Journal of Food Engineering 171 (2016) 200–207

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Effect of thermal treatment on phenolic compounds from plum (*prunus domestica*) extracts – A kinetic study

Mihaela Turturică [1, 2], Nicoleta Stănciuc [1, 2], Gabriela Bahrim [1], Gabriela Râpeanu [*, 1]

Dunărea de Jos University of Galati, Faculty of Food Science and Engineering, Domnească Street 111, 800201, Galati, Romania

ARTICLE INFO

Article history:
Received 27 February 2015
Received in revised form
9 October 2015
Accepted 21 October 2015
Available online 23 October 2015

Keywords:
Plum
Polyphenols
Anthocyanins
Thermal treatment
Fluorescence
Degradation kinetics

ABSTRACT

The effect of thermal treatment on the degradation of the polyphenolic compounds in plum extract was investigated in the range of 70–110 °C by means of fluorescence spectroscopy and spectrophotometric techniques. The fluorescence results suggested that plum extract represents a multicomponent system with different fluorescence species. The heating of plum extract resulted in structural changes that led to a significant decrease in fluorescence intensity at higher temperature when the solutions were excited at 300 nm, whereas, when excited at 410 nm, significant increase in fluorescence intensity was measured in the temperature range of 70 and 110 °C. Degradation rate constants were estimated using a first order kinetic model. Temperature dependence of the degradation rate constants were expressed according to the Arrhenius model. The total monomeric anthocyanins showed the highest degradation in comparison to other polyphenols, as well as to antioxidant activity.

1. Introduction

Nowadays consumers are demanding high quality, safe products with fresh appearance, that are minimum processed and have a natural flavor and taste (Oey et al., 2004). The bioactive compounds present in fresh fruits play an important role in health-promoting activity (Hannum, 2004). An increasing consumption of fruits has been associated with reduced prevalence of degenerative diseases, like cardiovascular diseases or cancer, due to their antioxidant activity (Schreiner and Huyskens-Keil, 2006).

Plum is a rich source of carbohydrates (i.e. glucose, fructose, sucrose), as well as fibers, tannins, enzymes, minerals and vitamins, potassium, phosphorus, calcium and magnesium (Ertekina et al., 2006). Owing to the high content in phytochemicals, such as flavonoids, phenols, anthocyanins and others, plum has a significant antioxidant capacity and may protect cells against the oxidative damage caused by free radicals (Chun et al., 2003). Plum consumption is useful to treat blood circulation disorder, measles, digestive disorder (Li, 2008), as well as to prevent cancer, diabetes, and obesity. Epidemiologic studies suggest that the consumption of anthocyanins lowers the risk of cardiovascular disease, diabetes, arthritis and cancer, because of their antioxidant and anti-inflammatory activities (Wang and Stoner, 2008). Anthocyanins are polyphenolic pigments belonging to a large group of plant secondary metabolites, known as flavonoids. Their color is pH-dependent, being red at pH below 2.0 and changing to blue for neutral pH and finally colorless as the pH increases (Clifford, 2000). Their concentration is mainly influenced by the distribution of various anthocyanins in the skin (Gao and Mazza, 1995), as well as by other factors, such as light, temperature, etc. (Lancaster et al., 1997). The main anthocyanins found in plum are cyanidin 3-xyloside, cyanidin 3-glucoside, cyanidin 3-rutinoside, peonidin 3-glucoside, and peonidin 3-rutinoside (Blažek, 2007; Usenik et al., 2008).

Many foods which contain polyphenols are thermally processed prior to consumption, which greatly influence the anthocyanin content in the final product (Giusti and Wrolstad, 2001). However, a thermal processing method is necessary to extend the shelf-life of the fruit-based products (Dewanto et al., 2002). Thermal processing involves temperatures from 50 to 150 °C, depending upon the pH of the product and desired shelf life, and imply short heating prior to further processing in order to enhance both quality and safety attributes (Abu-Ghannam and Jaiwal, 2015). Therefore, heating has

* Corresponding author. Dunărea de Jos University of Galati, Faculty of Food Science and Engineering, Domnească Street 111, Building E, Room 202, 800201, Galati, Romania.
E-mail address: Gabriela.Rapeanu@ugal.ro (G. Râpeanu).
[1] www.sia.ugal.ro, www.bioaliment.ugal.ro.
[2] Both authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jfoodeng.2015.10.024
0260-8774/

several benefits, such as inactivation of surface microflora, enhancement of the color and texture, inactivation of some quality and nutritional related enzymes (Jaiswal et al., 2012).

Chemical stability of anthocyanins is the principal subject of many recent studies due to their many potential applications, their beneficial effects and their use as alternative to artificial colorants in foods. It would appear from these studies that the stability of anthocyanins is a function of the processing temperature but is also influenced by the properties of the resulted product and also due to the entire process parameters such as: pH, storage temperature, chemical structure and concentration of anthocyanins, light, oxygen, enzymes, metallic ions, etc. (Rein, 2005). Thus, the time–temperature combinations, the type of vegetables and the maintenance of the enzyme activity after treatment may negatively influence the functionality of the phenolic compounds by destruction of phenolic acids and anthocyanins (García-Parra et al., 2014). In addition, thermal degradation of anthocyanins adversely affects the color of vegetables, an attribute particularly appreciated by consumers.

