IOCAG 2022

Proceeding Paper

Influence of Maturity Stage on Polyphenolic Content and Antioxidant Activity of Fig (*Ficus carica* L.) Fruit in Native Albanian Varieties †

Luziana Hoxha [1,*], Renata Kongoli [2] and Juljana Dervishi [2]

1 Agricultural University of Tirana, Faculty of Biotechnology and Food, Food Research Center, Tirana, Albania
2 Agricultural University of Tirana, Faculty of Biotechnology and Food, Agrifood Technologies Department, Tirana, Albania; rkongoli@ubt.edu.al (R.K.); j.dervishi@yahoo.com (J.D.)
* Correspondence: lhoxha@ubt.edu.al; Tel.: +355-698-602-117
† Presented at the 1st International Online Conference on Agriculture—Advances in Agricultural Science and Technology (IOCAG2022), 10–25 February 2022; Available online: https://iocag2022.sciforum.net/.

Abstract: Fig fruits are an important horticultural crop, which are traditionally grown in Albania, and has recently attracted the worldwide attention of many researchers, fruit cultivators, processors, and consumers. This study determined the content of polyphenolic compounds, antioxidant activity and some physico-chemical parameters of black and white varieties of *Shëngjinas* and *Kraps* autochthonous fig (*Ficus carica* L.) fruits, which were collected in Tirana, Albania. The influence of maturity stage on physico-chemical parameters such as dry matter, total soluble solids, titratable acidity, ash, vitamin C, total polyphenols content, flavonoids, anthocyanins, and antioxidant activity, were investigated at three maturity stages during the May-June harvesting period. For determination of physico-chemical parameters, the official methods were used, whereas for determination of total phenolic content, the Folin-Ciocalteu method was used. For total flavonoid content, the aluminum chloride colorimetric method was used. For total anthocyanin content, the pH difference method for used, and for antioxidant activity, the ABTS (2,2′-azinobis (3-ethylbenzthiazoline-6-acid) assay was used. In this study black varieties resulted in 86.92% higher content of polyphenols, and a decrease was noted during fruit development (till 59.16% in third maturity stage), total flavonoid content varied around 12.02–65.08 mg catechin equivalent/100 g, and antioxidant activity ranged 119.09–181.65 mg ascorbic acid/100 g, whereas anthocyanins were found in black varieties ranging 4.23–48.98 mg cyanidin-3-glucozide/100 g. Black varieties had higher polyphenol compounds and antioxidant activity, whereas *Shëngjinas* variety resulted in the highest values. During fruit development a decrease of 1.91-fold and 2.45-fold was seen, respectively in the second and third stage of maturation compared to the first one. The selected fig varieties may provide a good source of phytochemicals and nutrients, and the generated data may serve as a guide for its consumption in fresh state, or to be further processed.

Keywords: polyphenolic content; antioxidant activity; fig fruit; maturity stage

Citation: Hoxha, L.; Kongoli, R.; Dervishi, J. Influence of Maturity Stage on Polyphenolic Content and Antioxidant Activity of Fig (*Ficus carica* L.) Fruit in Native Albanian Varieties. *Chem. Proc.* **2022**, *4*, x. https://doi.org/10.3390/xxxxx

Academic Editor: Firstname Lastname

Published: date 25 Feburary 2022

1. Introduction

The fig tree (*Ficus carica* L.) (common figs, or simply, figs) is one of the unique Ficus species widely spread in tropical and subtropical countries which has edible fruits with high commercial value [1] and are believed to be one of the oldest cultivated plants. A large number of cultivated forms are known in which the fruits vary in shape, size, color of skin, color and flavor of flesh, and period of ripening [2]. The skin of the fruit is thin and tender when fresh and the fleshy wall is whitish, pale yellow, pink, rose, red, or purple, depending on the species [3].

For centuries, their fruits have been used fresh or dried as food for humans and their animals. Figs have been popular not only because of their pleasant taste but possibly also because of their medicinal properties [4].

Figs constitute an important part of the Mediterranean diet, either fresh or dried; figs are especially rich in fiber, trace minerals, polyphenols, proteins, and sugars and the levels of these compounds are strongly dependent on the fig cultivars and genotypes [4]. In addition, fig fruit also contains fat and cholesterol-free with a high number of amino acids. Similarly, to other fruit species, figs contain sugars and organic acids that influence their quality [5]. These nutritional and functional characteristics are closely related to fruit quality and are usually influenced by genotype and ripening stage, as well as by environmental conditions and orchard management practices [6].

