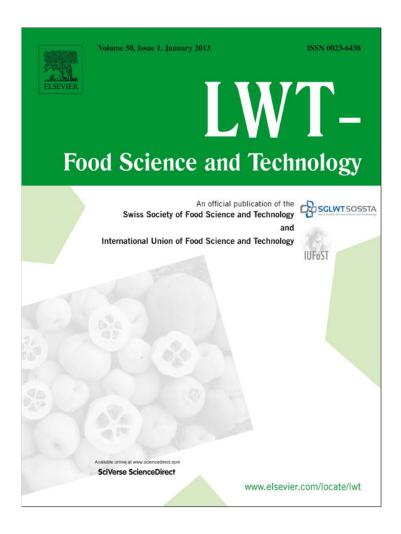
Provided for non-commercial research and education use. Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

Author's personal copy

LWT - Food Science and Technology 50 (2013) 139-145

FISEVIER

Contents lists available at SciVerse ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt



Functional quality and antioxidant composition of selected tomato (Solanum lycopersicon L) cultivars grown in Northern India

Charanjit Kaur^{a,*}, Suresh Walia^b, Shweta Nagal^a, Shweta Walia^a, Jashbir Singh^b, Braj Bhushan Singh^b, Supradip Saha^b, Balraj Singh^c, Pritam Kalia^d, Seema Jaggi^e, Sarika^e

- ^a Division of Post Harvest Technology, Indian Agricultural Research Institute, New Delhi 110 012, India
- ^b Division of Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi 110 012, India
- ^c Centre for Protected Cultivation and Technology, Indian Agricultural Research Institute, New Delhi 110 012, India
- ^d Division of Vegetable Science, Indian Agricultural Research Institute, New Delhi 110 012, India
- ^e Indian Agricultural Statistics Research Institute, Indian Agricultural Research Institute, New Delhi 110 012, India

ARTICLE INFO

Article history: Received 19 September 2011 Received in revised form 21 March 2012 Accepted 12 June 2012

Keywords: Antioxidant activity Lycopene Quercetin S. pimpinellifolium Tomato

ABSTRACT

Ten commercial and three exotic/wild cultivars (cvs) grown under Indian conditions were analyzed for variations in lycopene, β -carotene, total phenolics, quercetin, ascorbic acid and antioxidant activity (AOX). AOX was measured using three in vitro assays namely ferric reducing antioxidant power (FRAP), 2,2-diphenyl-1-picrylhydrazyl (DPPH) and Trolox equivalent antioxidant capacity (TEAC) assays. The lycopene content in tomato cvs ranged from 4.31 to 5.97 mg/100 g fw. The wild/exotic cvs had exceptionally high total phenolic content (141.98 mg/100 g fw), quercetin (56 μ g/g fw) and total AOX (5.39 μ mol TE/g fw). Solanum pimpinellifolium, with nearly six times lycopene content than commercial cvs, may serve as the most desirable gene pool in breeding programmes to develop functional tomatoes. Results suggest that TEAC may be more useful than DPPH assay for detecting total AOX in tomatoes.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Tomato (*Solanum lycopersicon* L) is one of the most consumed vegetables in the world, both as fresh and in processed form. It is widely available in various processed products such as puree, paste, whole peeled tomatoes, diced products, juice, sauces and soups. Although a tropical plant, tomato is grown in almost every corner of the world from the tropics to within a few degrees of the Arctic Circle. Fresh tomatoes and tomato products are rich source of bioactive compounds, including carotenes (lycopene, β - carotene), ascorbic acid, tocopherol, and phenolic compounds. Lycopene is a strong antioxidant and exhibits higher (2–10 times) singlet oxygen quenching ability compared with β -carotene and α -tocopherol, respectively (Dimascio, Kaiser, & Sies, 1989). It may prevent carcinogenesis or atherogenesis by interfering with

Abbreviations: FRAP, ferric reducing antioxidant power; DPPH, 2,2-diphenyl-1-picrylhydrazyl; TPTZ, 2,4,6-Tripyridyl-striazine; Trolox, 6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid; GAE, gallic acid equivalent; AOX, antioxidant activity; cv, cultivar; TEAC, Trolox equivalent antioxidant capacity; TE, Trolox equivalent.

oxidative damage to DNA and lipoproteins (Clinton, 1998). Numerous epidemiological and intervention studies have demonstrated that dietary intake of lycopene-rich foods results in decreased incidence of certain cancers, including prostate, lung, mouth, and colon cancers, coronary heart diseases and macular degeneration (Dillingham & Rao, 2009). Daily consumption of 15 mg of lycopene has been shown to reduce C-reactive proteins reported to be key marker of inflammation and a predictor of cardiovascular diseases (Rein et al., 2006). The major phenolics in tomato (chlorogenic acid, caffeic acid and rutin) also exhibit a wide range of physiological properties, such as anti-inflammatory, antimicrobial, cardio protective, hepatoprotective, hypoglycemic and antiviral effects (Navarro-González, García-Valverde, García-Alonso, & Periago, 2011). Ascorbic acid is another important antioxidant compound present in tomato. Although its content is moderate (84-590 mg/kg), but its contribution to diet is significant because of its high consumption. Synergistic interactions between various phytonutrients in tomatoes are responsible for its beneficial health effects. In this regard, tomato has been conferred the status of a "functional food" or nutraceutical" (Canene-Adams, Campbell, Zaripheh, Jeffery, & Erdman, 2005). The functional quality and antioxidant constituents of tomato are strongly influenced by environmental factors and genetics. Thus, it is important to assess

^{*} Corresponding author. Tel.: +91 011 25842155; fax: +91 011 258448428. E-mail address: charanjitkaur6@gmail.com (C. Kaur).

the performance of newly developed cultivars/varieties under changing global climactic patterns to ensure consistent functional quality.

