

Effect of semi-drying on the antioxidant components of tomatoes

Ramandeep K. Toor *, Geoffrey P. Savage

Food Group, Animal and Food Sciences Division, Lincoln University, Canterbury, New Zealand

Received 28 June 2004; received in revised form 20 October 2004; accepted 20 October 2004

Abstract

Three tomato cultivars (Excell, Tradiro, and Flavourine) grown under hydroponic conditions in a commercial greenhouse in New Zealand were semi-dried at 42 °C. The semi-dried tomatoes contained low levels of 5-hydroxymethyl-2-furfural and were significantly ($p < 0.05$) darker (lower CIELAB L^* values) and had a higher mean a^*/b^* value (1.6) than the fresh tomatoes (1.2). The mean total phenolics in the semi-dried samples of tomatoes (300 mg gallic acid equivalents, GAE/100 g dry matter (DM)) was significantly lower than that of fresh tomatoes (404 mg GAE/100 g DM). The mean total flavonoid, and lycopene contents in the fresh samples (206 mg rutin equivalents/100 g DM, 63 mg/100 g DM, respectively) also showed a significant decrease after semi-drying (179 mg rutin equivalents/100 g, 54 mg/100 g DM, respectively). Ascorbic acid content in fresh tomatoes (284 mg/100 g DM) decreased to 223 mg/100 g DM after drying. The total antioxidant activity of the semi-dried tomatoes (1783 μ mole trolox equivalents antioxidant capacity (TEAC)/100 g DM) was significantly ($p < 0.05$) lower than that of the fresh samples (2730 μ mole TEAC/100 g DM).

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Tomato; Processing or semi-drying; Total phenolics; Flavonoids; Lycopene; Ascorbic acid; Antioxidant activity

1. Introduction

Epidemiological studies which show that the consumption of tomato and tomato-based products can help to prevent various forms of cancers, especially prostate cancer, and heart diseases (George, Nuttall, & Kendall, 2001; Gerster, 1997; Giovannucci, 1999; Lister, 2003; Rao & Agarwal, 2000), have increased interest in the antioxidant components they contain, e.g. lycopene, ascorbic acid, phenolics and flavonoids (Abushita, Hebshi, Daood, & Biacs, 1997; Diplock, Charleux, Crozier-Willi, Kok, & Rice-Evans, 1998; Kaur, Savage, & Dutta, 2002; Paganga, Miller, & Rice Evans, 1999; Vinson et al., 1998). Demand for ready-to-use products, which have similar health benefits to the original raw products,

has also increased in recent years (Dewanto, Wu, Adom, & Liu, 2002).

Fresh tomatoes can be dried as halves, slices, quarters and powders and used as a component for pizza and various vegetable dishes (Giovannelli, Zanoni, Lavelli, & Nani, 2002). Industrial processing of tomatoes to a final moisture content of <15% often involves high temperatures (60–110 °C) for a period of 2–10 h in the presence of oxygen, and therefore, the products show some oxidative damage (Zanoni, Peri, Nani, & Lavelli, 1999). Considerable losses of ascorbic acid have been reported during the production of dried tomato halves and tomato pulp using high temperatures (Dewanto et al., 2002; Giovannelli et al., 2002; Zanoni et al., 1999). The loss of ascorbic acid is dependent on the drying temperature used and the moisture content in the final product; for instance, tomatoes dried at 80 °C contained 10% residual ascorbic acid while those dried at 110 °C contained none (Zanoni et al., 1999). Air-drying of

* Corresponding author. Tel.: +64 3 325 2811x8139; fax: +64 3 325 3851.

E-mail address: kaurr1@lincoln.ac.nz (R.K. Toor).

tomatoes also leads to an increase in the 5-hydroxymethyl-2-furfural (HMF) content which results in undesirable colour and appearance changes of dried tomatoes (Zanoni et al., 1999). Drying of tomato halves at 110 °C caused a 20-fold increase in HMF when compared to 80 °C (Zanoni et al., 1999). Olorunda, Aworh, and Onuoha (1990) report that an increase in drying time and temperature result in tissue darkening, while other studies report an increase in darkness (L^*) and decrease in redness (a^*/b^* value) of tomatoes after air-drying (Kerkhofs, 2003; Shi, Le Maguer, Kakuda, Liptay, & Niekamp, 1999).

Air-drying is reported to have little effect on the lycopene content of tomatoes (Giovanelli et al., 2002; Kerkhofs, 2003; Shi et al., 1999; Zanoni et al., 1999). The total phenolics and carotenoids of tomato have been reported to be quite stable during processing under high temperature conditions, and thermal processing has been reported to release more bound phenolics due to the breakdown of cellular constituents (Dewanto et al., 2002).

