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Quantitative Analysis of Ginger Components in Commercial Products Using Liquid Chromatography with Electrochemical Array Detection

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For the first time, a sensitive reversed-phase HPLC electrochemical array method has been developed for the quantitative analysis of 8 major ginger components ([6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione) in 11 ginger-containing commercial products. This method was valid with unrivaled sensitivity as low as 7.3−20.2 pg of limit of detection and a range of 14.5−40.4 pg for the limit of quantification. The levels of 8 ginger components in 11 different commercial products were quantified by use of this method. The results found that both levels and ratios among the 8 compounds vary greatly in commercial products.

KEYWORDS: Ginger; gingerols; shogaols; electrochemical array detection; quantification

INTRODUCTION

Ginger (*Zingiber officinale* Roscoe), a tropical and subtropical cultivated plant, is derived from Zingiberaceae and has been used worldwide as a spice, dietary supplement, and traditional medicine for centuries (*1*). Moreover, ginger has been suggested for the treatment of headaches, nausea, and colds in Asia, India, Arabia, and Africa since ancient times. In Western alternative medicine practice, ginger is primarily defined as a plant useful for the prevention of nausea and motion sickness (*2*). Recently, ginger has drawn much more attention for anti-inflammation, antioxidative, anticarinogenic, and antimutagenic properties due to the long history of medicinal use as well as being rich in bioactive constituents (*3*−*6*). A series of bioactive compounds such as gingerols, paradols, and shogaols have been identified in ginger and suggested to play significant roles in both flavoring and health contributions. Gingerols, a series of chemical homologues differentiated by the length of their unbranched alkyl chains, were identified as the major pungent components in the ginger oleoresin from fresh rhizome, with [6]-gingerol (**Figure 1**) being the most abundant. Gingerols are not stable during storage or thermal processing as they generate the dehydration products, shogaols, which are predominant pungent constituents in the ginger oleoresin from dried ginger (*7*, *8*). It has been reported that shogaols were minor components in fresh ginger, and the ratio of [6]-shogaol to [6]-gingerol was about 1:1 in dried ginger (*7*, *8*). Other gingerol- or shogaol-related compounds have also been reported in ginger rhizome, such as [6]-paradol, [1]-dehydrogingerdione, [6]- and [10]-gingerdione, [4]-, [6]-, [8]-, and [10]-gingerdiol, and diarylheptanoids (*7*, *9*). However, these minor compounds account for only about 1−10% of the overall amount of gingerols and shogaols (*7*, *9*).

Although most animal studies with ginger extract showed antioxidative, anti-inflammatory, and antitumor activities, no study has considered that the instability of gingerols during thermal processing and long-term storage will affect the chemical profile of the ginger extract used in their animal studies (*10*, *11*). They either did not quantify the levels of the active components in their raw material or simply used the total levels of gingerols as the standard. Therefore, fast and accurate analytical methods are needed for the determination and quantification of the active components in ginger and its related products.

A high-performance liquid chromatography (HPLC) method with a single-channel electrochemical detector was developed and used to analyze the pungent principles of ginger 20 years ago (*12*). However, a single-channel electrochemical detector usually cannot provide a sufficient profile of analytes' responses under different potentials in the same run. A gas chromatographic−mass spectrometric (GC-MS) method has also been used to analyze gingerols in the ginger extracts (*13*). However, the instability of gingerols under high temperature limits the application of this method. An HPLC-UV-ESI (electrospray ionization)-MS method has been developed by He et al. for the identification of major components in ginger extracts (*14*), but the high-price instrumentation and tedious sample preparation apparently limit the application of this method for samples with complex matrices, such as biofluids and ginger-containing commercial products. An HPLC photodiode array (PDA) method was also reported to analyze gingerols and shogaols in commercial products recently (*15*). Although the PDA detector provides a "third dimension" to

