Research Article

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Effects of industrial tomato paste processing on ascorbic acid, flavonoids and carotenoids and their stability over one-year storage

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Abstract

BACKGROUND: The effects of industrial tomato paste processing and long-term (12 months) ambient storage on the content and stability of quercetin, kaempferol, ascorbic acid (AA), dehydroascorbic acid (DHAA), β-carotene and lycopene were evaluated in a commercially produced tomato paste.

RESULTS: The initial thermal treatment (hot break; 93 °C for 5 min) resulted in significant reductions in quercetin (54%), kaempferol (61%), AA (63%) and β-carotene (30%), whereas subsequent processing steps (e.g. evaporation and sterilization) did not result in marked changes in these compounds. Lycopene was stable during hot break but decreased by 20% through evaporation and sterilization. The ratio of DHAA : vitamin C increased during hot break to 23%, whereas the ratio of DHAA : vitamin C remained relatively low in subsequent processing steps, indicating that AA was not oxidized. AA decreased with prolonged storage, with only 13% remaining at 12 months. The carotenoids and quercetin remained stable through 12 months of ambient storage.

CONCLUSIONS: Tomato pomace contained significant amounts of carotenoids and flavonoids, indicating that it may be an underutilized processing byproduct.

Keywords: tomato; processing; storage; ascorbic acid; vitamin C; flavonoids; carotenoids

INTRODUCTION

Tomato (*Lycopersicon esculentum)* is one of the most consumed vegetables (botanically a fruit) per capita in the USA, second only to the potato.[1] Owing to the high level of consumption, tomatoes are a significant source of vitamin C (19 mg 100 g^{-1} fresh weight (FW)), vitamin A (623 IU 100 g^{-1} FW), carotenoids (USDA/NCC) and flavonoids in the Western diet.[2] The main flavonoids found in tomatoes are quercetin and kaempferol. Quercetin predominates, with levels ranging from 0.03 to 2.76 mg 100 g^{-1} in fresh tomatoes and from 0.50 to 4.12 mg 100 g^{-1} in processed tomato products.[3] The main carotenoids in tomatoes are β-carotene and lycopene. Levels of β-carotene reported for fresh tomato and canned tomato sauce are 0.39 and 0.41 mg 100 g^{-1}, respectively, whereas the levels of lycopene are 3.02 and 15.91 mg 100 g^{-1}, respectively.[4]

Tomatoes are consumed either fresh (9.3 kg per capita in 2005) or more frequently as processed tomato products (33.3 kg per capita in 2005), which include sauces, canned products, ketchup and juice.[5] California is the leading producer of tomatoes in the USA, accounting for one third of fresh crop and 95% of processing tomato output.[5] Tomato paste accounts for about 75% of all processed tomato products produced in California annually, and is reconstituted for manufacturing tomato juice, ketchup, pizza sauce, pasta sauce and Mexican sauces, etc.[6] From 1980 to 2006, the quantity of processed tomatoes increased from 6.2 to 10.6 million tons in the USA.[7] This increase parallels the increasing demand for convenience foods (e.g. pizza and pasta sauces) that utilize tomato paste as a starting material.

In general, commercial tomato paste is made using a multi-step process that relies on an initial thermal treatment (called the *break*) followed by a series of pulping, filtering, evaporation and pasteurization steps (Fig. 1). Washed and color-sorted tomatoes are rapidly heated to produce either *hot break* paste (HBP) or *cold break* paste (CBP). Hot break processing involves rapidly heating tomatoes to approximately 95 °C, whereas cold break processing involves heating tomatoes to lower temperatures (approximately 65 °C). Hot break preserves viscosity with some loss in flavor, whereas cold break results in a less viscous but more flavorful paste. The tomatoes are then pressure forced through finishers of various sizes in a process called pulping. The resulting material is evaporated using multi-stage evaporators that range in time–temperature profiles depending upon the viscosity required for the finished product. Tomato paste can be produced to have anywhere from 21% to 37% soluble solids depending upon manufacturing needs. After evaporation, the paste is sterilized (approximately 100 °C for 3–5 min), flash cooled and packaged into aseptic containers. Although the time and temperature profiles used for the initial inactivation of enzymes,

