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Effect of Different Ripening Conditions on pigments of Pepper for Paprika Production in Green Stage of Maturity

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Abstract

Content and composition of pigments and CIELab color properties were compared in fruits ripened in the field with those obtained in ground paprika produced from green pepper fruits after postharvest ripening for 15 days in greenhouse under different conditions. Obtained data for pigment content, composition and esterification rate have shown that the processes of pigment biosynthesis in fruits ripened under greenhouse conditions are different from those occurring in naturally matured fruits in the field: red/yellow pigment ratio (3:1) in greenhouse ripened fruits is much higher than in naturally ripened pepper in breaker (1:1), but also in faint red (2:1) ripening stage from the field. Additionally, during the postharvest ripening of green pepper in the greenhouse esterification processes are less expressed than during the ripening of the fruits in the field. Postharvest ripening under natural daylight changes has resulted in higher content of red pigments, followed with higher ASTA value.

Key words:

Pepper, ground paprika powder, color, carotenoids, carotenoid esterification, ripening conditions

Introduction

One of the main characteristic of ground red paprika is its extractable color. Color, rated on the basis of ASTA[1] is the base for classification of ground red paprika products worldwide. The color of ground red paprika is also by rule listed among the specific properties in declarations of ground red paprika with protected denomination of origin (PDO) or with protected geographic identification (PGI) like Pimentón de Murcia (ASTA minimum 120) and Pimentón de la Vera (ASTA minimum 90).

Although widely accepted, ASTA method has its drawbacks: it requires equipped laboratory and it is time consuming (16 h). Color properties of ground red paprika expressed in CIELab system have been the subject of investigation of numerous authors using method for determining color change as a consequence of paprika storage,[2,3] paprika powder diameter,[4] ionizing radiation and steam,[5] drying rate.[6] Some authors successfully correlated quick and easy apparent (CIELab) and ASTA method.[7]

Color of ground red paprika highly depends on content and composition of carotenoids[8] present in the pepper fruits used in its production consequently resulting in research investigating dependence of carotenoid composition on pepper variety,[9,10] maturity stage of pepper fruits[11-13] and processing conditions.[14,15]

Regarding harvest in traditional, manual production, ripe red fruits are sequentially picked from the plant and left to be dried under natural conditions. High production costs as the consequence of such approach to the production of ground red paprika are acceptable only in the case of high added value products like PDO and PGI products. In a large scale production of ground red paprika, which is before all commercially very competitive because of its price, there is a tendency to perform harvest mechanically at the moment when majority of the fruits achieve the full ripeness. Nevertheless, at the harvesting moment some fruits on the plants are still not completely ripe, influencing thus the quality of ground red paprika predominantly by altering its color. Additionally, even when harvesting is performed manually, some pepper fruits remain unripe (green) at the end of the growing season and the question of possibility and effects of their utilization in ground red paprika production is still opened.

Nevertheless, there is no sufficient information on changes of pigment content and composition in unripe pepper fruits during their postharvest ripening and their influence on color properties of ground red paprika. The aim of present research is to analyze the differences in pigment content and composition in green pepper ripened in the field and in the greenhouse under different postharvest ripening conditions and to relate them to the color properties of produced ground red paprika.

Materials and methods

Sampling and postharvest treatment (ripening) of pepper fruits

Green pepper fruits (*Capsicum annum* L.) variety *"AlevaNK"* were picked manually from the field, located in the northern part of Serbia. During the production a good agricultural practice was applied including fertilization, irrigation and plant protection. Pepper fruits were sampled from the field when 80% of fruits were well developed in a green maturity stage. For fruits analyzed without postharvest ripening picking, measurement, transport from the field to the laboratory, preparation for drying, drying and grinding were performed in the period not exceeding three days. Remaining fruits were subjected to the postharvest ripening for 15 days under different conditions: with natural daylight changes and in the dark. For both ripening conditions treatment was conducted in greenhouse under semi-controlled temperature (25-45 ^{o}C) and humidity (40-60%). During the ripening pepper fruits were spread on flat surface. After postharvest ripening, fruits were dried under laboratory conditions in the same manner as fresh fruits (for 10 h with gradual increase of temperature from 40 °C at the beginning to 80 °C at the end of experiment). After drying, in order to obtain powdered pepper, pericarp was separated from seeds and grinded shortly, for 10 s, in a laboratory grinder in order to avoid sample heating, but long enough to obtain powder with over 90% of particles with size under 350 µm .

