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Full Length Research Paper

Functional compounds and antioxidant properties of dried green and red peppers

M. Ozgur[1]*, T. Ozcan[2], A. Akpinar-Bayizit[2] and L. Yilmaz-Ersan[2]

[1]Department of Horticulture, Faculty of Agriculture, Uludag University, Bursa, 16059, Turkey.
[2]Department of Food Engineering, Faculty of Agriculture, Uludag University, Bursa, 16059, Turkey.

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The effects of drying on chemical composition and functional compounds, including ascorbic acid, phenolics and carotenoids of hot-air-dried green and red peppers, were investigated. Drying significantly affected the dry matter, ash, pH, titritable acidity and chlorophyll values ($p < 0.01$). The rehydration ratios of the dried green and red peppers at 45°C were 5.57 and 4.27, respectively, and the coefficients of rehydration for the dried green and red peppers were calculated to be 0.65 and 0.82, respectively. Drying caused a more pronounced lightening of the vegetable surfaces with a loss of green color. The rehydrated pepper samples had a high total color difference (ΔE) indicating an obvious color change when the fresh peppers were dried. Although hot air-drying caused a more pronounced increase in the ascorbic acid and carotenoid contents of the green and red peppers there was a decrease in the total phenols and antioxidant capacities.

Key words: Green and red peppers, drying, carotenoids, phenolic compounds, antioxidant activity.

INTRODUCTION

With increasing evidences in chronic diseases, especially in industrialized countries, the researchers are focused on the health benefits of fruit and vegetables that are rich sources of essential dietary micronutrients, fibers and many other classes of bioactive compounds (Rechkemmer, 2001; Southohn and Faulks, 2002).

Capsicum is a genus of plants from the *Solanaceae* family that have a variety of names depending on location and type, and the most common pepper names are chili, bell, red, green or just pepper (Faustino et al., 2007). Peppers contain a wide array of phytochemicals, such as neutral and acidic phenolic compounds, which are important nutritional antioxidants that may reduce the risk of degenerative, mutagenic and chronic diseases (Lee et al., 1995a, b; Howard et al., 2000; Yahia, 2000). The anticarcinogenic activity of phenolic compounds is due to the inhibition of *N*-nitroso compound formation *in vitro* (Mennen et al., 2005).

The nutritive composition of peppers depends mainly on the variety and stage of maturity. The phytochemicals in peppers have been reported to possess many biochemical and pharmacological properties, such as antioxidant, anti-inflammatory, anti-allergic and anticarcinogenic activities (Rice-Evans et al., 1995; Lee et al., 2005). Ripe red peppers are naturally rich in ascorbic acid (vitamin C) and provitamin A (Niizu and Rodriguez-Amaya, 2005; Kidmose et al., 2006), which neutralize free radicals in the human body and, thus, reduce the risk of diseases, such as arthritis, cardiovascular disease (Kritchevsky, 1992) and cancer (Nishino et al., 2002, 2009), in addition to delaying the aging process (Packer, 1996). Carotenoids, which are fat-soluble antioxidants found in peppers, have received considerable interest by researchers due to their antioxidant properties (Rao and Rao, 2007) and the necessity for human epithelial cellular differentiation (Byers and Perry, 1992). In addition, several studies have demonstrated the antimicrobial activity of peppers (Cichewicz and Thorpe, 1996; Wahba et al., 2010).

Dried foods are more concentrated than fresh foods with low moisture contents and can be stored at ambient temperatures for longer periods. Due to a considerable decrease in the water activity of the material, dried foods have reduced microbiological activity with minimized

*Corresponding author. E-mail: mozgur@uludag.edu.tr.

physical and chemical changes (Araujo et al., 2004; Vega-Gálvez et al., 2007). Peppers, similar to other vegetables, are perishable resulting in high losses due to storage problems and marketing. An alternative to the consumption of fresh vegetables is their dried form, which allows their use during the off-season. However, food products are sensitive to drying temperatures and methods that can induce degradation (e.g., oxidation, loss of color, shrinkage or loss of texture) and change the nutritional and functional properties of the products (Attanasio et al., 2004).

Although studies have focused on the drying kinetics of pepper varieties in terms of an empirical model, the lack of published work on the effect of hot-air-drying on several physicochemical properties including phenolic compound, ascorbic acid and carotenoid contents of green and red peppers explains the interest for the present work.