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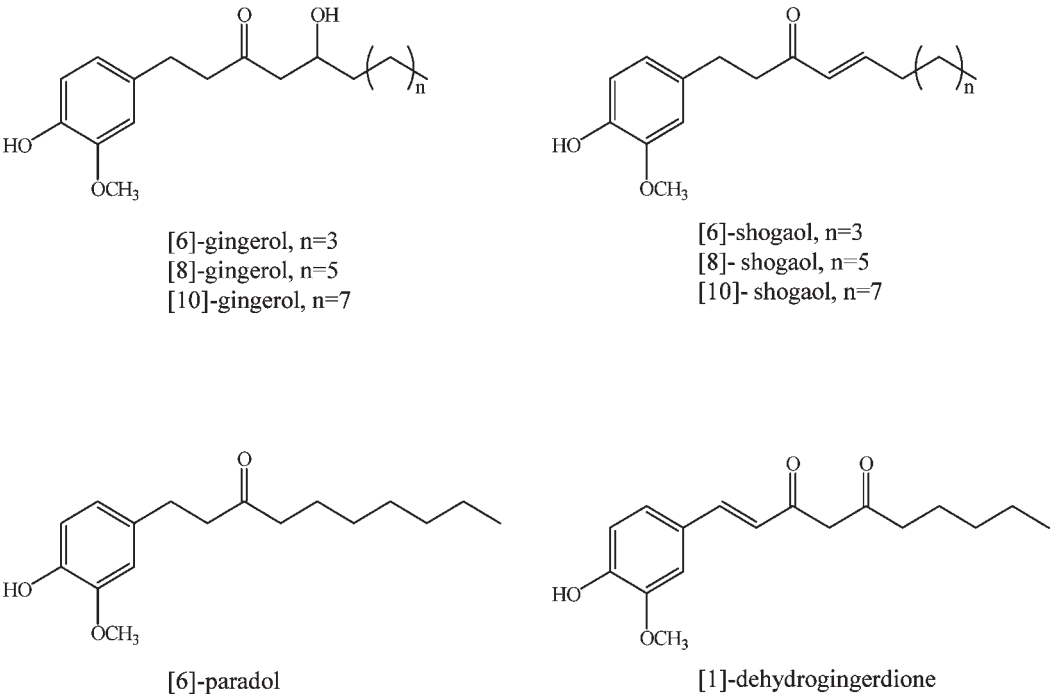

Figure 1. Chemical structures of [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione.

HPLC−absorbance techniques by examining an analyte's spectrum and identifying the compounds both by retention time and by spectral behavior, the low sensitivity and resolution limit the application of the PDA detector to a more complex sample matrix; coelution, misidentification, and quantification errors can still occur due to the inadequate sensitivity (*16*).

HPLC combined with an electrochemical array detector (ECD) offers several advantages over UV and MS detectors, especially the extraordinary sensitivity for redox sensitive compounds. Besides much higher sensitivity, a CoulArray ECD also offers online generation of qualitative data and the ability to resolve peaks due to different voltammetric characteristics. For gingerols and shogaols, the length of unbranched alkyl chains provides the polarity differences, and the hydroxyl groups offer differently sensitive voltammetric responses. Generally, frequent column maintenance and careful sample preparation are required during LC-MS analysis of biological substances. The clean cell activity using high electropotential in ECD cells after each run is another advantage of ECD compared to LC-MS, indicating the potential of applying this instrument to the analysis of biofluids and tissue samples. Clean cell activity is used to apply a high electropotential to the cells for a short period of time, to clean the electrode surfaces and prevent the contamination of later samples with previous samples. Due to this convenient function, frequent cleaning and maintenance are not needed. Several studies have proven the sensitivity, selectivity, and stability of HPLC-ECD in the analysis of biofluid samples, such as measuring the levels of tea polyphenols in human plasma, urine, and tissue samples (*17*−*19*).

In this study, we developed a very sensitive HPLC method coupled with electrochemical array detection for the quantitative analysis of [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione and quantified their levels in 11 different commercial ginger products.

