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Effect of UV radiation on postharvest conservation of blueberries

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ABSTRACT



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The objective of this work is to determine the variation in the nutritional and quality characteristics of blueberries subjected to UV radiation. Blueberries of the variety (JEWEL) provided by Tierra de blueberries, Oran, Monteros, Tucuman were used. The parameters analyzed were variations of the color and content of polyphenols by HPLC and UV-vis. Polyphenols determined by HPLC were: delphinidin-3-galactoside, delphinidine-3-glucoside, cyanidin-3-galactoside, delphinidin-3-arabinoside, cyanidin-3-glucoside, petunidin-3-galactoside, cyanidin-3-arabinoside, petunidin-3-glucoside, peonidin-3-galactoside, petunidin-3-arabinoside, malvidin-3-galactoside and malvidin-3-glucoside. From the results obtained, it is concluded that the polyphenol content varied in the irradiated fruits and in the untreated fruits as a function of time, with the values being closest to the initial time value (control) in the case of irradiated fruits. There were no appreciable differences in color change due to irradiation. At time 0, the color difference in the whole fruit between the treated sample (IFCO) and the standard (NFCO) gave ΔE^* values equal to 2.06. After 3 days, the color difference was 3.08 for the natural sample and 6.06 for the treated sample. For this reason, it is considered that irradiation of blueberries is a very appropriate method for conservation, maintaining the nutritional and quality characteristics of blueberries.

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1. Introduction

The blueberry is a berry-type fruit, considered within the group of fine fruits or berries, with a high content of antioxidants and is appreciated for its nutraceutical properties. It comes from a perennial shrub native to eastern North America, which belongs to the Ericaceae family, the genus *Vaccinium* [1]. It is characterized by having a low caloric value and a high water content (more than 80 % of the total weight of the fruit). Although its contribution to macronutrients is not remarkable, its nutritional quality is determined by being a good source of vitamins and minerals. In addition, it contains various phytochemicals, mainly phenolic in nature, related to different parameters of organoleptic, nutritional, and functional quality [2].

Among the beneficial effects of consuming blueberries, it is worth highlighting the ability to reverse memory loss associated with aging and the early stages of diseases such as Alzheimer's [3]. According to the same authors, blueberry polyphenols are capable of exerting their anti-inflammatory action at the cellular level. Since this cellular inflammation is the focus of numerous degenerative diseases associated with aging, blueberry consumption could prevent and/or delay said degenerative processes [4].

In Argentina, blueberries began to be cultivated in 1993, and Argentina has become an important counter-season supplier to supply the demand of the Northern Hemisphere. From August, the early fruit or scoop is obtained in marketable volumes. Tucumán Province is a major producer of blueberries for export. The plantations stretch about 1,200 ha, which represents 46% of the total area of Tucumán country [5]. It is a notable source of economic income and work in the province, since employees are required all year round in the field, and during the peak of the harvest it increases both in the harvesters and in packaging employees. Tucumán ranks second in terms of blueberry production at the country level, after Concordia. A essential advantage of blueberry production in Tucumán is that it occurs in the early counter-season, which allows for advantageous exports and increased employment in counter-season.

In recent years, there has been a growing demand for fresh products; this means that the food industry seeks nonthermal conservation technologies. The application of UV light to liquid or solid products is used in different sectors of the food industry, due to the harmful effect it causes on the DNA of many microorganisms [6].

Table 1. Peak wavelengths of the identified species.

| Anthocyanins | λ_{\max} | References |
|--------------|------------------|------------|
| Cyanidin | 506 (Orange-red) | [9] |
| Delphinidin | 508 (Blue-red) | [9] |
| Peonidin | 506 (Orange-red) | [9] |
| Petunidin | 508 (Blue-red) | [9] |
| Malvidin | 510 (Blue-red) | [9] |

The application of UV light is already used industrially, mainly as a disinfectant or as a germicide. There have been several attempts to use it as a germicide in vegetables and fresh fruits. Thus, it is necessary to evaluate the composition of vegetables and fruits in the post-harvest time and evaluate the advantages of the application of UV radiation; in our case pulsed on them to know if new compounds were generated or if there is a significant change in the amount of each over time. In this study, blueberries were evaluated, which are fine fruits that are produced in the region.