MATERIALS AND METHODS

Fresh and dried (green and red) pepper samples of *Capsicum annuum* L. cv. Yalova Yaglik 28 were obtained from a commercial plant that processes dried fruit and vegetables in Bursa, Turkey. The fresh pepper samples were washed in tap water, cut into pieces (diameter of 1.0 ± 0.1 cm and thickness of 3 to 4 mm) and placed on stainless steel trays in a forced-air drier at a temperature of 63 ± 2°C for 3 h with an air velocity of 2.5 m s^{-1}. The dried peppers were immediately packed in airtight, resealable polyethylene bags and stored at 25 ± 1°C in the dark.

For each physicochemical analysis, at least 500 g of fresh pepper was chopped in a domestic chopper (model *K 1191*, Arcelik Inc., Turkiye) resulting in a homogenized pepper extract, which was used for all analyses. Dried peppers were rehydrated prior to analysis, except determination of moisture content, and extracted as described for fresh peppers. Each sample was analyzed in triplicate. All chemicals and reagents used were of analytical grade.

Moisture contents, ash contents, pH levels and titritable acidity levels (expressed as %citric acid) were measured according to the Association of Office Analytical Chemists (AOAC, 2000). Dried green and red peppers were analyzed after rehydrating at 25°C for 3 h. Rehydration experiments were conducted as previously described by Ozgur et al. (2011). The rehydration ratio was expressed as the ratio of water absorbed by the dried sample (W_r) to the weight of the dried sample (W_d) (rehydration ratio, R_r) (Equation 1). The coefficient of rehydration (R_{cf}) representing water absorption during rehydration was determined as suggested by Rangana (1986) (Equation 2). The following equations were used to calculate the rehydration ratio and coefficient of rehydration:

$$R_r = W_r / W_d \quad (1)$$

$$CR = \frac{D_{wt}\, x\, (100 - A)}{(W_d - B) x\, 100} \quad (2)$$

Where D_{wt} is the drained weight of the rehydrated sample; A is the moisture of the sample before drying (%wet basis); W_d is the weight of the dried sample; and B is the moisture present in the dried sample taken for rehydration (% wet basis).

The extraction of chlorophyll *a* and *b* was done according to Wellburn (1994) and Butz et al. (2002). The absorbance of the extract was measured at 663, 645, 652 and 750 nm (reference= acetone). The E_{750} value was subtracted from the E_{663} (chlorophyll *a*), E_{645} (chlorophyll *b*) and E_{652} (total chlorophyll) values. The corrected values were used for the determination of chlorophyll *a*, chlorophyll *b* and total chlorophyll concentrations in the peppers.

Ascorbic acid content was determined using the 2, 6-dichlorophenol-indophenol (0.0012%) method at 520 nm as described by the Association of Official Analytical Chemists (AOAC, 1996). *L*-ascorbic acid was used to prepare a standard solution (1 mg mL^{-1}). The ascorbic acid concentration was calculated by comparison with the standard and expressed as mg 100 g dry $weight^{-1}$ (DW^{-1}).

The CIELAB coordinates (L^*, a^* and b^*) were measured using a Minolta Chromameter CR-300 (Minolta Camera Co. Ltd., Osaka, Japan). The chromameter consisted of a measuring area with a diameter of 8 mm, and diffuse illumination (0°) viewing was used. The measurements were taken with a pulsed xenon lamp. Color changes in the green and red pepper samples due to drying were evaluated by the total color difference (ΔE) (Equation 3) and hue angle (h) (Equation 4) as follows:

$$TCD\ (\Delta E) = \sqrt{([\Delta L])^2 + ([\Delta a])^2 + ([\Delta b])^2} \quad (3)$$

$$h = \tan^{-1}(b^* / a^*) \quad (4)$$

Where ΔL is the difference of lightness (L-L_0); Δa is the difference of redness (a-a_0); and Δb is the difference of yellowness (b-b_0). Determination of total phenolic content was based on a modified method described by Spanos and Wrolstad (1990) using a spectrophotometer (Hewlett Packard 8452A, Diode Array, USA) and a comparison against a blank. The absorbance readings of the reaction mixtures were measured at 725 nm. The phenolic contents, expressed in gallic acid equivalents (GAE), were estimated by derivation from a gallic acid (GA) standard curve (0 to 0.1 mg ml^{-1}). The results were expressed as milligrams of GAE per gram of dry weight.