Peeled or unpeeled, the fruits may be prepared in several ways, such as fig pies, puddings, cakes, or other bakery products. Figs can also be added to ice cream mixtures. Home growers preserve whole fruits in sugar syrup or prepare them as jam, marmalade, or paste. Plant parts and extracts of the fig tree have traditionally been used for internal, as well as external, application [7].

Fruits and vegetables, a rich source of metabolites such as flavonoids and phenolics, exhibit various protective effects [8]. In recent years, polyphenols have become an intense focus of research interest because of their potential health-beneficial effects with regard to their antioxidant capacity [9], and huge data have been generated on the presence of polyphenol compounds in a variety of food materials, including figs [6,10–12].

Fruit maturity is important to the overall quality of fruit and their derived products, and changes in polyphenol content and antioxidant capacity of fruits are often associated with ripening of fruits [13].

According to our knowledge, regarding changes in physico-chemical parameters and influence of maturity stage on polyphenolic content and anti-oxidant activity of fig (*Ficus carica* L.) fruit, literature is scarce for native Albanian varieties, even their evaluation for understanding the influence of the maturity stage may have an increased interest recently for the most productive figs. Therefore, the objectives of this study were to determine the changes in physico-chemical properties, polyphenol compounds and antioxidant activity in native Albanian fig fruit, during development and ripening.

2. Materials and Methods

Ficus carica L. fruits, *Shëngjinas* and *Kraps* varieties (black and white) collected manually in Tirana region in three maturity stages 12 May, 3 June, and 29 June 2016. Fig fruits, were harvested in the early morning and randomly sampled. The sampled fruits were subdivided into three maturity stage (early, mid and late), stage I: immature, fruit state greenish, pulp white, fruit hard; stage II: mature, fruit skin green & green-purple, pulp pale; and stage III: ripe, fruit skin green-yellow and purple-black, pulp rose & red. Fruit samples from each variety tree replications (for each sample was taken 3 kg) and kept separately in a properly labeled clean polyethylene plastic bag.

Extracts were prepared according to [10] with slight modifications, and analyzed for total polyphenols, flavonoids, anthocyanins and antioxidant activity.

The moisture content has been determined according to [14], result expressed as g/100 g FW. The total soluble solids (TSS) content of samples was measured at 25 °C using Abbe refractometer, results expressed in °Brix. The pH was determined using pH meter UB-10 (UltraBasic, Denver Instrument) [14], total acidity (expressed as % citric acid) was determined by titrating with 0.1 N NaOH solution and calculated as grams of citric acid per 100 g FW (fresh weight of sample) [14]. Determination of total ash of the samples by placing in muffle furnace at 550 °C according to [14], results expressed as g/100 g FW. Ascorbic acid determination was carried out by iodine titration [15], till the end point (appearance of the blue starch-iodine color). The iodine reagent was standardized by titrating it against 5 mL of 1.00% ascorbic acid solution (to which three drops of 1% starch was added) until the appearance of the blue starch-iodine color, results were expressed as mg/ 100 g FW.

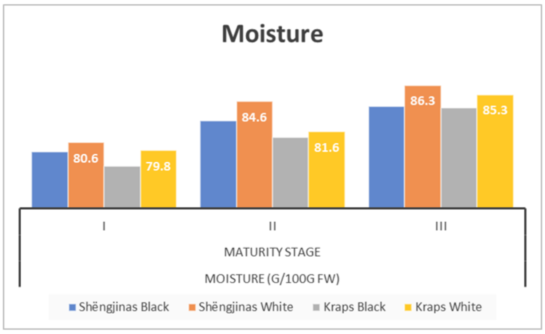
Total phenolic content of the extracts was determined according to the method of [10], and the measurement was compared to a standard curve (y= 0.0101x + 0.0024, R^2 = 0.9998) prepared with gallic acid solutions and expressed as milligrams of gallic acid equivalents (GAE) per gram of fresh weight (mg GAE/100 g FW). Total flavonoid content was measured colorimetrically using $AlCl_3$ [10], with some modification, and the measurement was compared to a standard curve (y = 0.0036x + 0.0007, R^2 = 0.9995) prepared with gallic acid solutions and expressed as milligrams of (+) catechin equivalents (mg CE /100 g FW). Total anthocyanin's content was measured according to the pH differential method [10]. The antioxidant capacity of extracts was determined as ABTS radical scavenging activity [10], with some modifications. The ABTS radical scavenging activity of the extract was compared to ascorbic acid, which was used as standard, and the results of the assay were expressed was expressed as mg acid ascorbic equivalent (mg AAE/100 g FW).