2. Experimental

2.1. Instrumentation

The samples were analyzed by UV-vis spectra, color chromatography, and HPLC chromatography techniques. HPLC-Agilent 1200 infinity series chromatography instrument was used for chromatography analysis (chromatographic conditions: Column: C18 (Phenomenex), F. Mobile: 1% Acetonitrile, T (column): 35 °C, Flow rate: 1.3 mL/min, Sample temperature: 4 °C, Injection volume: 20 μ L). For color determinations, a Konica Minolta Sensing CM-600d spectrophotometer was used. For UV-vis spectroscopy, the HITACHI U-1900 spectrophotometer was used.

2.2. Samples and methods

A sample of blueberries of the variety (JEWEL) provided by Tierra de Arándanos, Orán, Monteros, and Tucumán was obtained in October 2021. They were stored at -18 °C for 6 months and divided into four identical representative samples: (i) Natural Complete Fruit Witness (FCN: Natural whole fruit) at time 0 ($t = 0$); (ii) Sample without radiation preserved at room temperature and at 4 °C (FCHel: Whole fruit preserved in the refrigerator) evaluated at 3 days and 7 days; (iii) sample irradiated with 254 nm pulsed UV radiation measured at time 0 (FCIO: Irradiated whole fruit); (iv) Sample irradiated with pulsed UV radiation at 254 nm measured at 3 days and 7 days (FCI: Irradiated whole fruit).

From each sample, an extract was obtained weighing 4 g of each and was macerated in 15 mL of absolute ethyl alcohol. UV-vis spectra, color, and HPLC chromatography were performed for the initial time, corresponding to the moment of application and 3 and 7 days later. All samples, both control and irradiated, were stored at room temperature (average temperature 14 °C, 70% humidity, and atmospheric pressure (978 hPa). Furthermore, visible ultraviolet spectra were obtained on the peel and pulp of natural and irradiated fruits at zero time (CN: Natural fruit peel; CI: Irradiated fruit peel; PN: Natural fruit pulp; PI: Irradiated fruit pulp).

2.3. Colorimetry in the extracts

Color is a mental response to the stimulus produced in the retina by visible-light radiation, but the extent of this stimulus depends on the conditions that surround it. The most commonly used model to characterize the color of anthocyanin extracts is CIELAB [7]. This model, developed in 1976, established an international system based on the effect that any color can produce on a standard observer. For this, it was taken into account that the color is three-dimensional and that only

three numbers are enough to define it. The scale on which the color is measured, based on Hering's theory, is represented by the coordinates: clarity or luminosity (L^*), and colorimetric coordinates (a^*), (b^*). To determine the total color difference between the three coordinates, it was used [7].

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

where ΔE_{ab}^* : Overall color difference, L^* : Luminosity, ΔL^* : Difference in light and dark (+ = brighter, - = darker), a^* : Red/green coordinates (+a indicates red, -a indicates green), Δa^* : Difference in red and green, b^* : Yellow/blue coordinates (+b indicates yellow, -b indicates blue) and Δb^* : Difference in yellow and blue.

3. Results and discussion

To evaluate the composition of fruits in the postharvest time and the advantages of the application of UV radiation, in our case with a given frequency, chromatograms and UV-vis spectra of the peel and pulp extracts were performed. In addition, compounds of interest for blueberries were analyzed with UV-vis spectra in this study.

Anthocyanins have maximum absorption in both the visible and ultraviolet regions, which is essential for the structural characterization of these compounds [8]. The absorption spectra are characterized by two bands separated in the visible region between 465 and 550 nm and another smaller one in the UV around 275 nm (Figure 1). This is how anthocyanins can be identified by their absorption in the visible region. Table 1 shows the maximum wavelengths of the identified species [9].

Figure 1 shows the UV-Vis spectra obtained from the extracts of the whole blueberry fruit with (FCI) and without UV irradiation (FCN) at different storage times (0, 3 and 7 days). As can be seen in Figure 1, as the days pass, the concentration of compounds decreases gradually in the untreated sample, while in those subjected to preservation treatment, as the days pass, the concentration of compounds remains practically at values very close to the control sample (FCN at zero days).

