



## Drying effects on the antioxidant properties of tomatoes and ginger



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### ABSTRACT

In this study, the effects of four different drying processes, sun drying (SD), oven drying (OD), vacuum oven drying (VOD) and freeze drying (FD) for tomatoes (*Solanum lycopersicum*) and ginger (*Zingiber officinale*) in terms of thiolic and phenolic contents have been studied. Thiol content, total phenolic content (TPC), ascorbic acid (AA) content, and cupric ion reducing antioxidant capacity (CUPRAC) were determined in fresh and dried samples. Glutathione (GSH) and cysteine (Cys) were determined as the thiol contents of tomatoes and ginger. Significant losses were observed in the contents of TPC, AA, GSH and Cys and CUPRAC values in all samples that were dried using the thermal method. There was a statistically significant difference in the losses of the TPC, AA, and thiol contents between the use of thermal drying and freeze drying (except Cys in tomatoes) methods. Freeze dried tomato and ginger samples have been found to have better antioxidant properties.

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### 1. Introduction

Reactive oxygen species (ROS) can be spontaneously formed in living cells during normal metabolism. Antioxidants play an important role (as a defense mechanism) in ROS-induced damage. Many studies indicate that, if the diet has plenty of antioxidant-rich fruits, vegetables, plants, and “species”, the risk of getting age-related disorders, cancer, and atherosclerosis (all caused by free radical damage) will decrease (Chang, Lin, Chang, & Liu, 2006; Genkinger, Platz, Hoffman, Comstock, & Helzlsouer, 2004; Manda, Adams, & Ercal, 2010; Orak et al., 2012; Shukla & Singh, 2007; Stoilova, Krastanov, Stoyanova, Denev, & Gargova, 2007).

Thiols, characterised by having sulphhydryl derivatives of organic sulfurs, play a pivotal role in the antioxidant defense system as well as in protein synthesis, formation, redox-sensitive signal transduction, cellular growth and proliferation, organising programmed cell death, and the immune system. Recent studies show that fruits, vegetables, and species have significant amounts of biothiols like glutathione (GSH), cysteine (Cys), homocysteine (HCys), g-glutamyl cysteine (GGC), and captopril (CAP) (Demirkol, Adams, & Ercal, 2004; Manda et al., 2010).

Phenolic complexes, commonly found in fruits and vegetables, are antioxidants that scavenge free radicals, chelate metals, and

prevent lipid peroxidation (Escarpa & Gonzalez, 2001). In addition, they strongly affect the colour and aroma of foods. Studies show that polyphenols in the diet affect the treatment of cardiovascular disease, diabetes, cancer, and heart attacks (Crozier, Jaganath, & Clifford, 2009).

Ascorbic acid (AA), found in almost all living tissues, is a crystal-complex and its best known isomer is L-ascorbic acid. L-Ascorbic acid interrupts the chain reaction in the lipid peroxidation process by giving an electron. It does this by blocking “free radicals” before they reach the cellular membrane. AA functions as an antioxidant by removing singlet oxygen, eliminating peroxy radicals formed during lipid peroxidation and reducing  $\alpha$ -tocopherol radicals to  $\alpha$ -tocopherol. Humans, and a few other mammals, do not have the enzyme that converts glucose to vitamin C. In addition, GSH can be converted to isoform in the presence of AA (Chou & Khan, 1983; May, Qu, & Mendiratta, 1998; Padh, 1991; Wang et al., 2000).

Tomato intake has been shown by epidemiological studies to decrease the prevalence of some cancers and cardiovascular disorders, proving that tomatoes definitely belong to the functional food status. This preventive effect of tomatoes originates from its AA, flavonoid, vitamin E, lycopene, and other carotenoid antioxidant contents (George, Kaur, Khurdiya, & Kapoor, 2004; Raffo, La Malfa, Fogliano, Malani, & Quaglia, 2006). In general, known as “ginger”, *zingiber officinale*, is one of the most commonly used spices. Over the centuries, this has become an important medicine

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for treating colds, nervous system disorders, gingival infections, tooth-aches, asthma, paralysis, constipation, and diabetes (Ali, Blunden, Tanira, & Nemmar, 2008). Phytochemical studies show that ginger contains antioxidants that have anti-inflammatory and anticarcinogenic effects (Manju & Nalini, 2005; Stoilova et al., 2007; Thomson et al., 2002).