India ranks 4th among major tomato producing countries in the world after China, USA and Turkey. The estimated area and production of tomato in India is about 3,50,000 ha and 1,24,33,200 MT, respectively. Presently, India is the major exporter of tomatoes to $Pakistan, Bangladesh, U.A.E, Nepal, Maldives\ and\ Oman\ (Anonymous,$ 2010). The average consumption pattern of tomatoes in Indian diet is very high as they form an integral ingredient of ethnic cultural cuisine. In recent years, demand for processed tomato products (tomato ketchup and puree) has increased tremendously. Also there has been a stiff competition between the domestic and international brands of processed tomato products. To address these issues, industry requires quality raw material rich in lycopene. However, the commercial cultivars (cvs) are low in lycopene and the average content ranges between 2.8 and 7.0 mg/100 g (George, Kaur, Khurdiya, & Kapoor, 2004). Lack of quality raw material is driving tomato processors to import quality tomato paste from other countries. Tomato breeders are addressing this issue and are developing new varieties, lines and accessions with elevated levels of lycopene using their existing germplasm resources. However, information on phytochemicals and antioxidant properties of these cvs is lacking. Detailed information on antioxidant properties of these cvs with desired genetic pool rich in nutraceutical content will serve as a reference material to develop functional tomatoes. Generation of such information will benefit both breeders, general consumer and result in quality processed tomato products. The present study, therefore aims at determining the antioxidant quality (lycopene, β -carotene, ascorbic acid, phenolics, quercetin and AOX) and other quality attributes (color attributes, TSS and acidity) of ten commercial and three wild/exotic cvs grown under Indian conditions.

2. Material and methods

Freshly harvested, fully ripe red tomatoes grown under open field conditions of Indian Agricultural Research Institute (IARI), New Delhi were included in the present study. Ten commercial cultivars included Pusa Gauray, Pusa Ruby, Roma, Pusa Uphar, Pusa. Sadabhar, Pusa Sheetal developed by IARI and Arka Vikash developed by Indian Institute of Horticulture Research, Bangalore. Wild cultivar Solanum pimpinellifolium, (exotic lines EC-521083, EC-521086), Taiwan, Balkan and Chiku, were introduced by National Bureau of Plant Genetic Resources (NBPGR) New Delhi. Subsequent selections made from these lines are being maintained at Division of vegetable science, I.A.R.I. The field experiments were carried out in a field in IARI farm fields during the 2010-11 growing season (December-May). One month-old tomato seedlings were transplanted in an open field with a spacing of approximately 50 cm within the row and 100 cm between rows matching a density of about 20,000 plants/ha. The experimental design was a randomized complete block with three blocks (replicates). Standard agronomical techniques were used for plant nutrition and pathogen prevention. The fruits were randomly harvested from the rows and from the middle of each plant in the field from four different areas in the field. The fruits were pooled and 2 kg of visually selected healthy and injury free red-ripe tomato fruits were drawn from pooled lot. Sampled fruits for each cv were cut into small pieces and sequentially homogenized in a domestic blender (Inalsa, India) for 2 min and analyzed for various antioxidant constituents.

2.1. Extraction of carotenoids

The sample (5 g) of fresh tomato was weighed into 200 mL amber colored flask wrapped with aluminum foil and homogenized

in a blender. A mixture of hexane-ethanol, 1:1 (vol/vol), was then added to the flask and sonicated continuously for 10 min on an ultrasonicator (Misonix Ultrasonic Liquid Processor, NY, U.S.A). The extraction was repeated until sample became colorless. The combined extract was transferred to a separating funnel and 5 mL of distilled water was added to separate into two distinct polar and nonpolar layers. The non polar hexane layer containing carotene was collected and concentrated in a rotary evaporator (Heidolph, Germany) till dryness. Residue was dissolved in 25 mL of methyl tert-butyl ether (MTBE) and sample was analyzed by HPLC.

2.2. Determination of lycopene and β carotene content

Lycopene and β - carotene content was analyzed using HPLC method (Dewanto, Wu, Adom, & Li, 2002). HPLC apparatus consisted of a water e2695 quaternary pump with auto injector (20 μ L loop), and a 2998 photodiode array detector (Waters Corp., Milford, Mass., U.S.A.) and a 25 cm \times 4.6 mm dia and 5- μ m C30 YMC column (Waters Corp., Ireland). Two milliliters of each sample solution filtered through a 0.4- μ m nylon filter before injection into HPLC. The mobile phase comprised of isocratic mixture of MTBE: methanol, 70:30 (v/v) at a flow rate of 1 mL/min. Concentration of standard solutions was calculated using the molar extinction coefficient of 17.2 \times 10⁴ for lycopene and 13.9 \times 10 ⁴ for β -carotene, in hexane. Peaks were detected at 471 and 453 nm for lycopene and β -carotene respectively. Results were expressed as mg/100 g fresh weight. A computer using an "Empower" software programme integrated the peak areas automatically.

2.3. Determination of total phenolics and quercetin content

For extraction of total phenolics, 5 g of homogenized samples were extracted twice with 30 mL of ethanol (80%), by stirring and sonicating for 30 min in dark. The homogenate was then centrifuged for 15 min at $10,000 \times g$ at 4 °C (Eppendorf, Westbury, and U.S.A). The supernatant was then vacuum concentrated at 40 °C in a rota-evaporator and stored at -20 °C. The concentrated sample was used as sample extract for estimation of total phenolics and hydrophilic antioxidant activity. Total phenolics were estimated spectrophotometrically using Folin-Ciocalteu reagent (Singleton, Orthofer, & Lamuela-Ranventos, 1999). To the 100 µL of the sample extract (80% ethanol) 2.9 mL of deionized water, 0.5 mL of Folin-ciocalteu reagent and 2.0 mL of 20% Na₂CO₃ solution were added. The mixture was allowed to stand for 60 min and absorption was measured at 760 nm against a reagent blank in U.V. vis spectrophotometer (VARIAN Cary 50). Results were expressed as gallic acid equivalent (mg GAE/100 g fw).

The quercetin content in the samples was analyzed using the method described by Mazza, Fukumoto, Delaquis, Girard, and Ewert (1999). Briefly the ethanolic extract was evaporated to dryness and the residue dissolved in 250 μL of 0.1% HCL in 95% ethanol and 4.55 mL of 2% HCL. The solution was mixed and allowed to sit for approx 15 min and absorbance read at 360 nm. Results were expressed as μg quercetin/g fw.