All the compounds and parameters reported below were determined in triplicate, for each of the samples. Data were expressed as Mean ± Standard Deviation.

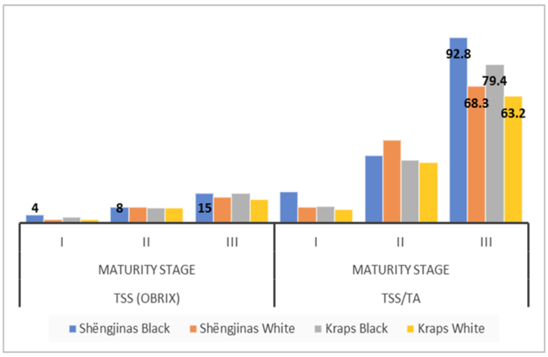
3. Results

3.1. Physico-Chemical Parameters Changes during Fruit Development

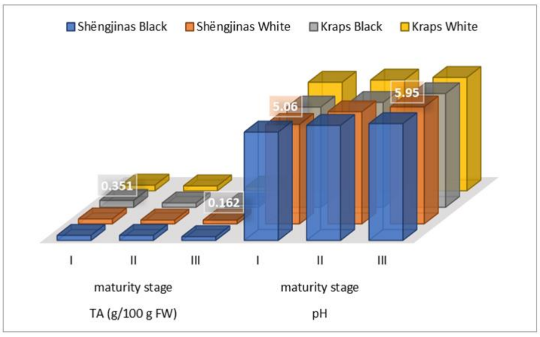
The changes of some physico-chemical characteristics of fig varieties *Shëngjinas* and *Kraps*, black and white varities used in this study are presented in the Figure 1a–d. Moisture in fig fruit was in ranges 78.2–80.6; 81.1–84.6; 84.0–86.3 g/100 g FW respectively for first, second and third maturity stages, and is noted as more immature fruit is higher dry matter has (Figure 1a). White varieties had higher values of moisture content in each of stages for *Shëngjinas* white variety had till 2.4% more, for *Kraps* white variety had till 1.9 % more moisture compared to respective black variety. Among varieties *Shëngjinas* had more moisture compared to *Kraps*, till 2% more in black varieties and till 3.7% more in white varieties. During fruit development and ripening, moisture changes in the fruit samples increased (dry matter decreased) from 2.3 to 6.9 %. During fruit development, the total soluble solids (TSS) content increased significantly from first to second stage 50–75%, and to third stage 73–85% among samples (Figure 1b). *Shëngjinas* black varieties had the highest values for each stage, whereas among same color varieties no significant differences existed. At the third stage (ripe), the change in TSS was significant (till 75–85% higher) and the final TSS content was 12–15°Brix (Figure 1b). Accordingly, the TSS/TA ratio during fruit development increased significantly from first to second stage 53.7–80.1%, and to third stage 83.1–89.2% among samples. *Shëngjinas* black varieties had the highest values for each stage, whereas among same color varieties no significant differences existed. At the third stage (ripe), the change in TSS was significant (till 75–85% higher) and the final TSS content was 12–15°Brix. TSS/TA ratio linking total acidity (sourness) and sugar level (sweetness), is considered as maturation index is regarded as the most reliable measure of fruit quality. In Figure 1c are represented pH values ranging 5.06–5.95, which increased 5.1–12% during fruit development and ripening. Acidity was in range 0.35–016 g/100 g FW, showed a gradual decrease from 15.8% to 45.8%. TA was inversely correlated to pH, the ripe fruit sample which had a low acid content, had a correspondingly high pH. Organic acids usually decline during ripening as they are respired or converted to sugars, and pH is becoming increasingly recognized for its important contribution to product quality. In Figure 1d, total ash was highest for the first stage of maturity 0.75–0.84 g/100 g FW, and decreased in later maturity stages 10.8–12%. *Shëngjinas* variety had the higher content, and white varieties in general had highest values.



