

Influences of γ -Irradiation and Storage on the Carotenoids of Sun-Dried and Dehydrated Paprika

AYHAN TOPUZ AND FERAMUZ OZDEMIR*

Department of Food Engineering, Faculty of Agriculture, Akdeniz University, 07059 Antalya, Turkey

The effects of drying methods, γ -irradiation, and storage on the carotenoids (capsanthin, capsorubin, zeaxanthin, capsolutein, violaxanthin, β -carotene, and β -cryptoxanthin) of paprika were investigated. Sun-dried and dehydrated paprika samples were irradiated in a ^{60}Co γ -irradiator at five doses (0, 2.5, 5.0, 7.5, and 10 kGy) in polyethylene bags and stored for 10 months at ambient temperature. Individual carotenoid analyses were carried out on the paprika and fresh red pepper during a 2 month period using the reverse phase HPLC technique. The concentrations of capsanthin and capsorubin, which are responsible for the attractive red color of sun-dried paprika, were higher than those of dehydrated paprika. Higher irradiation doses and a longer storage period resulted in a significant ($P < 0.01$) reduction of all the carotenoids, except capsorubin. There was no significant ($P < 0.05$) effect of irradiation dose on capsorubin destruction. The decrease of red carotenoids, for all irradiation treatments, was less than that of the storage period. Even the highest irradiation dose, 10 kGy, caused a 11.1% capsanthin reduction; however, 10 months of storage at the ambient temperature caused a 42.1% reduction of capsanthin. Yellow pigments of paprika (zeaxanthin, capsolutein, violaxanthin, β -carotene, and β -cryptoxanthin) were significantly ($P < 0.01$) decreased by all treatments. These yellow pigments were also found to be at high levels in those sun-dried samples with red pigments. This difference could be caused by the contribution of pigment biosynthesis during the sun-drying period. The most significant pigment reduction was realized in the processing and storage conditions of paprika, rather than in the irradiation process.

KEYWORDS: Paprika; carotenoids; γ -irradiation; storage

INTRODUCTION

Paprika, the dehydrated and ground fruit of a certain variety of red pepper (*Capsicum annuum* L.), is one of the oldest, most important, and widely used food colorants because of its high carotenoid content (1–3). The annual productions of paprika and paprika oleoresins all over the world are 60000 and 1400 tonnes, respectively (4). They are used in a variety of products, such as soups, stews, sausage, salad dressing, sauces, and pizzas (1, 5). It is well-known that both the pungency and aroma of paprika affect consumer preference. However, because the commercial value of the paprika depends primarily on the red coloring, the quantification and characterization of paprika carotenoids have always been of great interest (6). Furthermore, carotenoids have important biological properties, such as being antioxidants and free radical scavengers and reducing the risk of cancer. In addition, some of them (β -carotene, β -cryptoxanthin, etc.) have provitamin A activity (6–9).

Earlier research has stated that all of the carotenoid pigments present in paprika are C_{40} isoprenoids, containing nine conjugated double bonds in the central polyenic chain with different end groups (β , κ , and 3-hydroxy-5,6-epoxide), which change

the chromophore properties of each pigment, allowing them to be classified into two isochromic families: red and yellow. The red fraction (ketocarotenoids) contains the pigments exclusive to the *Capsicum* genus (capsanthin, capsanthin 5,6-epoxide, and capsorubin), and the yellow fraction contains xanthophylls (zeaxanthin, violaxanthin, antheraxanthin, β -cryptoxanthin, and capsolutein) and carotene (β -carotene). In the ripening process of the pepper, the yellow fraction acts as a precursor of the red carotenoids (7, 10, 11).

There are many technological and conditional factors that affect the carotenoids of paprika, apart from the maturity, variety, and genetic diversity of the red pepper (12–14). Many studies carried out on carotenoid losses in paprika have shown that both the drying and milling processes are the most effective in creating light, heat, and oxygen tension in the oxidation reaction (11, 15–17). Hence, several types of drying and milling methods were utilized to preserve the color of the paprika, besides food additives (3, 12, 18). The addition of seed to the flesh of red pepper before milling and storage under nitrogen also slowed the oxidation rate of carotenoids in paprika (18).

Many subsequent studies have been carried out on the discoloration mechanism of pepper or paprika carotenoids (13, 19, 20). It has been clarified that the carotenoids are present as partially or completely esterified with fatty acids, which prevent

* Author to whom correspondence should be addressed (telephone +90 242 310 24 34; fax +90 242 227 45 64; e-mail feramuz@akdeniz.edu.tr).

the possible thermo- or photooxidation reactions caused by the discoloration of pigment (21, 22). A previous study showed that the ketocarotenoids are mostly esterified with medium-chain saturated fatty acids, such as lauric (C_{12:0}) and myristic (C_{14:0}) acids, whereas the xanthophylls are esterified mainly by unsaturated long-chain fatty acids, such as oleic (C_{18:1}) and linoleic (C_{18:2}) acids (11). Hence, the stability of every pigment is different, due to the different degree of esterification and the nature of the esterified fatty acid.