Simultaneously, the ripening of pepper was observed at the same field and pepper fruits were picked manually at the time when majority (approximately 80%) of fruits reached breaker (8 days after picking green fruits) and faint red (another 10 days after picking breaker) stage of ripening. Pericarp of fresh fruits was separated from seeds and used for the analysis. Complete scheme of conducted experiment is presented in Figure 1.

Analytical methods

Color of fresh fruits and powder samples was measured as a reflected color in the CIELab color space. Measurements were performed using a MOMCOLOR 101 (MOM – Budapest) and *MOMCOLOR computing unit* was used for calculation of lightness of color (L*), ratio between red/green (a*) and yellow and blue (b*) from measured $x1$, $x2$, y and z values. Ten readings were performed for each sample. For fresh fruits color measurements were performed on visually even color characteristic for each maturity stage (green, breaker and faint red). Powder samples were spread in 0.5 cm layer and color was measured at ten different points. Dominant wavelength was estimated from chromaticity diagram, while the color difference between two samples (ΔE_{ab}^*) was calculated as the square root from sum of squared differences between measured L*, a* and b* values of compared samples. Method proposed by American Spice Trade Association[1] was used for the measurement of extractable red color and result is expressed in ASTA units.

In all samples moisture content was determined by drying sample to the constant mass at 105 °C. Chlorophyll content was determined by extraction of chlorophyll from 10 g of the representative pepper pericarp sample with acetone (P.A. grade, J.T. Baker, Deventer, Holland), under dim light and by measuring absorption of the extract at 662 and 664 nm. Calculation of chlorophyll *a* and *b* content was conducted according to Wettstein.[16]

Extraction of carotenoids from the pepper pericarp was performed according to Mínguez-Mosquera and Hornero-Méndez[17]. Separation of extracted carotenoids was performed according to the method of Morais et al.[18] with minor modifications by Kevrešan et al[19]. HP1090 (Agilent Technologies, CA, USA) HPLC system with DAD detector equipped with Zorbax SB C18 column (3.0×250 mm i.d., particle size 5 µm) and the same precolumn (Zorbax SB C18, 4.6×12 mm i.d., particle size 5 µm) was used. Separation of pigments was carried out at ambient temperature (24±1 °C). Flow rate was 1.5 mL/min. Two eluents were used A: acetone-water (75:25, v/v) and B: acetone-methanol (75:25, v/v) with following gradient: from 0% to 25% B in 10 min, from 25% to 100% B in 35 min, 100% B for 10 min. All reagents used for separation were HPLC quality grade purchased from J.T. Baker (Deventer, Holland), while water was grade 1 quality according to ISO 3696:1987. After each analysis eluent B was reduced to 0% in 20 min and then the system was left running under these conditions for 15 min before the next analysis. Carotenoids were detected at 460±4 nm. For each peak the whole spectrum (from 300 – 550 nm) was recorded. Peaks were identified by comparing retention time and/or spectra with carotenoid standards (capsorubin, antheraxanthin, zeaxanthin, violaxanthin and β-carotene). Standards were acquired from Carotenature, Switzerland, while capsanthin was purchased from Hoffman La

Roche, Switzerland. All unidentified yellow carotenoids were calculated as β-carotene equivalents. Results for pigment content were expressed per dry weight.