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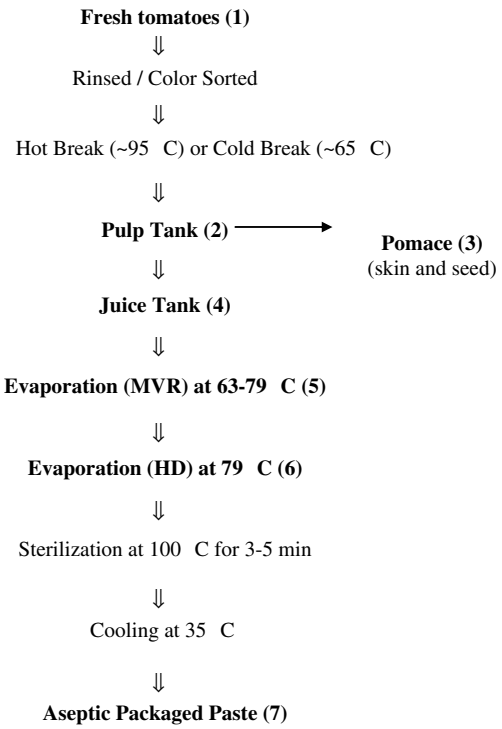

Figure 1. General flow diagram for commercial tomato paste processing. The seven-inlet points sampled for this study are in bold and numbered.

evaporation and sterilization of the tomato paste can vary, most commercial tomato processing facilities use very similar practices.

As the prevalence of processed tomato products has increased in the Western diet, more emphasis is being placed on understanding how commercial processing influences the levels and stability of bioactives with the goal of improving processed food quality. The disposition of bioactives during tomato processing is influenced by numerous factors, including the chemical and thermal stability of the compounds, length and temperature used for thermal treatments, oxidation, presence of metals and the presence of ingredients added for improving taste and flavor.[8–11] Ascorbic acid (AA) is labile and is known to decrease in processed tomato products in response to prolonged thermal processing.[9,10,12] Of the AA present in raw tomatoes, only about half is retained in the final tomato paste after processing.[13] Carotenoids are relatively thermally stable; however, heating can result in some losses and in *cis–trans* bond isomerization.[14,15] For example, thermal treatments ranging from 90 to 150 °C produced up to a 35% loss in lycopene in tomato purée and increased with cooking times from 0.15% at 5 min to 3.47% at 60 min at 100 °C.[15] Takeoka *et al*. also demonstrated that lycopene decreased significantly 9–28% during tomato paste processing, whereas levels of other carotenoids, including phytofluene, phytoene and ζ-carotene, were not affected.[16]

Accordingly, the goal of the present study was to evaluate the levels of the flavonoid aglycones of quercetin and kaempferol as well as other key bioactives – AA, total vitamin C (the sum of AA and dehydroascorbic acid (DHAA), β-carotene and lycopene – in tomato samples collected from seven inlet points during typical industrial tomato paste processing and through 12 months of storage. To date, there are no studies evaluating the influence of long-term storage on the disposition of the range of these bioactives in tomato paste.

MATERIALS AND METHODS

Materials

Lycopene (all-*trans* form from tomato), β-carotene and quercetin dihydrate (2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4*H*-1-benzopyran-4-one dihydrate) were purchased from Sigma (St Louis, MO, USA). Kaempferol (3,5,7-trihydroxy-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one) was obtained from Indofine (Hillsborough, NJ, USA). AA, *m*-phosphoric acid (85%) and solvents for high-performance liquid chromatography were from Fisher Scientific (Fair Lawn, NJ, USA). DL-1,4-Dithiothreital (DTT) was purchased from Acros Organics (Geel, Belgium).

