Food Chemistry 138 (2013) 644–649

Contents lists available at SciVerse ScienceDirect

Food Chemistry

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

Reduction of acrylamide formation by vanadium salt in potato French fries and chips

Diganta Kalita, Sastry S. Jayanty *

San Luis Valley Research Center, Department of Horticulture and Landscape Architecture, Colorado State University, 0249 East County Road 9N Center, CO 81125, USA

ARTICLE INFO

Article history:
Received 22 June 2012
Received in revised form 29 August 2012
Accepted 25 September 2012
Available online 10 November 2012

Keywords:
Vanadyl sulphate
Acrylamide
Potato
French fries
Chips

ABSTRACT

The effects of vanadyl sulphate on the formation of acrylamide have been studied in fried potato products, such as French fries and chips. Acrylamide formation was inhibited by 30.3%, 53.3% and 89.3% when the sliced potato strips were soaked in 0.001, 0.01 and 0.1 M vanadyl sulphate ($VOSO_4$) solutions, respectively, for 60 min before frying. Moreover, 57.7%, 71.4% and 92.5% inhibition of acrylamide formation was observed when chips were soaked in the respective vanadyl sulphate solution before frying. In a separate model reaction, a solution containing an equimolar concentration of L-asparagine and D-glucose showed a significant inhibition of acrylamide formation when heated at 150 °C for 30 min in the presence of vanadyl sulphate ($VOSO_4$). The results indicate that the binding of VO^{2+} to asparagine and the decrease in the pH of the potato samples resulted in a significant reduction of acrylamide formation in fried potato products.

1. Introduction

The detection of acrylamide in carbohydrate-rich cooked food (Swedish National Food Administration, 2002) has led to considerable attention worldwide because acrylamide is known to be a neurotoxin and genotoxin (Calleman, Bergmark, Stern, & Costa, 1993). Acrylamide is also classified as a "probable carcinogen to humans" (Group 2A) (IARC, 1994). Since the discovery of acrylamide in such commonly consumed foods (Tareke, Rydberg, Karlsson, Eriksson, & Törnqvist, 2002), several studies have reported on understanding the formation and mitigation of acrylamide in processed foods (Friedman, 2003; Friedman & Levin, 2008; Medeiros Vinci, Mestdagh, & De Meulenaer, 2012; Zhang, Ren, & Zhang, 2009). It is well established that acrylamide is formed via the Maillard reaction when asparagine and reducing sugars are heated at high temperature (Stadler & Scholz, 2004; Stadler et al., 2002). Potatoes have considerable amounts of these precursors and therefore, fried potato products, such as French fries and chips, have been found to contain high levels of acrylamide (Lineback, Coughlin, & Stadler, 2012; Medeiros Vinci et al., 2012). The potato is one of the most important vegetable with respect to its value of production and nutritional impact. Coloured potatoes, which are called specialties, are rich in antioxidants (Perla, Holm, & Jayanty, 2012a). Previous reports from our research team identified number of potato cultivars that are rich in selenium (Perla, Holm, & Jayanty, 2012b).

Acrylamide formation depends upon many factors, such as the amount of reducing sugars and free asparagine, the cooking process, including the temperature and the time, the pH and the surface-to-volume ratio of the food materials (Friedman, 2003; Rydberg et al., 2003). Taking these factors into account, several effective measures have been suggested to reduce acrylamide levels in food materials; these include the modification of the raw materials (Rommens, Yan, Swords, Richael, & Ye, 2008), the optimization of heat processing parameters, the addition of various compounds, including pH modifiers (Kita, Brathen, Knutsen, & Wicklund, 2004), and blanching with proteins or amino acids (Mestdagh et al., 2008). Decreasing the pH has been suggested as a way to reduce the amount of acrylamide in processed food (Jung, Choi, & Ju, 2003). Pretreatment with citric acid and some organic acids decreased the pH of processed food and were reported to be effective agents in reducing acrylamide levels (Jung et al., 2003; Kita et al., 2004). Recent studies indicate that metal cations, including mono-, di- and trivalent cations, efficiently reduce acrylamide formation in a solution of asparagine–glucose and in some other food model systems, including potato and wheat (Gökmen & Şenyuva, 2007a; Kolek, Šimko, & Simon, 2006).