Obtained results were analyzed by analysis of variance (ANOVA), followed by comparison of means with Duncan´s test at significance level of 0.01, using the Statistica 10.0 software.[20]

Results and discussion

In the first step of analysis of obtained results, the comparative overview of differences in pepper pigment composition of paprika fruits ripened in the field and paprika obtained from green pepper fruits ripened in the greenhouse under different conditions is presented and related with color properties in CIELab system and ASTA value of analyzed samples.

Changes in pigment content and composition during the ripening process of investigated pepper (*Capsicum annum*) variety *AlevaNK* in the field, from green, over breaker to faint red maturity stage are presented in Table 1.

In green pepper, dominant pigments are chlorophylls and yellow carotenoids emphasizing photosynthesis as the dominant biochemical process. Red pigments, capsanthin and capsorubin were not identified in green paprika fruits, but the intermediate products of their synthetic pathways, including zeaxanthin, antheraxanthin and violaxanthin were identified, indicating initiation of biochemical changes leading to formation of red pigments (Table 1).

Towards the breaker phase, content of chlorophyll is reduced to the half in green fruits, while the total of carotenoids content is doubled. Red pigments start to be accumulated with content of capsanthin being up to 7 fold higher than content of capsorubin. More or less equal content of red and yellow pigments was registered in fruits at breaker maturity phase. Pepper at breaker phase starts to accumulate β-carotene, and the quantity of zeaxanthin is increased in comparison to green fruits. On the other hand, content of antherxanthin remains at the same level as in the green fruits, while the content of violaxanthin significantly decreases. Variation in the content of yellow pigments in pepper ripening stages reported for variety Bola[21] pointed out gradual but permanent increase of these intermediate products of red pigments during the ripening process in the field. At the same time findings of Deli et al.[12], based on the research on Szentesi Kosszarvu pepper variety, are mainly aligned with our findings. These contrasting results indicate that the stage of development, variety and ripening conditions influence the dynamic of pigment synthesis and intermediate products equilibrium.

Total carotenoid content in faint red pepper fruits is significantly higher than in breaker stage and especially higher compared to green fruits. In faint red pepper content of red pigment is twice as high as content of total yellow pigments and the content of capsanthin is over 10 times higher than the content of capsorubin. In faint red paprika fruits content of β-carotene and zeaxanthine is multiply increased in comparison to breaker phase, while oppositely to findings of Mínguez-Mosquera and Hornero-Méndez[22] and Deli et al.[12,13] antheraxantin was not identified.

Carotenoids synthesized during the pepper fruit maturation undergo the esterification process.[21,23] Esterification of carotenoids in investigated fruits of pepper variety AlevaNK is presented in Table 2. It is obvious that in green pepper almost only non-esterified forms of pigments are present, in breaker stage quantity of pigments in esterified forms is more or less at the level of nonesterified pigments, while in faint red fruits zeaxanthin, capsathin and capsorubin are present more in esterified than in nonesterified forms with major quantity being in diesterified form. These results confirm the findings presented by Mínguez-Mosquera and Hornero-Méndez.[21]

Described changes of pigment content, composition and esterification in pepper fruits ripening in the field are further compared with pigment composition in ground paprika obtained from pepper fruits picked at green maturity stage and have been subjected to different postharvest treatments

(Tables 3 and 4). Even in green paprika, dried and grinded shortly after harvesting, some quantities of β-carotene and capsorubin have been registered, oppositely to fresh green pepper fruit. Other sign indicating instant changes in the pigment composition after picking of green fruits is a complete disappearance of antheraxanthin and violaxanthin, as well as chlorophyll and multitude of unidentified yellow pigments. Although the complete processing procedure of fresh green pepper fruits was conducted in less than three days and under usual processing conditions used in ground paprika production it is obvious that significant changes in carotenoid content occurred. Such results can be easily ascribed to changes causing partial or complete destruction of certain pigments even under very mild processing conditions, but also to dynamic biochemical processes in the first days after paprika harvesting.[14,15,21,22] Nevertheless, it is quite obvious that balance of pigments in paprika dried and grinded shortly after harvesting is quite different than in green fresh fruits. This points out that also color changes reflecting more red but less green and yellow tones than fresh fruit, can be expected (Table 3). In ground paprika obtained from the green pepper without postharvest ripening, pigments are dominantly in nonesterified form (Table 4).