Drying is one of the most practiced food storage procedures. This process occupies an important place in the food industry due to the fact that it increases the shelf life of food, it decreases the cost of packaging and transporting the food, as well as providing numerous environmental advantages (Chang et al., 2006; Doymaz, 2007). Dried products allow the consumption of fresh fruits and vegetables during the off-season. On the other hand, some foods are extremely sensitive to the application of oxygen and heat, and the drying process may cause food degradation (oxidation, discolouration, shrinkage, or loss of tissue) and change the food's nutritional value (Attanasio, Cinquanta, Albanese, & Di Matteo, 2004; Orak et al., 2012; Ozgur, Ozcan, Akpinar-Bayazit, & Yilmaz-Ersan, 2011).

This study investigates the effects of some drying processes (sun drying, oven drying, vacuum oven drying and freeze drying) on the phenolic amount, antioxidant capacity, thiol concentration, and AA content of tomatoes and ginger that are commonly used and have a very high antioxidant and nutritional value.

## 2. Materials and methods

### 2.1. Reagents and chemicals

Acetonitrile, acetic acid, and phosphoric acid [all high-performance liquid chromatography (HPLC) grade] were purchased from Fisher (St. Louis, MO). GSH and Cys were purchased from Sigma (St. Louis, MO). N-(1-Pyrenyl)maleimide (NPM), Folin–Ciocalteu reagent, 2,6-dichloroindophenol sodium salt (DCPI) was purchased from Aldrich (Milwaukee, WI). Sodium carbonate, gallic acid, oxalic acid, ascorbic acid, hydrochloric acid, sodium acetate, copper(II) chloride, ammonium acetate, ethanol, methanol and glacial acetic acid (all analytical grade) were purchased from Merck (Darmstadt, Germany). Trolox [(±)-6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid] was purchased from Aldrich (Steinheim, Germany). Neocuproine was purchased from Carlo Erba Reagents (Milano, Italy).

### 2.2. Samples

Tomatoes and ginger were purchased from major chain supermarkets in Sakarya, from June 2011 to July 2012.

### 2.3. Drying process

Samples were subject to four different drying methods, i.e., sun-, oven-, vacuum oven-, and freeze drying.

#### 2.3.1. Sun drying (SD)

Ginger and tomato slices were distributed on stainless steel trays (size  $1 \times 1 \text{ cm}^2$ ) and dried under direct sunlight at temperatures between 25 and 30 °C, for 3 days with about 36 h of daylight, between 16 July and 19 July 2011.

#### 2.3.2. Oven drying (OD)

Ginger and tomato slices were distributed on stainless steel trays (size  $1 \times 1 \text{ cm}^2$ ) and dried in an oven (Binder, model 115) at 60 °C for 36 h.

#### 2.3.3. Vacuum oven drying (VOD)

Ginger and tomato slices were distributed on stainless steel trays (size  $1 \times 1 \text{ cm}^2$ ) and dried in a vacuum oven (Jeiotechi, model OV-12) at 60 °C and 0.025 mbar vacuum pressure for 36 h.

#### 2.3.4. Freeze drying (FD)

Ginger and tomato slices were distributed on steel trays (size  $1 \times 1 \text{ cm}^2$ ) and dried in a freeze drier (Labconco Freezone 6 litre Benchtop, model 7752030) at  $-50 \text{ °C}$  and 0.133 mbar vacuum pressure for 24 h.

The conditions for oven drying (Muratore, Rizzo, Licciardello, & Maccarrone, 2008), vacuum oven drying (Wu, Orikasa, Ogawa, & Tagawa, 2007) and freeze drying (Chang et al., 2006) were determined with some modifications of the methods in the previous studies. All samples were dried to 80–90% dry matter content.