Sampling

Commercial tomato processing was carried out at a commercial facility (Dixon, CA, USA) on 9 October 2007. Tomatoes from local fields (mixed cultivars AB2, Peto 849, Heinz 9995 and Heinz 9780) were loaded into washing flumes and immediately processed. Tomato samples were taken at seven independent points along the processing line and include: (1) mixed fresh tomatoes washed with water; (2) crushed tomatoes after hot break at 93 °C for 5–10 min; (3) tomato pomace, i.e. tomato paste processing wastes consisting mainly of skin and seed; (4) pulped tomato juice; (5) tomato juice after stage I mechanical vapor recompression (MVR) evaporation at 63–79 °C; (6) tomato paste concentrated to 28 °Brix after the stage II HD evaporator at 79 °C; and (7) final tomato paste from aseptic bag sterilized at 99 °C for 3–5 min. Three individual samples were taken at each processing step at different times through the processing load. Samples were transported on ice and stored at −80 °C in a freezer until chemical analysis. Frozen tomato pomace was lyophilized for 3 days using a Virtis Freeze Drier (Model: 50-SRC, Gardiner, NY) to stabilize bioactives. Dried pomace samples were ground in a food mill to a homogeneous powder and kept frozen at −80 °C until analyzed.

Storage of tomato paste

Aseptic 8 L plastic bags filled with tomato paste samples were placed in the dark at room temperature to simulate storage conditions in the facility. Two different bags of paste were randomly taken after 1, 3, 6, 9 and 12 months of storage for analysis of vitamin C, flavonoids and carotenoids. The tomato paste within each bag was mixed prior to sampling.

Determination of moisture

The moisture content of all samples was determined by vacuum oven method. Samples (10 g) were weighed into aluminium weighing dishes (VWR, West Chester, PA, USA) and placed in a vacuum oven (National Appliance Company, Winchester, VA, USA) at 60 °C until the weight of the sample reached a constant value.

Determination of Brix

With the exception of the tomato pomace, fresh tomatoes and processing samples were homogenized and filtered to remove skin and seeds as they can interfere with the measurement of soluble solids. Brix was determined using a digital refractometer (RFM 80, Bellingham + Stanley Ltd, Tunbridge Wells, UK). Freeze-dried pomace was pulverized, mixed with distilled water to reconstitute the actual moisture content and measured as described above.

Determination of ascorbic acid

AA was determined using the method of Sánches-Mata *et al*. (2000) with a slight modification.[17] Either a 20.0 g or 5.0 g sample (for the more concentrated samples) was mixed with 25 mL of 2.5% *m*-phosphoric acid, vortexed and centrifuged at 4000 × *g* for 20 min at 4 °C. The supernatant was decanted into a 50 mL volumetric flask and the residue was reconstituted with 20 mL of 2.5% *m*-phosphoric acid and centrifuged at 4000 × *g* for 20 min at 4 °C, brought to volume, and filtered through a 0.45 m PTFE membrane with glass microfiber pre-filter (Whatman, Florham Park, NJ, USA). A 1.0 mL aliquot of the filtrate was treated with 0.20 mL DTT (40 mg mL^{-1} solution) at 40 °C for 2 h in order to reduce DHAA to AA. Samples, treated with DTT (vitamin C) or not (AA), were analyzed using a Hewlett Packard series 1090 liquid chromatograph (Agilent, Palo Alto, CA, USA) equipped with a diode array detector monitoring at 245 nm. Isocratic separation was achieved using an Agilent Zorbax Eclipse XDB C_{18} column (4.6 × 250 mm, 5 m) equipped with a guard column (4.6 × 12.5 mm, 5 m) of the same material. The mobile phase consisted of 0.05 mol L^{-1} KH_2PO_4 (pH 2.6) at 1.0 mL min^{-1}. The linear range of quantification for AA was determined as 0.001–0.20 mg mL^{-1}.