Paprika has a great amount of mold, yeast, bacteria, and insect contaminant. This restricts or decreases the commercial value because of the strict hygienic demand in spices. Therefore, they are obligatorily sterilized or fumigated in some way (4, 23–25). Because of its low moisture content, paprika is a micro-biologically stable product; however, when it is added to water-rich foods, microorganisms can proliferate quickly. Additionally, paprika is not usually used immediately after processing, but is stored for varying periods of time before use. Because of this, the irradiation of paprika is one of the safest, most efficient, and widely used methods to obtain a microorganism-free product. Furthermore, it is also important to establish suitable conditions for its storage, so that there is a reduction in its microbiological and chemical deterioration.

The objective of the present study was to determine the comparative effects of γ -irradiation and the duration of storage on the color constituents of sun-dried and dehydrated paprika so as to ensure the safest and most stable product.

EXPERIMENTAL PROCEDURES

Materials. Fully ripe peppers, of an unnamed Turkish paprika cultivar, were harvested by farmers from their own fields during the harvesting season in the province of Kahramanmaraş, Turkey. The pepper harvesting season begins in September and continues until the end of October. Kahramanmaraş is one of the most intensive pepper production areas in Turkey, and it is located in southern Turkey, ~650 m above sea level with ~700 mm of annual rainfall. For each experimental trial, 100 ± 10 kg of harvested ripe pepper pods was sampled.

Processing of Paprika. Pepper pod samples were processed into paprika using two different paprika processing systems used commercially in Turkey. Paprika processing was carried out at the two plants that belong to the Musan and Godeler Co. (Kahramanmaraş, Turkey).

Sun-Drying. In Turkey, this method is traditionally used by farmers owing to its low cost. Pepper samples were spread out on fields and left under sunlight exposure for 5–7 days. After drying, the moisture content of the pods had dropped to between 12 and 14%. Impurities of dried pods were cleaned and seeds were removed. The seeds of 30% of the sample were re-added to the deseeded dried pepper before milling. The milling process consisted of coarse grinding by two hammer mills. Flakes were separated into two classes (<1 or 1–3 mm) using mechanically shaken sieves, whereas the coarse particles were sent back to another hammer mill. Paprika of 1–3 mm was used for this study.

Oven-Drying. The drying consisted of washing equipment, a chopper, a hotted washing cylinder, and drying equipment. Stalks and seeds were removed before being chopped into a 9 mm square shape. Then the chopped pepper was dehydrated in a tunnel dryer with a hot air stream for 90 min. The temperature of the air at the entrance of the tunnel was ~70 °C. After drying, the moisture content of the chopped pepper dropped to between 11 and 12%. After the addition of 30% seed, it was crushed using a hammer mill and classified into the flakes and powder that were previously explained.

Salting and Polishing. Salt (10%) and oil [8% olive oil and cotton seed oil (1:1)] were added into the sun-dried and dehydrated paprika flakes. This process is a common traditional application in Turkey.

The final product was packaged in polyethylene bags before undergoing γ -irradiation and subsequent storage.

Irradiation of Paprika. Paprika samples were irradiated at the Nuclear Agriculture and Animal Science Research Center, Ankara, Turkey. The irradiation process of samples was carried out in a ⁶⁰Co γ -irradiator (Gamma Cell 220) at average absorbed doses of 2.5, 5.0, 7.5, and 10.0 kGy, with a maximum dose rate of 0.042 kGy/min. These doses were chosen according to the predictive microbiological load of sun-dried and dehydrated paprika samples. Treatments were performed on the eight samples at each step, due to the restricted volume of the irradiator cell at ambient temperature. The absorbed doses of samples were confirmed at each step by putting a Harwell Amber Perspex dosimeter in the center and the outer side of the eight bags wrapped around in a cylinder shape, using sticky ribbon.

The irradiation treatment was conducted in duplicate for every dose. All of the irradiation treatments were completed in 3 days.

Samples were stored at room temperature in the dark. Carotenoids of the samples were extracted at the end of every 2 month storage period within 10 months.

Pigment Extraction. The extraction of carotenoids was carried out according to the method used in a previous study (26). To achieve this, 1.5 g of paprika flakes (from 10 g of the pulp of red pepper) was extracted four times, with 50 mL of acetone in an Ultra Turrax homogenizer for 3 min, until no more color was extracted. Each extract was collected in a round-bottom flask and then evaporated (at 50 °C and 500 mmHg vacuum) until a 50 mL final volume was attained. The concentrate was transferred into the decanting funnel before 100 mL of diethyl ether and 100 mL of sodium chloride solution (10%) were added. When the phases were separated, the aqueous phase was discarded. The supernatant was then washed with 100 mL of an anhydrous Na₂SO₄ (2%) solution to remove all of the remaining water. For the saponification reaction at room temperature, 50 mL of potassium hydroxide solution (10%) in methanol was added and shaken vigorously before being left in a dark place for 1 h. The solution was separated by adding 100 mL of sodium chloride solution (10%) at the end of the saponification process. For subsequent quantification, 500 μ L of the standard solution (500 μ g/mL) of β -apo-8'-carotenal in 40–60 °C light petroleum ether was added, and then the aqueous phase was discarded. The organic phase was first washed several times with 100 mL of distilled water, until the wash was neutral, and then once in 100 mL of an anhydrous Na₂SO₄ (2%) solution. After that, diethyl ether was evaporated (at 30 °C and 500 mmHg vacuum) to dryness in the flask of the rotary evaporator (Janke Kunkel), and the pigments were dissolved in acetone to a volume of 100 mL and kept at –18 °C in an Eppendorf until HPLC analysis. The extract was passed through the 0.45 μ m membrane filter (Millipore) before injection.