Within the series of metal cations, VO^{2+}, a dicationic form of vanadium, is biologically and pharmaceutically important (Nechay et al., 1986). $VOSO_4$, which contains the VO^{2+} dication, is a potent antidiabetic agent and is used as a nutritional supplement (Verma, Cam, & McNeill, 1998). The therapeutic value of inorganic vanadium as an orally active agent against diabetes has been well documented. Vanadium is also available in various foods such as mushrooms, shellfish, black pepper, parsley, dill weed, beer, wine, grain and grain products, and artificially sweetened drinks (Manna,

* Corresponding author. Tel.: +1 7194809042; fax: +1 7197542619.
E-mail addresses: diganta.kalita@colostate.edu (D. Kalita), sastry.jayanty@colostate.edu (S.S. Jayanty).

0308-8146/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodchem.2012.09.123

Das, Chatterjee, Janarthan, & Chatterjee, 2011). The combination of vanadium with other food supplements has been developed to have potent antidiabetic and anticancer activity (Manna et al., 2011; Mukherjee, Pessoa, Kumar, & Sarkar, 2011; Refat & El-Shazly, 2010).

Although significant work has been performed investigating the role of metal salts in reducing acrylamide formation, there are no reports on the effect of vanadium salt in reducing the amount of acrylamide in processed food. In this paper, we report the possible inhibitory effect of $VOSO_4$ on the formation of acrylamide in an aqueous model system (asparagine and glucose) and a food model system (French fries and potato chips).

2. Materials and methods

2.1. Chemicals and materials

L-Asparagine, D-glucose, acrylamide, bromine, hydrobromic acid, potassium bromide, sodium sulphate, $VOSO_4$, and $^{13}C_3$-acrylamide (99% purity) were purchased from Sigma–Aldrich (St. Louis, USA). All other chemicals were of analytical grade.

Electronic scanning absorption spectra (450–900 nm) were obtained with a UV–Visible spectrophotometer (DU® Series 700, Beckman Coulter, Inc., Fullerton, CA) using a 1 cm quartz cuvette. To estimate the concentration of asparagine and sugars, absorbances were recorded at 340 and 570 nm respectively in a plate reader (Power Wave XS2, BioTek instruments, Winooski, VT) using a flat bottom 96-well plate (Costar, Corning, NY). Rio Grande Russet tubers were harvested in September 2011 from San Luis Valley Research Center, Colorado, USA and maintained at 7.2 °C with a high relative humidity. Samples were prepared after 2 months of storage.

2.2. Acrylamide formation in the aqueous model reaction

In the aqueous model reaction, mixtures of solutions were prepared containing 12 mM of asparagine and 12 mM of glucose in 3 ml of distilled water and transferred to a 10 ml glass vial with a screw cap having a Teflon® septum. To each mixture, aliquots of $VOSO_4$ were added to a final concentration of 1, 3 and 6 mM $VOSO_4$, respectively, and vials were closed tightly and wrapped with Teflon® tape. The glass vials containing the reaction mixtures were heated at 150 °C for 30 min in a commercial oven after the oven had reached the desired temperature. Each reaction mixture was immediately cooled in an ice bath and then prepared for further acrylamide analysis.

2.3. Acrylamide formation in the potato model reaction

Two grams of raw potato powder, collected from 5 tubers, that were ground earlier after flash freezing in liquid nitrogen, was mixed with 3 ml of distilled water and homogenised for 5 min, and the pH was adjusted to 4.0, 5.0, 6.0 and 7.0 with 1 N HCl or 1 N NaOH. The glass vials were tightly closed, wrapped with Teflon® tape, heated at 150 °C for 30 min and then cooled immediately by placing them in an ice bath. In addition, the acrylamide content was estimated in each sample using gas chromatography–mass spectrometry (GC–MS) as described in Section 2.5.

