JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Determination of Phenolic Compounds and Ascorbic Acid in Different Fractions of Tomato by Capillary Electrophoresis with Electrochemical Detection

YOUYUAN PENG,*,† YINGWU ZHANG,† AND JIANNONG YE§

Department of Chemistry, Quanzhou Normal University, Quanzhou 362000, China, and Department of Chemistry, East China Normal University, Shanghai 200062, China

Tomato (*Lycopersicon esculentum* Mill.), one of the most important crops worldwide, contains different classes of substances with antioxidant properties such as carotenoids, vitamin C, and phenolics. A method based on capillary electrophoresis with electrochemical detection has been developed to analyze ascorbic acid and phenolics in the peel, pulp, and seeds of tomatoes. Operating in a wall-jet configuration, a 300 µm diameter carbon disk electrode was used as the working electrode, which exhibits a good response at +0.90 V (vs saturated calomel electrode) for the analytes. Under optimum conditions, the analytes were baseline separated within 20 min in a 50 mmol/L borate buffer (pH 8.7). Notably, excellent linearity was obtained over 3 orders of magnitude with detection limits (S/N = 3) ranging from 1×10^{-8} to 2×10^{-7} g/mL for all analytes. This proposed method has been successfully applied to monitor the content of ascorbic acid and phenolics in real samples, and the assay results were satisfactory.

KEYWORDS: Tomato; capillary electrophoresis; electrochemical detection; ascorbic acid; phenolics

INTRODUCTION

The awareness of harmful effects of free radicals for human health has recently increased. Free radicals are very unstable molecules arising physiologically during cellular aerobic metabolism(~2–3% of oxygen consumed by a cell is converted into free radicals) (*1*). They react quickly with other compounds, beginning chain reactions. Once the process is started, it can cascade, finally resulting in disruption of a living cell or in molecular and cellular DNA damage (*2*). Normally, the human body can handle these compounds, but if their amount becomes excessive, damage can occur. Free radicals have been indicated as probable pathogenesis determinants of many degenerative and chronic diseases that develop with age, such as cancer, cardiovascular disease, cataract, and immunity system dysfunctions (*2*). For their potential role in preventing such diseases, natural compounds with antioxidant activity have gained the attention of researchers and nutritionists. Estimation of the antioxidant activity is becoming, in fact, an evaluation parameter for the nutritional quality of food.

A large number of fresh fruits and vegetables are primary sources of antioxidants. Tomatoes (*Lycopersicon esculentum* Mill.), commonly used in the Mediterranean diet, are a major source of antioxidants and contribute to the daily intake of a significant amount of these molecules. Tomatoes are consumed fresh or as processed products (sauces, juice, ketchup, soup). The consumption of fresh tomatoes and tomato products has been inversely related to the development of some types of cancer (*3*) and to plasma lipid peroxidation (*4*). Tomato contains different classes of substances with antioxidant properties such as carotenoids, ascorbic acid, and phenolics. Lycopene is the major carotenoid present in tomato and shows strong antioxidant activity both in vitro and in vivo (*5*). It is possible that these phenolics in tomato can act synergistically with lycopene in preventing cell damage. This latter possibility seems to be plausible because lycopene-containing tomato diets appear to be more effective in cancer prevention than is pure lycopene (*6, 7*).

Chlorogenic acid (5′-caffeoylquinic acid), a hydroxycinnamic acid conjugate, is the main phenol in tomato (*8, 9*). Rutin (quercetin-3-rhamnosylglucoside) and naringenin are representative flavonoids of tomato, respectively conjugated and nonconjugated (*9, 10*), and flavonols such as myricetin are also found in tomato and its products (*7*). More recently, resveratrol, which is found primarily in the grape skin and reported to possess cancer prevention properties based on in vitro assay results (*11*), is also found to exist in both nontransgenic (*12*) and transgenic tomatoes (*13*).

The most widely used method for the analysis of phenolic compounds in plants and fruits is high-performance liquid chromatography (HPLC) with photodiode array (PDA) detection (*7, 13–16*); the effectiveness of HPLC with mass spectrometric detection for analyzing polyphenols in plant extracts and food has been explored, too (*13, 15*). However, HPLC has some shortcomings including time-consuming sample pretreatment

* Corresponding author (telephone 86-595-22919530; fax 86-595-22919530; e-mail youyuanpeng@hotmail.com).
† Quanzhou Normal University.
§ East China Normal University.