### 2.4. Preparation of aqueous sample extracts for determination of thiol content

Extracts were prepared according to the literature procedure described by Demirkol et al. (2004). Ginger (0.1 g/ml) and tomatoes (0.5 g/ml) were placed in a serineborate buffer solution (100 mM Tris–HCl, 10 mM borate, 5 mM serine, and 1 mM diethylenetriaminepentaacetic acid, pH 7.0) to prevent artifactual oxidation. The samples were homogenised with a tissue tearor (Wiggen Hauser, model D-130 handheld disperser) on ice for 2 min, with 5 s intervals of homogenisation, and then centrifuged at 2000g for 15 min; supernatants were used for the thiol content.

### 2.5. Preparation of aqueous sample extracts for determination of total phenolic content

Extracts were prepared according to the literature procedure, with a few modifications of Wojdylo, Oszmianski, and Czemerz (2007). Samples (1 g) were weighed and placed into a test tube. A total of 10 ml of 70% aqueous methanol was added, and homogenised with tissue tearor. Tubes were sonicated twice for 15 min at room temperature (20 °C). The extract was centrifuged for 10 min (1500g), and supernatants were used to determine the antioxidant activity of the total phenolic content.

### 2.6. Preparation of aqueous sample extracts for determination antioxidant capacity

Extracts were prepared according to the literature procedure described by Capanoglu, Beekwilder, Boyacioglu, Hall, and Vos (2008). 3 ml of 75% methanol was added to sample (0.5–1 g) and sonicated for 15 min. After centrifugation at 2500 rpm for 10 min, the supernatant was collected, 75% methanol (3 ml) was added to the pellet, and the extraction procedure was repeated. Both supernatants were combined and adjusted to a final volume of 10 ml.

### 2.7. Preparation of aqueous sample extracts for determination of ascorbic acid content

Extracts were prepared according to the literature procedure with a few modifications of Durust, Sumengen, and Durust (1997). Samples (5 g) were homogenised with tissue tearor in 50 ml of 0.4% aqueous oxalic acid solution and filtered through filter paper.

### 2.8. Determination of GSH and Cys, by the HPLC Method

The GSH and Cys contents of extracts were measured by the chromatographic method developed by Winters, Zukowski, Ercal,

Matthews, and Spitz (1995) to analyse  $\gamma$ -glutamyl cycle intermediates and modified by Demirkol et al. (2004). The supernatants prepared for the thiol contents (250  $\mu$ l for ginger, 50  $\mu$ l for tomato) were derivatised with NPM. This compound reacts with free sulfhydryl groups to form fluorescent derivatives. Each sample was first diluted with distilled water to make the volume up to 250  $\mu$ l, and then 750  $\mu$ l of NPM (1 mM in acetonitrile) were added. The resulting solution was mixed and incubated at room temperature for 5 min. 10  $\mu$ l of 2 N HCl were added to stop the reaction. After filtration through a 0.2  $\mu$ m acrodisc, the derivatised samples were injected onto a 5  $\mu$ m C<sub>18</sub> column in a reverse phase HPLC system. GSH and Cys were determined concurrently since all known monothiols form fluorescent derivatives with NPM. All determinations were performed in triplicate ( $n = 3$ ).

## 2.9. HPLC system

The HPLC system (Shimadzu) was comprised of a model LC-10A pump, a Rheodyne injection valve with a 20  $\mu$ l injection filling loop, and a model RF535 fluorescence spectrophotometer operating at an excitation wavelength of 330 nm and an emission wavelength of 375 nm. The HPLC column was a Reliasil ODS-1 C18 column (5  $\mu$ m packing material) with 250  $\times$  4.6 mm i.d. The mobile phase was 30% water and 70% acetonitrile, containing 1 ml/l acetic acid and 1 ml/l *o*-phosphoric acid. The NPM derivatives were eluted from the column isocratically at a flow rate of 1 ml/min. Quantitation of the peaks from the HPLC system was performed with a Chromatopac, model C-R601 (Shimadzu).