MATERIALS AND METHODS

General. [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione standards were purified from ginger extract in our laboratory (*20*). In brief, the ginger standards were purified using different column chromatographies, and the structures of these eight compounds were confirmed on the basis of their ^{1}H and ^{13}C NMR analyses (*20*). Sodium phosphate, phosphoric acid, HPLC-grade methanol, acetonitrile, and tetrahydrofuran were obtained from Fisher Scientific (Fair Lawn, NJ). HPLC-grade water was prepared using a Millipore Milli-Q Academic purification system (Bedford, MA). All of the ginger-related products were purchased from local supermarkets.

Preparation of [6]-, [8]-, and [10]-Gingerol, [6]-, [8]-, and [10]-Shogaol, [6]-Paradol, and [1]-Dehydrogingerdione Standards. HPLC-grade methanol was added to each standard to produce a stock standard of 10 mg/mL and stored at −80 °C for future use. We found that all eight ginger standards are stable under −80 °C. Serial dilutions of the 10 mg/mL stock standards were prepared using methanol (100%) for calibration studies. Concentration ranges of each standard were determined to ensure that the calibration curve can cover the level of each component in all commercial products.

Sample Preparation of Ginger-Containing Commercial Products. The levels of [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione were determined in 11 ginger-containing commercial products from local supermarket including 3 crystal ginger beverages (manufactured in granule form), 5 ginger tea bags (tea bag with dried rhizome and tea leaves in it), and 3 ground ginger powders (dried ginger rhizome). Crystal ginger products were ground to fully mix, weighed, and placed into a 50 mL centrifuge tube. The fine powders of products were dissolved in the deionized water to make 10 mg/mL solutions. Then the solutions were filtered by nylon syringe filter (0.45 μm) obtained from Fisher Scientific (Fair Lawn, NJ) and diluted 10-fold with HPLC-grade methanol (100%) for further analysis. Three tea bags from each brand of product were mixed together. The mixed tea leaves and dried ginger rhizome in tea bags were then ground, weighed, and placed in 50 mL centrifuge tubes. The fine powders were extracted three times with methanol, each time for 24 h at room temperature. The final concentration was adjusted to 10 mg of ginger product powder/mL of methanol. Then the solutions were centrifuged at 17000*g* (accuSpin Micro, Fisher Scientific, PA) for 5 min at room temperature. The supernatant was further filtered by syringe filter and diluted 10-fold with HPLC-grade methanol for HPLC analysis. Ground ginger powder was directly weighed, placed in a 50 mL centrifuge tube, and extracted three times, 24 h each with methanol at room temperature. The final concentration was adjusted to 10 mg of ginger product powder/mL of methanol. The solutions were centrifuged, filtered, and diluted following the same procedure as for tea bags. Triplicate samples were prepared for all commercial products.