10.1021/jf0727544 CCC: $40.75
Published on Web 02/20/2008

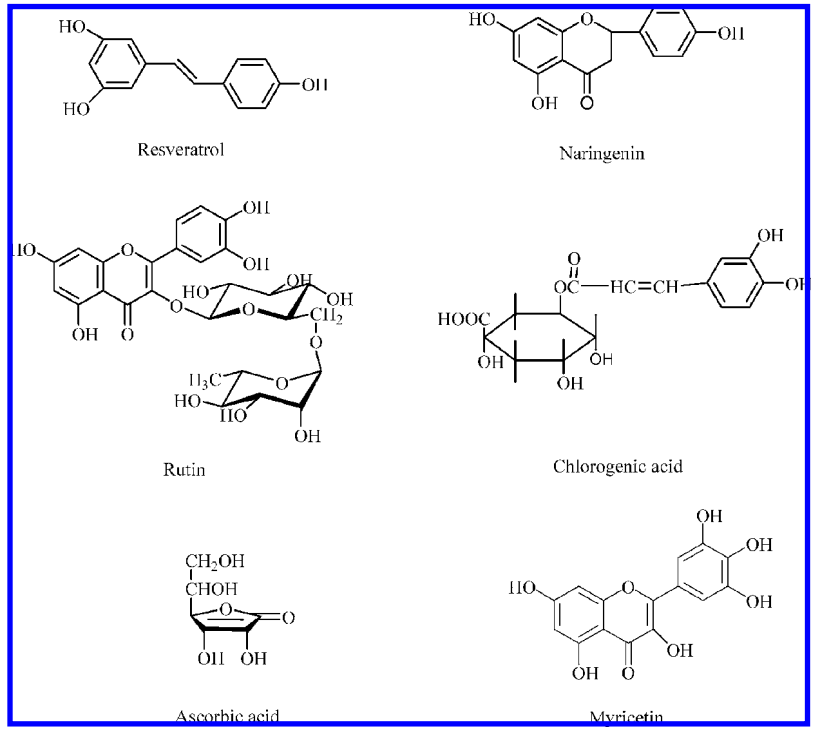

Figure 1. Molecular structures of resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin.

and short column lifetime owing to numerous coexistent interferences in real samples. Now, capillary electrophoresis (CE) is becoming increasingly recognized as an important analytical separation technique for charged compounds and partially charged organics such as phenolic compounds. It provides faster analysis time and better separation efficiency than HPLC and consumes only small amounts of aqueous solvents. CE does have environmental and economic advantages; however, HPLC is better in terms of accuracy, sensitivity, and precision. Therefore, CE has been proposed as a complementary technique to HPLC for the separation of phenolic compounds present in herbs such as phenolic acids and flavones (*17*). In combination with electrochemical detection (ED), CE-ED offers high sensitivity and good selectivity; the limitation of this method is that it could be applied only to electroactive analytes.

The aim of the present study was to provide an easy and feasible method to detect the contents of ascorbic acid and polyphenols in different fractions of tomato. With these results, it might be possible to get new insights in the quality control of tomato and tomato products. CE-ED was proposed for the determination of resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin (**Figure 1**) in different fractions of tomato. To our best knowledge, there are no studies published on the simultaneous determination of the target analytes in tomato by CE-ED. The optimization, detailed characterization, and advantages of the CE-ED approach are reported here.

MATERIALS AND METHODS

Apparatus. In this work, a capillary zone electrophoresis with amperometric detection system was laboratory-built. A ±30 kV high-voltage dc power supply (Shanghai Institute of Nuclear Research, Shanghai, China) provided a voltage between the ends of the capillary. The inlet of the capillary was held at a positive potential, and the outlet end of the capillary was maintained at ground. The separations were undertaken in a 80 cm length, 25 µm i.d., and 360 µm o.d. fused silica capillary (Polymicro Technologies, Phoenix, AZ). To protect the operator from the high voltage and ensure the safety of the CE-ED system, the entire capillary, the buffer reservoirs for CE, and all electrodes were enclosed in a Plexiglas box with a safety switch wired to turn off the power supply whenever the box was opened. The whole system was assembled in a 10 m^2 faraday room that was air-conditioned at 20 °C to minimize the effects of external noise sources.

A three-electrode cell system consisting of a 300 µm diameter carbon disk working electrode, a platinum auxiliary electrodes, and a saturated calomel electrode (SCE) as the reference electrode was used in combination with a BAS LC-3D amperometric detector (Bioanalytical Systems, West Lafayette, IN). Before use, the carbon disk electrode was polished with emery paper, then sonicated in doubly distilled water, and finally positioned carefully opposite the outlet of the capillary and arranged in a wall-jet configuration (*18*). The distance between the tip of the working electrode and the capillary outlet was adjusted to about 25 µm by comparison with the bore (25 µm) in the capillary while being viewed under a microscope. The electropherograms were recorded using a chart record (XWTD-164, Shanghai Dahua Instrument Factory, China). CE was performed under optimized conditions; 50 mmol L^{-1} borate buffer (pH 8.7) was used as the running buffer at a separation voltage of 16 kV. The potential applied to the working electrode was 0.90 V (vs SCE). A special syringe from Instrument Manufactory of Shanghai Medical School was used for rinsing the capillary, and no pressure from outside was needed. Before each run in CE experiments, the capillary was sequentially rinsed with 0.1 mol L^{-1} hydrochloric acid, doubly distilled water, and 0.1 mol L^{-1} sodium hydroxide 3 min for each and running buffer until the current inside of the capillary was stable, which was important to get a reproducible electro-osmotic flow (EOF). Samples were injected electrokinetically at 16 kV for 8 s.

Reagents and Solutions. Resveratrol, naringenin, chlorogenic acid, and myricetin were purchased from Sigma (St. Louis, MO); rutin and L-ascorbic acid was obtained from Shanghai Reagent Factory (Shanghai, China). Stock solution of ascorbic acid (1.0×10^{-3} g/mL) was freshly prepared in distilled water every day and stored in the dark at 4 °C,l the stability of the ascorbic acid solution was checked by measuring the peak height and migration time by capillary electrophoresis at the end of each day; it has been proved to be stable under the conditions. Stock solutions of the other analytes (1.0×10^{-3} g/mL each) were prepared in anhydrous ethanol (A.R. grade) and were diluted to the appropriate concentration with running buffer (50 mmol/L borate buffer, pH 8.7) for the construction of calibration curves. Before use, all solutions were filtered through 0.22 µm nylon filters.