Pigment Separation and Quantification by HPLC. The carotenoid profile of the samples was quantified using β -apo-8'-carotenal as the internal standard. The chromatographic separation was performed on a reversed phase column (Nucleosil 5 C₁₈, 250 × 4 mm i.d.). The binary gradient (acetone/water, at the beginning 75:25) elution was run by means of a solvent delivery system (Varian 9010) at the flow rate of 1.5 mL/min. The gradient was initiated with the beginning proportion for 5 min, then linearly increased to 95:5 for 5 min, and subsequently maintained at this level for 10 min. At the end of the analysis, the column was washed with acetone for 3 min and conditioned with the initial proportion for 10 min. Detection was performed at 450 nm with the UV detector (Varian 9050). The guard cartridge (Nucleosil 5 C₁₈ 4 × 4 mm i.d.) was used to protect the main column for each of the 10 samples. The duplicate chromatographic separation of the specific samples was performed at room temperature, with a 20 μ L injection volume.

Identification of Pigments. Identification of the pigments was carried out according to the method of Minguez-Mosquera and Hornero-Mendez (26), which consists of thin layer cochromatography purification and identification. The obtained standard solution was used to differentiate each peak of the sample chromatogram.

Statistical Analysis. The experiment was conducted as a randomized plot with a factorial design in the drying methods, irradiation doses, and six periods of storage (2 × 5 × 6), using duplicate samples. Data were subjected to analysis of variance, and appropriate means separation was conducted using Duncan's multiple-range test analysis in SAS software.

Table 1. Carotenoid Composition of Fresh Red Pepper and Changes in Carotenoids during the Whole Process in Sun-Dried and Dehydrated Paprika (Milligrams per Kilograms of Dry Matter)^a

pigment	fresh fruit	sun-dried paprika	loss (%)	dehydrated paprika	loss (%)
capsanthin	4005.8 ± 175.9	818.12a ± 24.04	79.58	571.57b ± 14.13	85.73
capsorubin	381.6 ± 8.00	67.92a ± 1.70	82.20	62.54b ± 1.52	83.61
violaxanthin	392.2 ± 8.85	65.19a ± 3.08	83.38	50.95b ± 2.02	87.01
capsolutein	550.1 ± 20.02	86.40a ± 3.60	84.29	61.14b ± 2.40	88.89
zeaxanthin	1022.8 ± 28.13	191.35a ± 4.87	81.29	127.62b ± 3.17	87.52
β-carotene	359.6 ± 7.80	60.35a ± 1.67	83.21	54.47b ± 1.26	84.85
β-cryptoxanthin	430.4 ± 8.35	59.83a ± 1.48	86.10	50.10b ± 1.17	88.36
red pigments	4387.4 ± 171.2	886.04a ± 25.71	79.80	634.11b ± 15.30	85.55
yellow pigments	2755.1 ± 32.1	463.12a ± 14.29	83.19	344.28b ± 9.37	87.50
total carotenoids	7142.5 ± 211.3	1349.16a ± 39.73	81.11	978.39b ± 24.37	86.30

^a Values in a row followed by the different letters are significantly ($P < 0.05$) different (Duncan's multiple-range test). Mean value ± standard error (for fresh fruit $n = 3$; for sun-dried and dehydrated paprika $n = 60$).

RESULTS AND DISCUSSION

Pigments Present in Red Pepper. Color is the most important sensory characteristic of paprika. Carotenoids are responsible for the color of pepper and paprika. The carotenoid content of fully ripe red pepper (*Capsicum annuum* L.) was analyzed to estimate the rate of degradation during the processes of irradiation and storage. Capsanthin, capsorubin, violaxanthin, capsolutein, zeaxanthin, β-cryptoxanthin, and β-carotene were determined to be the main carotenoids of the samples (Table 1). Those pigments, which are responsible for color, are normally present in the greatest quantities in the fresh fruit. Although trace amounts of other pigments and cis isomers of capsanthin, zeaxanthin, and β-cryptoxanthin were also found in fresh red pepper, they have not been taken into account in this study, due to their negligible contribution to color. In a previous study (26) on red pepper, the same pigments were detected in a similar amount. Furthermore, the authors quantified a few more pigments. A number of papers have stated that the carotenoid content of red pepper may have different values depending upon the particular variety, the rate of maturity, genetic diversity, and conditions of growth (2, 9, 11, 27–29).