Polyphenols are absorbed in the ultraviolet (UV) region. In the case of flavonoid-type phenols, there are two characteristic absorption bands [10], the aromatic ring A band with maximum absorption in the range of 240-285 nm (benzoyl band) and another band of ring B with maximum absorption in the range 300-550 nm (cinnamoyl band). In Figure 1, as the days go by, it is observed that the concentration of compounds gradually decreases in the untreated sample, while in those exposed to conservation treatment it remains practically at values very close to the control sample (FCN at zero days). The UV-vis analysis of the different samples showed a maximum absorption band (composite structure) between 200 and 300 nm, which corresponds to the characteristic of a benzoyl band or band II. The aromatic ring A of flavonoids with peaks at 384, 366, and 322 nm and another very broad band at 520 nm, which is band I or the cinnamoyl band and corresponds to the aromatic ring B of the flavonoid structure. The displacement of this last band to a wavelength greater than 500 nm is characteristic for flavonoids of the anthocyanin group [11-13], thus verifying the presence of anthocyanins in addition to other phenolic substances. The absorption band at 515 nm is characteristic of anthocyanins.

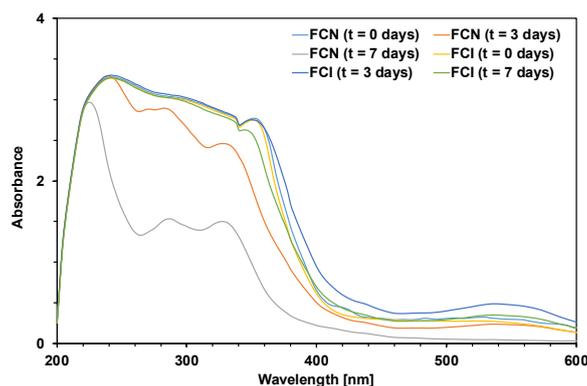


Figure 1. Ultraviolet-visible spectrum of solutions of blueberries. FCN (natural whole fruit); FCI (irradiated whole fruit).

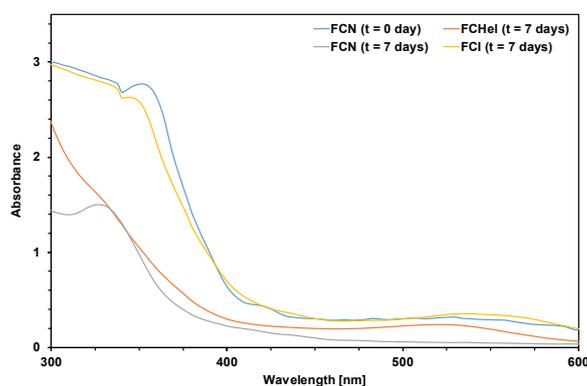


Figure 2. Ultraviolet-visible spectrum of solutions of blueberries. FCN (natural whole fruit); FCHel (full fruit in ice cream); FCI (irradiated whole fruit).

Figure 2 shows the UV-vis spectra obtained from the extracts of the entire blueberry fruit without treatment (at 0 and 7 days after storage), with conventional FCHel treatment at low temperature (4 °C) and with irradiation treatment (FCI) (at 7 days after storage). All were stored at an average temperature of 14 °C, 70% humidity, and 978 hPa atmospheric pressure. From the UV-Vis spectra, the presence of characteristic absorption bands is observed in the UV (250 and 400 nm) and visible region (500 to 545 nm), indicating the presence of anthocyanins, as obtained in different plant materials: fruits, juices and wines, as well as flowers [14]. Finally, it is observed that the fruits subjected to the proposed irradiation method are close to the control sample (FCN on day 0).