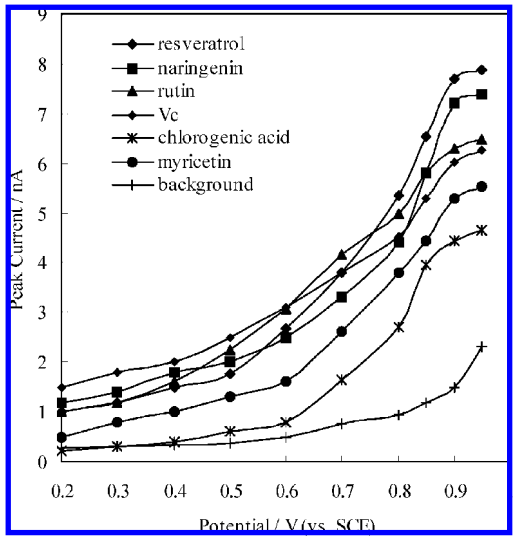

Figure 2. Hydrodynamic voltammograms (HDVs) for resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin in CE. Working conditions: fused-silica capillary, 25 µm i.d. × 70 cm; working electrode, 300 µm diameter carbon disk electrode; running buffer, 50 mmol/L borate buffer (pH 8.7); separation voltage, 16 kV; electrokinetic injection, 8 s (16 kV); concentrations, 1.0×10^{-6} g/mL for resveratrol, 2.0×10^{-5} g/mL for naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin.

Sample Preparation. The tomatoes used were regular red ripe tomatoes grown in village farm greenhouses and purchased from the local supermarket (Qilong, China) during June 2007; the samples were classified according to the varietal information given on the label (Anqi, Chunjiao, and Mava). Each tomato was about 110 g, and about 5 kg of tomatoes was separated into three different fractions: skin, pulp, and seeds. The peel (outer epidermis, ~2 mm thick) of the tomatoes was carefully separated from the fresh using a sharp knife. The seed fraction of the tomatoes consisted of the seeds along with the jelly portion. Pulp was the portion of tomato remaining after removal of the skin and seed fractions. All of the samples were frozen in liquid nitrogen, freeze-dried, and stored at −20 °C until analysis.

For extraction of the target analytes, the dried samples were ground to a fine powder using a mortar and pestle, and an accurate weight amount of the powders (2.0000 ± 0.0005 g) was extracted with 10 mL of 80% ethanol for 1 h in an ultrasonic bath at ambient temperature. Next, each of the samples was filtered through filter paper first, then through a 0.22 µm nylon filter. The pH of the sample solutions ranged from 4.2 to 4.7, and they were neutralized with NaOH and then diluted using the running buffer just prior to CE analysis.

RESULTS AND DISCUSSION

Hydrodynamic Voltammograms (HDVs). In amperometric detection the potential applied to the working electrode directly affects the sensitivity, detection limit, and stability of this method. Therefore, the effect of working electrode potential on the peak current (calculated by measuring the peak height) of the analytes was investigated by plotting peak currents versus detection potential to obtain optimum detection. As shown in **Figure 2**, all of the analytes display similar profiles, with a rapid increase of the response starting at +0.60 V (vs SCE). When the applied potential passes +0.90 V (vs SCE), however, the peak currents of the analytes increase much more slowly. Although an applied potential greater than +0.90 V (vs SCE) results in higher peak currents, both the baseline noise and the background current increase substantially. The high background current leads to an unstable baseline, which is a disadvantage for sensitive and stable detection. The potential applied to the working electrode was, therefore, maintained at +0.90 V (vs SCE), where the background current is not too high and the signal-to-noise (S/N) ratio is the highest.

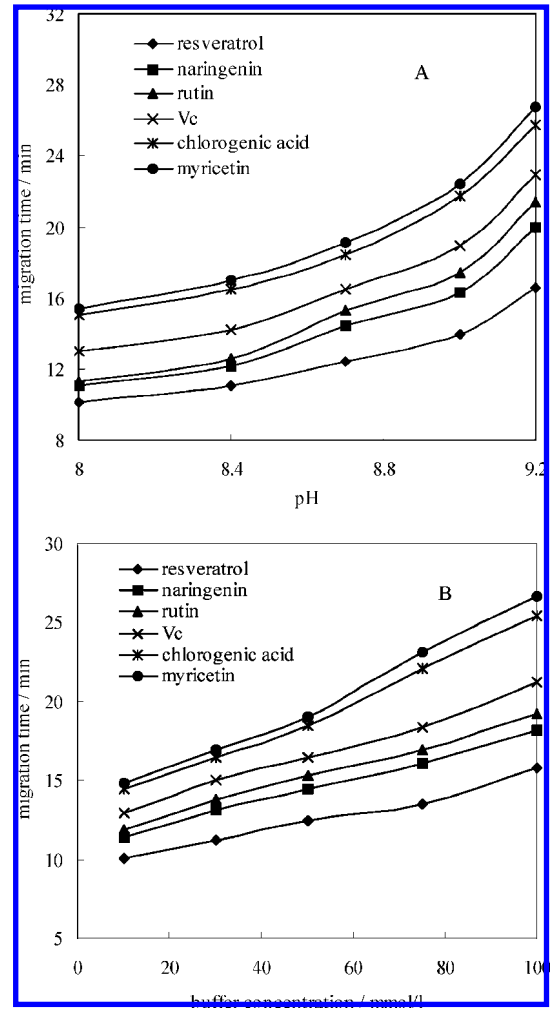

Figure 3. Effect of buffer pH (**A**) and concentration (**B**) on the migration time of resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin. Working potential, +0.90 V (vs SCE); other conditions as in **Figure 2**.