## 2.10. Calibration curves

Calibration curves were plotted by using a concentration of the x-axis versus peak areas as the y-axis. Linearity obtained for GSH

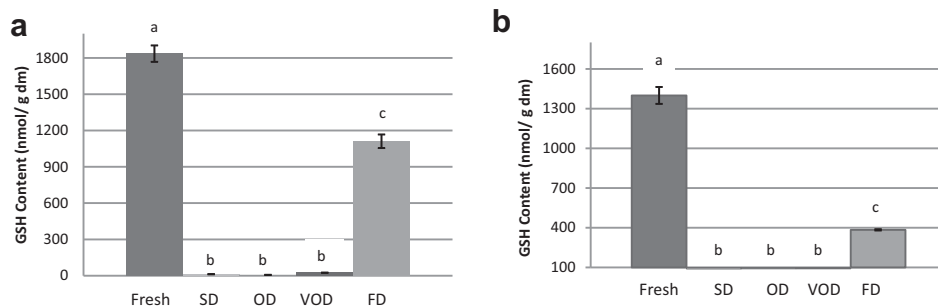
and Cys concentrations ranged from 0 to 5000 nM, with a regression constant of  $r^2 = 0.996$ .

## 2.11. Determination of total phenolic content

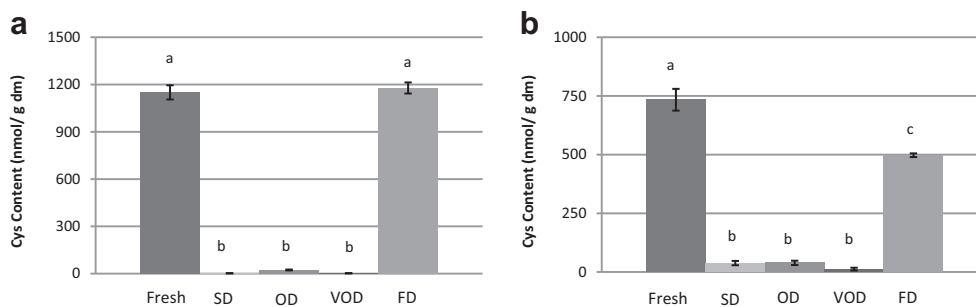
Total phenolic content (TPC) was measured using the Folin–Ciocalteu colorimetric method described previously (Wojdylo et al., 2007). Sample extracts prepared for total phenolic content (100  $\mu$ l), were mixed with 0.2 ml of Folin–Ciocalteu reagent and 2 ml of distilled water, and then incubated at room temperature for 3 min. Following the addition of 1 ml of 20% sodium carbonate to the mixture, total polyphenols were determined after 1 h of incubation at room temperature. The absorbance of the resulting blue colour was measured at 765 nm with a spectrophotometer (Shimadzu UV–1240). Quantification was done with respect to the standard curve of gallic acid ( $r^2 = 0.9985$ ). The results were expressed as gallic acid equivalents (GAE), milligrams per 100 g of dry matter (dm). All determinations were performed in triplicate ( $n = 3$ ).

## 2.12. Determination of ascorbic acid

Ascorbic acid (AA) content was measured by using a UV–VIS spectrophotometer according to the literature procedure of Durust et al. (1997). The spectrophotometer was adjusted to zero by using distilled water. The absorbance of mixing of 1 ml of oxalic acid solution with 8 ml of DCPI solution (12 mg of DCPI in 1000 ml of distilled water) and 1 ml of acetate buffer solution (300 g of anhydrous sodium acetate in 700 ml of distilled water with 1000 ml of glacial acetic acid) was recorded at the end of 15 s. This value was recorded as  $X_1$ . Then, the absorbance of the standard ascorbic acid solution (1 ml) with the acetate buffer solution (1 ml) and DCPI (8 ml) was recorded as  $X_2$ .  $X_1$  was the absorbance



**Fig. 1.** GSH content of fresh and dried tomato samples (a) and GSH content of fresh and dried ginger samples (b). Values are mean, ( $n = 3$ ). SD: sun dried, OD: oven dried, VOD: vacuum-oven dried, FD: freeze dried, dm: dry matter. For each column, values followed by the same letter (a–c) are not statistically different at  $p < 0.05$  as measured by the Duncan test ANOVA applies between fresh and dried samples.