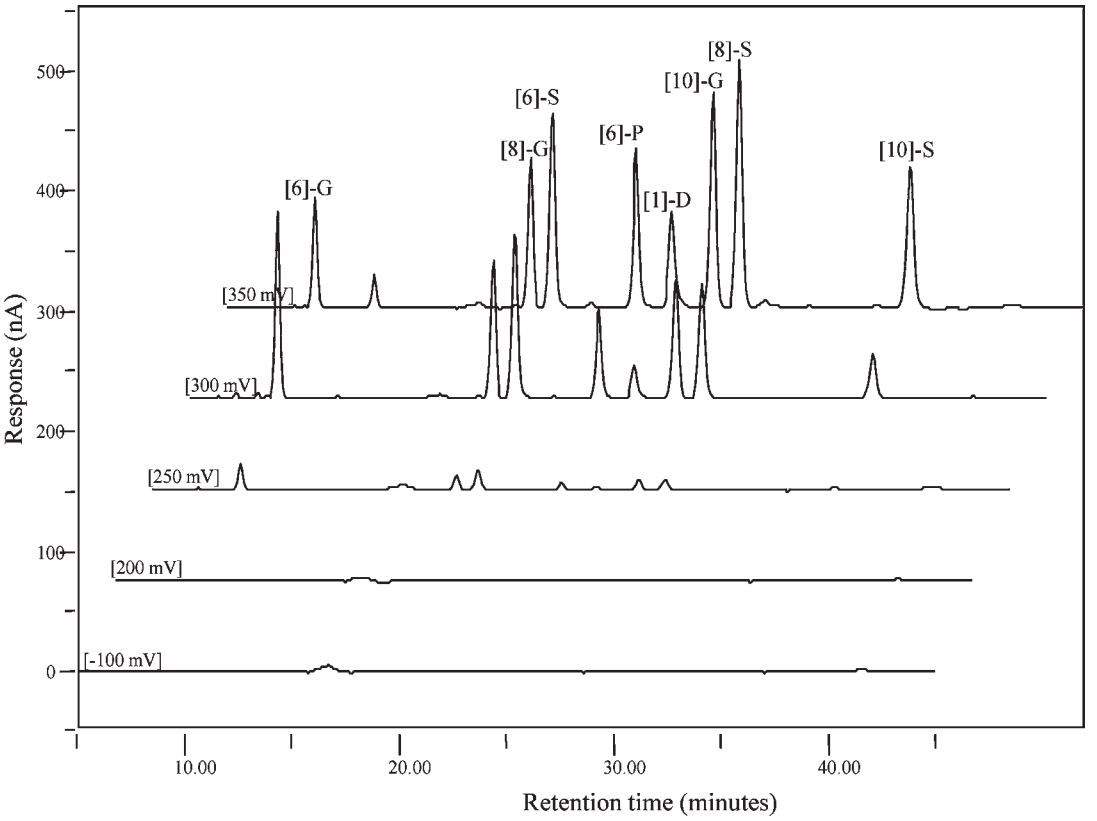

Figure 2. LC chromatograms of a mixed [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione standard (1 μg/mL) under different electrochemical potentials.

HPLC Analysis. An HPLC-ECD/UV system (ESA, Chelmsford, MA) consisting of an ESA model 584 HPLC pump, an ESA model 542 autosampler, an ESA organizer, an ESA coularray detector coupled with two ESA model 6210 four sensor cells, and an ESA 526 UV detector was used in our study. Chromatographic analysis was performed on a 150 mm × 4.6 mm, 5 μm, Supelcosil LC-18 column. The mobile phases consisted of solvent A (30 mM sodium phosphate buffer, pH 3.35) and solvent B (15 mM sodium phosphate buffer containing 58.5% acetonitrile and 12.5% tetrahydrofuran, pH 3.45). The gradient elution had the following profile: 50−55% B from 0 to 10 min; 55−60% B from 10 to 14 min; 60−65% B from 14 to 15 min; 65−100% B from 15 to 40 min; and then 50% B from 40.1 to 53 min with a flow rate of 1.0 mL/min. The cells were then cleaned at a potential of 1000 mV for 1 min. The injection volume of the sample was 10 μL. The peak identifications of all eight ginger components were based on the retention time of the standards and further confirmed by comparing their peak patterns under different voltammetric potentials to those of the individual standards.

Method Validation. This analytical method was validated by determining the linearity, limit of quantification (LOQ), limit of detection (LOD), recovery rate, and precision. The calibration curves were established individually for the eight ginger compounds using five different concentrations, and response linearity was assessed with standards diluted in 100% methanol using a least-squares regression analysis of peak area response versus concentration of the standards. The calibration curves of [6]-gingerol and [6]-shogaol were prepared in a range of 1.0−20.0 μg/mL and 1.0−5.0 μg/mL, respectively, in triplicate. The calibration curves for [8]-gingerol, [10]-gingerol, and [10]-shogaol were determined using five dilutions by methanol in the range of 0.1−3.0 μg/mL, in triplicate. The calibration curves for [8]-shogaol, [6]-paradol, and [1]-dehydrogingerdione were established using five dilutions by methanol in the range of 0.1−1.0 μg/mL, in triplicate. The linearity was evaluated in the most sensitive channel for each standard: the peak area of [6]-gingerol was determined on channel 4 with 300 mV of cell potential and the peak areas of [8]- and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione were obtained on channel 5 with 350 mV of cell potential. The intraday variations of [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione with a concentration of 1.0 μg/mL were measured using their dominant channels. The interday variations were determined by comparing the results obtained on three different days. Triplicate injections were performed to test both intraday and interday variations of each sample. LOD and LOQ were estimated using signal-to-noise ratios of 3:1 and 10:1, respectively. Recovery for each compound was calculated by the amounts obtained from the first two extractions and then divided by the total amounts obtained from all three extractions.