Determination of flavonoids

The flavonoid analysis was based on the method of Merken and Beecher.[18] Freeze-dried sample (1.0 g) was mixed with 80 mL methanol–water (62.5 : 27.5, v/v) in a 500 mL round-bottomed flask and spiked with 50 L of an internal standard of morin (1 mg mL^{-1} solution) to a final concentration of 0.005 mg mL^{-1}. The sample was refluxed for 2 h after adding 20 mL of 6 mol L^{-1} HCl. After acid hydrolysis, a 2 mL aliquot of the mixture was placed in a vial, cooled on ice and subsequently centrifuged on a Savant speed vacuum concentrator (Model SVC 100H, Savant Instruments, Inc., Hicksville, NY, USA). A 200 L aliquot of the supernatant was reconstituted with 200 L methanol. The mixture was placed in an ultrasonic water bath for 10 min and filtered using an Amicon ultracentrifuge MC 0.5 mL filtration tube (Millipore Corp., Bedford, MA, USA). Prepared samples were analyzed using an Agilent Zorbax Eclipse XDB C_{18} column (4.6 × 250 mm, 5 m) with a guard column (4.6 × 12.5 mm, 5 m) of the same material and monitored at 365 nm for kaempferol and at 375 nm for quercetin. The mobile phase consisted of 0.05% trifluoroacetic acid (TFA) in water (A), 0.05% TFA in methanol (B) and 0.05% TFA in acetonitrile (C). The linear gradients used at a flow rate of 1.0 mL min^{-1} were as follows: 90–85% A, 6–9% B, 4–6% C (0–5 min); 85–71% A, 9–17.4% B, 6–11.6% C (5–30 min); 71–0% A, 17.4–85% B, 11.6–15% C (30–60 min); and 0–90% A, 85–6% B, 15–4% C (60–71 min). The linear range of quantification of quercetin was 0.0005–0.01 mg mL^{-1}.

Determination of lycopene and β-carotene

Carotenoid analysis was based on the methods of Sadler *et al*. and Martínez-Valverde *et al*.[19,20] A 0.5 g of freeze-dried samples was weighed into a 125 mL Erlenmeyer flask wrapped with aluminium foil to exclude light. To this, 50 mL of the mixture of hexane–acetone–ethanol (2 : 1 : 1, v/v/v) was added to solubilize carotenoids. The mixture was extracted at room temperature for 30 min using a Lab-Line Orbit Environ-Shaker (Lab-Line Instruments, Inc, Melrose Park, IL, USA). This extract was reconstituted with 10 mL distilled water on a vortex mixer for 1 min, followed by standing until the two phases were separated completely. A non-polar phase containing carotenoids was decanted into a 50 mL volumetric flask and the residue was re-extracted using the same procedure described above. Non-polar phase extracts combined were volumerized to 50 mL and filtered through a 0.45 m Millex-FH filter (Millipore). Lycopene and β-carotene were determined using a C_{30} carotenoid column (4.6 × 250 mm, YMC, Wilmington, NC, USA) at 470 nm and 451 nm, respectively. The mobile phase consisted of methyl *tert*-butyl ether (MTBE) (solvent A) and methanol (solvent B). The linear gradients at a flow rate of 1.0 mL min^{-1} were as follows: 95% A, 5% B (0–25 min); 30% A, 70% B (25–30 min); 95% A, 5% B (30–35 min). Stock concentrations were determined using the Beer–Lambert equation employing the molar absorptivities of β-carotene (ε = 139 000) and lycopene (ε = 184 000) in hexane.[21,22] The stock solution was diluted with the mixture of methanol and MTBE (50 : 50, v/v). The linear ranges of quantification of lycopene and β-carotene were 0.42–21.0 and 0.11–1.13 g mL^{-1}, respectively.