2.4. Preparation of potato strips and slices for frying

Ten stored tubers were washed under running tap water and dried with paper towels. Five tubers were used to prepare French strips and five were used to make chip slices. The French strips and chip slices were made by a Dito Dean Food Prep French cutter (TR23, USA) using a C10 and FS10 blade. French strips and chip slices were divided into five sets. One set was used as a control without any treatments prior to frying. The remaining four sets were soaked in water or solutions of $VOSO_4$ and calcium chloride ($CaCl_2$) at three different concentrations: 0.001, 0.01 and 0.1 M. After 60 min of soaking at room temperature, potato strips or chip slices were removed from the solutions, dried at room temperature for 30 min and then fried in a 2 L capacity fryer (APW Wyott, Cheyenne, Wyoming) at 180 °C for 2 min in canola oil. The fried potato strips and chips were flash frozen in liquid nitrogen, ground to a fine powder using a mortar and pestle and stored at −80 °C until further analysis.

2.4.1. Extraction of acrylamide and sample preparation for GC–MS analysis

The samples were prepared according to the method described by Ono et al. (2003) in which the analyte was detected as a dibromo derivative (2,3-dibromopropionamide) by GC–MS with some modifications. Two grams of ground French fries and chips were weighed in a 50 ml polypropylene tube (Corning, NY). To this, 20 ml of water and 10 μl of $^{13}C_3$-acrylamide (1 mg/ml), as an internal standard, were added and vortexed at high speed for 2 min. The mixtures were then homogenised (Omni International homogenizer, Kennesaw, GA, USA) using an Omni Tip™ plastic generator probe at high speed for 5 min. The samples were defatted by adding 25 ml of hexane and vortexed for 5 min at high speed followed by centrifugation at 15,000 rpm for 30 min. A 5 ml aliquot of the aqueous phase was transferred to a 20 ml glass vial and stored on ice. The bromination reaction was performed by adding 200 μl of brominating reagent (KBr, 15.2 g; HBr, 0.8 ml; bromine water, 5 ml; water, 60 ml) to the sample glass vials on ice and storing them at 4 °C overnight. After bromination was complete, excess bromine was titrated by adding sodium thiosulphate solution (1 mol/L) until the reaction mixture became colourless. The reaction mixture was extracted by adding 10 ml of ethyl acetate and dried over sodium sulphate for 20 min. The ethyl acetate extract was reduced to approximately 2 ml under a stream of nitrogen gas (Reacti-Vap 18780, Pierce Chemical Company, Rockford, IL) and then filtered through a 0.45 μm nylon filter (Chromatography Research Supplies, Inc., USA). Finally, the sample was concentrated, and the volume was adjusted to 200 μl from which 1 μl was injected into a GC–MS instrument.

2.4.2. Analysis of acrylamide by GC–MS

The quantification of acrylamide was performed using a Varian Saturn 2000 GC–MS system equipped with a split–splitless mode injector and coupled to a mass selective detector. The chromatographic separations were performed using a capillary column, CP-Sil 24 CB (Agilent Technologies, Inc.), with the dimensions of 30 m × 0.25 mm and a 0.39 μm film thickness. The temperature regime of the column was the following: 50 °C for 1 min, 100 °C/min for 2 min followed by a 0.5 °C/min temperature gradient for 10 min and 100 °C/min until a final temperature of 235 °C was reached. The carrier gas was helium with a flow rate of 1.0 ml/min. The temperature of the injector was 250 °C in the splitless mode. Data acquisition was performed by using a selective ion monitoring (SIM) mode with positive electron impact ionisation. The qualitative analysis of acrylamide was conducted based on retention times and the specific ions of 2,3-dibromopropenamide at 150 and 152 m/z derived from acrylamide. Two other ions (153 and 155 m/z) were used to characterise those ions derived from isotopically marked [1,2,3-$^{13}C_3$]-acrylamide, used as an internal standard. Quantitative analyses were performed using a 6 point standard curve for acrylamide concentration ranging from 50 to 2000 ng/ml with an R^2 value of 0.9963 by considering the peak areas of 150 and 153 m/z.