An increase in oxidation has been reported to occur during dehydration if the moisture content falls below the monolayer moisture content of the product (Labuza, 1971; Zanoni, Pagliarini, & Foschino, 2000). Tomatoes dried at a lower temperature (60 °C) have been reported to imbibe more water on rehydration than those dried at 70 or 80 °C (Olorunda et al., 1990). It has been proposed by Zanoni et al. (1999) that modification of the operating conditions during air-drying of tomatoes, by (i) using low temperature treatments, (ii) reducing tomato thickness by using tomato slices or quarters, and (iii) partial removal of water (production of intermediate moisture tomatoes), can help to reduce oxidative damage in the final dried product. Kerkhofs (2003) used a low temperature treatment (42 °C) to dry tomatoes to a residual dry matter content of 77%. Improved colour retention occurred when compared to higher temperature treatments (Nicoli, Anese, Parpinel, Franceschi, & Lerici, 1997; Shi et al., 1999). Shi et al. (1999) also reported that the colour (L^* and a^*/b^* values) of tomatoes was retained best under conditions of osmotic dehydration at 25 °C. However, it is not known whether colour and the antioxidant components of tomatoes would be retained if lower temperatures and a higher moisture content product is produced. Recently, a new method has been developed to produce semi-dried tomatoes by drying at 42 °C for 18 h to a final dry matter (DM) content of about 19%. The bright-red semi-dried tomatoes are then packed in air-tight plastic bags after the addition of canola oil to extend their shelf life. It is hypothesised that these semi-dried tomatoes would retain high levels of antioxidant compounds. Therefore, the objective of this study was to investigate the potential retention of the major antioxidant compounds in three commercially grown tomato cultivars.

2. Materials and methods

2.1. Fruit sampling

Tomato fruit of three commercial tomato cultivars: Excell, Tradiro and Flavourine, which are mainly used for the local fresh consumption, were used for this study. The tomatoes had been grown using a hydroponic fertigation system and commercial conditions in a greenhouse located in Christchurch, New Zealand (43°40'S, 172°29'E). The tomatoes were harvested at the red-ripe stage (Maturity stage 6, Californian Tomato Commission, 2002).

2.2. Drying of tomatoes

Ninety kg of each tomato cultivar were divided into three replicates and the tomatoes were washed in 150 ppm hypochlorite chlorine-based surface sanitizer (Johnson Diversey, Papatoetoe, Auckland). The fruit were cut into quarters before drying. The tomato quarters were placed on stainless steel trays in a forced-air drier in a pilot plant and were dried at a temperature of 42 ± 1 °C for 18 h. The semi-dried tomatoes were immediately packed in resealable plastic bags and analysed fresh.

2.3. Analyses

Approximately 10 kg of each cultivar of semi-dried and fresh tomatoes were stored in resealable plastic bags at 10 °C and representative subsamples were taken for each analysis. All analysis was completed within 2 days.

2.4. Carpometric characteristics

The DM content of fresh and semi-dried tomatoes was determined by placing the samples in a 105 °C oven until a stable weight was reached (AOAC, 2000). The CIELAB coordinates, L^* , a^* (bluish-green/red-purple hue component, and b^* yellow/blue hue component) were measured on the skin of tomato fruit and dried tomatoes, using a Minolta Chroma Meter CR-210 (Minolta Camera Co. Ltd., Osaka, Japan). The chromameter consisted of an 8 mm diameter measuring area and diffuse illumination/0° viewing was used, and the readings were calibrated against a white tile. The a^*/b^* value is the ratio of red-green component of colour and relates better to the colour variation in tomatoes (Francis & Clydesdale, 1975).

For the determination of total soluble solids, the fresh tomatoes were homogenised and then centrifuged at 1474g for 10 min. The supernatant was used to measure the soluble solids, using a refractometer, DMA 35n density meter (Anton Parr GmbH, Graz, Austria), and the results were reported as °Brix at 20 °C. The titratable

acidity and pH were measured on fresh, homogenised samples using a Metrohm 670 titroprocessor (Metrohm Herisau, Switzerland) that measured the amount of 0.1 M NaOH required to neutralize the acids of the tomatoes. The results for titratable acidity were expressed as % citric acid. The water activity in the samples was determined with a Aqua Lab Model CX-2 water activity a_w meter (Decagon Devices, Pullman, Washington, USA).

2.5. HMF determination

For determination of HMF, the fresh and semi-dried tomato samples (8.5 g) were extracted in 10 ml of deionised water on a rotary mixer for 15 min. The samples were then centrifuged at 3400 rcf for 15 min, and the supernatant was then passed through a 0.45 μ m cellulose nitrate membrane filter (Sartorius, Goettingen, Germany) prior to injecting 25 μ l into the HPLC. A Waters 510 isocratic pump, Waters WISP 712 autoinjector/samplechanger (Waters Inc., Marlborough, Massachusetts) and Waters 441 UV/VIS detector (Waters Inc., Marlborough, Massachusetts, USA), set at 280 nm, using an Econosphere C₁₈ 250 mm \times 4.6 mm analytical column (Alltech Associates Inc., Deerfield, Illinois, USA) held at 30 °C, were used for HMF analysis. An isocratic mobile phase of 5% methanol and 0.5% acetonitrile (BDH, Poole, UK) was circulated at a flow rate of 1.5 ml/min. HMF was identified and quantified using a HMF standard (Sigma–Aldrich, St. Louis, Missouri, USA) at 2.5 μ l/ml.