Effects of the pH and Concentration of the Buffer. Borate buffer was employed as the running buffer in this work because borate can chelate with the analytes to form more soluble complex anions (*19*). The acidity and concentration of the running buffer play an important role in CE for its effect on zeta potential (ζ) and the electroosmotic flow (EOF), as well as the overall charge of all the analytes, which affect the migration time and the separation of the analytes. Therefore, it is important to study their influences on CE to obtain optimum separations. The effect of the running buffer pH on the migration time of the investigated analytes is shown in **Figure 3A**. When the running buffer pH increases, the resolution of all compounds is improved with migration time increased. At pH 8.7 the analytes can be well separated; it is also found that the peak current is low and the peak shape became poor when the pH value exceeds 8.7.

Increasing the running buffer concentrations (ionic strength) generally decreases the EOF, and thus lengthens the migration times. The reduced EOF with the increasing buffer concentrations is due to the decrease of the thickness of the diffusion of the double layer at the inner capillary wall. Thus, the resolution is also increased with the increasing ionic strength. Results show

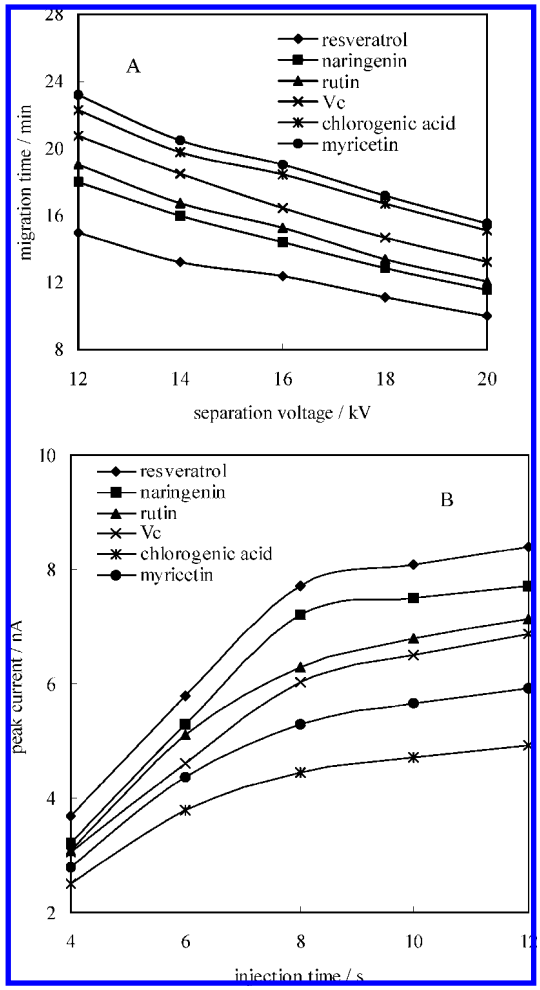

Figure 4. Effect of separation voltage on the migration time of resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin (**A**) and effect of injection time on the analytes peak current (**B**). Working potential, +0.90 V (vs SCE); other conditions as in **Figure 2**.

that higher buffer concentrations led to longer migration times and decreasing electrophoretic mobility. Moreover, higher buffer concentrations (>50 mmol/L) also have a negative effect on the detection limits because the peak currents of all analytes decrease and the effect of joule heat becomes more pronounced. At 50 mM, all compounds were well separated with the total migration time of 20 min, and the migration order was resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin, respectively (**Figure 3B**). Consequently, 50 mmol/L borate buffer (pH 8.7) was selected as a compromise between resolution, efficiency, and analysis time and employed for subsequent optimization.

Effects of Separation Voltage and Injection Time. The separation voltage affects the electric field strength, which in turn affects the EOF and the migration velocity of charged particles, which determine the migration time of the analytes. Moreover, higher separation voltage may result in higher joule heating. The effect of separation voltage on the migration time of the analytes is shown in **Figure 4A**: increasing the voltage gives shorter migration times but also increases the background noise, resulting in a higher detection limit. Although the resolution of analytes can be improved to some extent, too low a separation voltage will increase the analytical time considerably, which in turn causes severe peak broadening. On the basis of experiments, 16 kV was chosen as the optimum voltage to accomplish a good compromise.