**Fig. 2.** Cys content of fresh and dried tomato samples (a) and Cys content of fresh and dried ginger samples (b). Values are mean, ( $n = 3$ ). SD: sun dried, OD: oven dried, VOD: vacuum-oven dried, FD: freeze dried, dm: dry matter. For each column, values followed by the same letter (a–c) are not statistically different at  $p < 0.05$  as measured by the Duncan test ANOVA applies between fresh and dried samples.



loses were seen in GSH contents of thermal dried tomato and ginger samples (Table 1). Cys content of the samples also showed significant differences between the freeze dried and thermal dried samples. Also, Cys content of tomatoes did not change significantly by freeze drying. The losses seen in the GSH and Cys contents after using the thermal drying method may have been the result of accelerated degradation due to heat and oxygen. Freeze drying was achieved under vacuum at a low temperature. Besides, the freeze drying method, provided highly efficient extraction. The reason for this could originate from the ice crystals in the plant extract matrix damaged cellular structures, thereby causing intracellular components of the cells to reach the solvent to help provide better extraction (Asami, Hong, Barrett, & Mitchell, 2003). Our results are in agreement with previous studies. The samples from the FD method had more GSH loss than Cys loss, because the cellular GSH synthesis was limited due to the availability of Cys. In addition, GSH, a substrate for oxidative enzymes and non-enzymatic reductant for free radicals and peroxides, is a very active antioxidant (Kleinman & Richie, 2000; Sen & Packer, 2000).

Although we have not seen any study that investigates the effects of a drying process on the thiol contents of tomatoes and ginger, Qiang, Demirkol, Ercal, and Adams (2005) reported that the disinfection process significantly decreased biothiols in vegetables.

### 3.2. Total phenolic content

Drying is a commonly used method for conserving food. During this process, retaining the phenolic content is a significant issue because phenolic complexes play an important role in cells. Our results showed that fresh ginger and tomato are a good source of phenolic compounds. TPC of fresh ginger and tomato were  $1351.10 \pm 62.16$  and  $792.22 \pm 43.35$ , respectively. Furthermore, TPC of sun, oven, vacuum oven and freeze dried gingers were  $319.60 \pm 33.45$ ,  $354.05 \pm 40.60$ ,  $284.10 \pm 18.10$  and  $910.9 \pm 44.51$  mg GAE/100 g dm, respectively; for sun, oven, vacuum oven and freeze dried tomato, TPC were  $314.27 \pm 42.30$ ,  $346.10 \pm 49.68$ ,  $355.79 \pm 28.38$  and  $654.60 \pm 29.63$  mg GAE/100 g dm, respectively (Fig. 3). We observed less phenolic content in dried samples than in their fresh counterparts. There was no significant difference between TPC of freeze dried and fresh tomatoes, whilst TPC of thermal dried tomatoes decreased. ( $p < 0.05$ , Fig. 3). A slight decrease was observed in TPC of freeze dried ginger. However, this decrease was not significant when compared to the thermal drying method. Kerkhofs, Lister, and Savage (2005) and Toor and Savage (2006) reported that tomatoes dried at a low temperature ( $42^\circ\text{C}$ ), had lower phenolic content than that of fresh tomatoes. During the drying process, activation of oxidative enzymes, such as polyphenoloxidase and peroxidase, may have led to the loss of phenolic