2.6. Extraction method for separation of hydrophilic and lipophilic extracts

A modified method of Prior et al. (2003) was used to separate the hydrophilic and lipophilic extracts of fresh and semi-dried tomatoes. In brief, 4 g of finely homogenised sample were extracted twice with 10 ml hexane, in the dark, followed by centrifugation at 3400g for 10 min. The lipophilic extract was prepared by drying a known volume (4 ml) of the hexane extract under nitrogen flow. This was then re-dissolved in 0.5 ml of 100% acetone and vortexed for 2 min, followed by addition of 1.5 ml of 80% acetone. The samples were vortexed and sonicated for 5 min to completely dissolve the residue. After the hexane extraction, the sample was used for the extraction of hydrophilic antioxidants. The residual hexane in the samples was evaporated under nitrogen flow, followed by extraction of the residual pellet with 10 ml of acetone:water:acetic acid (70:29.5:0.5, v/v/v), then vortexed for 1 min, then sonicated for 5 min. The tubes were covered with aluminium foil and were placed on a rotary mixer for 15 min, followed by centrifugation at 3400 rcf for 10 min. The supernatant (hydrophilic extract) was then transferred to a new tube.

2.7. Total phenolics

Total phenolics were measured using the Folin–Ciocalteu method (Spanos & Wrolstad, 1990). In brief, the hydrophilic and lipophilic extracts were appropriately diluted and then oxidised with 2.5 ml of freshly diluted 0.2 M Folin–Ciocalteu reagent. This reaction was neutralised by adding 2.0 ml of 7.5% w/v sodium carbonate, and the samples were vortexed for 20 s. The samples were then incubated at 45 °C for 15 min and the absorbance of the resulting blue colour was measured at 765 nm on an UV–Vis recording spectrophotometer (UV-2100, Shimadzu, Corporation, Kyoto, Japan). Gallic acid was used as a standard, and results were expressed as gallic acid equivalents (GAE) per 100 g DM. The results were corrected for the contribution of ascorbic acid to the total phenolics, as described by Toor, Savage, and Lister (2004a).

2.8. Total flavonoids

The flavonoid content was measured using a colorimetric assay developed by Zhishen, Mengcheng, and Jianming (1999). A known volume (1 ml) of the extracts or standard solutions of rutin (Sigma–Aldrich, St. Louis, Missouri, USA) was added to a 10 ml volumetric flask. Distilled water was added to make a volume of 5 ml. At zero time, 0.3 ml of 5% w/v sodium nitrite was added to the flask. After 5 min, 0.6 ml of 10% w/v AlCl₃ was added and, after 6 min, 2 ml of 1M NaOH were added to the mixture, followed by the addition of 2.1 ml distilled water. Absorbance was read at 510 nm against the blank (water) and flavonoid content was expressed as mg rutin equivalents/100 g DM.

2.9. Lycopene

For extracting lycopene, 1 g of homogenised fresh or semi-dried tomato sample was weighed into a screw-top Kimax tube (Kimble Glass Inc., Vineland, New Jersey, USA), which was covered with aluminium foil to exclude light and the lycopene from the samples was extracted using the method of Sadler, Davis, and Dezman (1990). In brief, a 25 ml mixture of hexane–acetone–ethanol (2:1:1, v: v: v) was added to the samples, which were then placed on the rotary mixer for 30 min. Agitation was continued for another 2 min after adding 10 ml of distilled water. The solution was then left to separate into distinct polar and non-polar layers and then the hexane layer was collected in a 50 ml flask. The residual solids were re-extracted to ensure complete extraction of lycopene. The absorbance of the combined hexane layers was measured at 472 nm on a Unicam Helios Beta spectrophotometer (UVB 074115, Pye, Cambridge, UK) using hexane as a blank. The purity of the extracted standard lycopene was checked using its

extinction coefficient ($E_{1\text{ cm}}^{1\%}$) of 3450 (Davis, 1976) and a standard curve was prepared. The amount of lycopene in the tomato samples was determined from this standard curve, and the results were expressed as mg/100 g DM.

2.10. Ascorbic acid

Ascorbic acid in fresh and semi-dried tomatoes was measured by the Metrohm 670 titroprocessor (Metrohm Ltd., Herisau, Switzerland) using the AOAC method (AOAC, 2000). In brief, 1 g of sample was mixed with 40 ml of buffer (1 g/l oxalic acid plus 4 g/l anhydrous sodium acetate) and titrated against the dye solution containing 295 mg/l of DPIC (phenolindo-2,6-dichlorophenol) and 100 mg/l sodium bicarbonate. A standard curve was generated using L-ascorbic acid (BDH, Poole, UK). The ascorbic acid content in samples was determined from the standard curve and the results were expressed as mg/100 g DM.

2.11. Antioxidant activity

The radical-scavenging capacity (antioxidant activity) of the hydrophilic and lipophilic extracts of fresh and semi-dried samples was measured using the modified ABTS (2,2' azinobis 3-ethylbenzothiazoline-6-sulfonic acid diammonium salt, Sigma–Aldrich, St. Louis, Missouri, USA) radical decolourisation assay (Miller & Rice-Evans, 1997). The ABTS radical was generated with manganese dioxide. Then, 1 ml of the ABTS⁺ solution was added to 100 μ l of standard or sample (diluted as required) and vortexed for 10 s. The decolourisation caused by reduction of the cation by antioxidants from the sample was measured at 734 nm, with a UV–Vis recording spectrophotometer UV2100 (Shimadzu, Cor-

poration, Kyoto, Japan), at exactly 1 min after initial mixing. Assays were performed with three dilutions per extract, and in duplicate per dilution. ‘Trolox’® (6 hydroxy-2,5,7,8-trimethyl-chroman-2-carboxylic acid (Sigma–Aldrich, St. Louis, Missouri, USA)), a water-soluble vitamin E analogue, was used to prepare the standard curve and activity was reported as trolox equivalent antioxidant capacity (μ mole TEAC/100 g DM).