Majority of green pepper fruits subjected to postharvest ripening during 15 days period visually appeared as red fruits. Nevertheless, obtained data for pigment content, composition and esterification rate (Tables 3 and 4) have shown that the processes of pigment biosynthesis in fruits ripened in postharvest processes are different from those occurring in the naturally matured fruits in the field (Tables 1 and 2).

Quantity of red pigments in paprika produced from green pepper fruits ripened by greenhouse postharvest treatments during 15 days is over 3 times higher than the quantity of yellow pigments, providing the red/yellow pigment ratio (3:1) much above naturally ripened pepper at breaker (1:1), but also in faint red (2:1) ripening stage from the field. Furthermore, in greenhouse ripened fruits, oppositely to the fruits ripened in the field, no accumulation of β-carotene and zeaxanthine has occurred, but rather the biosynthesis process redirects the pathways to formation of red pigments, capsanthin and capsorubin. These findings are in contrast with the results of Markus et al.[24] who observed an increase of β-carotene content in paprika spice produced from overipened fruits harvested in later maturity stages. Also, small quantity of antheraxanthin, which has not been registered in faint red fruit from the field, is present in fruits ripened in the postharvest treatment. The quantity of violaxanthin is multiple times lower than in fruits ripen in the field (Tables 1 and 3). Different stress factors, such as salinity[25], water stress[26] and storage temperature[27] are proven to influence the carotenoid biosynthesis in edible plant organs. Harvest, as process by which fruit is detached from plant, is stress for both remaining plant and fruit, especially for green, non mature fruits and could be one of reasons for changing intensity of carotenoid biosynthesis in investigated green pepper fruits and consequently in obtained ground paprika.

By comparing pigment composition of ground paprika obtained from green pepper fruit ripened under natural daylight change and in the dark, it can be concluded that postharvest ripening under natural daylight changes is resulting in higher content of red pigments (both capsanthin and capsorubin), and in higher contents of β-carotene and zeaxanthin. At the same time contents of antheraxanthin and violaxanthin are at the same level regardless of applied postharvest ripening conditions. Quantity of capsanthin in paprika produced from the pepper ripened in the dark is more than 13 times higher than capsorubin content and for the postharvest treatment under natural daylight this ratio is similar to faint red pepper ripened in the field (Tables 1 and 3).

During the postharvest ripening of green pepper the esterification processes are less expressed then during the ripening of the fruits in the field. Zeaxanthin is not undergoing the esterification processes, and other yellow pigments are present only in monoesterified form. Esterification of red pigments is somewhat more expressed compared to yellow ones, and capsanthin is present in both mono and diesterified forms. Quantities of monoesterified pigments are aproximately doubled if the postharvest ripening is conducted under the natural daylight changes in comparison to the dark conditions. Regardless of postharvest ripening conditions diesterified form is synthesized only in the case of capsanthin with more diesterified form being produced again when postharvest ripening was conducted under the natural daylight changes. These findings are in accordance with results of Markus et al.[24] who concluded that more sunny days during the ripening period result in more pigments in esterified forms, which are more stable and thus result in better storage properties of produced paprika spice.

Color properties of the surface of fresh pepper fruits from the field in different maturity stage i.e. in fruits of very distinctive visual appearance regarding color when expressed in CIELab system (Table 5) indicate that there is no significant difference among fruits in different ripening stages regarding the lightness (L*) while the blue/yellow ratio (b*) only slightly changes to positive values as ripening progresses, indicating domination of yellow over blue color. The main change during ripening, which results in visual perception of fruit distinction, is related to change of green/red ratio (a*). The values of a* change from negative values (indicating green fruits) over to zero for breaker stage of maturity (indicating balanced ratio of red and green tones) to high positive values for faint red fruits. Differences in green/red ratio (a*) result also in significant differences in psychrometric chroma (C*) among fresh pepper fruits at different ripening stages. Dominant wavelength for green and breaker fruits is in the range of yellow part of the spectra while for faint red fruits it inclines more to the orange spectral range.