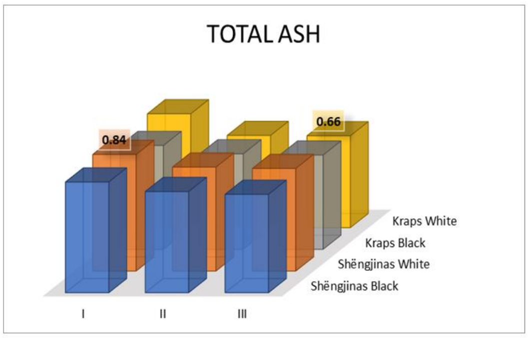
(**a**)



(**b**)



(**c**)



(**d**)

Figure 1. *Shëngjinas* and *Kraps* fig varieties (black and white) (g/100 g FW) in three maturity stages, (**a**) moisture content; (**b**) total soluble solids (°Brix) and TSS/TA; (**c**) total acidity and pH; (**d**) total ash.

The total vitamin significantly reduced its content from first stage 63.4–119.1, second stage 39.6–114.1 to third stage 30.3–37.9 mg/ 100 g FW. *Kraps* black variety had the higher content till 119.1 mg/100 FW, and ripe figs have not significant differences among varieties of the same colour from 0.2 to 5%.

3.2. Total Polyphenols, Flavonoids, Anthocyanins and Antioxidant Activity Changes during Fruits Development

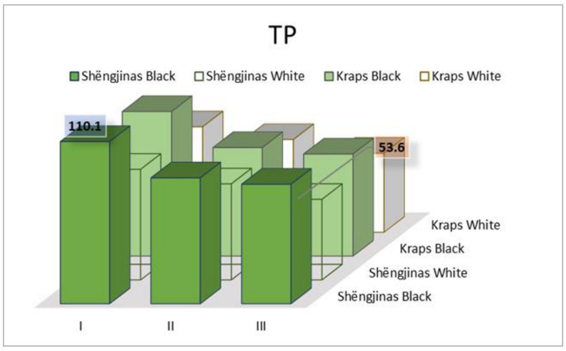
The changes of polyphenols, flavonoids, anthocyanins and antioxidant activity changes during fruits development of fig varieties *Shengjinas* and *Kraps* (black and white) are presented in the Figure 2a–d. The polyphenols (TP) (Figure 2a) analysed in our experiment were found at the mature stage I with 71.6–110.1 mg GAE/g FW, stage II 62.9–85.5 mg GAE/g FW, whereas, at the third maturity stage contained the lowest content 53.6–81.2 mg GAE/g FW. Black varieties had higher values of TP content compared to respective white variety till 86.92%. Comparing varieties, *Shëngjinas* had more TP content compared to *Kraps*, till 14.6% for black varieties and till 4.7% more in white varieties. Comparing the different stages of development and ripening it was noted that maturity stage influenced significantly the polyphenolic content (a decrease till 59.16% in third maturity stage).

The flavonoids (TF) of the fig fruits ranged 12.02–65.08 mg catechin equivalent/100 g FW, and results during development and ripening are presented in Figure 2b. From our experiment were found TF at the mature stage I with 42.1–65.08 mg CE/g FW, stage II 31.2–41.6 mg CE/g FW, whereas, at the third maturity stage contained the lowest content 12.0–31.2 mg CE/g FW. Black varieties had higher values of TF content compared to respective white variety, for *Shëngjinas* had till 45.6% more, for *Kraps* variety had till 59.3 %. Comparing varieties, *Shëngjinas* had more TF content compared to *Kraps*, till 7.3% for black varieties and till 29.3% more in white varieties. Comparing the different stages of development and ripening it was noted that maturity stage influenced significantly the polyphenolic content (a decrease about 13.5–71.4%).

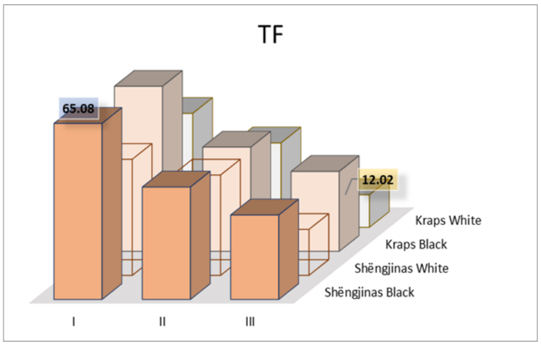
The total anthocyanin content (TA) of the fig fruits ranged 4.23–48.98 mg cyanidin-3-glucozide/ 100 g FW, and results during development and ripening are presented in Figure 2c. The study shows that the concentrations of anthocyanins increase with ripening of fruits, through a gradual accumulation in the course of ripening, TA has been detected at the second maturity stage 4.23–9.01 mg C3G/100 g FW, and the highest content of TA was at the third maturity stage 29.39–48.98 mg C3G/100 g FW.