2.12. Statistical analysis

All data are reported as means \pm standard error of means of three replicates. Two-way analysis of variance (ANOVA) was used and the least significant difference (LSD) at $p < 0.05$ was calculated using (Genstat, 2000) to determine significant differences between the fresh and semi-dried tomatoes.

3. Results and discussion

3.1. Carpometric characteristics

Excell and Tradiro were salad-type, large-sized tomato cultivars (mean weights of the fruit: 103 ± 3.1 g, and 101 ± 4.4 g respectively), and Flavourine was a smaller cultivar (mean weight of the fruit: 68 ± 2.6 g). Due to its small size, Flavourine had significantly higher soluble solids (5.1 ± 0.09 °Brix) than Excell and Tradiro (4.2 ± 0.10 and 4.7 ± 0.10 °Brix, respectively). The DM of fresh Flavourine was significantly higher than the other two cultivars (Table 1). The DM of the semi-dried Flavourine was also significantly ($p < 0.05$) higher (21.8%) than the other two cultivars (15.9–18.9%). The water activity (a_w) of the semi-dried tomatoes was quite

Table 1
Carpometric characteristics of fresh and dried tomatoes of the three cultivars (means \pm standard error, $n = 3$)

Cultivar/treatment	Mean weight of 20 fruit (g)	Dry matter (%)	HMF content (mg/kg DM)	Titratable acidity (% citric acid)	Chromaticity values			
					L^*	a^*	b^*	a^*/b^*
Excell								
Fresh	103 ± 3.1	5.1 ± 0.14	nd	0.55 ± 0.04	46.0 ± 0.81	33.6 ± 2.01	31.9 ± 1.27	1.05 ± 0.07
Dried		18.9 ± 0.64	8.1	1.13 ± 0.04	32.2 ± 1.24	24.7 ± 1.55	18.9 ± 1.99	1.32 ± 0.09
Tradiro								
Fresh	101 ± 4.4	5.6 ± 0.19	nd	0.41 ± 0.02	44.0 ± 0.72	39.4 ± 0.35	29.5 ± 0.98	1.34 ± 0.06
Dried		15.9 ± 0.23	7.1	1.30 ± 0.03	29.6 ± 1.18	27.7 ± 1.84	15.0 ± 0.91	1.84 ± 0.02
Flavourine								
Fresh	68 ± 2.6	6.2 ± 0.02	nd	0.56 ± 0.02	48.0 ± 1.34	39.5 ± 2.36	31.4 ± 1.32	1.26 ± 0.02
Dried		21.8 ± 0.39	7.3	1.95 ± 0.03	30.6 ± 0.46	26.5 ± 1.06	14.8 ± 0.70	1.79 ± 0.02
Source of variation	Probability							
Cultivar	***	***	NS	***	***	*	NS	***
Drying		***		***	***	***	***	***
Cultivar \times drying		***		***	***	NS	NS	NS

Significance: NS = not significant; nd = not detected.

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

high (Excel, 0.96; Tradiro, 0.95, Flavourine, 0.95) and this reduces their shelf-life. For commercial purposes, oil is commonly added to the semi-dried tomatoes to extend their shelf-life (Yumco, Christchurch, NZ). For the purpose of this study, all the analyses were carried out immediately after semi-drying of tomatoes. Addition of oil to the product was avoided in this study because it results in the absorption of oil by the semi-dried tomatoes, which could interfere with the analysis. The titratable acidity of the tomatoes showed a significant ($p < 0.05$) increase with semi-drying. The titratable acidities of fresh Excell and Flavourine were quite similar, but, after semi-drying, Flavourine retained a significantly higher titratable acidity than Excell (Table 1). This is probably because of the significantly higher DM content in semi-dried Flavourine.

After semi-drying of the tomatoes, an increase in the darkness (a decrease in the L^* value) was observed (Table 1). The amounts of sugar, acids (pH), and amino acids, as well as time of processing have been reported to affect the colour of processed tomato products by causing formation of brown pigments (Gould, 1983). Fresh Excell tomatoes had a significantly lower red colour ($+a^*$) value than the other two cultivars. The a^* value of all tomato cultivars declined by 28% after semi-drying. But the decline in b^* value was much higher (33–52%) in all three cultivars, and Excell had significantly higher b^* value for the semi-dried tomatoes than the other two cultivars. The higher decrease in b^* value than a^* value in semi-dried tomatoes resulted in an overall increase in a^*/b^* value. An a^*/b^* value is commonly used as an index to report the colour quality (brightness of red colour) of tomatoes (Arias, Lee, Logendra, & Janes, 2000; Francis & Clydesdale, 1975; Kerkhofs, 2003; Shi et al., 1999). Previous studies have reported a decrease in both L^* and a^*/b^* values after dehydration

