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Proceeding Paper

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

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Abstract: Fig fruits, are an important horticultural crop and traditionally grown in Albania. Recently have attracted the 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 up to 59.16% in the 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 decreases were seen for polyphenol compounds and antioxidant activity, respectively in the second and third stage of maturation 1.91-fold and 2.45-fold, 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

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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, are edible fruits with high commercial value [1], and is 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 has no cholesterol, 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) were collected in Tirana region in three maturity stages on 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 stages (early, mid and late).The first maturity stage included immature fruits, greenish skin and white pulp, hard in texture; the second maturity stage included mature fruit, with green skin and green-purple, pale pulp; third maturity stage included ripe fruits, with green-yellow and purple-black, and pulp rose and red. Fruit samples from each variety (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]. 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 in some physico-chemical characteristics of fig varieties *Shëngjinas* and *Kraps*, black and white varieties, used in this study are presented in Figure 1a–d. Moisture in the fig fruit was in the ranges 78.2–80.6, 81.1–84.6, and 84.0–86.3 g/100 g FW for first, second and third maturity stages, respectively, and it is noted that as more immature fruit is as lower is the moisture content (Figure 1a). White varieties had higher values of moisture content in each of the stages: the *Shëngjinas* white variety had up to 2.4% more moisture compared to *Shëngjinas* black variety, while *Kraps* white variety had up to 1.9% more moisture compared to *Kraps* black variety. Among varieties, *Shëngjinas* had more moisture compared to *Kraps*: up to 2% more in black varieties and up to 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 (till 75%), and then to third stage (till85%) among samples (Figure 1b). The *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 (up to 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 (up to 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, pH values are represented, ranging 5.06–5.95, which increased by 5.1–12% during fruit development and ripening. Acidity was in the range 0.35–016 g/100 g FW, which showed a gradual decrease from 15.8% to 45.8%. TA was inversely correlated to pH. Matured fruit, had a low acid content, and 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%. The *Shëngjinas* variety had the higher content, and white varieties in general had highest values.

