. The study shows alarming results that call for regulating the caffeinated product industry by setting legislations and standard protocols for product preparation in order to limit the acrylamide content and protect consumers. In order to avoid carcinogenic and neurotoxic risks, we propose that WHO/FAO set acrylamide levels in caffeinated beverages to 7000 μg acrylamide/kg sample, a value which is 4-folds lower than the average acrylamide levels of 29,176 μg/kg sample found in caffeinated beverages sold in the Lebanese market. Alternatively, consumers of caffeinated products, especially Lebanese coffee and espresso, would have to lower their daily consumption to 0.3–0.4 cups/day.

1. Introduction

Coffee products have been shown to possess antioxidant activity and their intake reduces the risk of development of some types of cancer, such as colon cancer (Tavani and La, 2000). This anti-cancer activity can be attributed to caffeine which is the active ingredient in such products and after which the beverage was named (Iwa et al., 2012). According to Iwa et al., chlorogenic acids included in green and roasted coffee beans possess various biological benefits such as antioxidant, radical scavenging, antimutagenic/anticarcinogenic as well as anti-inflammatory activities (Iwa et al., 2012). In addition, coffee consumption has been shown to aid the fight

* Corresponding author. Lebanese American University School of Arts and Sciences, Department of Natural Sciences Byblos, P.O Box 36. Lebanon.
E-mail address: robin.taleb@lau.edu.lb (R.I. Taleb).

https://doi.org/10.1016/j.chemosphere.2018.05.185
0045-6535/

against obesity while also limiting the effects of type II diabetes by decreasing glucose absorption (Bassoli et al., 2008). On the other hand, coffee is a main contributor to the human dietary intake of acrylamide, a chemical known to exhibit carcinogenic and neurotoxic risks (Guenther et al., 2007). In March 2018, a California judge ruled that "coffee firms must add cancer warning on their products". This verdict was based on the presence of toxic chemicals in coffee, of which only acrylamide was mentioned (CBSLA, 2018; Deabler, 2018; Turner, 2018).

Acrylamide (Fig. 1) is an odorless crystalline organic molecule that is primarily used as raw material in the production of polyacrylamide which in turn has various industrial applications. These applications include adhesives, paints and flocculants in addition to the textile and paper industries, wastewater treatment facilities, tunnels and sewers construction, electrophoresis gels and even cosmetics (Shipp et al., 2006). While polyacrylamide is not considered to be significantly toxic (Smith and Oehme, 1991), the acrylamide monomer is known to be toxic to the nervous system and fertility (Miller and Spencer, 1985; Dearfield et al., 1988). Acrylamide exerts genotoxic effects in cells through oxidative DNA damage induced by the build-up of intracellular reactive oxygen species (ROS) and the depletion of glutathione (GSH) (Jiang et al., 2007). In 1994, acrylamide was classified as "a probable human carcinogen, (Group 2A)" by the International Agency for Research on Cancer (IARC) (Anonymous, 1994). In 2002, Tareke et al. first reported the detection of acrylamide in a variety of heat-processed foods such as potato crisps, French fries, bread and hamburgers (Tareke et al., 2002). Few years later, reports claimed that acrylamide is also present in other food (especially plant derived foods) and beverages, such as biscuits, cereals, wafers, coffee, almonds, olives, potatoes, sweet potatoes, and baby food (Mizukami et al., 2006; Medeiros Vinci et al., 2012; Friedman, 2015). Acrylamide is a byproduct in industrially-prepared food/beverages which is formed as a result of the Maillard reaction of asparagine with reducing sugars, such as glucose, galactose, and fructose, at high temperatures (Mottram et al., 2002; Robert et al., 2004). The formation of acrylamide begins at a temperature exceeding 120 °C and reaches its peak at around 170 °C (Mottram et al., 2002). One way by which acrylamide levels in food products can be lowered is by utilizing industrial procedures that convert asparagine into aspartic acid and in the process lowering the rate of the Maillard reaction (Mottram et al., 2002; Akillioglu, 2014).