RESULTS AND DISCUSSION

Optimization of the Chromatographic Conditions. The mobile phase used for HPLC with an EC detector should meet several important criteria. The EC detector requires a stable level of electrolyte within a suitable range in the mobile phases. The level of electroactive impurities and noise may be promoted if the level of electrolyte is too high. However, a drifting baseline and poor signal for the analyte can occur if the mobile phase electrolyte concentration is too low. Under these circumstances, any pH changes due to the sample can then influence the signal from the analyte. To prevent those influences caused by pH changes and to provide greater stability for both the chromatographic and electrochemical reactions, buffered systems are usually used. In our study, 30 and 15 mM, respectively, sodium phosphate was added to mobile phase A and B to serve these purposes. The concentrations of sodium phosphate for both mobile phases A and B used in this study were directly adopted from previous laboratory protocol for the analysis of tea polyphenols in biological samples (*21*). Phosphate salt was chosen due to the low background current at high electrode potentials.

Once the chromatographic conditions have been optimized, a potential is usually chosen on the basis of experience or literature. For unknown compounds, a hydrodynamic voltammogram

(HDV) consisting of applied potential (mV) versus normalized response was used to determine the applied potential: it is usually best to start at −100 mV and then increment by +100 mV. This "rough" HDV can then be refined using smaller incremental potentials (typically 25 or 50 mV increments). Most HDVs generated by ESA application chemists are at the 50 mV resolution; this is an excellent compromise between time taken to generate the HDV and EC resolution.

Table 1. Linearity of Eight Ginger Standards

	concn range (μg/mL)	linear regression eq	r^2
[6]-gingerol	1.0−20.0	$y = 2.7084x + 1.7942$	0.9868
[8]-gingerol	0.1−3.0	$y = 3.2288x + 0.0477$	0.9988
[10]-gingerol	0.1−3.0	$y = 3.3596x + 0.1895$	0.9985
[6]-shogaol	1.0−5.0	$y = 3.8596x + 0.3068$	0.9977
[8]-shogaol	0.1−1.0	$y = 4.1659x + 0.0166$	0.9951
[10]-shogaol	0.1−3.0	$y = 1.8994x + 0.0786$	0.9990
[6]-paradol	0.1−1.0	$y = 3.1967x - 0.0199$	0.9964
[1]-dehydrogingerdione	0.1−1.0	$y = 1.7756x - 0.0116$	0.9923

Table 2. Validation Parameters for the HPLC-ECD Method

	interday variation (% RSD) (n = 3)	intraday variation (% RSD) (n = 3)	LOD (pg)	LOQ (pg)
[6]-G (300 mV)	6.87 ± 2.47	6.52 ± 0.85	8.3	16.6
[8]-G (350 mV)	5.76 ± 2.57	1.23 ± 0.10	9.6	19.1
[10]-G (350 mV)	5.54 ± 2.04	5.15 ± 0.33	7.3	14.5
[6]-S (350 mV)	4.68 ± 2.59	1.41 ± 0.19	11.3	22.6
[8]-S (350 mV)	4.32 ± 2.64	6.61 ± 0.53	20.2	40.4
[10]-S (350 mV)	4.57 ± 3.02	11.2 ± 0.53	8.6	17.2
[6]-P (350 mV)	4.83 ± 2.84	5.85 ± 0.44	17.8	35.5
1-D (350 mV)	9.27 ± 0.75	9.61 ± 0.73	8.5	17.1