Statistical analysis

Data were analyzed using the Statistical Package for the Social Sciences (SPSS, version 16.0, SPSS Inc., Chicago, IL, USA). Data were subjected to analysis of variance using a general linear model to determine the difference among samples collected from seven inlet points of an industrial tomato paste facility.

RESULTS AND DISCUSSION

Moisture, Brix, AA, vitamin C, flavonoids and carotenoid levels are presented in Table 1. These values are based on tomato wet weight and are relevant for nutritional comparisons. Moisture content did not change significantly from fresh tomatoes to juice tank and, as expected, decreased substantially upon evaporation (Table 1). Brix levels were increased from 4.9 to 27.5 °Brix, the maximum increase occurring during MVR evaporation. To avoid any misinterpretation arising from the removal of water when comparing the absolute amount of components, all values are also presented based upon a dry weight basis in Table 2.

The content of AA and vitamin C in raw tomatoes was 21.38 ± 0.71 and 24.76 ± 0.27 mg 100 g^{-1} FW, respectively (Table 1). Our value for vitamin C is about twofold higher than the value reported in the USDA database for fresh tomato (12.7 mg 100 g^{-1} FW).[7] Vitamin C is known to increase with tomato ripening and decrease with prolonged storage.[23,24] In general, commercial fresh tomatoes are harvested at a mature green stage and ripened to a red stage using ethylene gas prior to placement on the market shelves. Tomatoes used in the current study were processing tomatoes picked at a mature red stage and delivered directly to the facility, which may have resulted in the higher values for vitamin C. The content of vitamin C in this tomato paste displayed approximate threefold higher levels as compared to USDA values (67.54 mg 100 g^{-1} FW *versus* 21.9 mg 100 g^{-1} FW).[7] Again, this is likely due to sampling and storage as tomato paste is routinely stored for up to 2 years at ambient temperature prior to distribution and remanufacturing. Our tomato paste samples were immediately analyzed after processing, whereas no information is available regarding the length of storage post processing in the studies referred to in the USDA database.

Significant decreases in AA levels occurred when fresh tomatoes were processed into paste (Table 1). The greatest loss occurred during hot break (66%), indicating that this is a critical step for

Table 1. Content of moisture, Brix, ascorbic acid, vitamin C, quercetin, kaempferol, β-carotene and lycopene in tomato paste processing samples on a wet weight basis

Sample	Moisture[a]	°Brix	Ascorbic acid[b]	Vitamin C[c]	Quercetin[d]	Kaempferol[d]	β-Carotene[e]	Lycopene[e]
Fresh tomato	94.5 ± 0.4	4.9 ± 0.3	21.38 ± 0.71c	24.76 ± 0.27c	2.16 ± 0.12d	0.68 ± 0.02c	0.28 ± 0.03d	5.68 ± 0.56c
Pulp tank[g]	94.2 ± 0.7	5.0 ± 0.3	8.33 ± 0.64e	10.83 ± 0.11d	0.56 ± 0.10e	0.19 ± 0.03d	0.20 ± 0.03e	5.87 ± 0.23c
Juice tank[h]	95.0 ± 0.2	4.8 ± 0.1	8.81 ± 0.60e	10.59 ± 0.41d	2.26 ± 0.31d	0.03 ± 0.00d	0.18 ± 0.02e	4.79 ± 0.48c
MVR evaporator	93.3 ± 0.2	6.8 ± 0.1	12.57 ± 0.44d	14.35 ± 0.22d	2.02 ± 0.09d	0.04 ± 0.03d	0.17 ± 0.01e	4.61 ± 0.29c
HD evaporator	73.2 ± 0.9	25.8 ± 0.2	59.00 ± 1.82b	62.74 ± 1.69b	6.25 ± 0.70c	2.82 ± 0.05b	0.69 ± 0.03b	22.23 ± 1.04b
Tomato paste	73.1 ± 0.1	27.5 ± 0.2	66.32 ± 2.62a	67.54 ± 1.81a	9.90 ± 0.10b	3.86 ± 0.28a	1.00 ± 0.07a	26.61 ± 0.45a
Tomato pomace[f]	67.1 ± 0.3	5.9 ± 0.1	5.27 ± 0.07f	7.07 ± 0.12e	12.08 ± 0.88a	0.59 ± 0.14c	1.30 ± 0.06a	27.67 ± 0.21a