2.4. Antioxidant activity

2.4.1. Trolox equivalent antioxidant capacity (TEAC) assay

Antioxidant activity was measured using the ABTS decoloration method using radical ABTS (2,2-azino-di-(3-ethylbenzothialozine-sulphonic acid)) (Re et al., 1999). Hydrophilic and lipophilic antioxidants were extracted from 5 g of homogenized pulp with 80% of ethanol and 70% acetone respectively with ultrasonicator for 20 min. The lipohilic extract was, evaporated to dryness and residue was dissolved in n-hexane. AOX was measured in both hydrophilic

and lipophilic fractions and referred as HAA and LAA respectively. The ABTS^{+•} stock solution (7 mM) was prepared through reaction of 7 mM ABTS and 2.45 mM of potassium persulphate as the oxidant agent. The working solution of ABTS^{+•} was obtained by diluting the stock solution in ethanol to give an absorption of 0.70 \pm 0.02 at $\lambda = 734$ nm. Sample extract (10 μ L) was added to 90 μ L of ABTS⁺⁴ solution and absorbance readings at 734 nm were taken at 30 °C for exactly 10 min after initial mixing. The percentage inhibition of ABTS^{+•} of the test sample and known solutions of Trolox were calculated by the following formula: %Inhibition = $100 \times (A_0 - A)$ / A_0 where A_0 was the beginning absorbance at 734 nm, obtained by measuring the same volume of solvent, and A was the final absorbance of the test sample at 734 nm. The calibration curve between % inhibition and known solutions of Trolox (100-2000 μM) was then established. The radical-scavenging activity of the test samples were expressed as Trolox equivalent antioxidant capacity (µmol TE/g fw).

2.4.2. Free radical scavenging activity using DPPH assay

DPPH assay is based on the measurement of the scavenging ability of antioxidants toward the stable radical DPPH (Brand-Williams, Cuvelier, & Berset, 1995). A 3.9 mL aliquot of a 0.0634 mM of DPPH solution, in methanol (95%) was added to 0.1 mL of each extract and shaken vigorously. Change in the absorbance of the sample extract was measured at 515 nm for 30 min. The percentage inhibition of DPPH of the test sample and known solutions of Trolox were calculated by the following formula: %Inhibition = $100 \times (A_0 - A)/A_0$ where A_0 was the beginning absorbance at 515 nm, obtained by measuring the same volume of solvent, and A was the final absorbance of the sample extract at 515 nm. Methanol (95%) was used as a blank. Results were expressed as μ mol TE/g fw.

2.4.3. Determination of ferric reducing antioxidant power (FRAP) assay

FRAP was performed according to the procedure described by Benzie and Strain (1996). The FRAP reagent included 300 mM acetate buffer, pH 3.6, 10 mM TPTZ in 40 mM HCl and 20 mM FeCl₃ in the ratio 10:1:1 (v:v:v). Three mL of the FRAP reagent was mixed with 100 μ L of sample extract in a test tube and vortexed and incubated at 37 °C for 30 min in a water bath. Reduction of the ferric-tripyridyltriazine to the ferrous complex formed an intense blue color which was measured at a UV vis spectrophotometer (Varian Cary 50) at 593 nm at the end of 4 min. Results were expressed in terms of μ mol TE/g fw.

2.5. Determination of ascorbic acid content

Ascorbic acid content was quantified in accordance with the dinitrophenylhydrazine (DNPH) method, modified by Nunes, Brecht, Morais, and Sargent (1995). Ten grams of sample was homogenized in mortar pestle, with 20 mL of a mixture of 6% (w/v) metaphosphoric acid in 2 mol/L acetic acid. The mixture was centrifuged at $17,600 \times g$ for 15 min at 4 °C. The supernatant was filtered through Whatman filter paper (no:1). An aliquot of 0.05 mL of 0.2% (w/v) 2,6-dichlorophenolindophenol (DCPIP) was added to 1 mL of the supernatant and incubated at room temperature for 1 h. Thiourea solution (2%, w/v) in 5% metaphosphoric acid (w/v) and 0.5 mL of 2% (w/v) DNPH in 4.5 mol/L sulfuric acid were added and the solution was incubated at 60 °C for 3 h. Tubes were placed in an ice bath and 2.5 mL of ice cold 90% sulfuric acid were slowly added. Tubes were vortexed and absorbance measured at 540 nm. The concentration was calculated using a standard curve of ascorbic acid. Results were expressed as mg ascorbic acid/100 g fw.

2.6. Determination of quality attributes

To measure, total soluble solids (TSS) and titratable acidity (TA), fruits were crushed and mass placed in cheesecloth. Juice was squeezed by hand was measured with a hand-held refractometer (Atago, Tokyo, Japan) calibrated with distilled water. TA was determined from a 5 mL aliquot by titration with 0.1 mol/L NaOH with phenolphthalein as an indicator and results expressed as % citric acid. Peel percentage was calculated by taking the average weight of the peel tissues over the total fruit weight (w/w). Peels from ten representative fruits were removed manually. The fruits were steamed prior to peeling for ease of separation.

2.7. Color attributes

The external color of the tomato fruit was determined within 24 h of harvest. The measurements were taken at three different points on the equatorial regions of the fruits. The reflectance spectra were obtained using a portable HunterLab LabScan XE spectrocolorimeter (HAL, U.S.A, model $0^{\circ}/45^{\circ}$ standard, s/n LX17760) at 400-700 nm range spectral resolution of 10 nm and a wavelength accuracy of 1 nm under CIE Illumination D65 and d/ 10° illumination. Hue and chroma was calculated by the following equations.

Hue angle =
$$Tan^{-1}(b^*/a^*)$$

Chroma =
$$\sqrt{a2 + b2}$$

2.8. Statistical analysis

Data are presented as mean \pm SD of three replicates. The results were statistically analyzed by ANOVA and means compared using duncan's multiple range tests. Statistical significance was accepted at a level of 5% level.