of tomatoes (Kerkhofs, 2003; Shi et al., 1999). Shi et al. (1999) reported a 50% decrease in the a^*/b^* value when tomatoes were dehydrated to a moisture content of 3–4% using conventional air-drying at 90 °C. They also reported that preparation of intermediate dried tomatoes (with a moisture content of 50–55%) by osmotic dehydration at 25 °C was the best method to retain the colour (a^*/b^* value) of tomatoes, while production of intermediate dried tomatoes by air-drying at 95 °C decreased the a^*/b^* values by 26% when compared to fresh tomatoes. Kerkhofs (2003) observed a 21% decrease in the a^*/b^* values when tomatoes were dehydrated at 42 °C to a final DM content of 77%. However, in the present study, a significant increase in the a^*/b^* values was observed after semi-drying, and this is probably related to the use of low temperatures and a relatively high moisture content in the final product compared to the previous studies. Tradiro and Flavourine had significantly ($p < 0.05$) higher a^* and a^*/b^* values in the fresh and semi-dried tomatoes than Excell. Upon semi-drying, a 37–42% increase in the a^*/b^* value was observed in Tradiro and Flavourine, whereas this increase was only 25% in Excell.

The gradual browning of tomatoes during previous dehydration studies is due to non-enzymatic browning or Maillard reaction; HMF is an intermediate product (Zanoni et al., 1999). No HMF was detected in fresh tomatoes, while the HMF content in the semi-dried tomatoes of the three cultivars ranged from 7.1 to 8.1 mg/kg DM (Table 1). Zanoni et al. (1999) observed that the HMF content of dried tomatoes increased with an increase in drying temperature and time. Increase in time from 390 to 430 min resulted in a corresponding increase in HMF content from 10–36 mg/kg DM at 80 °C, and 18–512 mg/kg DM at 110 °C. They also reported that a HMF value > 20 mg/kg DM corresponded to a

Table 2
Antioxidant composition of fresh and dried tomatoes of the three cultivars (means \pm standard error, $n = 3$)

Cultivar/treatment	Total phenolics (mg GAE/100 g DM)		Total flavonoids (mg rutin eq/100 g DM)	Lycopene (mg/100 g DM)	Ascorbic acid (mg/100 g DM)	Antioxidant activity (μ mole TEAC/100 g DM)	
	Hydrophilic	Lipophilic				Hydrophilic	Lipophilic
Excell							
Fresh	314 \pm 14.5	63 \pm 3.7	210 \pm 7.2	44 \pm 1.5	296 \pm 12.6	2540 \pm 56.0	172 \pm 5.7
Dried	235 \pm 23.6	44 \pm 3.0	179 \pm 9.6	35 \pm 1.3	246 \pm 14.2	1554 \pm 99.1	101 \pm 2.9
Tradiro							
Fresh	342 \pm 48.8	51 \pm 4.1	211 \pm 10.7	76 \pm 4.3	310 \pm 12.6	2548 \pm 163.9	187 \pm 13.0
Dried	238 \pm 29.5	43 \pm 1.5	183 \pm 7.6	68 \pm 2.2	222 \pm 12.7	1841 \pm 119.7	108.2 \pm 4.5
Flavourine							
Fresh	387 \pm 19.8	56 \pm 3.6	197 \pm 13.6	68 \pm 4.0	247 \pm 10.5	2579 \pm 136.6	164 \pm 8.1
Dried	299 \pm 25.9	42 \pm 2.5	176 \pm 7.0	60 \pm 1.3	202 \pm 8.5	1638 \pm 67.3	107 \pm 3.3
Source of variation	Probability						
Cultivar	NS	NS	NS	***	**	NS	NS
Drying	**	***	**	**	***	***	***
Cultivar \times drying	NS	NS	NS	NS	NS	NS	NS

Significance: NS = not significant.

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

change in colour from red to brick-red, then to brown. The HMF values of the semi-dried tomatoes in this study are well below the limit of 20 mg/kg DM, which confirms the mild conditions used.

3.2. Antioxidant components

3.2.1. Total phenolics and flavonoids

Tradiro showed a significant ($p < 0.05$) decline in hydrophilic phenolics (30%) following semi-drying, whereas the decrease was non-significant for Excell and Flavourine (Table 2). Semi-dried Flavourine had significantly ($p < 0.05$) higher hydrophilic phenolics than Excell and Tradiro. Phenolics in the lipophilic extract accounted for only 13–16% of the total phenolic content of tomatoes (hydrophilic + lipophilic). A significant ($p < 0.05$) decrease was observed in the lipophilic phenolic content of Excell and Flavourine after semi-drying. The total flavonoids showed a 10–15% loss as a result of semi-drying, and this loss was significant for Excell only (Table 2). Kerkhofs (2003) also reported a significant decrease in total phenolics when tomatoes were dried under low temperature conditions (42 °C) to a final moisture content of 77%. The major losses of phenolics during processing are brought about by the action of oxidative enzymes such as polyphenoloxidases and peroxidases (Shahidi & Naczki, 1995). However, Lavelli, Hippeli, Peri, and Elstner (1999) reported that the total phenolics of tomatoes increased after air-drying at 80 °C for 7 h, and this was reportedly due to an increase in the number of free hydroxyl phenol groups as a result of hydrolysis of flavonoid glycosides and/or the release of cell wall phenolics. Gahler, Otto, and Böhm (2003) also observed an increase in the phenolic content of tomatoes as a result of thermal processing. Dewanto et al. (2002) reported that heating of tomatoes at 88 °C for 30 min did not affect the phenolic content of tomatoes. At cellular level, the phenolic compounds are located in the vacuoles and are separated from oxidative enzymes in an intact fruit (Macheix, Fleuriet, & Billot, 1990). However, the tomato structure collapses during dehydration and this may result in release of the oxidative and hydrolytic enzymes. Thermal processing at 88 °C has been reported to deactivate these enzymes to avoid losses of phenolic acids (Dewanto et al., 2002). However, in the present study, low temperatures were used for drying, which probably did not inactivate the oxidative enzymes completely, which may have in turn resulted in some oxidation of the phenolic substances and resulted in a relatively lower phenolic content in the semi-dried tomatoes than in fresh tomatoes.