Values are reported as the mean ± standard deviation. Means in a column with different letters are significantly different at $P < 0.05$.
[a] Percentage (%).
[b] mg ascorbic acid 100 g^{-1} FW
[c] Value based on the sum of AA and DHAA.
[d] mg 100 g^{-1} FW after acid hydrolysis.
[e] mg each carotenoid 100 g^{-1} FW.
[f] By-products consisted of skin and seed resulting from peeling and sieving.
[g] The pulp tank holds the washed, sorted, chopped and heated tomatoes.
[h] The juice tank holds the tomato pulp after it has been passed through finishers that extract seed and skin.

Table 2. Content of ascorbic acid, vitamin C, quercetin, kaempferol, β-carotene and lycopene in tomato paste processing samples on a dry weight basis

Sample	Ascorbic acid[a]	Vitamin C[b]	Quercetin[c]	Kaempferol[c]	β-Carotene[d]	Lycopene[d]
Fresh tomato	386.81 ± 12.91a	447.96 ± 4.86a	46.30 ± 9.86b	12.23 ± 0.41b	5.03 ± 0.51a	102.69 ± 11.14a
Pulp tank[f]	142.92 ± 11.01e	185.80 ± 1.83e	21.16 ± 0.51d	4.77 ± 0.71d	3.51 ± 0.60b	101.26 ± 4.04a
Juice tank[g]	174.62 ± 11.86d	209.79 ± 8.22d	58.17 ± 7.55a	1.40 ± 0.14f	3.58 ± 0.37b	95.90 ± 9.68a
MVR evaporator	186.50 ± 6.48d	212.90 ± 3.27d	39.60 ± 4.40b	1.16 ± 0.42f	2.49 ± 0.10c	68.80 ± 4.30c
HD evaporator	219.86 ± 6.77c	233.82 ± 6.31c	37.32 ± 0.45b	10.30 ± 0.17c	2.59 ± 0.13c	82.96 ± 3.88b
Tomato paste	246.66 ± 9.73b	251.23 ± 6.74b	36.37 ± 0.34bc	13.97 ± 0.91a	3.66 ± 0.04b	98.90 ± 1.66a
Tomato pomace[e]	19.32 ± 0.27f	78.75 ± 1.34f	16.78 ± 0.71e	2.23 ± 0.40e	3.96 ± 0.18b	84.09 ± 0.65b

Values are reported as the mean ± standard deviation. Means in a column with different letters are significantly different at $P < 0.05$.
[a] mg ascorbic acid 100 g^{-1} dry weight.
[b] Value based on the sum of AA and DHAA.
[c] mg 100 g^{-1} dry weight after acid hydrolysis.
[d] mg each carotenoid 100 g^{-1} dry weight.
[e] By-products consisted of skin and seed resulting from peeling and sieving.
[f] The pulp tank holds the washed, sorted, chopped and heated tomatoes.
[g] The juice tank holds the tomato pulp after it has been passed through finishers that extract seed and skin.

determining AA in finished tomato paste. This is in agreement with the results of other studies.[9,10,12,13] The content of DHAA, based on dry weight, in fresh tomatoes was found to be 14% of the total vitamin C (Table 2). Wills *et al*. (1984) reported that the proportion of DHAA to total vitamin C was 7% at harvest, increasing up to 20% within 2 days and continuing to increase with prolonged storage.[25] Herein, the ratio of DHAA to total vitamin C (DHAA : vitamin C) increased, with a maximum value of 23% after hot break, yet was only 1.8% of the total vitamin C in the finished paste. These findings indicate that hot break plays a key role in the oxidation of AA; however, subsequent processing steps do not significantly alter the DHAA : vitamin C ratio.