3. Results and discussion

3.1. Lycopene and β —carotene content

Lycopene and β -carotene content of thirteen tomato cvs are presented in Table 1. The lycopene content in commercial and

Table 1 Carotenoids (lycopene and β – carotene) and total phenolics and quercetin content of selected Indian tomato

Cultivar	Lycopene (mg/100 g fw)	β-carotene (mg/kg fw)	Total phenolics (mg GAE/ 100 g fw)	Quercetin (μg/g fw)
Taiwan	4.98 ± 0.38^{c}	$3.81 \pm 0.21^{\rm f}$	47.80 ± 1.20^{e}	10 ± 1 ^{ef}
Balkan	5.97 ± 0.50^c	6.74 ± 0.34^c	57.96 ± 1.34^{d}	13 ± 2.6^g
Pusa Gaurav	4.68 ± 0.13^c	3.42 ± 0.49^f	46.69 ± 3.09^{fe}	23 ± 1.4^{d}
Pusa Ruby	4.77 ± 0.55^c	3.80 ± 0.78^f	59.44 ± 1.53^{d}	21 ± 1.4^d
Roma	4.31 ± 0.50^c	2.71 ± 0.56^g	$41.13 \pm 1.94^{\rm f}$	20 ± 1.8^{ed}
Pusa Uphar	4.89 ± 0.35^{c}	$3.43\pm0.56^{\rm f}$	47.44 ± 0.69^{fe}	$14\pm0.6^{\rm fg}$
Pusa Sadabahar	4.76 ± 0.27^{c}	4.32 ± 0.23^e	66.08 ± 1.37^{c}	$24\pm2.3^{\rm d}$
Avikash	4.49 ± 0.52^{c}	$1.80\pm0.19^{\rm g}$	$26.34\pm0.77^{\mathrm{g}}$	15 ± 0.45^{fg}
Pusa Sheetal	4.72 ± 0.37^c	5.62 ± 0.67^{d}	45.75 ± 1.50^{fe}	18 ± 0.3^{efg}
Chiku	5.44 ± 0.31^{c}	4.50 ± 0.68^e	45.06 ± 2.11^{fe}	34 ± 5.6^c
S.pimpinellifolium	29.99 ± 2.28^a	12.01 ± 1.7^a	62.82 ± 2.50^{dc}	56 ± 0.6^a
EC-521083	26.53 ± 1.65^{b}	8.30 ± 1.2^b	141.98 ± 10.23^a	48 ± 3.6^{b}
EC-521086	25.59 ± 1.59^{b}	8.53 ± 1.6^{b}	76.79 ± 1.16^{b}	47 ± 4.5^{b}

S. pimpinellifolium, EC-521083 and EC-521086 represent the wild/exotic cvs respectively.

Values represent the mean of three replicates \pm standard deviation.

Mean followed by the same superscripts are not significantly different (P < 0.05).

exotic/wild cvs ranged from 4.31 to 5.97 and 25.59 to 29.99 mg/100 g respectively. The exotic cv, S. pimpinellifolium exhibited 5-6 times higher content than commercial ones depicting a significant difference (p < 0.05) between the two groups. Amongst the commercial cvs Balkan and Chiku had higher lycopene content (≥5 mg/100 g) than the rest. Similar variations in lycopene ranging from 3.0 to 11.0 mg/100 g have been reported in Hungarian, Spanish and Indian tomatoes (Adalid, Roselló, & Nuez, 2010). Cherry tomatoes have been shown to have higher content than local ones (Raffo, La Malfa, Fogliano, Maiani, & Quaglia, 2006). High pigmented cvs from Italy have as high as 20 mg/100 g (Ilahy, Hdider, Lenucci, Tlili, &Dalessandro, 2011). 'Kalvert' and "Lyco" cvs have been identified as highly pigmented cvs. However pertinent information regarding the parentage and fruit size is lacking. Probably some wild types may have been used as donor parent. Differences between commercial and high-pigmented cvs have been attributed to genotypic factors triggering enhanced enzymatic activity of phytoene synthase I that causes a massive production of lycopene precursors. Reduced cycling rate of this molecule to synthesize carotenes, results in accumulation of lycopene in ripening tomato fruits (Fraser, Enfissi, & Bramley, 2009). Another plausible explanation accounting for significant difference between the two distinct groups of tomato is related to their smaller fruit size and high peel percentage. All commercial cvs were normal sized (42.6-54.4 g) with low peel percentage (3-5%) except Balkan with intermediate size fruit $(26.84 \,\mathrm{g})$. The wild/exotic cvs were small sized fruits $(1.2-5.2 \,\mathrm{g})$ with high peel percentage (11–15%). Small sized fruits with high surface area to volume ratio have high peel percentage. In other words, the peels of small fruits represented 10-15% of the fruit weight in comparison to 3–5% in normal ones. As peels are the main reservoir of lycopene and accumulate 3–5 times higher content, small sized/ cherry tomatoes tend to have higher content than the commercial ones. This adequately explains highest lycopene content observed in cv Balkan in comparison to commercial cvs. Similar observations with regard to surface ratio, surface skin and fruit weight were made in small Corbarini and Campari cvs (Toor & Savage, 2005).

Apart from genotype, environmental factors such as temperature, plant nutrition, and light can also considerably affect the biosynthesis of carotenoids. Under North Indian conditions, fruits are usually harvested in mid-April to end May depending upon the prevailing temperature conditions. The months of March and April are extremely critical as synthesis of red pigment lycopene in fruits takes place during this period. Optimum temperature range for lycopene synthesis is between 12 and 32 °C.

Temperatures below 12 °C strongly inhibit the biosynthesis and above 32 °C obstruct the process altogether (Dumas, Dadomo, Lucca, & Grolier, 2003). In May, the average temperature during the day rises sharply above the 32 °C reaching steeply to 40 °C. This coupled with excessive sunlight hinders lycopene synthesis. On the contrary, in the Mediterranean region, the temperature during ripening period remains well below 30 °C thus promoting high lycopene synthesis. This seems to be one of the important factors responsible for high lycopene in Spanish and Italian tomatoes.

β-carotene constitutes a small fraction nearly 7–10% of total tomato carotenoids and is nutritionally important because of its provitamin A activity (Nguyen & Schwartz, 1999). The content in commercial cvs ranged between 2.7 and 6.7 mg/kg, however in wild/exotic cvs content ranged from 8.3 to 12.0 mg/kg, depicting a significant difference (p < 0.05) between the two groups. Of all the cvs S. pimpinellifolium and EC-521083 presented remarkable high values. Our results are in agreement with previous reported content (3.9–19.4 mg/kg) in Spanish tomatoes (Ilahy et al., 2011).