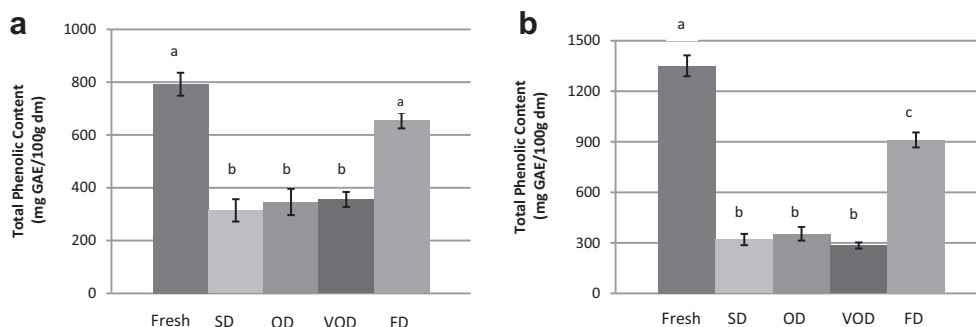
complexes. Besides, the structure of a tomato is disrupted during drying, and this may also cause the liberation of peroxidative and hydrolytic enzymes (Toor & Savage, 2006). In addition, other reasons for the loss of phenolic content could have been the binding of phenols to proteins, changes in chemical structures, or impossibility of extraction by presently available methods (Martin-Cabrejas et al., 2009; Miranda et al., 2010). However, Lavelli, Hippeli, Peri, and Elstner (1999) observed an increase in the phenolic content in tomatoes dried at  $80^\circ\text{C}$  for 7 h. Investigators explained that this was due to rehydration, along with the release of phenols from the cell walls and an increase in free hydroxyphenols. Dewanto, Wu, Adom, and Liu (2002) reported that high temperature applications, such as  $88^\circ\text{C}$ , to tomatoes did not affect their phenolic content. The same group indicated that the thermal process at  $88^\circ\text{C}$  deactivated oxidative and hydrolytic enzymes that may cause the loss of phenolic acids. Chan et al. (2009) reported that there was a decrease in TPC when leaves of ginger were dried by the sun, in an oven, and by microwaves. The same group found an increase in phenolic content in ginger leaves that had been freeze dried. However, results were not calculated on the basis of dried samples.

### 3.3. Ascorbic acid

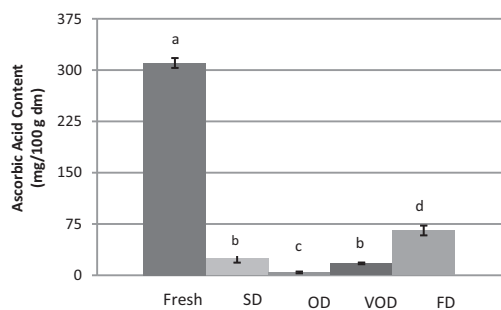
We observed that tomatoes had higher ascorbic acid (AA) than ginger. Kerkhofs et al. (2005) reported that the AA content in tomatoes was  $277$  mg/100 g dm, and a report by Giovanelli, Zanoni, Lavelli, and Nani (2002) showed  $330$  mg/100 g dm. In our study, AA contents of fresh ginger and tomatoes were  $79.86 \pm 4.37$  and  $310.34 \pm 7.23$  mg/100 g dm, respectively. For sun, oven, vacuum oven and freeze dried tomatoes, AA contents were  $24.39 \pm 5.93$ ,  $4.14 \pm 1.29$ ,  $17.37 \pm 1.25$  and  $65.47 \pm 7.1$  mg/100 g dm, respectively. We found that the AA content in dried tomatoes was less than that in fresh tomatoes (Fig. 4). Thermal methods caused much more loss when compared with freeze drying (Table 1).

The tomato is a very rich source of AA, a very sensitive vitamin. However, processing causes a negative effect on AA content. Previous studies indicated that the presence of oxygen and heat cause degradation of AA (Chang et al., 2006; Demiray, Tulek, & Yilmaz, 2013; Dewanto et al., 2002; Lavelli et al., 1999; Toor & Savage, 2006; Zanoni, Peri, Nani, & Lavelli, 1998). For example, Chang et al. (2006) reported that AA content decreased by 61% when dried by heat, whereas Lavelli reported that the AA content decreased by 88% when the moisture in tomatoes was lower than 10%.