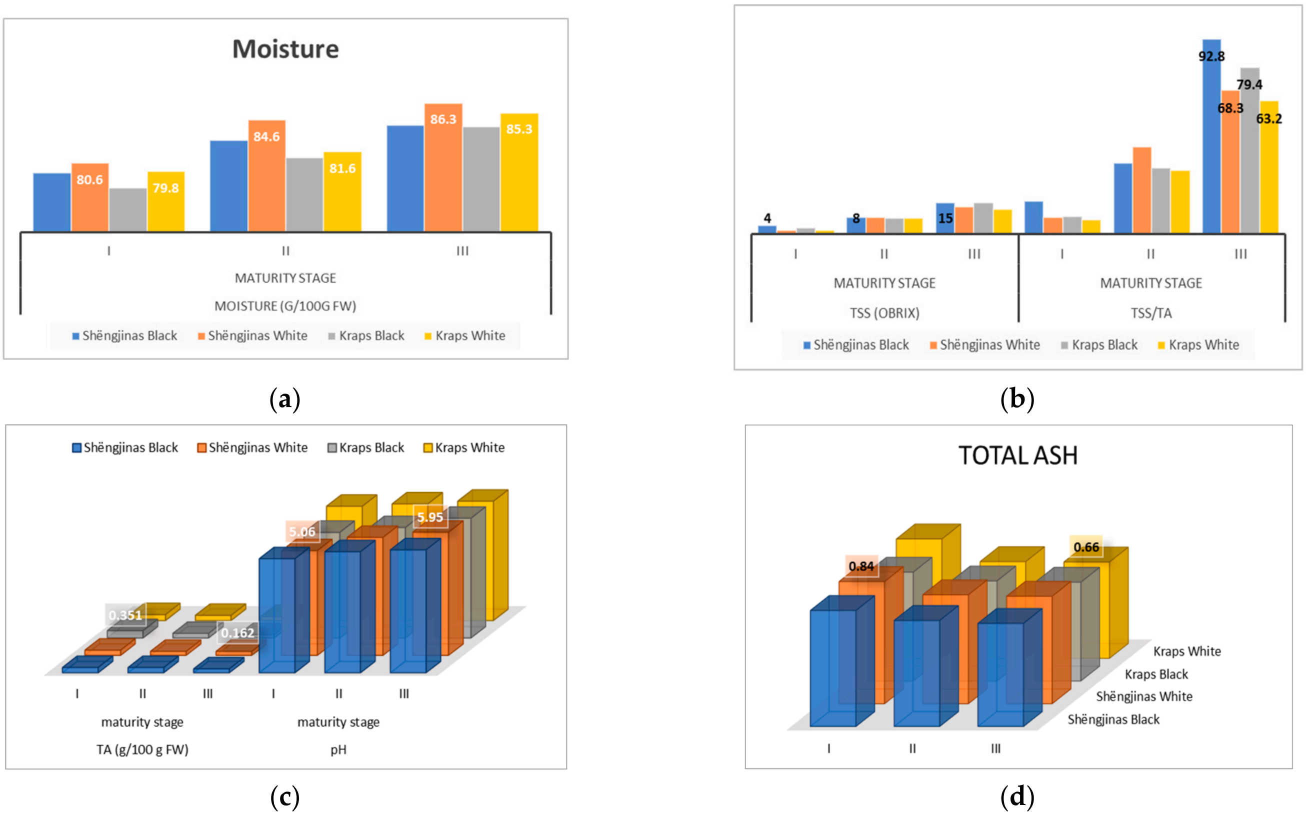

Figure 1. *Shëngjinas* and *Kraps* fig varieties (black and white) (g/100 g FW) in three maturity stages: (**a**) moisture content; (**b**) total soluble solids (°Brix) and TSS/TA; (**c**) total acidity and pH; (**d**) total ash.

The total vitamin content significantly reduced during maturity for white and black fig varieties, respectively the content of vitamin C was in the first stage 63.4 and 119.1 mg/100 g FW, in second stage 39.6 and 114.1 mg/100 g FW, and in the third stage 30.3–37.9 mg/100 g FW. The *Kraps* black variety had the highest content up to 119.1 mg/100 FW. Among fully matured fig varieties there were no significant differences for vitamin C content.

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

The changes in polyphenols, flavonoids, anthocyanins and antioxidant activity changes during fruits development of fig varieties *Shengjinas* and *Kraps* (black and white) are presented in Figure 2a–d. The polyphenols (TP) (Figure 2a) analyzed in our experiment were found for white and black varieties at the first maturity stage 71.6 and110.1 mg GAE/g FW, at the second maturity stage 62.9–85.5 mg GAE/g FW, whereas at the third maturity stage contained the lowest content 53.6 and 81.2 mg GAE/g FW. Black varieties had higher values of TP content compared to the white varieties (up to 86.92%). Comparing varieties, *Shëngjinas* had more TP content compared to *Kraps*, with up to 14.6% for black varieties and up to 4.7% more in white varieties. Comparing the different stages of development and ripening, it was noted that the maturity stage significantly influenced the polyphenolic content (a decrease of up to 59.16% in the third maturity stage).