Besides sugars and organic acids, polyphenols as secondary metabolites, to a certain extent can also contribute to sweet, bitter or astringent flavours of fruit, while they can also contribute to aroma [16]. According to [17], the decrease in polyphenol content of fruits causes a loss in astringency and bitterness during ripening. In our study, the quantity of TP and TF were in accordance to those values reported by [6] on fig fruits, also they found that (−)-epicatechin, (+)-catechin and rutin, were the main polyphenols of this fruit, which remained relatively high in quantity during fruit development and ripening. As anthocyanins are members of the group of polyphenolics, which are responsible for the colour of black fig varieties and contribute to the red and purple colours of fig fruit tissues, and so they can largely contribute to the visual quality of fruits. The changes in TA concentrations agree with [18] for arbutus berry fruit.

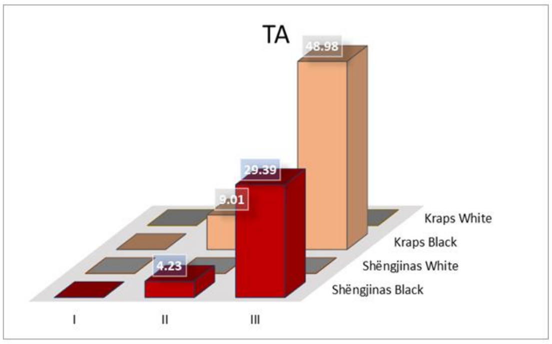
The antioxidant activity (TAA) (Figure 2d) ranged 119.09–181.65 mg ascorbic acid/100 g and were found that trend of content was: at the mature stage I < stage II < stage III. Accordingly, to above results on polyphenolic compounds black varieties had higher values of TAA content compared to respective white variety, for *Shëngjinas* had till 18.1% more, for *Kraps* variety had till 17.4 %. When, comparing varieties, *Shëngjinas* had more TAA content compared to *Kraps*, till 14.3% for black varieties and till 7.4% more in white varieties. Comparing the different stages of development and ripening it was noted that maturity stage influenced the antioxidant activity content with a decrease about 3.6–15.6%.



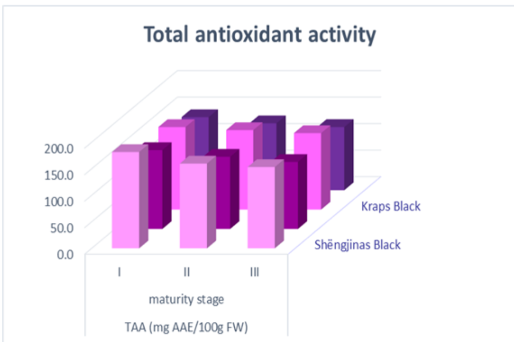
(**a**)



(**b**)



(**c**)



(**d**)

Figure 2. *Shëngjinas* and *Kraps* fig varieties (black and white) (g/100 g FW) in three maturity stages, (**a**) total polyphenols (mg GAE/100 g FW);(**b**) total flavonoids (mg CE/100g FW); (**c**) total anthocyanins (mg C3G/100g FW); (**d**) total antioxidant activity (mg AAE/100g FW).

The total phenolic content (TP) and antioxidant activity (AA) tended to decrease continuously during fruit development and ripening. During fruit development a decrease of 1.91-fold and 2.45-fold was seen, respectively in the second and third stage of maturation compared to the first one. A number of studies have shown that the presence of polyphenols in food and especially in fruit, can be particularly important for consumers, because of their beneficial health properties [9]. Black varieties had higher polyphenol compounds and antioxidant activity, whereas *Shëngjinas* variety resulted in the highest values. This study in regard with other studies done before confirmed again suggesting that among all common fruits and vegetables in the diet, berries, and figs, especially those with dark blue or red colors, have the highest antioxidant capacity [11,12]. The selected fig varieties may provide a good source of phytochemicals and nutrients, and the generated data may serve as a guide for its consumption in fresh state, or to be further processed.