It has been suggested that fluorescence investigations, apart from the standard methods of visible absorption spectroscopy, may extend the possibilities of analysis and registration of the changes of anthocyanins (Drabent et al., 1999). However, to our knowledge this method has not been used to estimate the thermal degradation of anthocyanins in plant foods. Therefore, the purpose of the present study was to investigate the effect of thermal treatment at temperatures ranging from 70 to 110 °C on plum extracts in buffer solutions by using fluorescence spectroscopy techniques. The kinetics of the thermal degradation of the total phenolic content (TPC), total anthocyanin content (TAC), total flavonoid content (TFC), and antioxidant activity were also evaluated and described by using the biphasic model.

2. Materials and methods

2.1. Chemicals

2,2-Diphenyl-1-picrylhydrazyl (DPPH), 6-Hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox), Folin–Ciocalteu reagent, sodium carbonate, sodium hydroxide, sodium acetate, sodium nitrite, potassium chloride, aluminum chloride, gallic acid, potassium persulfate, formic acid, ethanol and methanol (HPLC grade) were obtained from Sigma Aldrich Steinheim, Germany. Cyanidin and pelargonidin standards were obtained from Extrasynthèse (Z.I Lyon Nord, France).

2.2. Plum fruits

Plums (*Prunus domestica* var. *Vanette*) were purchased from the local market (Galați) in the months of June and July of the year 2014. Plum samples were washed with tap water using plum:water ratio of 1:2 (w/w). The skins and seeds were manually separated from the pulp, washed with distilled water and then blotted on paper towels to remove any residual pulp. Skins were freeze-dried and stored at −20 °C until analyses.

2.3. Anthocyanins extraction

For the extraction of anthocyanins, 1 g of freeze-dried plum skin was suspended in ethanol (70%), homogenized and placed on an orbital shaker at room temperature for 2 h. After collecting, the supernatant was washed after centrifugation and the extraction step was repeated. Both supernatants were mixed and centrifuged at 11800 × *g*, and 10 °C for 10 min. The resulting supernatant was then concentrated under reduced pressure at 35 °C till dryness (AVC 2-18, Christ, UK). The anthocyanin solutions were obtained by dissolving 1 g of extract in 10 mL of 0.4 M acetate buffer at pH 3.0.

2.4. Heat treatment

For the heat-treatment experiments, 100 μL of the aforementioned anthocyanin solutions (0.4 M acetate buffer at pH 3.0) were dispensed in Eppendorf tubes (1 cm diameter), the later being submerged in a thermostatic bath (RaypaTrade BBO-4, Barcelona, Spain) kept at temperatures ranging from 25 to 110 °C for 10 min. For the thermal degradation kinetic studies, the tubes were maintained at constant temperature for different treatment times (0–20 min). A heating-up time of 30 s was employed at each experiment. After the thermal treatment, the tubes were immediately cooled in ice water in order to prevent further degradation.

2.5. Determination of total anthocyanins (TAC)

The plum extracts were analyzed for TAC content by using AOAC official method - pH differential, which is a quick method that does not require prior hydrolysis of the raw material. Monomeric anthocyanin pigments reversibly change color with a change in pH; the colored oxonium form exists at pH 1.0, and the colorless hemiketal form predominates at pH 4.5. The difference between the absorbance of the pigments at 520 and 700 nm is proportional to the pigment concentration. Briefly, 1–5 mL of the phenolic extract was diluted between 2 and 100 times with 0.025 M potassium chloride solution (pH 1.0) and 0.4 M sodium acetate buffer (pH 4.5), respectively. After 15 min of incubation, the absorbance was measured at 520 and 700 nm vs. the blank (water). The content of total anthocyanins was expressed as mg of cyanidin 3-glucoside equivalents (CGE) per 100 g dry weight (DW). A molar absorption coefficient of 26,900 L/mol·cm (cyanidin 3-glucoside) was used to calculate the concentration of total anthocyanins in solution.

2.6. Total phenolic content (TPC)

The TPC in the plum extracts was determined using the slightly modified Folin–Ciocalteu colorimetric method described by Gutfinger (1981). The plum extracts were totally dissolved in deionized water (1 mg/mL). In brief, 200 μL aliquots of the resulting solution were mixed with 125 μL of 2 N Folin–Ciocalteau's phenol reagent, diluted 1:2 (v/v). After 3 min of mixing, 125 μL of 20% Na_2CO_3 and 550 μL of deionized water was added to the mixture. The resulting mixture was allowed to stand for 30 min at room temperature in the dark; after that the mixture was centrifuged at 8200 × *g* for 10 min. Absorbance was measured at 765 nm. Results were expressed as mg of gallic acid equivalents (GAE) per 100 g DW.

2.7. Total flavonoid content (TFC)

The TFC of the plum extracts was determined using a modified colorimetric method (Dewanto et al., 2002). Briefly, each diluted plum extract (0.25 mL) was mixed with 1.25 mL of distilled water and, subsequently, with 0.075 mL of 5% $NaNO_2$ solution and kept to react for 5 min. After 6 min, 150 μL of 10% $AlCl_3 \cdot H_2O$ solution were added. Finally, 0.5 mL of NaOH (1 M) solution was added and the total volume was made up to 3.0 mL with deionized water. The absorbance of the mixture was immediately measured at 510 nm against a prepared blank. Results were expressed as mg of catechin (Sigma–Aldrich, Steinheim, Germany) equivalents (CE) per 100 g DW.