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

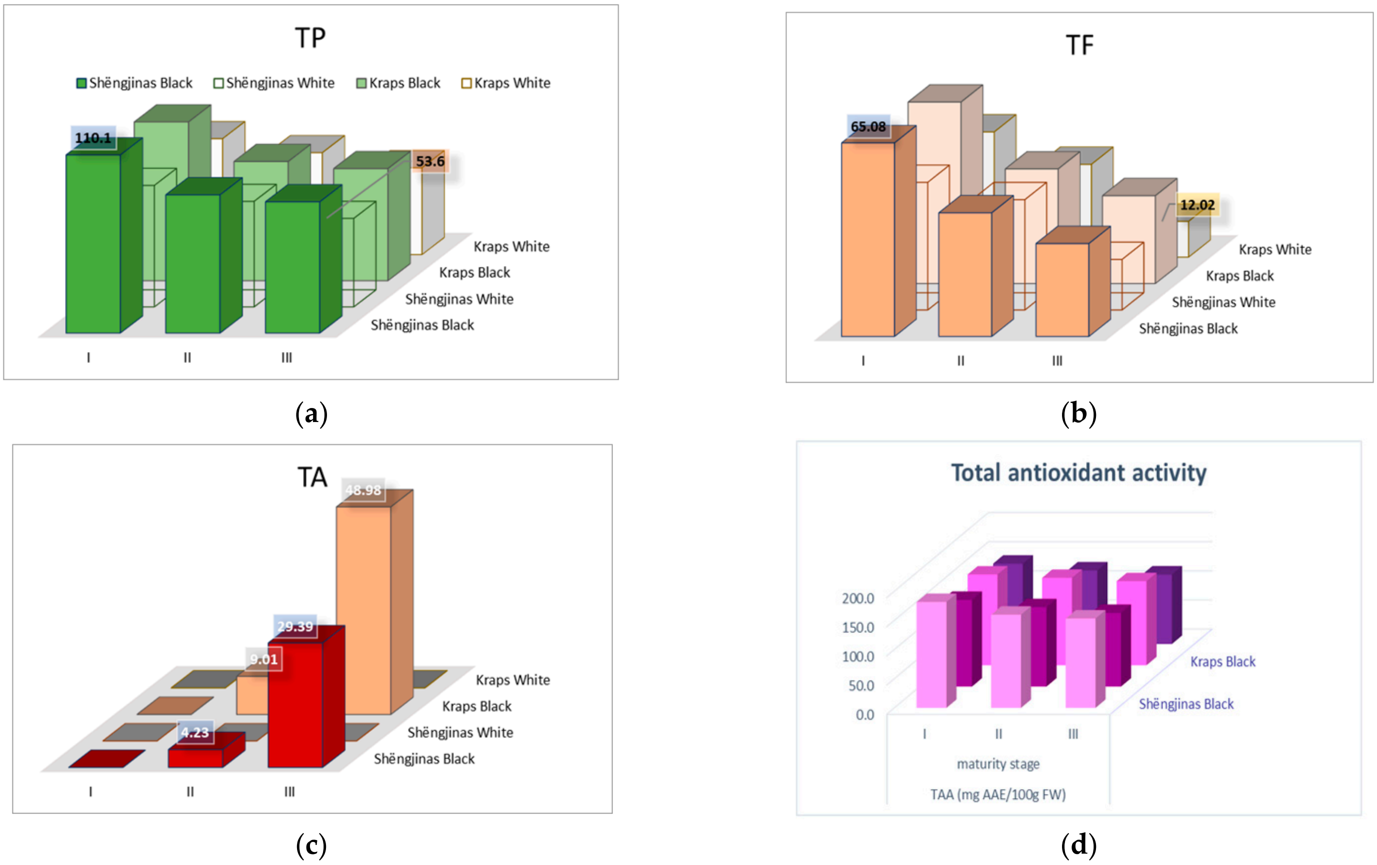

Figure 2. *Shëngjinas* and *Kraps* fig varieties (black and white) (g/100 g FW) in three maturity stages. (**a**) Total polyphenols (mg GAE/100 g FW); (**b**) total flavonoids (mg CE/100 g FW); (**c**) total anthocyanins (mg C3G/100 g FW); (**d**) total antioxidant activity (mg AAE/100 g FW).

The total anthocyanin content (TA) of the fig fruits ranged 4.23–48.98 mg cyanidin-3-glucozide/100 g FW, and the 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, and to a certain extent can also contribute to sweet, bitter or astringent flavors 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; which founded 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 color of black fig varieties and contribute to the red and purple colors 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, with regard to the above results on polyphenolic compounds, the black varieties had higher values of TAA content compared to their corresponding white variety:

the *Shëngjinas* variety had up to 18.1% more, while the *Kraps* variety had up to 17.4% more. When comparing varieties, *Shëngjinas* had more TAA content compared to *Kraps*, among black varieties *Shwngjinas* had up to 14.3% more than *Kraps*, and among white varieties *Shwngjinas* had up to 7.4% more than *Kraps*. Comparing the different stages of development and ripening, it was noted that maturity stage influenced the antioxidant activity content, with a decrease of about 3.6–15.6%.

The total phenolic content (TP) and antioxidant activity (AA) tended to decrease continuously during fruit development and ripening. During fruit development, 1.91-fold and 2.45-fold decreases were seen in the second and third stage of maturation, respectively, 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 the *Shëngjinas* variety resulted in the highest values. This study, confirms the suggestion 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.

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