3.2. Total phenolic and quercetin content

The total phenolic content ranged from 26.34 to 66.08 and 62.82 to 141.98 mg GAE/100 g in commercial and exotic/wild cvs respectively. On an average, values were nearly two fold higher in exotic/wild cvs (Table 1). The reported levels are slightly higher than our earlier reported range but in agreement with levels in Italian and Spanish cvs (27.2-49.8, 10-51 mg GAE/100 g) (Ilahy et al., 2011). Although genetics is the primary factor, levels may be affected by light and temperature under open field conditions. Field -grown tomato fruits, which receive a higher amount of light and UV radiation, contain a higher amount of phenolics in comparison to their counterparts (Jagadeesh et al., 2009). High total phenolics content in exotic/wild cv (S. pimpinellifolium) may be ascribed to their high lycopene traits. In high-pigment mutants there is a concomitant increase in carotenoid content along with other compounds such as flavonoids and vitamin C due to a mutation that exaggerates the phytochemical response leading to phenolics accumulation. Quercetin is the major flavonol compound reported in tomato and the content in commercial cvs ranged from 10 to 34 μ g/g (Table 1). Scottish tomatoes have been reported to contain 7.19-43.59 µg/g (Martínez-Valverde, Periago, Provan, & Chesson, 2002). S. pimpinellifolium, however had elevated levels

Table 2Antioxidant activity in selected Indian tomato using three different assays.

Cultivar	DPPH*μmol TE/g fw.		TEAC*μmol TE/g fw.		FRAP*µmol TE/g fw.
	HAA	LAA	HAA	LAA	
Taiwan	2.77 ± 0.38^{d}	0.23 ± 0.3°	4.37 ± 0.29^{dc}	$0.34 \pm 0.36^{\text{ed}}$	2.47 ± 0.39^{c}
Balkan	$3.08\pm0.49^{\mathrm{dc}}$	0.21 ± 0.1^{c}	5.43 ± 0.30^a	0.36 ± 0.33^{ed}	2.45 ± 0.30^{c}
Pusa Gaurav	2.51 ± 0.36^{d}	0.24 ± 0.2^{c}	5.40 ± 0.23^a	0.43 ± 0.45^{cd}	2.33 ± 0.11^{c}
Pusa Ruby	3.5 ± 0.26^{bc}	$\textbf{0.24} \pm \textbf{0.8}^{c}$	3.56 ± 0.32^e	0.33 ± 0.33^{ed}	2.67 ± 0.22^{c}
Roma	$2.74\pm0.68^{\rm d}$	0.17 ± 0.1^{c}	$2.74\pm0.22^{\rm f}$	$0.21 \pm 0.16^{\rm f}$	2.48 ± 0.37^{c}
Pusa Uphar	$3.15\pm0.10^{\text{dc}}$	0.12 ± 0.5^{c}	$4.66\pm0.45^{\mathrm{bdc}}$	0.32 ± 0.27^{ef}	2.25 ± 0.18^{c}
Pusa Sadabahar	$2.9\pm0.3^{\rm dc}$	0.21 ± 0.1^{c}	4.23 ± 0.26^{d}	0.23 ± 0.23^{ef}	2.52 ± 0.30^{c}
Avikash	$2.60\pm0.42^{\rm d}$	0.19 ± 0.15^{c}	4.95 ± 0.72^{bac}	$0.24 \pm 0.23^{ m ef}$	2.33 ± 0.23^{c}
Pusa Sheetal	4.61 ± 0.26^{ba}	0.22 ± 0.1^{c}	5.56 ± 0.33^a	0.25 ± 0.22^{ef}	2.34 ± 0.39^{c}
Chiku	$2.50\pm0.27^{\rm d}$	0.17 ± 0.1^{c}	5.62 ± 0.33^a	$0.58 \pm 0.55^{\mathrm{cb}}$	2.50 ± 0.26^c
S.pimpinellifolium	4.37 ± 0.25^a	0.82 ± 0.6^a	5.57 ± 0.26^{ba}	1.1 ± 1.33^a	3.68 ± 0.11^{b}
EC-521083	4.56 ± 0.29^a	$0.56\pm0.4^{\mathrm{ba}}$	5.73 ± 0.14^a	0.49 ± 0.46^{cd}	4.56 ± 0.29^a
EC-521086	4.60 ± 0.28^a	$0.60 \pm 0.5^{\mathrm{b}}$	5.39 ± 0.41^{a}	0.53 ± 0.64^{b}	4.67 ± 0.23^{a}

 $[\]textit{S. pimpinellifolium, EC-521083} \ \text{and EC-521086} \ \text{represent the wild/exotic cvs respectively.}$

Values are mean of three replicates \pm standard deviation.

DPPH * - 2,2-diphenyl-1-picrylhydrazyl, TEAC*-Trolox-equivalent antioxidant capacity; FRAP*-Ferric reducing antioxidant power; HAA- Hydrophilic antioxidant activity; LAA-Lipophilic antioxidant activity.

C. Kaur et al. / LWT - Food Science and Technology 50 (2013) 139-145

Table 3TSS, ascorbic acid and acidity of selected Indian tomato.

Cultivar	r TSS (°B) Ascorbic acid (mg/100 g)		Acidity (%)	
Taiwan	4.66 ± 0.11^{g}	34.26 ± 2.0^{c}	0.43 ± 0.03^{c}	
Balkan	5.32 ± 0.08^f	28.54 ± 1.62^{fe}	0.34 ± 0.02^{f}	
Pusa Gaurav	5.86 ± 0.05^{ed}	34.26 ± 0.19^{c}	0.63 ± 0.03^a	
Pusa Ruby	5.23 ± 0.13^{f}	30.32 ± 3.4^{dc}	$0.33\pm0.01^{\rm f}$	
Roma	4.38 ± 0.54^g	26.85 ± 2.5^{dc}	0.38 ± 0.01^{e}	
Pusa Uphar	5.01 ± 0.60^{fg}	32.65 ± 3.6^{dce}	0.4 ± 0.01^{dce}	
Pusa Sadabahar	5.26 ± 0.16^{f}	30.76 ± 3.0^{de}	0.31 ± 0.02^{f}	
Avikash	5.31 ± 1.65^{ef}	$27.91 \pm 2.8f^{e}$	$0.33\pm0.03^{\rm f}$	
Pusa Sheetal	4.7 ± 0.31^g	25.65 ± 2.1^{f}	0.51 ± 0.01^{b}	
Chiku	5.05 ± 0.15^{fg}	32.21 ± 2.7^{cde}	0.45 ± 0.02^c	
S pimpinellifolium	7.64 ± 0.23^a	50.21 ± 4.5^{a}	0.41 ± 0.01^{dce}	
EC-521083	6.11 ± 0.06^{b}	46.32 ± 3.9^{b}	0.42 ± 0.01^{dc}	
EC-521086	6.14 ± 0.91^{cb}	46.63 ± 2.1^{b}	0.32 ± 0.01^{de}	

TSS - Total soluble solids.