Observations regarding the CIELab color properties of ground red paprika obtained from green pepper fruits ripened under different postharvest treatments (Table 6) illustrate that the most intensive red color was obtained for ground paprika produced from green fruits ripened under natural daylight changes. Ground paprika produced from the fruit ripened in the dark had less apparently visible red color while in paprika ground from directly dried green pepper the a* value indicates balanced intensity of green and red tones.

The positive value of b* confirms domination of yellow tones for all examined samples, with more intensive yellow tone for paprika produced from pepper ripened by postharvest treatment under natural daylight changes than in the dark. This observation can be related to higher ratio of red/yellow pigment and higher capsanthin content in respect to capsorubin in paprika from pepper ripened in the dark (Table 3). Ground red paprika, regardless of ripening conditions of pepper fruits from which were produced showed dominant wavelengths in yellow spectral range.

ASTA value increased from 3.97 in ground paprika obtained from green pepper dried and grinded shortly after the harvest to 23.10 in ground paprika obtained from green pepper ripened for 15 days in the dark and even to 42.75 for ground paprika obtained from green pepper ripened for 15 days under natural daylight changes.

Based, on the L*, a* and b* values from Table 6 color differences (ΔE_{ab}*) between ground red paprika samples obtained under different ripening conditions were calculated. Color differences between ground paprika obtained from green pepper dried and grinded shortly after the harvest and ground paprika obtained from green pepper ripened for 15 days in the dark and under the natural daylight changes were 6.18 and 10.51 respectively, while the difference between two postharvest ripening treatments was 5.22. Color difference (ΔE_{ab}*) indicates the degree of color difference between two samples. ΔE_{ab}* value in the range of 0–0.5 signifies an imperceptible difference in color between two samples, 0.5–1.5 a slight difference, 1.5–3.0 a just noticeable difference, 3.0–6.0 an apparent difference, 6.0–12.0 an extremely apparent difference and above 12.0 a color of a different shade.[28,29] Obtained results indicate that color differences are apparent to extremely apparent with less expressed difference for paprika which has ripened in the dark.

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Figure 1. Scheme of conducted experiment

Table 1. Pigment Content (mg/kg dry matter) in Fresh Pepper Fruits Ripenedd in the Field.

Total content of pigments	**Fresh pepper picked from the field in different ripening stages**		
	Green	Breaker	Faint red
YELLOW PIGMENTS			
β-carotene	N.D. [1]	22.7[b]	207.8[c]
Zeaxanthin	28.2[a]	41.5[b]	211.6[c]
Antheraxantin	9.4[a]	9.6[a]	N.D. [1]
Violaxanthin	50.7[a]	18.3[b]	63.4[a]
Non identified yellow pigments	268.6[b]	212.9[a]	480.7[c]
RED PIGMENTS			
Capsanthin	N.D. [1]	293.1[b]	1841.9[c]
Capsorubin	N.D. [1]	40.7[b]	162.4[c]
GREEN PIGMENTS			
Chlorophyl (*a+b*)	126.64[a]	69.04[b]	N.D. [1]

[1]N.D. - not detected

Means within the same row followed by different letters were significantly different at $p \leq 0.01$.

Table 2. Contents of Pigments in Ester Forms (mg/kg dry matter) in Fresh Pepper Fruits Ripened in the Field.

