Food Control 84 (2018) 478–484

Contents lists available at ScienceDirect

Food Control

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

Effect of organic acid ingredients in marinades containing different types of sugar on the formation of heterocyclic amines in grilled chicken

S. Jinap [a, b, *], N.D.S. Hasnol [a], M. Sanny [a], M.H.A. Jahurul [c]

[a] Department of Food Science, Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
[b] Food Safety and Food Integrity (FOSFI), Institute of Tropical Agriculture and Food Security, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
[c] Faculty of Food Science and Nutrition, Universiti Malaysia Sabah, 884000 Kota Kinabalu, Sabah, Malaysia

ARTICLE INFO

Article history:
Received 12 May 2017
Received in revised form
6 August 2017
Accepted 20 August 2017
Available online 22 August 2017

Keywords:
Heterocyclic amines
Lemon
Tamarind
Calamansi
Marinated grilled chicken

ABSTRACT

The aim of the study was to determine the use of alternative organic acids in formulating marinade ingredients to reduce heterocyclic amines (HCA) in grilled chicken (satay). Samples were marinated with table sugar, brown sugar, and honey with the addition of tamarind, lemon, lime, and calamansi for 24 h at 4 °C. The pH readings before and after marinating were measured. HCA concentrations before and after grilling were quantified. There was a significant difference ($p<0.05$) in the combined HCAs among the control and marinated grilled chickens. Using lemon in marinades containing table sugar, concentrations of DiMeIQx were significantly reduced ($p < 0.006$) from 16.5 ng/g (low) to 8.30 ng/g for (high) concentrations of organic acid ingredients. The mean pH of the treated samples was significantly lower ($p<0.05$) than in the control samples. Calamansi was found to reduce HCAs in marinades containing table sugar and brown sugar, whereas tamarind in marinades containing honey.

1. Introduction

The International Agency for Research Cancer (IARC) has categorized five heterocyclic amines (HCAs), i.e., IQ (2-amino-3 methylimidazo[4,5-f]-quinoline), MeIQ (2-Amino-3,4-dimethyl-3H-imidazo[4,5-f]-quinoline), MeIQx (2-amino-3,8-dimethlimidazo [4,5-f]-quinoxaline), DiMeiQx (2-Amino-3,4,8-trimethyl-3H-imidazo[4,5-f]-quinoxaline), and PhIP (2-Amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine), as probable human carcinogens (class 2A) (IARC, 1993). HCAs are formed in a complex series of reactions that involves free amino acids, reducing sugars, and creatine through a Maillard reaction (Chiu, Yang, & Chen, 1998). The formation of HCAs has been reported in cooked food, especially in broiled and grilled meat as well as fish dishes (Felton, Fultz, Dolbeare, & Knize, 1994). Grilled meat is a popular dish around the world, and these dishes are normally marinated before being grilled (Lu, Kuhnle, & Cheng, 2017; Viegas, Novo, Pinto, Pinho, & Ferreira, 2012). Marinades can act as a barrier to avoid the direct contact of flame with the meat (Emamgholizadeh, 1993), and substantial reductions in the concentrations of MeIQ, PhIP, DiMeIQx, IQ, IQx, and Norharman were reported in grilled chicken, grilled beef, and deep fried lamb meat marinated with honey and local spices (Hasnol, Jinap, & Sanny, 2014; Jinap, Iqbal, & Selvam, 2015; Jinap, Iqbal, Talib, & Hasnol, 2016).