Table 1 shows the quercetin content of fresh tomatoes (1.11 mg 100 g^{-1} FW) and is within the range of USDA values (0.03–2.77 mg 100 g^{-1}). Hot break treatment produced the greatest losses in flavonoid content, which decreased by 54% for quercetin and by 61% for kaempferol as compared to fresh tomatoes (Table 2). Subsequent processing steps (e.g. evaporation and sterilization) did not result in marked changes in quercetin content; however, kaempferol levels declined. Dewanto *et al*. (2002) reported that heating tomatoes at 88 °C resulted in no significant changes in total flavonoid content.[9] This group suggested that thermal processing would deactivate oxidative and hydrolytic enzymes, which would produce losses of phenolic compounds. It appears that the initial hot break produces the greatest level of oxidative stress (and loss of phenolics); however, as the enzymes are deactivated subsequent losses are not significant.

The levels of lycopene and β-carotene in processed samples are shown in Tables 1 and 2. Fresh tomatoes contained 5.68 ± 0.56 mg lycopene 100 g^{-1} FW, which is similar to findings of other investigators[20,25–27] and is higher than the USDA value of 3.02 mg 100 g^{-1} FW for fresh tomato.[7] The content of β-carotene was 0.28 ± 0.003 mg 100 g^{-1} FW in fresh tomatoes and is similar to other reported values.[13] On a dry weight basis, the levels of lycopene in fresh tomatoes, hot break juice and paste are close to those reported by Takeoka *et al*.[16] Our results indicate that lycopene is more stable during paste processing as compared to β-carotene (96% of lycopene is retained *versus* 73% for

Table 3. Content of moisture, ascorbic acid, vitamin C, flavonoids and carotenoids in tomato paste over 1 year of storage at room temperature (mg 100 g^{-1} fresh weight)

	Storage time					
Compound	1 day	1 month	3 months	6 months	9 months	12 months
Moisture	73.11 ± 0.13	71.94 ± 0.15 (98%)	71.99 ± 0.29 (98%)	71.20 ± 0.74 (97%)	70.91 ± 0.69 (97%)	71.88 ± 0.31 (98%)
Ascorbic acid	66.32 ± 2.62	49.92 ± 1.75 (75%)	45.15 ± 2.96 (68%)	33.12 ± 2.34 (50%)	33.29 ± 0.15 (50%)	8.92 ± 0.97 (13%)
Vitamin C	67.54 ± 1.81	51.05 ± 1.29 (77%)	45.83 ± 3.05 (65%)	37.14 ± 3.60 (59%)	34.60 ± 2.86 (54%)	11.92 ± 0.92 (19%)
Quercetin	9.93 ± 0.12	10.08 ± 0.03 (102%)	10.06 ± 0.08 (101%)	10.44 ± 0.04 (104%)	11.07 ± 0.33 (115%)	10.19 ± 0.21 (103%)
Kaempferol	3.79 ± 0.34	3.64 ± 0.16 (96%)	3.63 ± 0.05 (96%)	3.69 ± 0.10 (96%)	2.47 ± 0.06 (65%)	2.34 ± 0.03 (62%)
β-Carotene	1.00 ± 0.07	1.15 ± 0.04 (115%)	1.19 ± 0.08 (119%)	1.08 ± 0.04 (108%)	1.07 ± 0.01 (107%)	0.96 ± 0.01 (96%)
Lycopene	26.61 ± 0.45	37.13 ± 0.65 (140%)	37.40 ± 0.84 (140%)	26.63 ± 0.71 (100%)	27.20 ± 1.29 (102%)	26.68 ± 0.94 (100%)

Values in parentheses represent the percentage of retention as compared to 1-day starting paste.