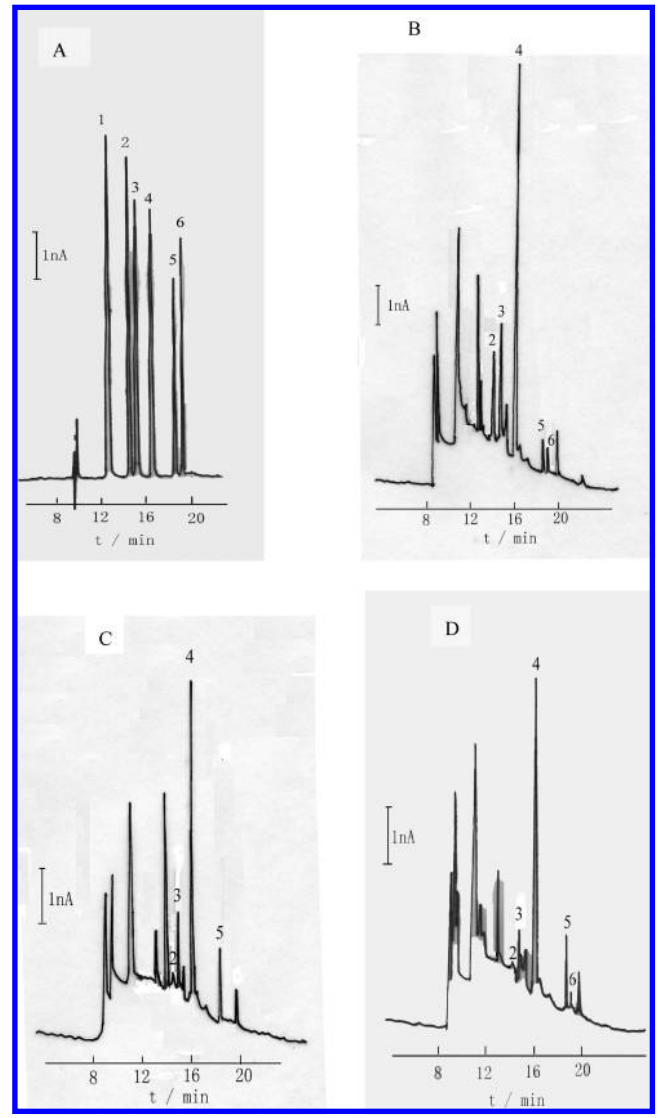

Figure 5. Electropherogram of a standard mixture solution (1.0×10^{-6} g/mL for resveratrol, 2.0×10^{-5} g/mL for naringenin, rutin, ascorbic acid, chlorogenic acid and myricetin) (**A**) and typical electropherograms of tomato (variety Mava) (**B**, peel; **C**, pulp; **D**, seed) (dilution for all samples, 1:100, dry weight). Peak identification: (1) resveratrol; (2) naringenin; (3) rutin; (4) ascorbic acid; (5) chlorogenic acid; (6) myricetin. Working potential, +0.90 V (vs SCE); other conditions as in **Figure 2**.

The effect of injection time on CE separation was investigated by varying the injection time (4, 6, 8, 10, 12 s at a voltage of 16 kV, as shown in **Figure 4B**). It was found that both the peak current and the peak width increase with increasing sampling time. When the injection time is longer than 8 s, peak current levels off and peak broadening becomes severe. In this experiment, 8 s (16 kV) is selected as the optimum injection time.

Through the experiments above, the optimum conditions for the determination of resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin were decided. The typical electropherogram for a standard solution of the analytes is shown in **Figure 5A**, as we can see baseline separation could be achieved within 20 min.

Precision, Linearity, and Detection Limits. The precision of the method was determined by measuring the repeatability of successive injection ($n = 7$) and intraday ($n = 10$), and interday ($n = 7$) analyses using the standard mixture solutions of 1.0×10^{-6} g/mL resveratrol and 2.0×10^{-5} g/mL

Table 1. Weights and Dry Matter of the Skin, Pulp, and Seed Fractions of Tomatoes and Percent Contributions of Each Fraction to Fresh Matter (FW) of Whole Tomato ($n = 3$)

cultivar/fraction	wt (kg)	dry matter (%)	contribution to FW (%)
Mava			
peel	0.55	5.6	10.2
pulp	3.14	4.2	63.5
seeds	1.26	6.5	26.3
total	4.95		
Anqi			
peel	0.59	5.8	11.7
pulp	3.18	4.6	63.1
seeds	1.27	6.3	25.2
total	5.04		
Chunjiao			
peel	0.52	5.5	10.4
pulp	3.22	4.3	64.7
seeds	1.24	6.2	24.9
total	4.98		

Table 2. Injection and Intraday and Interday Precision of the Analytes in the Standard Solution[a]

	precision (%RSD)					
	peak height			migration time		
compound	injection ($n = 7$)	intraday ($n = 10$)	interday ($n = 6$)	injection ($n = 7$)	intraday ($n = 10$)	interday ($n = 6$)
resveratrol	2.2	2.5	3.5	0.6	1.2	1.5
naringenin	1.5	2.0	3.6	0.8	1.0	1.6
rutin	2.0	3.2	3.5	1.0	1.3	1.2
ascorbic acid	2.5	3.0	4.2	1.2	1.3	1.5
chlorogenic acid	1.6	3.0	2.5	0.8	0.7	0.9
myricetin	2.5	2.2	4.8	0.8	0.9	1.2

[a] Working potential is +0.90 V (vs SCE). Other conditions as in **Figure 2**.

naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin under the optimum conditions. The results are listed in **Table 2**. The relative standard deviations (RSDs) of peak current varied from 1.5 to 4.8%, and the migration time varied from 0.6 to 1.6% for the analytes.