Effects of Drying Methods on the Carotenoids of Paprika. The total carotenoid content drastically decreases during processing. During the entire process, the losses of red pigments (capsanthin and capsorubin) and yellow pigments (violaxanthin, capsolutein, zeaxanthin, β-cryptoxanthin, and β-carotene) were 79.8 and 83.2% in sun-dried paprika and 85.5 and 87.5% in dehydrated paprika, respectively (Table 1). Minguez-Mosquera et al. (12) reported that a total loss of 54% in carotenoids occurred between the fresh fruit stage and the paprika stage, with 25% being lost in the drying process. It was reported that the milling step was the more destructive, leading to a loss of from 42.7 to 55.2% in the total carotenoid content, depending on the variety of fruit. In the present study, however, the decrease during processing seems to be >80%. This can undoubtedly be attributed to two causes. On the one hand, the carotenoid concentrations may decrease with the effect of the drying and milling processes, which would consequently increase the rate of the oxidation reaction. On the other hand, the dilution could result from the addition of a high portion of seeds (30% of weight), salt (10% of weight), and oil (8% of weight) to achieve a more homogeneous product with regard to color and texture. Markus et al. (28) studied the effect of seed addition to pericarp and grinding on the storage stability of paprika pigments. They reported that, with all pigments, there were losses of 15–90 and 0–74% in both the non-seed-containing and seed-containing samples, respectively. Seed addition is a normal practice in the industrial process of paprika

powder. However, paprika flake (1–3 mm) processing involved not only seed addition but also the addition of salt and oil. In Turkey, both paprika flakes and paprika powder are produced, but the consumer usually prefers paprika flakes. We must emphasize that the present study was carried out on paprika flakes.

The concentration of red and yellow pigments is higher in sun-dried paprika than in dehydrated paprika (Table 1). The difference between pigment concentrations can be related to the biosynthesis of carotenoids during the sun-drying period. As a matter of fact, many authors indicated that the drying process induces the synthesis of red pigment from their yellow precursors and that new carotenoid biosynthesis is associated with the incomplete maturation of fruit depending on its drying time and temperature (11, 12). The carotenoid biosynthesis can last until the dry matter content of pepper is reduced to 40% (12).

From the above-mentioned results, it could be concluded that the reasons for the significant decrease in carotenoids are a result of the drying and milling processes. It may also be due to dilution, because of the additions of seeds, salt, and oil. During the process, more decreases in yellow pigments were seen than in red pigments. With respect to the drying methods, the sun-drying process provides superior color properties in paprika compared with the dehydration process.

Effects of γ-Irradiation on the Carotenoids of Paprika. The concentrations of individual carotenoids were significantly ($P < 0.01$) decreased as a function of γ-irradiation doses of up to 10 kGy, but the pigment profile was not changed (Table 2). It is well-known that paprika can be successfully sterilized by γ-irradiation at the dose of 10 kGy without using any chemicals (25, 27). However, it has an unfavorable effect on paprika pigments. This finding coincides with that of other authors (30). Only capsorubin was not decreased by the irradiation dose of 10 kGy. Capsolutein and zeaxanthin pigments in paprika are the most sensitive to γ-irradiation. A dose of 10 kGy leads to losses of 14.90% in capsolutein and 15.08% in zeaxanthin. However, the pigments capsanthin, β-carotene, and β-cryptoxanthin are also significantly ($P < 0.01$) affected by γ-irradiation. The effect of γ-irradiation on violaxanthin was less significant ($P < 0.05$). Table 3 shows that changes in the red, yellow, and total carotenoids of the samples, as a result of the irradiation process, are very similar. However, the ratio of total red pigment loss was 10.41%, whereas the total yellow pigment loss was 12.77% with the highest dose. It is possible to say that the yellow carotenoids are a little more sensitive to this treatment. In general, there is no statistical difference between the treatments of 7.5 and 10 kGy on the pigment reduction. It can be stated that >97.4% of the destruction of the carotenoids

Table 2. Means Squares from Analysis of Variance of Paprika Carotenoids^a

DF	source of variation							
	drying method (D)	irradiation dose (I)	storage period (S)	D × I	D × S	I × S	D × I × S	error
	1	4	5	4	5	20	20	60
capsanthin	1919384.60**	27893.10**	450823.51**	2687.24 ^{NS}	38421.04**	2458.97 ^{NS}	1963.55 ^{NS}	1860.57
capsorubin	861.46**	42.61 ^{NS}	2944.66**	53.02*	221.98**	49.96**	30.06 ^{NS}	19.77
violaxanthin	6162.62**	126.84**	7883.55**	101.73*	499.77**	169.26**	43.31 ^{NS}	33.44
capsolutein	18851.39**	760.82**	11205.90**	117.77*	614.51**	112.25**	38.08 ^{NS}	35.39
zeaxanthin	123450.26**	3136.99**	18341.09**	242.50 ^{NS}	917.01**	229.45 ^{NS}	138.56 ^{NS}	132.45
β -carotene	1055.30**	254.23**	2548.59**	24.00 ^{NS}	86.45**	26.47*	17.75 ^{NS}	12.71
β -cryptoxanthin	3304.77**	216.34**	1780.81**	7.88 ^{NS}	82.61**	30.79 ^{NS}	28.75 ^{NS}	20.80
red pigments	2002264.17**	29529.97**	525083.16**	2314.38 ^{NS}	40772.61**	2572.86 ^{NS}	1963.52 ^{NS}	2037.96
yellow pigments	427157.25**	14794.12**	169884.32**	1347.80 ^{NS}	8276.40**	1588.00**	649.28 ^{NS}	565.16
total carotenoids	4282627.48**	85159.67**	1282586.60**	6994.32 ^{NS}	84342.77**	7549.21*	3996.79 ^{NS}	4262.30