The extraction of carotenoids (lycopene and carotene) was performed according to the method previously described by Konings and Roomans (1997) with methanol/tetrahydrofuran (THF) (1:1; v/v) using Na_2SO_4 and $MgCO_3$ as desiccants until colorless. The extracts were analyzed with a non-aqueous reversed-phase (NARP) HPLC system (Varian Vista 5500 liquid chromatographs, Varian) that was equipped with Varian UV-200 detectors and Varian 4270 integrators. In the NARP chromatography, the Zorbax ODS column (5 µm; 250 × 4.6 mm; i.d.; DuPont) was preceded by a guard column (5 × 0.46 cm; i.d.) packed with Bondapak AX/Corasil (37 to 50 pm) (Waters). The elution mixture was a mixture of methanol and THF (95:5; v/v), and the flow rate was 0.8 mL min^{-1}. Carotenoids were detected at 450 nm, and the columns were run at 30°C. Approximately 20 µl of both standards and samples were injected into the system. The separated peaks were recorded, and the peak areas were determined. The carotenoid concentrations in the samples were identified by comparing their retention times to those of authentic standards.

The ferric reducing ability of plasma (FRAP) assay was performed according to the method described by Ozgur et al. (2011). Readings of the colored product (ferrous tripyridyltriazine complex) were taken at a wavelength of 593 nm against a blank. The standard curve was constructed using ferrous sulfate standard solutions over the linearity range of 0.2 to 1.0 µmol L^{-1}. The antioxidant activities of the samples were determined from the standard curve of ferrous sulfate using their measured absorbance values. The results were converted to µmole Trolox equivalent (TE) per gram of DW^{-1}.

Table 1. Proximate composition of fresh and dried pepper samples (means, n = 3).

Sample		Moisture (g 100 g^{-1})	Ash (g 100 g^{-1})	pH	Titritable acidity (%)	Rehydration ratio(R_r)	Rehydration coefficient (R_{cf})	Chlorophyll content(mg kg^{-1})		
								a	*b*	Total
Green pepper	Fresh	94.50±0.113[a]	0.31±0.042[b]	5.43±0.133[a]	0.16±0.045[b]	--	--	21.70±1.669[b]	24.03±1.799[a]	55.07±3.056[b]
	Dried	9.23±1.110[b]	4.14±0.031[a]	5.29±0.425[b]	1.10±0.040[a]	5.57[a]	0.65[ns]	45.810±4.291[a]	47.05±3.619[b]	107.10±6.125[a]
Red pepper	Fresh	92.40±0.163[a]	0.44±0.084[b]	5.21±0.010[b]	0.18±0.223[b]	--	--	---	---	---
	Dried	9.57±0.537[b]	4.22±0.092[a]	5.01±0.164[c]	1.16±0.080[a]	4.27[b]	0.82[ns]	---	---	---

[a-c] Means superscript with different alphabets in the same column differ significantly ($p < 0.01$). ns: not significant.

All of the quantitative analyses were expressed as the mean values ± standard deviations for three replications. Data for each attribute of fresh and dried pepper samples were analyzed statistically by analysis of variance (ANOVA) using the Minitab package program (Minitab Release 10.51). The differences between the means were compared with the least significant difference test, and differences at $p < 0.01$ were considered to be significant.

RESULTS AND DISCUSSION

Table 1 shows the chemical composition of fresh and dried green and red peppers. The moisture contents of the dried green and red pepper samples were 9.23 and 9.57 g 100 g^{-1}, respectively. The ash content of the red pepper samples was found to be higher (4.22 ± 0.092%) than the ash content of the green pepper samples (4.14 ± 0.031%). As expected, the application of hot-air-drying significantly increased the dry matter and ash values due to the removal of water from the peppers. Similar results were observed for the contents of chlorophyll *a* and *b*, which were mainly in accordance with the increase in dry matter as dried green peppers had a higher total chlorophyll content (107.10 ± 6.125 mg kg^{-1}) when compared to the fresh green pepper samples (55.07 ± 3.056 mg kg^{-1}). The pH and titritable acidity values were significantly affected by the drying process ($p < 0.01$). However, the difference in these values between the green and red varieties was not significant. Total titritable acidity in terms of citric acid was found to be lower in the fresh pepper samples than in the dried pepper samples. In general, the raw material affected the amount and quality of components in the pepper samples during drying because the nutritional composition depends on the variety, environment, soil type and stage of maturity (Lee et al., 2005; Niizu and Rodriguez-Amaya, 2005; Kidmose et al., 2006).