β-carotene), in agreement with the results reported by Abushita *et al*. and Nguyen and Schwartz.[13,14] Losses in lycopene occurred between the juice tank and first-stage evaporation step, whereas losses in β-carotene (30%) occurred during the initial hot break. In contrast to our results, Abushita *et al*. reported no change in lycopene content during the production of tomato paste.[13] Losses in lycopene and β-carotene during processing can occur through *cis-trans* isomerization, oxidation reactions and co-oxidation by lipoxygenases and peroxidases.[28,29] In the current study, all-*trans* lycopene was the predominant geometric isomer in processed samples and the *cis* counterpart was below the limit of detection – a result similar to that of Gärtner *et al*.[30] These findings suggest that conditions used in tomato paste processing do not induce *cis-trans* isomerization of lycopene or that other components present in tomatoes prevent isomerization during processing.

Tomato paste production yields processing wastes (i.e. tomato pomace), which consist primarily of tomato skin and seed. Tomato flesh contains about twofold higher amounts of vitamin C as compared to peel (230 ± 6 g 100 g^{-1} *versus* 127 ± 10 g 100 g^{-1}).[10] As expected, tomato pomace contained significantly lower levels of AA as compared to the fresh tomatoes (Table 1). Conversely, tomato pomace contained about fivefold higher levels of quercetin than the fresh tomatoes. It is well established that plants, including tomatoes, accumulate flavonoids and their derivatives in the skin in response to ultraviolet-B radiation.[31,32] In addition, the content of lycopene and β-carotene in pomace was ~400% higher than that of fresh tomatoes. Tomato skin comprises more than 40% of tomato pomace and contains much higher levels of lycopene and β-carotene than tomato flesh.[33] Separating the skin and seed from process tomatoes results in significant decreases in bioactives, especially quercetin and lycopene. Given the yield (4%) of tomato pomace from fresh tomatoes[34] and the amount of processed tomatoes (12.3 million tons in 2004) in the USA,[35] the production of tomato pomace is estimated as about half a million (492×10^3) tons in a year and may be an excellent source of carotenoids and flavonoids.

Long-term storage of tomato paste indicated a loss in quality. The content of vitamin C in tomato paste decreased with increasing storage time, the greatest loss occurring between 9 and 12 months (Table 3). At 12 months only 17.6% of the vitamin C remained. The oxidation of AA to DHAA also occurred during storage as the ratio of DHHA : vitamin C increased during long-term storage after 6 months (3%), rising to 25% at 12 months of storage. The levels of quercetin did not change over the 12 months; however, levels of kaempferol decreased during storage. Flavonoids have been shown to be stable during long-term storage (up to 12 months) in regular and controlled atmosphere conditions in apples and onions.[36,37] Herein, the carotenoids studied were relatively stable throughout 12 months of storage. The all-*trans* lycopene predominated, whereas the *cis* isomers were present at the detection limit. Total lycopene levels did decrease by ~40% after 3 months of storage; however, they then remained stable. This result is similar to short-term studies by Lavelli and Giovanelli (2003) demonstrating that lycopene content of tomato paste remained stable after storage for 90 days at 30 °C.[38] Levels of β-carotene remained constant through 12 months of storage.

In conclusion, our study showed that the hot break step produces greatest losses in the flavonoids quercetin (54%) and kaempferol (61%), as well as AA (63%) and β-carotene (30%), whereas subsequent processing steps (e.g. evaporation and sterilization) did not result in marked changes in these bioactives. Conversely, lycopene was stable during hot break but decreased by 20% through evaporation and sterilization. The ratio of DHAA : vitamin C increased during hot break to 23%; however, ratios of DHAA : vitamin C remained relatively low, indicating that AA was not oxidized through subsequent processing. As expected, AA decreased with prolonged storage, with only 13% remaining at 12 months. The carotenoids and quercetin, but not kaempferol, remained stable through 12 month of ambient storage. Our results also indicate that the tomato pomace byproduct is an excellent source of carotenoids and flavonoids.

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