^a NS, nonsignificant at $P > 0.05$, *, significant at $P < 0.05$; **, significant at $P < 0.01$.

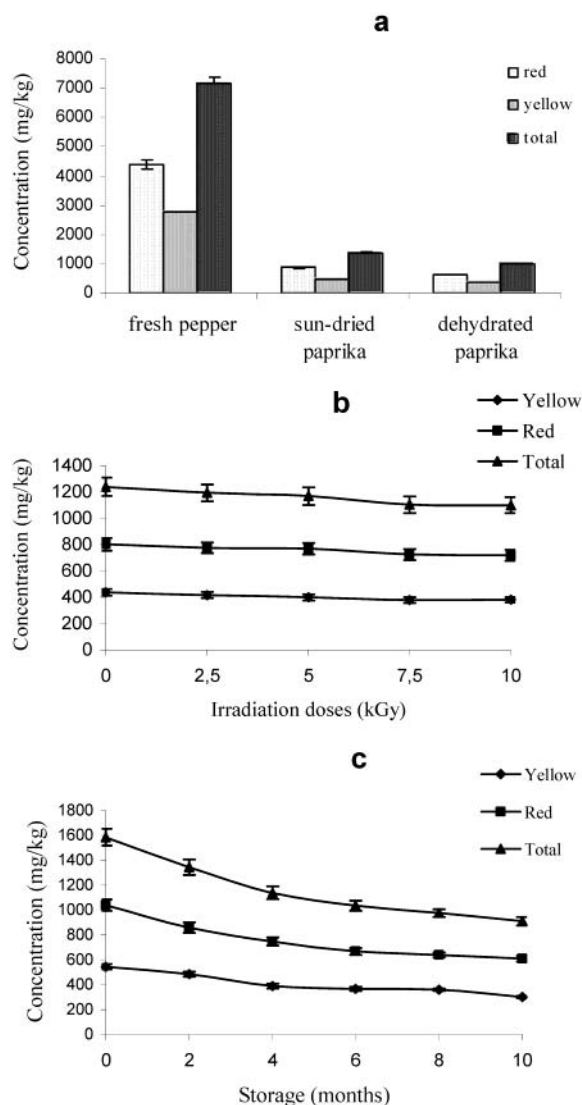


Figure 1. Variation of the contents of red, yellow, and total carotenoids of paprika with drying method (a), irradiation dose (b), and storage period (c). Values are the mean \pm standard error.

occurred with a dose of 7.5 kGy. The influence of irradiation on carotenoids reduction intensifies between doses of 5 and 7.5 kGy. This may be attributed to absorbed energy assisted by irradiation doses of >5 kGy and/or increases in the rate of the oxidation reaction of the paprika pigments.

Pigment reductions due to the irradiation are possibly caused by an increase of the oxidation reaction under γ -irradiation and also the secondary oxidative effects of free radical (H_2O_2 , O_3 , and $\cdot OH$) formation during irradiation.

It was inferred from the results of β -carotene and β -cryptoxanthin that the irradiation process lowers the pigments' stability for sun-dried paprika, but the same effect was not observed for dehydrated paprika. This difference may be explained by the de-esterification effect of γ -irradiation on sun-dried paprika owing to its high moisture content. The relationship between moisture content, water activity, and pigment stability will be studied to clarify the effect of moisture.

Research has been mostly carried out on the apparent and extractable color of paprika. However, research on the relationship between irradiation and the individual carotenoid of paprika has been limited. An earlier work (30) concluded that changes of the carotenoids in paprika were not significant with regard to practical application. Therefore, the results of the present study should be taken into consideration for the optimization of the irradiation process, whereby the loss of desirable compounds is decreased.