The World Health Organization (WHO) has set guideline values for acrylamide content in tap water, yet no country has set any regulations regarding acrylamide content in food and beverages (Narita and Inouye, 2014). A recent study carried out in our laboratories revealed a high acrylamide content in local and imported potato-based and corn-based chips (Hariri et al., 2015). In addition to the high consumption of chips, the Lebanese community has a unique attachment to caffeinated beverages (Melki, 2016).

The present study aims to determine the carcinogenic and neurotoxic risks associated with the daily consumption of acrylamide from local and imported caffeinated beverages that include Lebanese coffee, American coffee, espresso and hot chocolate. In line with this target, we aim to propose to the World Health Organization guideline values for acrylamide levels in caffeinated beverages.

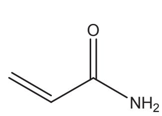

Fig. 1. Structure of acrylamide.

2. Materials and methods

2.1. Acrylamide analysis

Local and imported brands of ground coffee, coffee beans and hot chocolate were collected randomly from various locations across Lebanon (Byblos and Beirut) as duplicates with different production dates. Samples (56) were classified as follows: Lebanese coffee ($n = 19$), American coffee ($n = 5$), espresso ($n = 5$), instant coffee ($n = 10$) and hot chocolate ($n = 17$).

2.1.1. Chemicals and reagents

Chemicals and reagents used in this study were of analytical grade. Acrylamide (standard grade), n-hexane (95%), dichloromethane (DCM, LC-MS grade), propan-1-ol (99%) and acetonitrile (LC-MS grade) were purchased from Sigma–Aldrich, Germany. Distilled water was prepared using a Millipore system.

2.1.2. GC-MS analysis

Acrylamide was extracted according to the method proposed by Biedermann (Biedermann et al., 2002). A sample of solid hot chocolate or coffee (0.5 g) was mixed with water (5 mL) and heated at 70° C for 30 min. The homogenate was mixed with propanol (10 mL) and centrifuged for 10 min at 2200 rpm and 20° C (for Lebanese coffee, the homogenate was extracted with 2 mL of DCM prior to the addition of propanol). The supernatant was concentrated under reduced pressure. Acetonitrile (2 mL) and hexane (5 mL) were added and the mixture was sonicated for 3 min. The acetonitrile layer was re-extracted with hexane (5 mL), filtered using a C18-SPE cartridge and analyzed on a Gas Chromatogram Mass Spectrometer (GC-MS; Hewlett Packard, HP6890 series) fitted with a fused silica HP5-MS 5% phenyl methyl siloxane cap column; $30.0 \text{ m} \times 250.00 \mu\text{m}$ i.d., film thickness 0.25 μm; and directly coupled to the MS. The carrier gas was helium with splitless injection and the flow rate of 1.2 mL/min was applied. The temperature program was 15.0 min at 75 °C, from 75 °C to 230 °C at 10 °C/min and hold for 45.0 min. An HP5973 mass selective detector was used in full scan electron ionization (EI) mode. Identification of acrylamide was achieved by comparing mass spectral data against the NIST11 and Wiley9 MS databases along with selective ion monitoring of the molecular ion at an m/z of 71 and a daughter fragment at an m/z of 55. The concentration of acrylamide (μg/kg coffee) was determined by comparing experimental results against a calibration curve obtained from standard acrylamide solutions prepared in the range of 50–500 mg/L. The limit of quantitation (LOQ) was found to be 5.0 μg/L while the limit of detection (LOD) was found to be 0.5 μg/L. Acrylamide recovery was 92% which is higher than the reported average of 70–80% (Biedermann et al., 2002). The precision and accuracy of the GC method was validated using the Biedermann method by analyzing a 5 g crushed biscuit sample (powder) spiked with 50 mg of standard acrylamide (Biedermann et al., 2002).

2.2. Community survey

A survey targeting the Lebanese population (children, teenagers, young adults and adults) was conducted across south, central and north Lebanon to determine the consumption of hot caffeinated beverages nationwide. Data were collected from 918 subjects from December 2016 to January 2017. Subjects were interviewed about body weight, type of caffeinated beverage, brand, and daily recall consumption. Below is the URL link to the survey conducted:

https://docs.google.com/forms/d/e/1FAIpQLSc4KSm1rtnGbJD47M5q_-P_Mq-lf82akrQK-w5BDe7j0nfekA/viewform#start=openform