Values represent the mean of three replicates \pm standard deviation.

Mean followed by the same superscripts are not significantly different (P < 0.05).

nearly 4 fold higher than the average content found in commercial cvs. Flavonoids are potentially health-protecting components in diet and may offer protection against major diseases such as coronary heart diseases and cancer (Slimestad & Verheul, 2009). Wild type germplasm are known to accumulate higher flavonoid content however the trait is slowly missing from domesticated and commercial cvs. Willits et al. (2005) critically highlighted the opportunities for developing high flavonoid tomato using the wild tomato species (*Lycopersicon pennellii v. puberulum*). Utilization of these genetic resources can help restore functional pathways, resulting in production of healthier tomatoes.

3.3. Antioxidant activity

The total AOX represented the sum of HAA and LAA. In TEAC assay, HAA ranged from 2.74 to 5.62 μmol TE/g whereas LAA ranged from 0.21 to 0.58 μmol TE/g (Table 2). In both extracts, the upper case value corresponded to exotic/wild cvs. Hydrophilic fraction contributed to 78–96% of total AOX whereas LAA accounted for 3.4–21%. Reported results are in line with those observed by Navarro-González et al. (2011). In variance with our results, llahy et al. (2011) reported 3–5 fold higher LAA values (3–5 μmol/L) in pigmented Spanish tomatoes which they attributed to high

lycopene traits. However, we did not observe a similar pattern in exotic/wild type cvs with high lycopene content. Our results draw support from a recent publication by Kotíková, Lachman, Hejtmánková, and Hejtmánková (2011). The authors concluded that pure lycopene does not show dose response curve and there is an inverse relationship between the lycopene concentration and scavenging capacity. The lowest lycopene concentration produced the highest scavenging capacity and increasing lycopene does not necessarily increase AOX. The trend in DPPH assay was similar to that observed in TEAC assay; LAA was significantly lower than HAA. The HAA ranged from 2.5 to 4.6 μmol TE/g (Table 2). Interestingly, the overall values of total AOX in DPPH were lower than those obtained in TEAC assay. Matrix interference with DPPH has been shown to account for lower values in carotenoid rich extracts. This suggests that TEAC is more appropriate than DPPH assay for measuring AOX in high carotenoid containing commodities such as tomatoes. New studies have made similar conclusions (Floegel, Kim, Chung, Koo, & Chun, 2011). In FRAP assay, the HAA values ranged from 2.25 to 4.67 $\mu mol\,TE/g\,(Table\,2)$ and S. pimpinellifolium/ g had ~2 fold higher values than commercial cvs. With regard to LAA we did not get satisfactory results as there was a solubility issue with solvent system (containing carotenoids) and FRAP reagent. Consequently, our results were not consistent with replicates. There are conflicting reports about the applicability of FRAP assay for evaluating the lipophilic fractions. Earlier reports of Pulido, Bravo, and Saura-Calixto (2000) also confirm the inability of carotenoids to reduce ferric chloride in FRAP reagent. In a recent publication Halvorsen and Blomhoff (2011) have also referred to the solubility issue of pure carotenoids in FRAP assay. Thus, it seems that ABTS is better assay for measuring AOX of tomato extracts in comparison to DPPH and FRAP assay. Overall results suggest that exotic/wild cvs are potential gene pool with significant high AOX.

3.4. Ascorbic acid

Ascorbic acid is a powerful water-soluble antioxidant and plays an important role in the suppression of free radicals. The content ranged between 25.65 and 50.21 mg/100 g (Table 3). S. pimpinellifolium and EC-521083 had significantly (p < 0.05) higher content (2-fold) than the commercial tomatoes. Wild progenitors such as Solanum pennellii have also been reported to have high content than cultivated varieties (Di Matteo et al., 2010). High levels of ascorbic acid in tomato fruits provide health benefits for humans and also play an important role in several aspects of

Table 4Color attributes of selected Indian tomato.