Effects of Storage on the Carotenoids of Paprika. Changes in the individual carotenoid contents of paprika during the storage period are given in Table 4. Overall, during the different stages of the storage period, the same pigments in the red pepper were found. Throughout the 10 months of storage, all carotenoids were significantly ($P < 0.05$) decreased. During storage, capsorubin is the most stable pigment of paprika. Despite that, it gradually decreased to the proportion of 32.83%. Capsanthin, the other red pigment, was a little more sensitive. The fact that red pigments are the most stable to the oxidation reaction was found in earlier research (19). However, the present study showed that zeaxanthin, β -cryptoxanthin, and β -carotene are also stable in storage, even more so than capsanthin. This phenomenon can be attributed to several factors, such as the nature of the oil added during the manufacturing process, the state of pigment esterification, and the origin of raw material. As explained under Experimental Procedures, cottonseed oil and olive oil are added to paprika during the process. The long-chain fatty acids are the main fatty acids of these oils, and they might increase the stability of yellow pigments. Minguéz-Mosquera and Pérez-Galvez (22) reported that yellow xanthophylls are esterified mainly by long-chain fatty acids. However, to our knowledge, there are no studies about the impact of irradiation on the oxidative stability of paprika pigments related to their oils. The destruction rate of violaxanthin was the highest, with the value of 62.30%. In general, yellow pigments decreased

Table 3. Quantitative Changes in the Carotenoid Composition of Irradiated Paprika (Milligrams per Kilogram of Dry Matter)^a

carotenoid	control	irradiation doses			
		2.5 kGy	5.0 kGy	7.5 kGy	10 kGy
capsanthin	736.3a ± 43.06	710.7b ± 36.09	702.5b ± 38.69	662.0c ± 38.12	654.5c ± 37.67
capsorubin	66.2a ± 2.54	65.3a ± 2.86	66.6a ± 2.77	63.4a ± 2.13	64.5a ± 2.11
violaxanthin	59.8ab ± 4.32	60.5a ± 4.13	58.3abc ± 4.63	55.0c ± 4.39	56.3c ± 4.20
capsolutein	80.0a ± 5.53	78.7a ± 5.47	73.6b ± 5.90	67.7c ± 4.87	68.1c ± 4.89
zeaxanthin	175.8a ± 9.98	163.9b ± 9.16	157.8b ± 8.71	148.5c ± 8.02	149.3c ± 7.83
β-carotene	62.1a ± 2.80	59.3b ± 2.24	56.2c ± 2.36	54.8c ± 2.26	54.4c ± 1.89
β-cryptoxanthin	59.7a ± 2.48	55.1b ± 2.22	54.0bc ± 2.29	52.4c ± 1.95	53.4bc ± 1.95
red pigments	802.5a ± 46.75	776.3b ± 40.48	769.2b ± 43.33	725.5c ± 41.98	718.9c ± 41.14
yellow pigments	437.3a ± 24.49	417.5b ± 22.62	399.8c ± 23.54	378.5d ± 21.44	381.5d ± 20.37
total carotenoids	1239.8a ± 70.66	1193.7b ± 62.68	1169.0b ± 66.75	1104.0c ± 63.06	1100.4c ± 60.98

^a Values in a row followed by different letters are significantly ($P < 0.05$) different (Duncan's multiple-range test). Mean value ± standard error ($n = 24$).

Table 4. Quantitative Changes in the Carotenoid Composition of Paprika during Storage (Milligrams per Kilogram of Dry Matter)^a

carotenoid	control	duration of storage				
		2 months	4 months	6 months	8 months	10 months
capsanthin	951.38a ± 41.61 ^a	787.40b ± 39.07	686.94b ± 29.62	609.67c ± 24.74	584.37c ± 17.90	550.77c ± 20.61
capsorubin	87.45a ± 1.99	71.55ab ± 2.07	61.22ab ± 1.07	58.21ab ± 0.76	55.01b ± 1.06	58.74b ± 0.97
violaxanthin	87.98a ± 3.22	74.23b ± 2.50	56.68c ± 3.85	51.60d ± 1.91	45.32e ± 1.11	33.17f ± 0.94
capsolutein	98.42b ± 4.74	107.75a ± 4.07	69.00c ± 3.87	64.33d ± 3.22	57.90e ± 1.98	45.86f ± 1.71
zeaxanthin	206.33a ± 9.51	185.92b ± 9.27	155.71c ± 8.00	143.94d ± 7.51	136.79d ± 5.92	128.29e ± 5.59
β-carotene	78.35a ± 1.72	60.93b ± 1.29	55.80c ± 1.30	53.53c ± 1.28	49.10d ± 0.72	47.37d ± 1.04
β-cryptoxanthin	73.95a ± 1.79	56.88b ± 1.51	53.02c ± 1.32	53.45c ± 1.53	46.99d ± 1.17	45.88d ± 1.08
red pigments	1038.8a ± 45.55	859.0b ± 43.29	748.2c ± 32.55	667.9d ± 27.04	639.4e ± 20.26	609.5e ± 23.47
yellow pigments	545.0a ± 21.43	485.7b ± 19.55	390.2c ± 18.21	366.9d ± 15.26	361.1e ± 10.30	300.6f ± 9.90
total carotenoids	1583.9a ± 66.93	1344.7b ± 62.33	1138.4c ± 50.26	1034.7d ± 41.75	975.5e ± 29.95	910.1f ± 33.17

^a Values in a row followed by the same letters are not significantly ($P < 0.05$) different (Duncan's multiple-range test). Mean value ± standard error ($n = 20$).

more than red pigments during storage. However, it can be clearly seen from **Figure 1** that almost half of the amount of paprika carotenoids is lost during the 10 month storage period at ambient temperature. There are significant ($P < 0.05$) differences in the pigment content of paprika between the stages of storage. However, almost 85% of pigment losses occurred in the first 6 months. Only the capsorubin decreases were not significant during this period, due to resistance in oxidation reaction. The carotenoid oxidation reactions follow the first-order kinetic (19). The rate of the first-order reaction is dependent upon the initial concentration of the reactant (31).