The rehydration ratios of the dried green and red peppers at 45°C were 5.57 and 4.27, respectively, and the coefficients of rehydration for the dried green and red peppers were calculated to be 0.65 and 0.82, respectively. Assuming that perfect rehydration yields a product with similar proximate composition of the raw material, rapid and complete rehydration is an essential quality parameter of any dried product. In this study, the dried green peppers had higher water absorption when compared to the dried red peppers due to the cell/tissue matrix and chemical composition. The rate of water absorption is related to the pectic contents in dried vegetables (Levi et al., 1988; Femenia et al., 1997, 2000).

Drying caused a more pronounced lightening of the vegetable surfaces with a loss of green color, which is an important parameter for overall sensorial and color perception of the dried products. The average values of the color parameters (L^*, lightness; a^*, redness; and b^*, yellowness), total color difference (TCD; ΔE) and hue angle (H^0) for fresh, air-dried and rehydrated green and red peppers are presented in Figure 1. The total color difference, which is a combination of the L^*, a^* and b^* values as calculated by Equation 3, is a colorimetric parameter extensively used to characterize the variation of color in foods during processing. The rehydrated pepper samples had a high ΔE (23.31 for green peppers and 33.14 for red peppers), which indicated an obvious difference in color attributes. Dried red peppers also had a difference in color but to a lesser extent (ΔE = 4.20) (data not shown). These results demonstrated an increase of L^*, a^* and b^* values with rehydration. The L^* values for fresh, dried and rehydrated red peppers were lower than the L^* values for green peppers. The a^* and b^* values were significantly different between the pepper varieties ($p<0.01$). The a* values for the fresh and dried green peppers were negative, which implied that these values were within the green color space. The decrease in the a^* and b^* values may have been due to non-enzymatic reactions and the decomposition of chlorophyll and other pigments (Maskan, 2001).