HCA are formed on the surface of meat products through the Maillard reaction due to heat treatment, which involves free amino acids, creatinine, and reducing sugars (glucose and fructose, directly or via hydrolysis of sucrose) as precursors (Hwang & Ngadi, 2002; Hasnol et al., 2014). Our previous study has established relationships between different types of sugar (i.e., table sugar, brown sugar, and honey) in marinades on the formation of HCAs in grilled chicken (Hasnol et al., 2014). However, in addition to different types of sugars, acidic conditions significantly influence the mechanism of HCA formation (Alaejos & Afonso, 2011; Oz & Cakmak, 2016). Amino acids and carbonyl groups are crucial participants in the formation of HCAs by the Amadori rearrangement and the final Strecker degradation mechanism of the Maillard reaction (Skog, Johansson, & Jägerstad, 1998). It is generally known that a Schiff base formation is the initial reaction step in the Strecker

* Corresponding author. Department of Food Science, Faculty of Food Science and Technology, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia.
E-mail addresses: jinap@upm.edu.my, sjinap@gmail.com (S. Jinap).

http://dx.doi.org/10.1016/j.foodcont.2017.08.025
0956-7135/

degradation reaction (Turesky, 2007). The formation of the Schiff base is influenced by pH because at low pH values, the amino group of an amino acid is nearly completely protonated and no reaction with carbonyl groups takes place (Ables, 2006; Farhadian, Jinap, Hanifah, & Zaidul, 2011). The conversion from a free non-protonated amine to a protonated amine is easily obtained by lowering the pH of the system. However, a reduction in HCA formation by lowering the pH of a food system has not been reported in the literature.

Giarratana et al. (2016) reported that the essential oil such as limonene improved food quality of fish fillets. In another study, Giarratana et al. (2015) evaluated the activity of limonene and suggested its potential use in the industrial marinating process. Organic acids such as citric acid are mostly found in lemons and limes (Hiu, Jozsef Barta, & Pilar Cano, 2006). Salmon et al. (1997) reported that grilled chicken marinated with lemon juice as one of the ingredients decreased PhIP concentration by 92–99%. To the best of our knowledge, studies on HCA reduction using organic acidic ingredients have rarely been published in the literature. In addition to lemon, this study has explored other sources of citric acid such as lime and calamansi, as well as tamarind as a source of tartaric acid. The objective of the present study was to determine the effect of different concentrations of four different types of organic acidic ingredients in marinades containing different types of sugar on the formation of HCAs in grilled chicken. Four different types of organic acidic ingredients (i.e., tamarind, lemon, lime, and calamansi) and three different types of sugars (i.e., table sugar, brown sugar, and honey) were used. Three levels of concentration of organic acidic ingredients (i.e., low, medium and high concentrations) were prepared. The HCA concentrations of grilled chicken (control and treatment) samples were determined. Control samples were grilled without the addition of organic acidic ingredients, and treatment samples were marinated with three different concentrations of organic acidic ingredients.

2. Materials and methods

2.1. Preparation of chicken marinades

Raw chicken breasts were purchased from the local wholesale market at Selangor, Malaysia and stored at −20 °C until used. Onion (fresh), table sugar, brown sugar, lemongrass (fresh), salt, turmeric powder, cooking oil and organic acid ingredients, i.e., tamarind, lemon, lime, and calamansi, were purchased from a wholesale market (Sri Kembangan, Selangor, Malaysia), and pure honey *(Koompassia excelsa)* was purchased directly from an established honey farm in Bukit Katil, Melaka, Malaysia. The purchased table sugar, brown sugar, and honey were used as is to reflect the common cooking practice of marinating grilled chicken.

The marinade formulations containing table sugar, brown sugar and honey, and organic acid (i.e., tamarind, lemon, lime, and calamansi) were prepared the next day. The amounts of other ingredients, onion (fresh), lemongrass (fresh), salt, turmeric powder, and cooking oil, were the same for all three marinades. The marinade recipe was obtained from a qualified chef from the Department of Food Service and Management, Faculty of Food Science and Technology, Universiti Putra Malaysia, Malaysia. Organic acid was extracted from four different sources, i.e., tamarind, lemon, lime and calamansi. Semi-ripened fruit, which contain citric acid and tartaric acid, were chosen. For the tamarind marinade, the fruit was boiled for 15 min and the juice was manually extracted and filtered. For lemon, lime and calamansi, their juices were extracted using a juice extractor and then filtered. The total acidity of each organic acid was first determined using the method described by (Darias-Martín, Socas-Hernández, Díaz-Romero, & Díaz-Díaz, 2003). Next, the relative sourness of each organic acid was determined using tamarind as a reference. Three levels of concentrations of organic acids (i.e., low, medium and high concentrations) were prepared using the method described by (Shin, Rodgers, Gomaa, Strasburg, & Gray, 2002). The formulation of each organic acid ingredient is shown in Fig. 1.