Author Contributions: Conceptualization, L.H., R.K. and J.D.; methodology, L.H.; investigation, L.H. and J.D.; resources, L.H. and J.D.; data curation, L.H.; writing—original draft preparation, L.H.; writing—review and editing, L.H. and R.K.; supervision, L.H. and R.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Irget, M.E.; Aksoy, U.; Okur, B.; Ongun, A.R.; Tepecik, M. Effect of calcium based fertilization on dried fig (*Ficus carica* L. cv. Sarılop) yield and quality. *Sci. Hortic*. **2008**, *118*, 308–313.
2. Sinha, K.K. San Pedro Fig. In *Encyclopedia of Food Sciences and Nutrition*, 2nd ed.; Academic Press: Cambridge, MA, USA, 2003.
3. Stover, E.; Aradhya, M.; Ferguson, L.; Crisosto, C.H. The fig overview of an ancient fruits. *HortScience* **2007**, *42*, 1083–1087.
4. Ercisli, S.; Tosun, M.; Karlidag, H.; Dzubur, A.; Hadziabulic, S.; Aliman, Y. Color and antioxidant characteristics of some fresh fig (*Ficus carica* L.) genotypes from Northeastern Turkey. *Plant Foods Hum. Nutr.* **2012**, *67*, 271–276.
5. Mahmoudi, S.; Khali, M.; Benkhaled, A.; Boucetta, L.; Dahmani, Y.; Attallah, Z.; Belbraouet, S. Fresh figs (*Ficus carica* L.): Pomological characteristics, nutritional value, and phytochemical properties. *Eur. J. Hortic. Sci*. **2018**, *83*, 104–113.
6. Veberic, R.; Colaric, M.; Stampar, F. Phenolic acids and flavonoids of fig fruit (*Ficus carica* L.) in the northern Mediterranean region. *Food Chem.* **2008**, *106*, 153–157.
7. Veberic, R.; Mikulic-Petkovsek, M. Phytochemical Composition of Common Fig (*Ficus carica* L.) Cultivars. In *Nutritional Composition of Fruit Cultivars*; Elsevier: Amsterdam, The Netherlands, 2016.
8. Alibabic, A.; Skender, A.; Orascanin, M.; Sertovic, E.; Bajric, E. Evaluation of morphological, chemical, and sensory characteristics of raspberry cultivars grown in Bosnia and Herzegovina. *Turk. J. Agric. For*. **2018**, *42*, 7–74.
9. Stoclet, J.C.; Chataigneau, T.; Ndiaye, M.; Oak, M.H.; El Bedoui, J.; Chataigneau, M.; Schini-Kerth, V.B. Vascular protection by dietary polyphenols. *Eur. J. Pharm*. **2004**, *500*, 299–313.
10. Hoxha, L.; Kongoli, R.; Hoxha, M. Antioxidant activity of some dried autochthonous Albanian fig (*Ficus carica* L.) cultivars. *Int. J. Crop Sci. Technol*. **2015**, *1*, 20–26.
11. Hoxha, L.; Kongoli, R. Evaluation of antioxidant potential of Albanian fig varieties “Kraps Zi” and “Kraps Bardhe” cultivated in the region of Tirana. *J. Hyg. Eng. Des.* **2016**, *16*, 70–74.
12. Hoxha, L.; Kongoli, R. Comparative Study of Antioxidant Activity of Fruit, Peel and Pulp of Six Albanian Fresh Fig (*Ficus carica*) Varieties. *Online Int. Interdiscip. Res. J.* **2017**, *VII*, 34–42.
13. Amiot, M.J.; Tacchini, M.; Aubert, S.Y.; Oleszek, W. Influence of cultivar, maturity stage, and storage conditions on phenolic composition and enzymatic browning of pear fruits. *J. Agric. Food Chem*. **2015**, *43*, 1132–1137.
14. AOAC. *Official Methods of Analysis*, 18th ed.; The Association of Official Analytical Chemists: Gaithersburg, MD, USA, 2005.
15. Ikewuchi, C.J.; Ikewuchi, C.C. Iodometric determination of the ascorbic acid (vitamin C) content of some fruits consumed in a university community in Nigeria. *Glob. J. Pure Appl. Sci.* **2011**, *17*, 47–49.

16. Tomas-Barberan, F.A.; Espin, J.C. Phenolic compounds and related enzymes as determinants of quality in fruits and vegetables. *J. Sci. Food Agric*. **2001**, *81*, 853–876.
17. Vidal, S.; Francis, L.; Noble, A.; Kwiatkowski, M.; Cheynier, V.; Waters, E. Taste and mouth-feel properties of different types of tannin-like polyphenolic compounds and anthocyanins in wine. *Anal. Chim. Acta* **2004**, *513*, 57–65.
18. Alarcao-E-Silva, M.L.C.M.M.; Leitao, A.E.B.; Azinheira, H.G.; Leitao, M.C.A. The arbutus berry: Studies on its color and chemical characteristics at two mature stages. *J. Food Comp. Anal*. **2001**, *14*, 27–35.