3.2.2. Lycopene

There was no significant difference between the lycopene contents of fresh and semi-dried tomatoes of Tradiro and Flavourine (Table 2). However, lycopene

content of semi-dried Excell was significantly ($p < 0.05$) lower than that of fresh tomatoes. In addition, Excell had significantly ($p < 0.05$) lower lycopene content in the fresh tomatoes than did Tradiro and Flavourine. Thermal processing of tomatoes has been reported to increase the extractable lycopene content in processed products when compared to fresh tomatoes (Dewanto et al., 2002; Tonucci et al., 1995). This is probably because lycopene is mostly attached to the skin and insoluble fibre portion of tomatoes (Sharma & Le Maguer, 1996; Toor & Savage, 2004b), and heat processing may cause an increased release of lycopene from the cell matrix. However, Takeoka et al. (2001) reported significant losses in the lycopene content during production of tomato paste from fresh tomatoes using high temperature conditions. The reasons for this observation were not clear. However, Kerkhofs (2003) observed a significant increase in lycopene content upon air-drying of tomatoes at 42 °C to a final DM content of 77%. Lavelli et al. (1999) observed no significant change in lycopene content of air-dried tomatoes processed at 80 °C for 7 h (83 mg/100 g DM) when compared to fresh tomatoes (85 mg/100 g DM). Zanoni et al. (1999) reported a significant loss (12%) of lycopene during air-drying of tomatoes at 110 °C, whereas no significant loss occurred during air-drying at 80 °C. Shi et al. (1999) observed a 3.2% loss in lycopene in vacuum-dried tomatoes (55 °C for 4–8 h) and 3.9% loss in air-dried tomatoes (95 °C for 10 h). The presence of both light and oxygen could lead to a significant loss of lycopene during processing of tomato (Cole & Kapur, 1957a, 1957b; Zanoni et al., 1999). Oxygen permeability, light exposure, and presence of some metals in the processing system favour the isomerisation and oxidation of lycopene during dehydration (Shi et al., 1999).

3.2.3. Ascorbic acid

Semi-dried tomatoes showed a significant, but smaller loss of ascorbic acid when compared to previous studies, and this is mainly due to the lower temperature conditions used. Flavourine had a significantly ($p < 0.05$) lower amount of ascorbic acid in the fresh, as well as semi-dried tomatoes, when compared to the other two cultivars (Table 2). Tradiro showed a greater loss of ascorbic acid (27%) than did Excell and Flavourine (both at 17%). There are many reports of peroxidase activity in all common fruits, and this enzyme catalyses the oxidation of different substrates such as ascorbic acid and phenols (Dilley, 1970).

Tomatoes are a rich source of ascorbic acid (Abushita et al., 1997; Kaur et al., 2002); however, processing of tomatoes has been reported to have a very detrimental effect on their ascorbic acid content (Dewanto et al., 2002; Takeoka et al., 2001). The temperature at which tomato products are heated in the presence of air is the most important factor affecting the rate of ascorbic

acid destruction (Gould, 1983). Previous studies, using higher temperature conditions for drying of tomatoes, have reported a significant loss of ascorbic acid. For example, Lavelli et al. (1999) observed an 88% loss in ascorbic acid when tomatoes were dehydrated at 80 °C for 7 h to a 10% moisture content. Zanoni et al. (1999) showed that the loss of ascorbic acid was largely dependent on temperature, and reported significant losses of ascorbic acid (40 and 80% at temperatures of 80 and 110 °C, respectively) at 80% moisture content.

3.2.4. Antioxidant activity

The hydrophilic antioxidant activity was decreased by 28–38% in semi-dried tomatoes compared with the fresh (Table 2). Tradiro showed a lower decrease in antioxidant activity (28%) than the other two cultivars; therefore, this cultivar may be ideal to make processed products. Ascorbic acid and phenolic compounds are the main contributors of the hydrophilic antioxidant activity of tomato (Toor et al., 2004a). Declines in both total phenolics and ascorbic acid during processing are likely to be responsible for the observed decreases in antioxidant activity in the semi-dried tomatoes. The contributions of antioxidant activity of the lipophilic extract, of fresh and semi-dried tomatoes, to their total antioxidant activity (hydrophilic + lipophilic) were similar (7%). There were no differences in the lipophilic antioxidant activities of tomatoes of different cultivars, and a 35–42% decrease was observed in the semi-dried compared to fresh tomatoes (Table 2), which could be related to the decline in the lipophilic phenolics.