Cultivar	L*	a*	b*	Ratio a*/b*	Hue	Chroma
Taiwan	37.13 ± 1.62 ^{bc}	32.38 ± 3.15 ^{bc}	17.04 ± 1.94^{a}	2.35 ± 0.13 ^{bc}	27.84 ± 4.81^{ba}	36.68 ± 1.98^{ba}
Balkan	35.09 ± 2.26^{c}	31.93 ± 1.48^{dc}	13.66 ± 1.18^{ed}	2.34 ± 0.11^{bc}	$23.07 \pm 0.99^{\mathrm{ed}}$	34.74 ± 1.80^{bdc}
Pusa Gaurav	36.2 ± 1.59^{bc}	33.44 ± 1.40^{bac}	$14.98 \pm 0.55^{ m bedc}$	2.23 ± 0.15^{cd}	24.08 ± 1.41^{dc}	36.65 ± 0.70^{ba}
Pusa Ruby	$38.54\pm0.86^{\mathrm{bac}}$	30.37 ± 1.91^{edc}	$14.23 \pm 0.51^{\text{edc}}$	2.13 ± 0.13^{cd}	25.07 ± 1.42^{bdc}	33.55 ± 1.80^{d}
Roma	41.45 ± 1.26^a	28.63 ± 0.44^{e}	$16.18 \pm 0.50^{\mathrm{ba}}$	1.77 ± 0.51^{e}	29.39 ± 0.71^{a}	32.89 ± 0.53^{d}
Pusa Uphar	36.66 ± 2.55^{bc}	30.74 ± 1.93^{edc}	15.29 ± 0.12^{bdc}	2.01 ± 0.11^{d}	26.41 ± 1.29^{bac}	34.34 ± 1.77^{bdc}
Pusa Sadabahar	39.48 ± 3.5^{ba}	$30.79 \pm 1.69^{\text{edc}}$	$14.18 \pm 0.54^{\mathrm{ed}}$	2.17 ± 0.75^{cd}	24.68 ± 0.75^{bdc}	33.90 ± 1.72^{dc}
Avikash	35.85 ± 1.43^{c}	32.99 ± 1.61^{bc}	$15.15 \pm 0.35^{\mathrm{bdc}}$	2.17 ± 0.13^{cd}	24.63 ± 1.31^{bdc}	36.31 ± 1.42^{bac}
Pusa Sheetal	36.85 ± 2.73^{bc}	29.02 ± 0.98^{ed}	$15.81 \pm 0.93^{\mathrm{bac}}$	1.64 ± 0.29^{e}	28.49 ± 0.60^{a}	33.05 ± 1.31^{d}
Chiku	37.65 ± 1.16^{bc}	33.44 ± 0.91^{bac}	$14.23 \pm 0.55^{ m edc}$	2.35 ± 0.74^{bc}	22.99 ± 0.65^{ed}	36.34 ± 0.98^{bac}
S pimpinellifolium	28.81 ± 0.90^{d}	36.12 ± 1.16^{a}	13.70 ± 0.30^{ed}	2.63 ± 0.98^a	20.73 ± 0.71^{e}	38.63 ± 1.10^{a}
EC-521083	27.04 ± 0.46^d	36.32 ± 1.17^{a}	13.42 ± 0.96^{e}	2.71 ± 0.22^a	20.23 ± 1.52^{e}	38.73 ± 1.11^{a}
EC-521086	26.73 ± 1.01^{d}	35.31 ± 1.53^{ba}	14.11 ± 0.67^{ed}	2.50 ± 0.22^{ab}	21.75 ± 1.82^{ed}	38.04 ± 1.16^{a}

 L^* is the approximate measure of lightness, a^* takes positive values for reddish colors and negative values for greenish ones, b^* is positive for yellowish color and negative for the bluish.

Values represent the mean of three replicates \pm standard deviation.

Mean followed by the same superscripts are not significantly different (P < 0.05).

S. pimpinellifolium, EC-521083 and EC-521086 represent the wild/exotic cvs respectively.

All values are on fresh weight basis.

S. pimpinellifolium, EC-521083 and EC-521086 represent the wild/exotic cvs respectively.

All values are on fresh weight basis.

plant life. Our results are in the range reported elsewhere (Martínez-Valverde et al., 2002). Agronomical conditions, light, temperature and varietal differences may account for significant variations in ascorbic acid.

3.5. Quality characteristics and color attributes

TSS is a key determinant of shelf life and quality of the crop, whether it is for the fresh produce or for processing. Furthermore, TSS levels also contribute strongly to the tomato flavor and consistency (Stevens, Kader, Albright-Holton, & Algazi, 1997). TSS ranged from 4.38 in Roma to 7.64° Brix in S. pimpinellifolium (Table 3). Organic acids are important quality factor for determining characteristic tomato flavor. Acids also govern microbial stability and influence the processing time and temperature of tomato products. The acidity in cvs ranged between 0.31 and 0.63%, which is a desirable trait for processing cvs (Gould, 1992). Fruit color is a quality characteristic that has received intensive attention by fresh-market and processing tomato industries as well as consumers. It is also an important indicator of stage of ripeness. The final color in tomato fruit is conditioned by the total amount and proportion of different carotenoids. L^* (lightness) values ranged from 26.73 to 41.81, a* (redness) value from 26.02 to 36.32, b* (yellowness) value from 13.42 to 16.18. The quantitative attribute of color, ratio of a^*/b^* ranged from 1.64 to 2.71 CIELAB units (Table 4). The upper case corresponded to exotic/S. pimpinellifolium. There was slight difference with respect to the ratio a^*/b^* between the commercial cvs indicating that they were all at the same stage of ripeness. Hue and chroma values in tomato cvs ranged from 20.23 to 29.39 and 32.89 to 38.73 respectively.

3.6. Correlation between total phenolics and antioxidant activity

Total phenolics were found to correlate well with hydrophilic AOX in FRAP assay ($R^2 = 0.536$; P < 0.01). However no significant correlation existed in DPPH and TEAC assays. This could be probably because of the influence of other antioxidant system of tomato (glutathione and enzymatic components) with the reactions chemicals used for AOX measurement. Also the diverse sensitivity of different classes of hydrophilic antioxidants, could also influence the net activity in FRAP and TEAC assays. With regard to LAA we observe positive correlation in both DPPH and TEAC assays $(R^2 = 0.94 \text{ and } 0.60)$ respectively. Our results draw support from Raffo et al. (2006).

4. Conclusions

There is considerable variation between commercial tomato and wild/exotic cvs in terms of their antioxidant composition and antioxidant activity. This variability offers an opportunity to improve the functional quality of Indian tomatoes. Exotic/wild cvs with significant high lycopene can be useful in breeding programs for developing high pigmented tomatoes for processing industry and fresh market.

Acknowledgments

This study was supported from the World Bank funded project by National Agricultural Innovative Programme (NAIP) of Indian Council of Agricultural Research. The authors are thankful to Division of Agricultural chemistry and Division of Post Harvest Technology for providing laboratory facilities.

References

- Adalid, A. M., Roselló, S., & Nuez, F. (2010). Evaluation and selection of tomato accessions (Solanum section Lycopersicon) for content of lycopene, β-carotene and ascorbic acid. Journal of Food Composition and Analysis, 23, 613-618.
- Anonymous (2010). National Horticultural Board, (NHB), India. http://nhb.gov.in/. Benzie, I. F. F., & Strain, J. J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": the FRAP assay. Analytical Biochemistry, 239,
- Brand-Williams, W., Cuvelier, M. E., & Berset, C. (1995). Use of a free radical method to evaluate antioxidant activity. Lebensmittel-Wissenschaft und - Technologie, 28, 25-30,
- Canene-Adams, K., Campbell, I. K., Zaripheh, S., Jefferv, E. H., & Erdman, J. W., IR. (2005). The tomato as a functional food. Journal of Nutrition, 135, 1226–1230.
- Clinton, S. K. (1998). Lycopene chemistry, biology and implications for human health diseases. Nutrition Reviews, 56, 35-51.
- Dewanto, V., Wu, X. Z., Adom, K. K., & Li, 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.