The bands in the zones from 200 to 400 nm decrease significantly. Zones 400 to 600 nm decreased slightly, while fruits subjected to the proposed irradiation method are close to the control sample (FCN at 0 days). Some studies found an increase in the total phenol content in other berries, such as cherries stored at 4 °C for 7 days, which showed an increase of 7.5%. In strawberries, the increase in total phenolic compounds after 11 days of storage at 4 °C was 12.4%, and storage at 25 °C of the analyzed small fruits facilitated a faster deterioration [15]. In blackberries refrigerated at 1 °C for 15 days, the content of phenolic compounds increased from 9.5% to 54.1% [16,17]. Furthermore, an increase of 65.4% of anthocyanins in cherries was demonstrated after one week of storage at 4 °C. Storage at 4 °C preserved the quality of the analyzed fruits for a prolonged period of time compared to storage at room temperature, and the values of antioxidant capacity were higher in fruits stored at 4 °C, instead of 25 °C [17]. The variation of total polyphenols in berries depends on various elements such as environmental conditions, degree of maturity, crop variety, storage, and processing of the fruits [17,18].

Figure 3 shows the UV-vis spectra obtained from the peel extracts (C) and the pulp (P) of the blueberry fruit with and without treatment at 0 days. It is observed that the shell is more affected by irradiation, as expected when this irradiation method is proposed. In other words, a superficial effect is produced on the fruit when treatment is performed. The pulp is practically without effect despite irradiation. It is observed that the varieties studied exhibit a phenolic behavior similar to those found in the bibliography for cultivated blueberries from different sources, where it is inferred that the extracts from the blueberry peel have a greater capacity to trap radicals. The intake of phenolic compounds in the daily diet is variable; the highest levels of intake are observed in populations with a high consumption of fruits and vegetables [19]. Blueberries have a high polyphenol content, especially anthocyanins [20].

Table 2 shows the compounds identified in the chromatograms, according to the literature. The chromatograms obtained by HPLC show that: (i) At time zero, irradiation increases compounds such as delphinidin-3-galactoside, delphinidin-3-glucoside, delphinidin-3-arabinoside, cyanidin-3-glucoside, petunidin-3-galactoside, petunidin -3-glucoside, malvidin-3-galactoside and malvidin-3-glucoside, and (ii) Other compounds are maintained in greater amounts without irradiation (cyanidin-3-galactoside, cyanidin-3-arabinoside, peonidin-3-galactoside and petunidin-3-arabinoside). The chromatograms obtained for the peel and pulp of the fruits with and without irradiation at the beginning of the study show that the natural and irradiated fruit peel has a higher anthocyanin content compared to the pulp. The changes observed in the maximum intensity with the treatment are consistent with those obtained by UV-vis spectroscopy.

Table 2. Phenolic compounds in blueberries identified in the chromatograms.

| Peak | Compounds | t_R (min) |
|------|---------------------------|-------------|
| 1 | Delphinidin-3-galactoside | 16.6 |
| 2 | Delphinidin-3-glucoside | 17.5 |
| 3 | Cyanidin-3-galactoside | 17.9 |
| 4 | Delphinidin-3-arabinoside | 18.5 |
| 5 | Cyanidin-3-glucoside | 18.9 |
| 6 | Petunidin-3-galactoside | 19.4 |
| 7 | Cyanidin-3-arabinoside | 20.0 |
| 8 | Petunidin-3-glucoside | 20.5 |
| 9 | Peonidin-3-galactoside | 21.0 |
| 10 | Petunidin-3-arabinoside | 22.0 |
| 11 | Malvidin-3-galactoside | 23.4 |
| 12 | Malvidin-3-glucoside | 24.5 |

Table 3. Coordinates L^* , a^* , and b^* for each sample #.