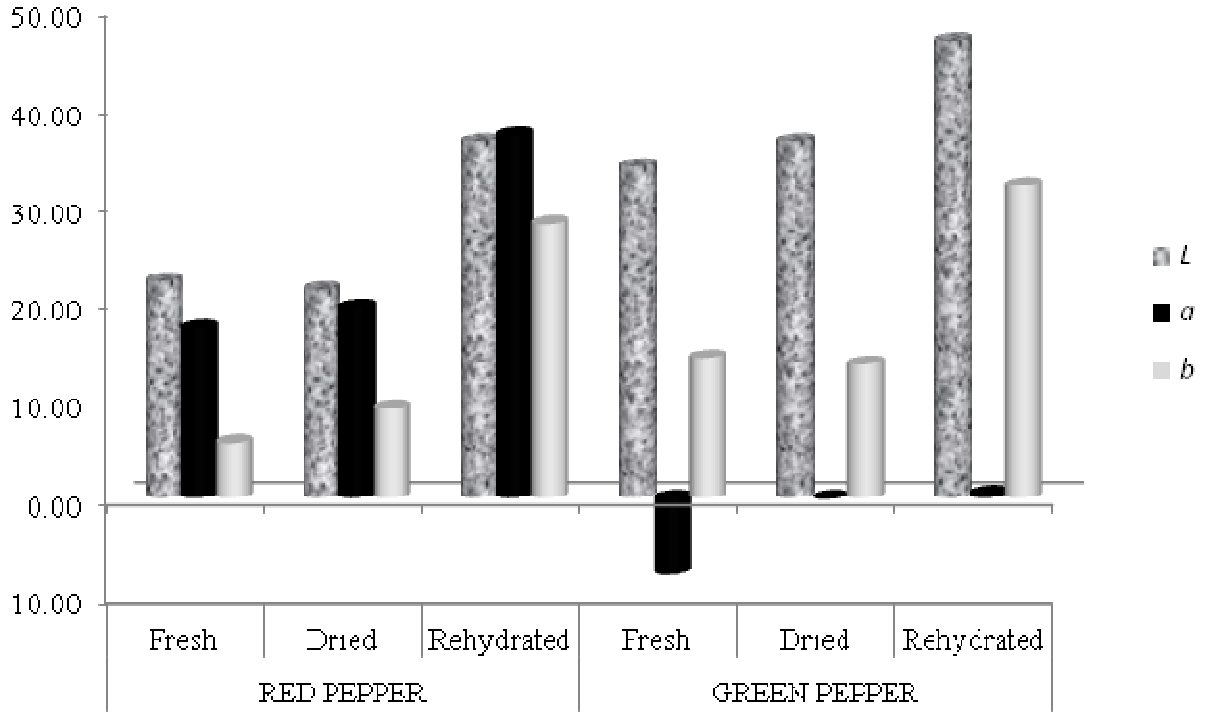

Figure 1. *L*, a**and *b** values of green and red peppers.

The antioxidant components of the green and red peppers are shown in Table 2. Peppers are well-known sources of vitamin A precursors, vitamin C precursors, neutral phenolic compounds and acidic phenolic compounds. Levels of these components can vary with genotypic differences, preharvest climatic conditions, cultural practices, maturity, harvesting methods, and postharvest handling procedures (Mejia et al., 1988; Biles et al., 1993; Ottaway, 1993; Luning et al., 1994; Niklis et al., 2002). Vitamin C, including ascorbic acid and its oxidation product (dehydroascorbic acid), has many biological activities in the human body due to its antioxidant properties (Davey et al., 2000; Lee and Kader, 2000; Yahia et al., 2001). The highest ascorbic acid content was found in the dried red peppers (108.65±6.481 mg 100 g DW^{-1}). As expected, drying caused the values of ascorbic acid to be increased due to the increase in dry weight. The loss of ascorbic acid is dependent on several factors including the type of heavy metals (copper and iron), light, pH level, water activity level, dissolved oxygen and drying temperature (Villota and Hawkes, 1992). There is a general trend that the ascorbic acid content showed an increase as the pepper fruit ripened (Howard et al., 1994; Luning et al., 1994). Therefore, it is possible that there is an interaction between genotype variation and stage of ripening. Niklis et al. (2002) reported that maturation and ripening affects the color changes and ascorbic acid contents of sweet peppers and that these changes are positively correlated with the changes in dry matter and soluble solids. Osuna-García et al. (1998) and Aniel-Kumar and Subba-Tata (2009) investigated the ascorbic acid content of chili peppers, and they reported that the ascorbic acid content gradually increases from green to red ripening but decreases in lateral stages, such as in partially or fully dried peppers.

As shown in Table 2, the fresh red peppers had higher phenolic contents (130.79 ± 2.141 mg GAE g DW^{-1}) when compared to the other samples. Meyer et al. (1998) reported that the antioxidant activities of phenolic compounds in different vegetables significantly vary, and they suggested that these variations may be due to the differences in the phenolic compound structures primarily related to their hydroxylation and methylation patterns. Kevers et al. (2007) reported that yellow and red peppers are the vegetables with the highest phenolic content followed by green peppers, spinach, and broccoli.

Carotenoids are yellow, orange, and red pigments present in many fruits and vegetables. Several of these carotenoids are precursors to vitamin A (β-carotene and β-cryptoxanthin). Due to their conjugated double bonds, β-carotene and β-cryptoxanthin are both radical scavengers and quenchers of singlet oxygen molecules v(Rice-Evans et al., 1997). Lycopene, which is found in peppers, is another compound with potential antioxidant activity similar to β-carotene. Lycopene has been found to prevent oxidative damage to DNA and liver necrosis in rats (Matos et al., 2001), and lycopene has also been shown to reduce the risk of prostate cancer (Giovannucci et al., 2002). Carotene content was found higher in the

Table 2. The antioxidant components of fresh and dried pepper samples (means, n=3)