Consequently, manufacturing is the most destructive stage for the paprika carotenoids. The destructive effects of both drying methods are similar on paprika carotenoids, but the sun-drying process provides better color quality because of biosynthesis or the low oxidation rate of the carotenoid during a long-term drying period under low temperature. The rate of oxidation reaction of paprika carotenoids increases with increasing temperature. Hence, the dehydration process, which is practically applied in the paprika industry, must be improved. The irradiation process of a dose up to 10 kGy is significant, but it is less destructive to paprika pigments than processing and long-term storage. This undesirable effect of irradiation is negligible with regard to the practical aspects of preservation, because the process is the best alternative method of spice sterilization. The storage of paprika also leads to a substantial decrease in the amount of carotenoids. The pigment reduction during storage is higher than that caused by irradiation treatment, and the irradiation and storage stabilities of both sun-dried and dehydrated paprika pigments are almost the same. Individual carotenoids are affected to varying degrees in every treatment.

ACKNOWLEDGMENT

We thank the Atomic Energy Agency of Turkey for collaboration and S. Delacour for checking the language of the manuscript.

LITERATURE CITED

- Reeves, M. J. Re-evaluation of *Capsicum* color data. *J. Food Sci.* **1987**, *52*, 1047–1049.
- Deli, J.; Molnár, P.; Matus, Z.; Toth, G. Carotenoid composition in the fruits of red paprika (*Capsicum annuum* var. *Lycopersiforme rubrum*) during ripening; biosynthesis of carotenoids in red paprika. *J. Agric. Food Chem.* **2001**, *49*, 1517–1523.
- Ladron-Guevara, R. G.; Gonzalez, M.; Garcia-Meseguer, M. J.; Nieto, J. M.; Amo, M.; Varon, R. Effect of adding natural antioxidants on colour stability of paprika. *J. Sci. Food Agric.* **2002**, *82*, 1061–1069.
- Buckenhüskes, H. J. Actual requirements on paprika powder for the food industry. Presented at the XIth EUCARPIA Meeting on Genetics and Breeding of Capsicum and Eggplant, Antalya, Turkey, April 9–13, 2001.
- Krajayklang, M.; Klieber, A.; Dry, P. R. Acceleration of the drying rates of paprika fruit with drying oil and cutting. *Int. J. Food Sci Technol.* **2001**, *36*, 207–214.
- Hornero-Mendez, D.; Minguez-Mosquera, M. I. Rapid spectrophotometric determination of red and yellow isochromic carotenoid fractions in paprika and red pepper oleoresins. *J. Agric. Food Chem.* **2001**, *49*, 3584–3588.
- Hornero-Mendez, D.; Ladron de Guevara, R. G.; Minguez-Mosquera, M. I. Carotenoid biosynthesis changes in five red pepper (*Capsicum annuum* L.) cultivars during ripening. Cultivar selection for breeding. *J. Agric. Food Chem.* **2000**, *48*, 3857–3864.