A series of standard solutions of resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin ranging from 1.0×10^{-8} to 1.0×10^{-3} g/mL in concentration were tested to determine the linearity of the determination. Results from regression analysis of calibration curves are listed in **Table 3**. Sensitivity was evaluated by determination of the limit of detection (LOD) and the limit of quantification (LOQ) (see **Table 3**). The LOD was determined as the concentration with a S/N ratio of 3, whereas the LOQ was the concentration with a S/N ratio of 10.

Sample Analysis and Recovery. The weights of the whole tomatoes and their fractions were recorded (**Table 1**), and the dry matter in the tomato fractions was determined. Under optimum conditions, the determination of resveratrol, naringenin, rutin, ascorbic acid, chlorogenic acid, and myricetin in real samples was carried out according to the procedures described earlier. Typical electropherograms of different fractions of tomatoes (Mava) are shown in **Figure 5B−D**, respectively. The migration times in CZE in fused-silica capillary tubes can be varied about 1–2% due to the nonrepeatable EOF, which is caused by the unstable surface condition of the inner wall of the tubes and the change in the effective electric field strength. Peaks were identified by migration time; further identification is confirmed by spiking experiments. The assay results are listed in **Table 4**.

Among the three fractions of tomato, the skin was found to contain the highest levels of ascorbic acid, which ranged from 7.52 to 15.8 mg/100 g (FW); this finding is consistent with the results of Toor and Savage (*20*), who showed that the mean ascorbic acid content in the skin of tomato cultivars (15.7−18.6 mg/100 g of FW) was significantly higher compared to the those of the pulp and seeds. The results of this study are also in accordance with George et al. (*21*), who have reported that the ascorbic acid content ranged from 8 to 56 mg/100 g (FW) in the skin and from 8 to 32 mg/100 g in the pulp of Indian tomatoes.

Phenolic compounds tend to accumulate in the dermal tissues of plant body because of their potential role in protection against ultraviolet radiation and to act as attractants in fruit dispersal and as defense chemicals against pathogens and predators (*22*). Flavonoids are often subject to acid or enzymatic hydrolysis to remove sugar moiety, and flavonoids are determined as their aglycones. The samples were prepared without acid hydrolysis or enzymatic hydrolysis in this work, and the naturally occurring variations of the phenolic components were detected. The amount of phenolics except chlorogenic acid was found to be higher in the skin of tomatoes compared to the pulp and seeds. The values of rutin (from 0.18 to 5.33 mg/100 g of FW) fall within the range reported by Schindler et al. (*23*), who reported that the natural amount of rutin in mature tomatoes varied from 2.78 to 53.4 ppm and that of naringenin from 0.29 to 12.2 ppm. In our work, the highest level of naringenin was detected in the peel of Mava to be 3.41 mg/100 g of FW, and naringenin was not found in the pulp and seed of the variety of Anqi, which agrees with the results of Raffo et al. (*24*); they found that naringenin was present mainly in a conjugated form, and its content before hydrolysis (in the free state) was negligible. The content of chlorogenic acid ranged from 1.08 to 3.69 mg/100 g (FW); the results are in accordance with the report of Periago (*9*), chlorogenic acid being found to vary from 1.4 to 3.2 mg/100 g (FW). Resveratrol was not found in all of the samples, which may depend on the variety of tomatoes.

By comparing with the electropherogram of the standard solution (**Figure 5A**), it was found that all samples have similar profiles on the basis of relative peak heights and migration time. As seen from the electropherograms, these results show that the skin and seed fractions are important contributors to the major antioxidants and overall antioxidant activity of tomatoes. Therefore, removal of tomato skin and seeds during their fresh consumption or home cooking means a significant loss of the antioxidants, it is important to consume whole tomatoes along with their skins and seeds to obtain maximum health benefits. The proposed method provided a simple and reliable way to not only determine the active compounds in tomatoes but also to provide some useful information about how to improve the intake of the antioxidants in our daily diet.

The recovery and reproducibility experiments under the optimum conditions were also conducted to evaluate the precision and accuracy of the method. Recovery was determined by standard addition method; accurate amounts of the analytes were added to the diluted extracts of the samples, and the recovery values were obtained using their peak currents from the calibration curve under the same conditions. The results obtained from seeds of tomato are listed in **Table 5**. The recovery for all samples varied from 95 to 105%. The results above indicate that this method is accurate, sensitive, and reproducible, providing a useful quantitative method for the analyses of active ingredients in tomato.