Sample		Ascorbic acid (mg 100 g DW^{-1})	Total phenols (mg GAE g DW^{-1})	Lycopene (mg kg DW^{-1})	Carotene (mg kg DW^{-1})	Total antioxidant capacity (µmole TE g DW^{-1})
Green pepper	Fresh	64.07±1.850^{c}	96.04±1.282^{b}	6.71±0.148^{d}	10.29±0.012^{d}	1233.36±37.259^{b}
	Dried	88.25±2.468^{b}	55.47±3.118^{d}	171.55±0.127^{a}	173.37±0.045^{b}	262.49±19.220^{d}
Red pepper	Fresh	87.13±3.729^{b}	130.79±2.141^{a}	13.45±0.099^{c}	158.31±0.127^{c}	8720.70±65.730^{a}
	Dried	108.65±6.481^{a}	89.82±4.721^{c}	123.89±0.170^{b}	2282.45±5.362^{a}	694.55±14.584^{c}

$^{a-d}$Means superscript with different alphabets in the same column differ significantly ($p < 0.01$).

dried red peppers as (2282.45 ± 5.362 mg kg DW^{-1}). The hot-air-drying caused a more pronounced increase of β-carotene content in both green and red peppers ($p < 0.01$). Shi et al. (1999) reported that oxygen permeability, light exposure, and the presence of several metals in the processing system favor the isomerization and oxidation of lycopene during dehydration. Dewanto et al. (2002) stated that an increase in the extractable lycopene content in processed tomato products when compared to fresh tomatoes is likely caused by lycopene being mostly attached to the skins and insoluble fiber portions of the tomatoes, and they suggested that heat processing may cause an increased release of lycopene from the cell matrix. Moreover, it is important to consider the synergic action of carotenoids with other bioactive compounds present in fruits and vegetables (Rao and Agarwal, 2000; Sharoni et al., 2002).

In this study, the total antioxidant capacity of the peppers significantly decreased with drying (Table 2). The antioxidant capacity of the fresh red peppers (8720.70 ± 65.730 µmol TE g DW^{-1}) was significantly higher than the antioxidant capacity of the other samples. While heat applied during the dehydration process is the main cause of antioxidant compound depletion, heat can also induce the formation of compounds, such as melanoidins, by the Maillard reaction, which can contribute to the antioxidant activity (Nicoli et al., 1997; Anese et al., 1999).

Vegetables contain other antioxidants in addition to phenolic compounds and ascorbic acid, such as proteins, β-carotene, α-tocopherol, and lycopene, which may have a role in the increase of total antioxidant activity. Moreover, heat application can increase the level of free flavonols with the antioxidant effect (Stewart et al., 2000). Kevers et al. (2007) demonstrated that peppers (red, yellow, or green) have a higher antioxidant capacity than other vegetables.

Using an antioxidant activity assay, Zhang and Hamauzu (2003) reported that green pepper phenolic extracts have the highest activity among the phenolic extracts of green, red and yellow bell peppers. Perucka and Materska (2001) found that red peppers are characterized by high antioxidant activity in both of their capsaicin and flavonoid fractions.

Conclusion

In this study, the application of hot-air-drying to green and red peppers significantly increased the dry matter and ash values due to removal of water from the peppers. Similar results were observed for the chlorophyll *a* and *b* contents in the peppers. The pH and titritable acidity values of the peppers were significantly affected by the drying process ($p < 0.01$). However, these values were not significantly different between the two varieties. Dried green peppers displayed higher water absorption due to the cell/tissue matrix and chemical composition.

Drying caused a more pronounced lightening of the vegetable surfaces with a loss of green color, which is an important parameter for overall sensorial and color perception of the dried products. The rehydrated pepper samples had a high total color difference ΔE, which indicated an obvious color change from fresh peppers to dried peppers.

The L^*, a^* and b^* values for the pepper samples were significantly different among the samples depending on the pepper variety and drying process ($p < 0.01$), which may be explained by the heat-induced degradation of the color pigments. The highest ascorbic acid content was found in the dried red peppers, and the highest phenolic content wasfound in the fresh red peppers. The results from the carotenoid analysis showed that the hot-air-drying caused a more pronounced increase of carotenoid content in both green and

red peppers ($p < 0.01$). Moreover, the total antioxidant capacity of the peppers significantly decreased with drying, which may have been due to the depletion of antioxidant compounds. However, heat application can induce the formation of compounds that can contribute to the antioxidant activity. In addition, heat application can increase the level of free flavonols with the antioxidant effect. Overall, these results suggested that drying had a significant impact on the chemical composition, phenolic components and antioxidant properties of the peppers.

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