Despite a decrease in the ascorbic acid, an increase in the antioxidant activity has been reported in the tomato products processed at higher temperatures (Dewanto et al., 2002; Gahler et al., 2003; Giovanelli et al., 2002; Nicoli et al., 1997). While heating is the main cause of depletion of antioxidants such as ascorbic acid, heating can induce the formation of compounds such as melanoidins in the Maillard reaction, and these compounds can have some antioxidant effects (Anese, Manzocco, Nicoli, & Lericci, 1999; Nicoli et al., 1997). However, because high temperature was not used in this study, this effect was not observed. It is suggested that the use of higher temperatures (90 °C) for a short period of time during processing could help the formation of melanoidins, which may increase the antioxidant activity in the semi-dried tomatoes but this, in turn, may lead to some additional losses of ascorbic acid.

4. Conclusions

This study shows that semi-drying of tomatoes allows the retention of colour with only low levels of HMF in the final product. This method of drying is particularly suitable for processors who are interested in retaining

maximum ascorbic acid contents. Retention of high levels of antioxidants is important as the product is likely to undergo further heat treatments in the home and this will lead to additional losses of antioxidants (Sahlin, Savage, & Lister, 2004). Out of the three cultivars studied, Tradiro appears to be the most suitable cultivar for this type of processing as it has a good colour and size and retains high levels of antioxidants and antioxidant activity after semi-drying.

Acknowledgements

The New Zealand Ministry of Foreign Affairs and Trade (MFAT) supported this research by providing a New Zealand Official Development Assistance (NZODA) doctoral fellowship to Ramandeep K. Toor. We thank Dr. Carolyn E. Lister, New Zealand Institute for Crop & Food Research Ltd., Lincoln, Canterbury for her useful comments and use of laboratory facilities. The local tomato grower helped this research by generous supply of tomatoes.

References

- Abushita, A. A., Hebshi, E. A., Daood, H. G., & Biacs, P. A. (1997). Determination of antioxidant vitamins in tomatoes. *Food Chemistry*, *60*, 207–212.
- Anese, M., Manzocco, L., Nicoli, M. C., & Lericci, C. R. (1999). Antioxidant properties of tomato juice as affected by heating. *Journal of the Science of Food and Agriculture*, *79*, 750–754.
- AOAC (2000). *Official methods of analysis of AOAC International* (17th ed.). Gaithersburg, MD, USA.
- Arias, R., Lee, T. C., Logendra, L., & Janes, H. (2000). Correlation of lycopene measured by HPLC with the *L*, *a*, *b* colour readings of a hydroponic tomato and the relationship of maturity with colour and lycopene content. *Journal of Agricultural and Food Chemistry*, *48*, 1697–1702.
- Californian Tomato Commission (2002). Available: <http://www.tomato.org/retail/color.html>.
- Cole, E. R., & Kapur, N. S. (1957a). The stability of lycopene. I. Degradation by oxygen. *Journal of Science of Food and Agriculture*, *8*, 360–365.
- Cole, E. R., & Kapur, N. S. (1957b). The stability of lycopene. II. Oxidation during heating of tomato pulps. *Journal of the Science of Food and Agriculture*, *8*, 366–368.
- Davis, B. H. (1976). Carotenoid. In T. W. Goodwin (Ed.), *Chemistry and biochemistry of plant pigments* (pp. 38–165). London: Academic Press.
- Dewanto, V., Wu, X. Z., Adom, K. K., & Liu, R. H. (2002). Thermal processing enhances the nutritional value of tomatoes by increasing total antioxidant activity. *Journal of Agricultural and Food Chemistry*, *50*, 3010–3014.
- Dilley, D. R. (1970). Enzymes. In A. C. Hulme (Ed.), *The biochemistry of fruits and their products* (pp. 179–204). New York: Academic Press.
- Francis, F. J., & Clydesdale, F. H. (1975). *Food colorimetry: Theory and application* (pp. 179–215). Westport, NJ: AVI Publishing Co.
- Gahler, S., Otto, K., & Böhm, V. (2003). Alterations of vitamin C, total phenolics, and antioxidant capacity as affected by processing