This paper presents the first application of CE-ED for the determination of resveratrol, naringenin, rutin, ascorbic acid,

Table 3. Results of Regression Analysis on Calibration and the Detection Limits[a]

compound	regression eq[b] $y = a + bx$	correl coeff (R)	linear range (µg/mL)	LOD[c] (g/mL)	LOQ[d] (g/mL)
resveratrol	$y = 7000000x + 0.0363$	0.9999	0.05−100	1×10^{-8}	2×10^{-8}
naringenin	$y = 361429x - 0.2$	0.9998	1−1000	2×10^{-7}	5×10^{-7}
rutin	$y = 310357x + 0.25$	0.9997	1−1000	2×10^{-7}	5×10^{-7}
ascorbic acid	$y = 304000x - 0.18$	0.9998	1−1000	2×10^{-7}	6×10^{-7}
chlorogenic acid	$y = 220500x - 0.11$	0.9996	2−1000	1×10^{-6}	3×10^{-6}
myricetin	$y = 268214x - 0.25$	0.9995	2−1000	1×10^{-6}	5×10^{-6}

[a] Working potential is +0.90 V (vs SCE). Other conditions as in **Figure 2**. [b] Where y and x are the peak current (nA) and concentration of the analytes (g/mL), respectively. [c] Limit of detection, corresponding to concentrations giving signal-to-noise ratio of 3. [d] Limit of quantification, corresponding to concentrations giving signal-to-noise ratio of 10.

Table 4. Assay Results of the Analytes in Tomato Fractions of Different Varieties ($n = 3$, mg/100 g)[a]

		Anqi		Chunjiao		Mava	
sample	ingredient	found FW	found DW	found FW	found DW	found FW	found DW
peel	resveratrol	NF[b]	NF	NF	NF	NF	NF
	naringenin	0.38	6.55	0.85	15.5	3.41	63.9
	rutin	0.62	10.69	3.65	66.4	5.33	95.2
	ascorbic acid	15.2	262	32.8	596	18.65	333
	chlorogenic acid	1.08	18.6	1.46	26.5	2.14	38.3
	myricetin	0.42	7.24	0.63	11.5	1.27	22.6
pulp	resveratrol	NF	NF	NF	NF	NF	NF
	naringenin	NF	NF	0.12	2.8	0.243	5.8
	rutin	0.20	4.35	1.28	29.8	1.77	42.2
	ascorbic acid	8.5	184.8	15.8	367.4	7.52	179
	chlorogenic acid	1.54	33.5	2.08	48.4	2.55	60.8
	myricetin	NF	NF	NF	NF	NF	NF
seed	resveratrol	NF	NF	NF	NF	NF	NF
	naringenin	NF	NF	0.10	1.61	0.199	3.06
	rutin	0.18	2.86	1.39	22.4	1.53	23.5
	ascorbic acid	8.2	130.2	16.5	266	11.7	180
	chlorogenic acid	2.83	44.9	3.26	52.6	3.69	56.8
	myricetin	NF	NF	0.32	5.16	0.638	9.81

[a] Working potential is +0.90 V (vs SCE). Other conditions as in **Figure 2**. FW, fresh weight. DW, dried weight. [b] Not found.

Table 5. Results of the Recovery of This Method ($n = 3$, 10^{-5} g/mL)[a]

compound	original amount	added amount	found amount	recovery (%)	RSD (%)
resveratrol	NF	0.10	0.102	102	2.6
naringenin	0.0306	0.10	0.136	105	3.8
rutin	0.235	0.10	0.33	95	2.5
ascorbic acid	1.80	1.0	2.76	96	3.2
chlorogenic acid	0.568	0.5	1.058	96	3.0
myricetin	0.0981	0.10	0.201	103	1.8

[a] Working potential is +0.90 V (vs SCE). Other conditions as in **Figure 2**. NF, not found.

chlorogenic acid, and myricetin in different parts of tomato. The realization of such analysis is more economical in comparison to HPLC because the consumption of electrolytes is negligible, the use of organic solvents is practically avoided, and the capillary is much easier to wash. The reproducibility of quantitative analysis is satisfactory. ED coupled with CE enabled selective and sensitive detection of the electroactive constituents in the food matrix, and simplification of the electropherograms for only electroactive constituents could be detected. Consumer demand for healthy food products provides an opportunity to develop foods rich in antioxidants as new functional foods. The proposed method could be used also for quantitative analysis for the phenolics in different products of tomatoes and different genetic type of tomato; it is expected that CE-ED would be a powerful technique for the constituents and quality control of natural foods and an alternative, competitive, and supplementary method for HPLC because of its special attributes.

LITERATURE CITED

(1) Wickens, A. P. Ageing and the free radical theory. *Respir. Physiol.* **2001**, *128*, 379–391.

(2) Halliwell, B.; Gutteridge, J. M. C. *Free Radicals in Biology and Medicine*, 3rd ed.; Oxford University Press: Oxford, U.K., 1999.

(3) Giovannucci, E. Tomatoes, tomato-based products, lycopene, and cancer: review of the epidemiologic literature. *J. Natl. Cancer Inst.* **1999**, *91*, 317–331.

(4) Parfitt, V. J.; Rubba, P.; Bolton, C.; Marotta, G.; Hartog, M.; Mancini, M. A comparison of antioxidant status and free radical peroxidation of plasma lipoproteins in healthy young persons from Naples and Bristol. *Eur. Heart J.* **1994**, *15*, 871–876.

(5) Agarwal, S.; Rao, A. V. Tomato lycopene and its role in human health and chronic diseases. *Can. Med. Assoc. J.* **2000**, *163*, 739–744.

(6) Friedman, M. Tomato glycoalkaloids: role in the plant and in the diet. *J. Agric. Food Chem.* **2002**, *50*, 5751–5780.