The frozen raw chicken breasts were thawed at 4 °C for six hours and then cut into small cubes (1 cm × 1 cm dimension). For every 100 g of chicken breast cubes, the following basic ingredients were used: fresh onion (15 g), fresh lemongrass (10 g), turmeric powder (5 g), salt (1 g), and cooking oil (1 ml). The weights of the three sugars, i.e., 10.0 g for table sugar, 10.3 g for brown sugar, and 14.7 g for honey, were added individually into the standard recipe. In addition, the amount of each acidic ingredient described in Fig. 1 was also added individually into the standard recipe. All of the ingredients were mixed for 3 min at speed no. 2 using a Waring blender (model MX337, Panasonic Corp, Osaka, Japan), and the marinade was then thoroughly mixed into the chicken breast cubes. The marinated chicken cubes were then skewered onto bamboo skewers (4 pieces/skewer) and kept in sealed polyethene bags (4 skewers per bag) at 4 °C for 24 h.

2.2. Grilling condition

For each marinade, 100 g of chicken cubes skewered onto bamboo skewers (4 pieces/skewer) were grilled for 4 min per side (total duration for both sides was 8 min), using an electric grill (model R-360J(S), Sharp Electronic Corp., New Jersey, USA), in which the temperature was set at 300 °C. The internal temperature of the chicken breast was measured during grilling at 0, 4 and 8 min using a thermocouple thermometer (A type-K, Fluke Corporation, Everett, USA). Chicken cubes marinated with each type of sugar (control samples) were also treated identically to the treatment samples, except that their marinades did not contain the organic acid ingredients. All samples were prepared separately in triplicate.

2.3. Analysis method

2.3.1. pH determination

The pH of the marinated chicken cubes was determined after 24 h of marinating (before grilling). The pH was measured according to the method of Jang et al. (2008). Five grams of fine ground sample was added to 45 mL of distilled water and blended for 30 s at medium speed using a Waring blender (Panasonic, MX-798S, Selangor, Malaysia). The pH of each sample was then measured using a portable pH meter (Mettler Toledo GmbH, Schwerzenbach, Switzerland). The pH value was calculated through the average of three measurements for each sample.

2.4. Analysis of heterocyclic amines

2.4.1. Chemicals and reagents

Nine HCA standards, 2-amino-3-methyl-3H-imidazo[4,5-F] quinoline (IQ), 2-amino-3-methyl-3H-imidazo[4,5-f]quinoxaline (IQx), 2-amino-3,4-dimethyl-3H-imidazo[4,5-f]quinoline (MeIQ), 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline (MeIQx), 2-amino-3,4,8-trimethyl-3H-imidazo[4,5-f]quinoxaline (4,8-DiMeIQx), 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP), 2-amino-9H-pyrido[2,3-*b*]indole (AαC), 1-methyl-9H-pyrido-[4,3-*b*]indole (Harman), and 9H-pyrido-[4,3-*b*]indole (Norharman), were obtained from Toronto Research Chemicals (Ontario, Canada). Acetonitrile, ethyl acetate, hydrochloric acid, methanol, sodium hydroxide, acetic acid, ammonium acetate and ammonium hydroxide (25%) were purchased from Merck (Darmstadt, Germany). All chemicals were of HPLC grade. Ultra-pure water was