- tomatoes to different products. *Journal of Agricultural and Food Chemistry*, 51, 7962–7968.
- Genstat (2000). *Genstat release 4.2 reference manual*.
- George, J., Nuttall, S. L., & Kendall, M. J. (2001). Prostate cancer and antioxidants. *Journal of Clinical Pharmacy and Therapeutics*, 26, 231–233.
- Gerster, H. (1997). The potential role of lycopene for human health. *Journal of the American College of Nutrition*, 16, 109–126.
- Giovannucci, E. (1999). Tomatoes, tomato-based products, lycopene, and cancer: review of the epidemiological literature. *Journal of the National Cancer Institute*, 91, 317–331.
- Giovanelli, G., Zanoni, B., Lavelli, V., & Nani, R. (2002). Water sorption, drying and antioxidant properties of dried tomato products. *Journal of Food Engineering*, 52, 135–141.
- Gould, W. A. (1983). *Tomato production, processing, and quality evaluation* (2nd ed., pp. xii). Westport, CT: The AVI Publishing Company, Inc.
- Kaur, R., Savage, G. P., & Dutta, P. C. (2002). Antioxidant vitamins in four commercially grown tomato cultivars. *Proceedings of the Nutrition Society of New Zealand*, 27, 69–74.
- Kerkhofs, N. S. (2003). An investigation of the influence of air-drying on the antioxidant components and antioxidant activity of New Zealand grown tomatoes. B.Sc. (Honours), Lincoln University.
- Labuza, T. P. (1971). Kinetics of lipid oxidation in foods. *CRC Critical Review of Food Technology*, 0, 355–405.
- Lavelli, V., Hippeli, S., Peri, C., & Elstner, E. F. (1999). Evaluation of radical scavenging activity of fresh and air-dried tomatoes by three model reactions. *Journal of Agricultural and Food Chemistry*, 47, 3826–3831.
- Lister, C. E. (2003). *Antioxidants: a health revolution*. New Zealand Institute for Crop & Food Research.
- Macheix, J.-J., Fleuriet, A., & Billot, J. (1990). *Fruit phenolics*. Boca Raton, FL: CRC Press, Inc.
- Miller, N. J., & Rice-Evans, C. A. (1997). Factors influencing the antioxidant activity determined by the ABTS⁺ radical cation assay. *Free Radical Research*, 26, 195–199.
- Nicoli, M. C., Anese, M., Parpinel, M. T., Franceschi, S., & Lericci, C. R. (1997). Loss and/or formation of antioxidants during food processing and storage. *Cancer Letters*, 114, 71–74.
- Olorunda, A. O., Aworh, O. C., & Onuoha, C. N. (1990). Upgrading quality of dried tomato: effects of drying methods, conditions and pre-drying treatments. *Journal of the Science of Food and Agriculture*, 52, 447–454.
- Paganga, G., Miller, N., & Rice Evans, C. A. (1999). The polyphenolic content of fruit and vegetables and their antioxidant activities. What does a serving constitute?. *Free Radical Research*, 30, 153–162.
- Prior, R. L., Hoang, H., Gu, L., Wu, X., Bacchiocca, M., Howard, L., et al. (2003). Assays for hydrophilic and lipophilic antioxidant capacity (oxygen radical absorbance capacity (ORAC)) of plasma and other biological samples. *Journal of Agricultural and Food Chemistry*, 51, 3273–3279.
- Rao, A. V., & Agarwal, S. (2000). Role of antioxidant lycopene in cancer and heart disease. *Journal of American College of Nutrition*, 19, 563–569.
- Sadler, G., Davis, J., & Dezman, D. (1990). Rapid extraction of lycopene and β -carotene from reconstituted tomato paste and pink grapefruit homogenate. *Journal of Food Science*, 55, 1460–1461.
- Sahlin, E., Savage, G. P., & Lister, C. E. (2004). Investigation of the antioxidant properties of tomatoes after processing. *Journal of Food Composition and Analysis*, 17, 635–647.
- Shahidi, F., & Naczk, M. (1995). *Food phenolics*. Lancaster, USA: Technomic Publishing Company, Inc.
- Shi, J., Le Maguer, M., Kakuda, Y., Liptay, A., & Niekamp, F. (1999). Lycopene degradation and isomerization in tomato dehydration. *Food Research International*, 32, 15–21.
- Spanos, G. A., & Wrolstad, R. E. (1990). Influence of processing and storage on the phenolic composition of Thompson seedless grape juice. *Journal of Agricultural and Food Chemistry*, 38, 1565–1571.
- Takeoka, G. R., Dao, L., Flessa, S., Gillespie, D. M., Jewell, W. T., Huebner, B., et al. (2001). Processing effects on lycopene content and antioxidant activity of tomatoes. *Journal of Agricultural and Food Chemistry*, 49, 3713–3717.
- Toor, R. K., Savage, G. P. & Lister, C. E. (2004a). Antioxidant activities of New Zealand grown tomatoes. *International Journal of Food Sciences and Nutrition* (in press).
- Toor, R. K. & Savage, G. P. (2004b). Antioxidant activity in different fractions of tomato cultivars. *Food Research International* (in press).
- Tonucci, L. H., Holden, J. M., Beecher, G. R., Khachik, F., Davis, C. S., & Mulokozi, G. (1995). Carotenoid content of thermally processed tomato-based food products. *Journal of Agricultural and Food Chemistry*, 43, 579–586.
- Vinson, J. A., Hao, Y., Su, X., Zubik, L., Hao, Y., & Su, X. H. (1998). Phenol antioxidant quantity and quality in foods: vegetables. *Journal of Agricultural and Food Chemistry*, 46, 3630–3634.
- Zanoni, B., Peri, C., Nani, R., & Lavelli, V. (1999). Oxidative heat damage of tomato halves as affected by drying. *Food Research International*, 31, 395–401.
- Zanoni, B., Pagliarini, E., & Foschino, R. (2000). Study of the stability of dried tomato halves during shelf-life to minimise oxidative damage. *Journal of the Science of Food and Agriculture*, 80, 2203–2208.
- Zhishen, J., Mengcheng, T., & Jianming, W. (1999). The determination of flavonoid contents in mulberry and their scavenging effects on superoxide radicals. *Food Chemistry*, 64, 555–559.