- (8) Maoka, T.; Mochida, K.; Kozuka, M.; Ito, Y.; Fujiwara, Y.; Hashimoto, K.; Enjo, F.; Ogata, M.; Nobukuni, Y.; Tokuda, H.; Nishino, H. Cancer chemopreventive of carotenoids in the fruits of red paprika *Capsicum annuum* L. *Cancer Lett.* **2001**, *172*, 103–109.
- (9) Russo, V. M.; Howard, L. R. Carotenoids in pungent and non-pungent peppers at various developmental stages grown in the field and glasshouse. *J. Sci. Food Agric.* **2002**, *82*, 615–624.
- (10) Ittah, Y.; Kanner, J.; Granit, R. Hydrolysis study of carotenoid pigments of paprika (*Capsicum annuum* L. var. *Lehava*) by HPLC/photodiode array detection. *J. Agric. Food Chem.* **1993**, *41*, 899–901.
- (11) Minguez-Mosquera, M. I.; Hornero-Mendez, D. Comparative study of the effect of paprika processing on the carotenoids in peppers (*Capsicum annuum*) of the *Bola* and *Agridulce* varieties. *J. Agric. Food Chem.* **1994**, *42*, 1555–1560.
- (12) Minguez-Mosquera, M. I.; Jaren-Galan, M.; Fernandez-Garrido, J. Competition between the processes of biosynthesis and degradation of carotenoids during the drying of peppers. *J. Agric. Food Chem.* **1994**, *42*, 645–648.
- (13) Jaren-Galan, M.; Miguez-Mosquera, M. I. Quantitative and qualitative changes associated with heat treatments in the carotenoid content of paprika oleoresins. *J. Agric. Food Chem.* **1999**, *47*, 4379–4383.
- (14) Ade-Omowaye, B. I. O.; Rastogi, N. K.; Angersbach, A.; Knorr, D. Osmotic dehydration behavior of red paprika (*Capsicum annuum* L.). *J. Food Sci.* **2002**, *67*, 1790–1796.
- (15) Biacs, P. A.; Daood, H. G.; Huszka, T. T.; Biacs, P. K. Carotenoids and carotenoid esters from new cross-cultivars of paprika. *J. Agric. Food Chem.* **1993**, *41*, 1864–1867.
- (16) Goda, Y.; Nakamura, H.; Sakamoto, S. S.; Ishikawa, K.; Maitani, T.; Yamada, T. Photo-stability of coloring constituents in paprika color. *J. Food Hyg. Soc. Jpn.* **1997**, *38* (4), 240–247.
- (17) Minguez-Mosquera, M. I.; Hornero-Mendez, D. Change in provitamin A during paprika processing. *J. Food Prot.* **1997**, *60*, 853–857.
- (18) Klieber, A.; Bagnato, A. Colour stability of paprika and chili powder. *Food Aust.* **1999**, *51*, 592–596.
- (19) Perez-Galvez, A.; Minguez-Mosquera, M. I. Structure–reactivity relationship in the oxidation of carotenoid pigments of the pepper (*Capsicum annuum* L.). *J. Agric. Food Chem.* **2001**, *49*, 4864–4869.
- (20) Shin, J. H.; Chung, H. L.; Seo, J. K.; Sim, J. H.; Huh, C. S.; Kim, S. K.; Baek, Y. J. Degradation kinetics of capsanthin in paprika (*Capsicum annuum* L.) as affected by heating. *Food Chem. Toxicol.* **2001**, *66*, 15–19.
- (21) Biacs, P. A.; Daood, H. G.; Pavisa, A.; Hajdu, F. Studies on the carotenoid pigments of paprika (*Capsicum annuum* L. Var Sz-20). *J. Agric. Food Chem.* **1989**, *37*, 350–353.
- (22) Minguez-Mosquera, M. I.; Perez-Galvez, A. Study of lability and kinetics of the main carotenoid pigments of red pepper in the de-esterification reaction. *J. Agric. Food Chem.* **1998**, *46*, 566–569.
- (23) Narvaiz, P.; Lescano, G.; Kairiyama, E.; Kaupert, N. Decontamination of spices by irradiation. *J. Food Saf.* **1989**, *10*, 49–61.
- (24) Sharma, A.; Padwal-Desai, S. R.; Nair, P. M. Assessment of microbiological quality of some gamma irradiated Indian spices. *J. Food Sci.* **1989**, *54*, 489–490.
- (25) Subbulakshmi, G.; Udipi, S.; Raheja, R.; Sharma, A.; Padwal-Desai, S. R.; Nair, P. M. Evaluation of sensory attributes and some quality indices of irradiated spices. *J. Food Sci. Technol.* **1991**, *28* (6), 396–397.
- (26) Minguez-Mosquera, M. I.; Hornero-Mendez, D. Separation and quantification of the carotenoid pigments in red peppers (*Capsicum annuum* L.), paprika, and oleoresin by reverse-phase HPLC. *J. Agric. Food Chem.* **1993**, *41*, 1616–1620.
- (27) Nieto-Sandoval, J. M.; Almela, L.; Fernandez-Lopez, J. A.; Munoz, J. A. Effect of electron beam irradiation on color and microbial bioburden of red paprika. *J. Food Prot.* **2000**, *63*, 633–637.
- (28) Markus, F.; Daood, H. G.; Kapitany, J.; Biacs, P. A. Change in the carotenoid and antioxidant content of spices red pepper (paprika) as a function of ripening and some technological factors. *J. Agric. Food Chem.* **1999**, *47*, 100–107.
- (29) Kim, S.; Park, J. B.; Hwang, I. K. Quality attributes of various varieties of Korean red pepper powders (*Capsicum annuum* L.) and color stability during sun light exposure. *J. Food Sci.* **2002**, *67*, 2957–2961.
- (30) Zachariev, G.; Kiss, I.; Szabolcs, J.; Toth, G.; Molnar, P.; Matus, Z. HPLC analysis of carotenoids in irradiated and ethylene oxide treated red pepper. *Acta Aliment.* **1991**, *20*, 115–122.
- (31) Villota, R.; Hawkes, D. R. Reaction kinetics in food systems In *Handbook of Food Engineering*; Heldman, D. R., Lund, D. B., Eds.; Dekker: New York, 1992; pp 39–144.

Received for review February 21, 2003. Revised manuscript received June 14, 2003. Accepted July 1, 2003. We thank the Scientific Research Fund of Akdeniz University for a grant.

JF034177Z