 Dillingham, B. L., & Rao, A. V. (2009). Biologically active lycopene in human health.
- International Journal of Naturopathic Medicine, 4, 23–27.
- Dimascio, P., Kaiser, S., & Sies, H. (1989). Lycopene as the most effective biological carotenoid singlet oxygen quencher. Archives of Biochemistry and Biophysics, 274, 532-538.
- Di Matteo, A., Sacco, A., Anacleria, M., Pezzotti, M., Delledonne, M., Ferrarini, A., et al. (2010). The ascorbic acid content of tomato fruits is associated with the expression of genes involved in pectin degradation. BMC Plant Biology, 163,
- Dumas, Y., Dadomo, M., Lucca, G. D., & Grolier, P. (2003). Effects of environmental factors and agricultural techniques on antioxidant content of tomatoes. Journal of Science of Food and Agriculture, 83, 369-382.
- Floegel, A., Kim, D., Chung, S., Koo, S., & Chun, O. (2011). Comparison of ABTS/DPPH assays to measure antioxidant capacity in popular antioxidant-rich US foods. *Journal of Food Composition and Analysis*, 24, 1043–1048.
- Fraser, P. D., Enfissi, E. M. A., & Bramley, P. M. (2009). Genetic engineering of carotenoid formation in tomato fruit and the potential application of systems and synthetic biology approaches. Archives of Biochemistry and Biophysics, 483, 196-204.
- George, B., Kaur, C., Khurdiya, D. S., & Kapoor, H. C. (2004). Antioxidants in tomato (Lycopersium esculentum) as a function of genotype. Food Chemistry, 84, 45-51. Gould, W. A. (1992). Tomato production, processing and technology. Baltimore, USA: CTI Publications.
- Halvorsen, B. L., & Blomhoff, R. (2011). Validation of a quantitative assay for the total content of lipophilic and hydrophilic antioxidants in foods. Food Chemistry, 127, 761-768
- llahy, R., Hdider, C., Lenucci, M. S., Tlili, I., & Dalessandro, G. (2011). Phytochemical composition and antioxidant activity of high-lycopene tomato (Solanum lycopersicum L.) cultivars grown in Southern Italy. Scientia Horiculturae, 127, 255–261.
- Jagadeesh, S. L., Charles, M. T., Gariepy, Y., Goyette, B., Raghavan, G. Vigneault, C. (2009). Influence of postharvest UV-C hormesis on the bioactive components of tomato during post treatment handling. Food Bioprocess Tech-
- nology, 1–10. Kotíková, Z., Lachman, J., Hejtmánková, A., & Hejtmánková, K. (2011). Determination of antioxidant activity and antioxidant content in: tomato (varieties and evaluation of mutual interactions between antioxidants). LWT - Food Science and Technology, 44, 1703-1710.
- Martínez-Valverde, I., Periago, M. J., Provan, G., & Chesson, A. (2002). Phenolic compounds, lycopene and antioxidant capacity in commercial varieties of tomato (Lycopersicum esculentum). Journal of Science Food Agriculture, 82, 323-330.
- Mazza, G., Fukumoto, L., Delaquis, P., Girard, B., & Ewert, B. (1999). Anthocyanins, phenolics, and color of Cabernet Franc, Merlot, and Pinot Noir wines from British Columbia. Journal of Agricultural and Food Chemistry, 47, 4009–4017.
- Navarro-González, I., García-Valverde, V., García-Alonso, J., & Periago, M. J. (2011). Chemical profile, functional and antioxidant properties of tomato peel fiber. Food Research International, 44, 1528-1535.
- Nguyen, M. L., & Schwartz, S. J. (1999). Lycopene. Food Technology, 53(2), 38-45. Nunes, M. C. N., Brecht, J. K., Morais, A. M. M. A., & Sargent, S. A. (1995). Physical and chemical quality characteristics of strawberries after storage are reduced by a short delay to cooling. Postharvest Biology and Technology, 6, 17-28.
- Pulido, R., Bravo, L., & Saura-Calixto, F. (2000). Antioxidant activities of dietary phenols are determined by a modified ferric reducing/antioxidant power assay. Journal of Agricultural and Food Chemistry, 48, 3396–3402.
- Raffo, A., La Malfa, G., Fogliano, V., Maiani, G., & Quaglia, G. (2006). Seasonal variations in antioxidant components of cherry tomatoes (Lycopersicon esculentum cv. Naomi F1). Journal of Food Composition and Analysis, 19, 11-19.
- Rein, D., Schijlen, E., Kooistra, T., Herbers, K., Verschuren, L., Hall, R., et al. (2006). Transgenic flavonoid tomato intake reduces C-reactive protein in human Creactive protein transgenic mice more than wild-type tomato. Journal of Nutrition, 136, 2331-2337.
- Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M., & Rice-Evans, C. (1999). Antioxidant activity applying an improved ABTS radical cation decolorization assay. Free Radical Biology and Medicine, 26, 1231-1237.
- Singleton, V. L., Orthofer, R., & Lamuela-Ranventos, R. M. (1999). Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin—Ciocalteu reagent. Methods in Enzymology, 299, 152—178.

- Slimestad, R., & Verheul, M. (2009). Review of flavonoids and other phenolics from fruits of different tomato (*Lycopersicon esculentum Mill.*) cultivars. *Journal of the Science of Food and Agriculture*, 89, 1255–1270.
- Stevens, M. A., Kader, A. A., Albright-Holton, M., & Algazi, M. (1997). Genotypic variation for flavor and composition in fresh tomatoes. *Journal of the American Society for Horticultural Science*, 102, 680–689.
- Toor, R. K., & Savage, G. P. (2005). Antioxidant activities in different fractions of tomato. *Food Research International*, 38, 487–494.
- Willits, M. G., Kramer, C. M., Prata, R. T., De Luca, V., Potter, B. G., Steffens, J. C., et al. (2005). Utilization of the genetic resources of wild species to create a non-transgenic high flavonoid tomato. *Journal of Agricultural and Food Chemistry*, 53, 1231–1236.