The choice of the potential in this study was established by plotting the current values measured at different applied potentials after the injection of 10 μL aliquots of 1 μg/mL of eight ginger standards mixture solution (**Figure 2**). The testing potential starts at −100 mV to reduce all of the possible impurities, thereby decreasing the interference of chromatography background, with 50 mV as the incremental potential until 400 mV. On the basis of the chromatogram profile shown in **Figure 2**, maximum currents of 300 mV for [6]-gingerol and 350 mV for [8]- and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione were observed. The responses of those eight compounds at 400 mV were very low (data not shown). The peak area ratios at 300 vs 350 mV for each compound were calculated. By comparing the ratios of gingerols and shagaols side by side ([6]-G vs [6]-S, 1.72 vs 0.87; [8]-G vs [8]-S, 0.95 vs 0.48; and [10]-G vs [10]-S, 0.57 vs 0.30), we found that gingerols were more easily oxidized under lower potential (300 mV), which could be due to the additional hydroxyl group on the side chain compared to shogaols. Also, the ratios of peak area at 300 and 350 mV for both gingerols and shogaols decreased when the side-chain length increased, indicating that the length of the side chain was related to the oxidation efficacy under potential charge.

Method Development and Validation. On the basis of the developed analytical method, the calibration curves for the eight ginger standards have been established as shown in **Table 1**. As described under Materials and Methods, all standards were prepared in a range to cover the concentration of correlated compounds in commercial samples. Regression analysis performed by the least-squares method yielded the standard curve equations and correlation coefficients (**Table 1**).

Linearity data obtained from diluted standards are shown in **Table 1**. The slope obtained from least-squares regression analysis indicates high sensitivity (μC/μg) for all analytes. On the basis of a

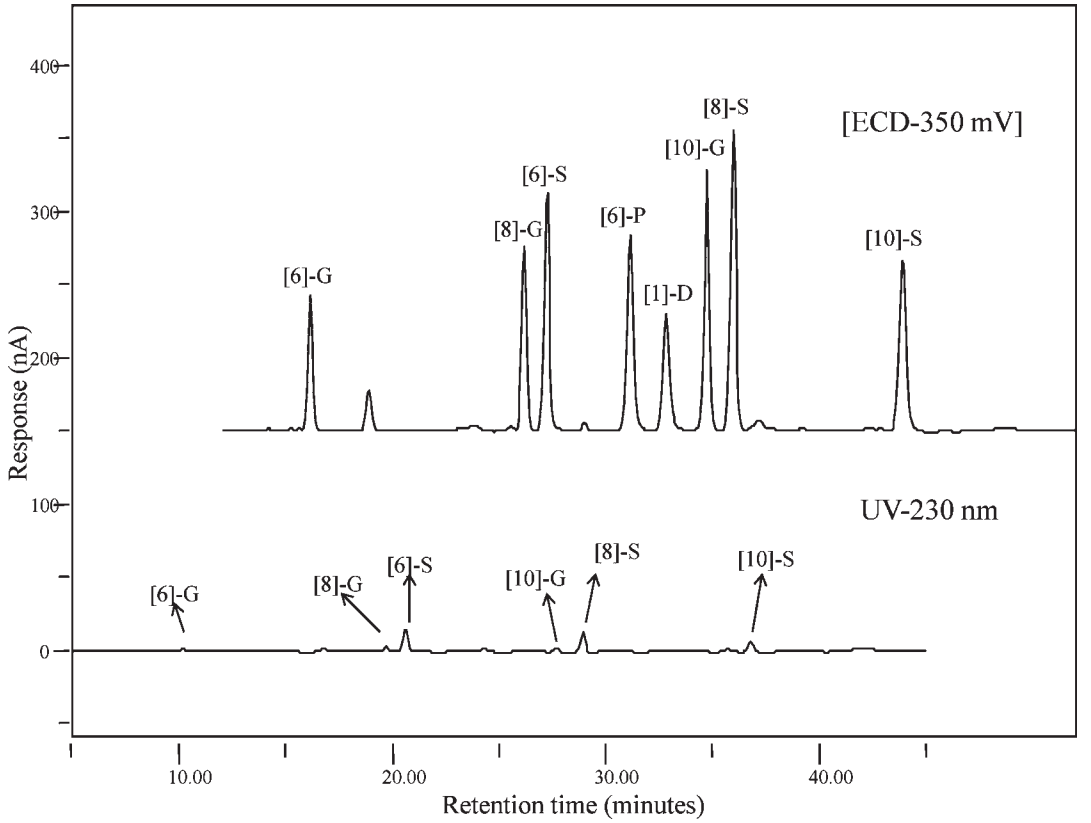

Figure 3. LC chromatograms of a mixed [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione standard (1 μg/mL) obtained by electrochemical (350 mV) and UV detection (230 nm).