Pigments	**Esterification**	**Fresh pepper picked from the field in different ripening stages**		
		Green	Breaker	Faint red
Zeaxanthin	nonesterified	28.2	20.6	60.2
	monoesterified	N.D. [1]	N.D. [1]	N.D. [1]
	diesterified	N.D. [1]	20.9	151.4
Yellow pigments	nonesterified	348	259.0	590.2
	monoesterified	8.9	25.1	221.9
	diesterified	N.D. [1]	20.9	151.4
Capsanthin	nonesterified	N.D. [1]	111.4	325.8
	monoesterified	N.D. [1]	72.0	621.9
	diesterified	N.D. [1]	109.7	894.2
Capsorubin	nonesterified	N.D. [1]	23.4	19.4
	monoesterified	N.D. [1]	6.6	69.4
	diesterified	N.D. [1]	10.7	73.6

[1] N.D. - not detected

Table 3. Pigment Content (mg/kg dry matter) in Ground Paprika Obtained From Green Pepper Ripened Under Different Postharvest Ripening Conditions.

Total content of pigments	**Green pepper dried and grinded after different postharvest ripening treatments**		
	Dried without ripening	Ripened in the dark	Ripened under natural daylight changes
YELLOW PIGMENTS			
β-carotene	14.34[a]	7.48[b]	14.50[a]
Zeaxanthin	32.94[a]	4.56[b]	8.45[b]
Antheraxantin	N.D. [1]	3.32[b]	4.41[b]
Violaxanthin	N.D. [1]	4.76[b]	4.79[b]
Non identified yellow pigments	4.00[a]	23.99[b]	33.79[b]
RED PIGMENTS			
Capsanthin	N.D. [1]	146.39[b]	200.66[c]
Capsorubin	7.27[a]	10.48[ab]	17.54[b]
GREEN PIGMENTS			
Chlorophyl (*a+b*)	N.D. [1]	N.D. [1]	N.D. [1]

[1]N.D. - not detected

Means within the same row followed by different letters were significantly different at $p \leq 0.01$.

Table 4. Contents of Pigments in Ester Forms (mg/kg dry matter) in Paprika Ripened in the Field and Under Different Postharvest Ripening Conditions.

Pigments	**Esterification**	**Green pepper dried and grinded after different postharvest ripening treatments**		
		Dried without ripening	Ripened in the dark	Ripened under natural daylight changes
Zeaxanthin	nonesterified	32.94	4.56	8.45
	monoesterified	N.D. [1]	N.D. [1]	N.D. [1]
	diesterified	N.D. [1]	N.D. [1]	N.D. [1]
Yellow pigments	nonesterified	47.28	38.82	55.57
	monoesterified	4.00	5.29	10.37
	diesterified	N.D. [1]	N.D. [1]	N.D. [1]
Capsanthin	nonesterified	N.D. [1]	70.03	83.32
	monoesterified	N.D. [1]	18.73	41.66
	diesterified	N.D. [1]	57.63	75.68
Capsorubin	nonesterified	3.03	2.89	4.20
	monoesterified	4.24	7.59	13.34
	diesterified	N.D. [1]	N.D. [1]	N.D. [1]

[1]N.D. - not detected

Table 5. CIELab Color Properties of Surface of Fresh Pepper Fruits From the Field in Different Ripening Stages.