| Sample | L^* (D65) | a^* (D65) | b^* (D65) | ΔE^* |
|--|-------------|-------------|-------------|------------------|
| Natural whole fruit at zero time (NFC0) | 4.4±0.2 | 27.3±0.4 | 7.6±0.2 | - |
| Natural fruit peel at zero time (NC0) | 11.6±0.3 | 40.5±0.6 | 19.9±0.7 | - |
| Natural fruit pulp at zero time (NP0) | 35.8±0.5 | 31.0±1.0 | 6.2±0.3 | - |
| Irradiated whole fruit at zero time (IFC0) | 5.0±0.4 | 29.0±1.0 | 8.6±0.7 | 2.06 (NFC0-IFC0) |
| Irradiated fruit peel at zero time (IC0) | 4.5±0.3 | 28.0±1.0 | 7.8±0.5 | - |
| Irradiated fruit pulp at zero time (IP0) | 28.1±0.8 | 42.0±2.0 | 1.1±0.8 | - |
| Natural whole fruit on day 3 (NFC3) | 5.4±0.3 | 30.5±0.8 | 9.4±0.5 | 3.08 (NFC0-NFC3) |
| Irradiated whole fruit on day 3 (IFC3) | 6.5±0.5 | 32.0±1.0 | 10.8±0.6 | 6.06 (NFC0-IFC3) |

Color differences are calculated on the whole fruit.

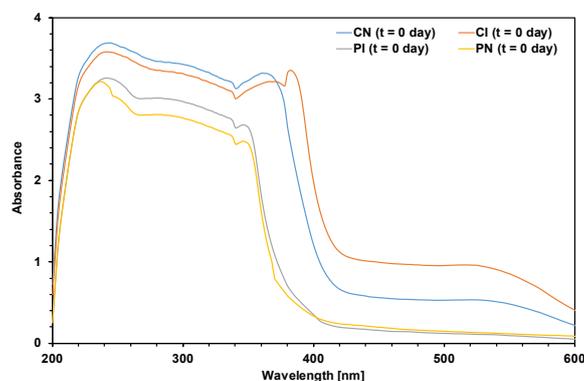


Figure 3. Ultraviolet-visible spectrum of solutions of blueberries. CN (natural fruit peel); CI (irradiated fruit peel); PN (natural fruit pulp); PI (irradiated fruit pulp). All at zero time.

Table 3 shows the values of the colorimetric coordinates obtained in the natural and irradiated samples at zero time and at three days. The values of the samples treated with UV-C radiation appeared in a color similar to that of the witness and similar to the bibliography [21]. Immediately after the application of the treatment, the values of luminosity (L^*), the a^* parameter and the b^* parameter of the treated blueberries were similar to the control sample. Rodoni *et al.* found no differences in the luminosity L^* of fresh peppers cut by the effect of UV-C radiation [22]. Ortiz Araque *et al.* found no differences in strawberry tone before and after UV-C radiation treatment, but a reduction in L^* [23]. One of the best parameters to describe the variation in color is the difference of color (ΔE^*), since it reflects the total change in all parameters L^* , a^* , and b^* .

4. Conclusions

The polyphenol content varied for both irradiated and untreated fruits depending on time. Fruits irradiated and preserved at room temperature show a behavior after several days similar to that of natural fruits at zero time. There were no appreciable differences in color change due to irradiation. For this reason, it is considered that the irradiation of blueberries is a very valuable method for the conservation of the nutritional characteristics and quality of blueberries.

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CRedit authorship contribution statement

Conceptualization: Eliana Vanesa Campero, María Julia Barrionuevo, Ana Clelia Gomez Marigliano; Methodology: Eliana Vanesa Campero, María Julia Barrionuevo, Ana Clelia Gomez Marigliano; Validation: Eliana Vanesa Campero, María Julia Barrionuevo; Formal Analysis: Eliana Vanesa Campero, María Julia Barrionuevo; Investigation: Eliana Vanesa Campero, María Julia Barrionuevo, Ana Clelia Gomez Marigliano; Resources: Eliana Vanesa Campero, María Julia Barrionuevo, Ana Clelia Gomez Marigliano; Writing - Original Draft: Eliana Vanesa Campero; Writing - Review and Editing: Eliana Vanesa Campero, María Julia Barrionuevo, Ana Clelia Gomez Marigliano; Visualization: Eliana Vanesa Campero, María Julia Barrionuevo, Ana Clelia Gomez Marigliano; Funding acquisition: María Julia Barrionuevo, Ana Clelia Gomez Marigliano; Supervision: María Julia Barrionuevo, Ana Clelia Gomez Marigliano; Project Administration: María Julia Barrionuevo; Ana Clelia Gomez Marigliano.

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