(7) Shen, Y. C.; Chen, S. L.; Wang, C. K. Contribution of tomato phenolics to antioxidation and down-regulation of blood lipids. *J. Agric. Food Chem.* **2007**, *55*, 6475–6481.

(8) Fleuriet, A.; Macheix, J. J. Quinyl esters and glucose derivatives of hydroxycinnamic acids during growth ripening of tomato fruit. *Phytochemistry* **1981**, *20*, 667–671.

(9) Martinez-Valverde, I.; Periago, M. J.; Provan, G.; Chesson, A. Phenolic compounds, lycopene and antioxidant activity in commercial varieties of tomato (*Lycopersicon esculentum*). *J. Sci. Food Agric.* **2002**, *82*, 323–330.

(10) Crozier, A.; Lean, M. E. J.; Morag, S. M.; Black, C. Quantitative analysis of the flavonoid content of commercial tomatoes, onions, lettuce and celery. *J. Agric. Food Chem.* **1997**, *45*, 590–595.

(11) Jang, M.; Cai, L.; Udeani, G. O.; Slowing, K. V.; Thomas, C. F.; Beecher, C.W. W.; Fong, H. H. S.; Farnsworth, N. R.; Kinghorn, A. D.; Mehta, R. G.; Moon, R. C.; Pezzuto, J. M. Cancer chemopreventive activity of resveratrol, a natural product derived from grapes. *Science* **1997**, *275*, 218–220.

(12) Ragab, A. S.; Van Fleet, J.; Jankowski, B.; Park, J. H.; Bobzin, S. C. Detection and quantitation of resveratrol in tomato fruit (*Lycopersicon esculentum* Mill.). *J. Agric. Food Chem.* **2006**, *54*, 7175–7179.

(13) Nicoletti, I.; De Rossi, A.; Giovinazzo, G.; Corradini, D. Identification and quantification of stilbenes in fruits of transgenic tomato plants (*Lycopersicon esculentum* Mill.) by reversed phase HPLC with photodiode array and mass spectrometry detection. *J. Agric. Food Chem.* **2007**, *55*, 3304–3311.

(14) Long, M.; Millar, D. J.; Kimura, Y.; Donovan, G.; Rees, J.; Fraser, P. D.; Bramley, P. M.; Bolwell, G. P. Metabolite profiling of carotenoid and phenolic pathways in mutant and transgenic lines of tomato: identification of a high antioxidant fruit line. *Phytochemistry* **2006**, *67*, 1750–1757.

(15) Justesen, U.; Knuthsen, P.; Leth, T. Quantitative analysis of flavonols, flavones, and flavanones in fruits, vegetables and beverages by high-performance liquid chromatography with photodiode array and mass spectrometric detection. *J. Chromatogr., A* **1998**, *799*, 101–110.

(16) Harnly, J. M.; Doherty, R. F.; Beecher, G. R.; Holden, J. M.; Haytowitz, D. B.; Bhagwat, S.; Gebhardt, S. Flavonoid content of U.S. fruits, vegetables, and nuts. *J. Agric. Food Chem.* **2006**, *54*, 9966–9977.

(17) Peng, Y. Y.; Ye, J. N.; Kong, J. L. Determination of phenolic compounds in *Perilla frutescens* L. by capillary electrophoresis with electrochemical detection. *J. Agric. Food Chem.* **2005**, *53*, 8141–8147.

(18) Ye, J. N.; Baldwin, R. P. Determination of amino acids and peptides by capillary electrophoresis and electrochemical detection at a copper electrode. *Anal. Chem.* **1994**, *66* (17), 2669–2674.

(19) Hoffstetter-Kuhn, S.; Paulus, A.; Gassmann, E.; Widmer, H. M. Influence of borate compexation on the electrophoretic behavior of carbohydrates in capillary electrophoresis. *Anal. Chem.* **1991**, *63*, 1541–1547.

(20) Toor, R. K.; Savage, G. P. Antioxidant activity in different fractions of tomatoes. *Food Res. Int.* **2005**, *38*, 487–494.

(21) George, B.; Kaur, C.; Khurdiya, D. S.; Kapoor, H. C. Antioxidants in tomato (*Lycopersicon esculentum*) as a function of genotype. *Food Chem.* **2004**, *84*, 45–51.

(22) Strack, D. Phenolic metabolism. *Plant Biochemistry*; Dey, P. M., Harborne, J. B., Eds.; Academic Press: London, U.K., 1997.

(23) Schindler, M.; Solar, S.; Sontag, G. Phenolic compounds in tomatoes. Natural variations and effects of gamma-irradiation. *Eur. Food Res. Technol.* **2005**, *221*, 439–445.

(24) Raffo, A.; Leonardi, C.; Fogliano, V.; Ambrosino, P.; Salucci, M.; Gennaro, L.; Bugianest, R.; Giuffrida, F.; Quagllar, G. Nutritional value of cherry tomatores (*Lycopersicon esculentum* cv. Naomi F1) harvested at different ripening stages. *J. Agric. Food Chem.* **2002**, *50*, 6550–6556.

Received for review September 16, 2007. Revised manuscript received January 11, 2008. Accepted January 13, 2008. We are grateful for the financial support provided by the Natural Science Foundation of Fujian province of China (Grant 2007J0009) and the Science Foundation of Quanzhou (Grant 2007Z47).

JF0727544