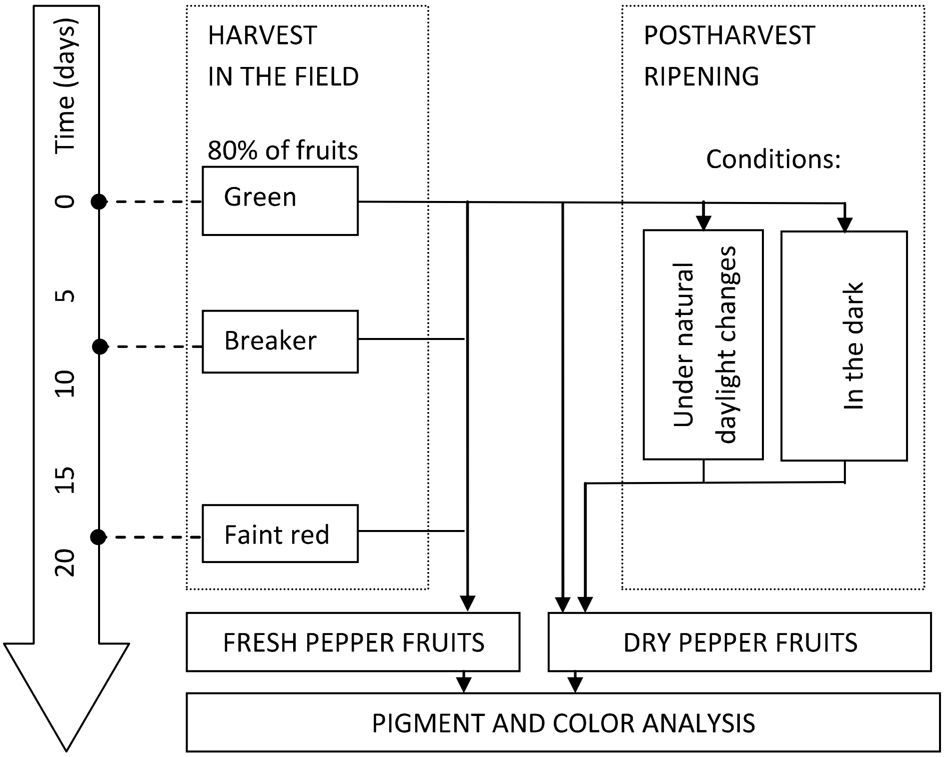
CIELab color properties	Fresh pepper picked from the field in different ripening stages		
	green	breaker	red
L*	35.80^{a}	33.16^{a}	33.77^{a}
a*	-17.65^{a}	1.20^{b}	39.23^{c}
b*	27.00^{ab}	33.16^{a}	22.98^{b}
C*	30.78^{b}	14.09^{a}	44.05^{c}
Dominant wavelength (µm)	562^{a}	579^{b}	615^{c}

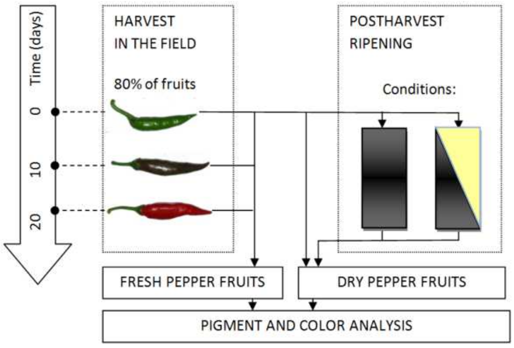
Means within the same row followed by different letters were significantly different at $p \leq 0.01$.

Table 6. ASTA and CIELab color properties of ground paprika obtained from green pepper ripened under different postharvest ripening conditions.

	Without ripening	Ripening in the dark	Ripening under natural daylight changes
CIELab color properties			
L*	41.42^{c}	39.20^{c}	38.67^{c}
a*	2.22^{c}	7.97^{b}	11.94^{a}
b*	22.33^{b}	21.88^{b}	25.23^{a}
C*	20.92^{c}	21.76^{b}	26.40^{a}
Dominant wavelength (µm)	579.0^{c}	584.0^{b}	588.5^{a}
ASTA	3.97^{c}	23.10^{b}	42.75^{a}

Means within the same row followed by different letters were significantly different at $p \leq 0.01$.


Time (days)
0
5
10
15
20
HARVEST
IN THE FIELD
80% of fruits
Green
Breaker
Faint red
POSTHARVEST
RIPENING
Conditions:
Under natural daylight changes
In the dark
FRESH PEPPER FRUITS
DRY PEPPER FRUITS
PIGMENT AND COLOR ANALYSIS



Time (days)
0
10
20
HARVEST
IN THE FIELD
80% of fruits
POSTHARVEST
RIPENING
Conditions:
FRESH PEPPER FRUITS
DRY PEPPER FRUITS
PIGMENT AND COLOR ANALYSIS