In the literature, a study of the AA content of ginger has not been made, to the best of our knowledge. However, Oboh, Akinyemi, and Ademiluyi (2012) reported that the AA content in red and white ginger was  $1.83$  mmol/100 g and  $0.91$  mmol/100 g, respectively. In our study, we found that the AA content in fresh



**Fig. 3.** Total phenolic content of fresh and dried tomato samples (a) and total phenolic content of fresh and dried ginger samples (b). Values are mean, ( $n = 3$ ). SD: sun dried, OD: oven dried, VOD: vacuum-oven dried, FD: freeze dried, dm: dry matter. For each column, values followed by the same letter (a–c) are not statistically different at  $p < 0.05$  as measured by the Duncan test ANOVA applies between fresh and dried samples.



**Fig. 4.** Ascorbic acid content of fresh and dried tomato samples. Values are mean, ( $n = 3$ ). SD: sun dried, OD: oven dried, VOD: vacuum-oven dried, FD: freeze dried, dm: dry matter. For each column, values followed by the same letter (a–d) are not statistically different at  $p < 0.05$  as measured by the Duncan test ANOVA applies between fresh and dried samples.

**Table 2**

Cupric ion reducing antioxidant capacity (CUPRAC) of fresh, sun dried, oven dried, vacuum oven dried, freeze dried tomato and ginger samples. Results are given as dry matter (dm) basis.

Samples	CUPRAC Values (mg trolox/100 g dm)	
	Tomato	Ginger
Fresh	1424.79 ± 53.19 <sup>a</sup>	2176.13 ± 68.47 <sup>a</sup>
Sun dried	873.32 ± 40.43 <sup>b</sup>	1220.616 ± 66.68 <sup>b</sup>
Oven dried	1012.80 ± 49.77 <sup>b,c</sup>	1470.043 ± 56.13 <sup>c</sup>
Vacuum oven dried	1148.86 ± 13.05 <sup>c</sup>	1486.884 ± 42.40 <sup>c</sup>
Freeze dried	1699.59 ± 45.24 <sup>d</sup>	2555.574 ± 48.01 <sup>d</sup>

Values represent mean ± SD ( $n = 3$ ). For each column, values followed by the same letter (a–d) are not statistically different at  $p < 0.05$  as measured by the Duncan test ANOVA applies between fresh and dried samples.

ginger was 0.45 mmol/100 g dm (recalculated). After drying, however, the AA content could not be determined in the ginger samples. Our results showed that the AA content in ginger, which was lower than that of tomatoes to begin with, was entirely lost during the drying process.

#### 3.4. Cupric ion reducing antioxidant capacity

Tomatoes and ginger were found to be rich sources for antioxidants by analysis of the CUPRAC of these samples. Table 2 shows CUPRAC values of fresh and dried ginger and tomato samples. The results showed that CUPRAC values of tomatoes and ginger samples decreased by thermal drying. On the contrary, CUPRAC of freeze dried samples were determined to be increased.

Kerkhofs et al. (2005) and Toor and Savage (2006) reported that the antioxidant activity decreased in proportion to the loss of phenolic content and AA content. We also believe that a decrease in antioxidant activity in our samples may have been due to the lower levels of AA and phenolic content. However, it can be said that the reason for the increase in CUPRAC values of freeze dried samples might be due to increased extraction efficiency and reduced losses of components with antioxidant activity.

#### 4. Conclusion

As a result, antioxidant capabilities of tomatoes and ginger were significantly affected by all of the drying techniques. The three drying methods in which heat was applied caused more losses when compared to the freeze drying method (Table 1). Unfortunately, freeze drying is a costly procedure that limits its usage in the food industry. Because fresh tomatoes and ginger are excellent sources of antioxidants, the antioxidants in tomatoes and ginger should be

maintained by minimising the adverse effects of all technological processes. This study aims to make consumers aware of the effects of drying and that they should become accustomed to eating seasonal fresh fruits and vegetables. Besides, antioxidant-rich freeze dried tomatoes and ginger are becoming important sources for functional foods that are increasingly popular today.

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