signal-to-noise ratio of 3:1, the LODs for the eight standard compounds were approximately from 7.3 to 20.2 pg (**Table 2**). The LOWs were calculated on the basis of a signal-to-noise ratio of 10:1 with a range of 14.5−40.4 pg for all analytes (**Table 2**). These results are 620−1725-fold lower than the previously published HPLC-UV method at 25 ng, indicating the potential of applying our method to the analysis of biofluids and tissue samples (*15*). For replicate injections of mixture standards, intraday response coefficients of variation ranged from 1.23 to 11.2% for all analytes as shown in **Table 2**. The interday coefficients of variation were also determined by comparing the results obtained on three different days and ranged from 4.32 to 9.27%.

To compare the sensitivity of our method to the ordinary UV analysis, 10 μL of mixed standard solution with a concentration of 1 μg/mL was analyzed by both the UV and EC detectors in the same run. The UV channel was selected at 230 nm as a specific wavelength for detection of gingerols and shogaols on the basis of reference data obtained by He et al. (*14*). As **Figure 3** shows, all eight standards showed much better responses at 350 mV than at 230 nm, indicating that the ECD performed with extraordinary sensitivity compared to the traditional UV detector. The peak areas of all eight ginger standards measured by ECD were 1.31, 2.12, 3.35, 3.06, 4.01, 2.67, 2.66, and 1.76 μC for [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione, respectively. The peak areas measured by UV detector for all eight ginger standards in the same order as listed above were 0.0323, 0.0418, 0.223, 0.0379, 0.0107, 0.045, 0.197, and 0.112 μC, respectively.

Table 3. Recovery Percentages and Relative Standard Deviations of Eight Ginger Components

	% recovery	% RSD (n = 3)
[6]-gingerol	96.93	4.20
[8]-gingerol	97.86	2.52
[10]-gingerol	97.92	3.10
[6]-shogaol	97.52	2.32
[8]-shogaol	97.01	2.86
[10]-shogaol	97.10	2.77
[6]-paradol	98.82	1.48
[1]-dehydrogingerdione	99.40	0.66

In our previous study, the detector response of the tea polyphenol peaks was found to be associated with the percentage of organic solvent in the samples (*21*). In this study, we compared the electrochemical response of eight ginger standards in different solvent systems. Five mixed standards were prepared by combining the eight ginger standards (100 ng/mL) in water, 20, 40, 60, and 80% aqueous methanol, respectively, and 100% methanol. The chromatograms shown in **Figure 4** clearly demonstrate how the solvent affected the ECD's sensitivity of our standards. By comparison of the peak areas of each compound at the 350 mV channel, the sensitivities of [6]-gingerol, [8]-gingerol, [6]-shogaol and [6]-paradol were discovered to be almost 2-, 15-, 5-, and 13-fold higher in methanol (100%) than in water (100%). Also, the detections of [1]-dehydrogingerdione, [10]-gingerol, [8]-shogaol, and [10]-shogaol were 7, 12, 5, and 11 times more sensitive in methanol (100%) than in methanol/water (20/80%). (Those compounds are not detectable in water.) On the basis of the above conclusions, we prepared all of the samples using 100% methanol.

Analysis of Commercial Products. The recovery of each ginger component using our extraction method is shown in **Table 3**. The chromatograms of ginger-containing commercial products are presented in **Figure 5**. **Figure 5A** represents commercial products in three different forms (ground ginger powder, ginger tea leaf,

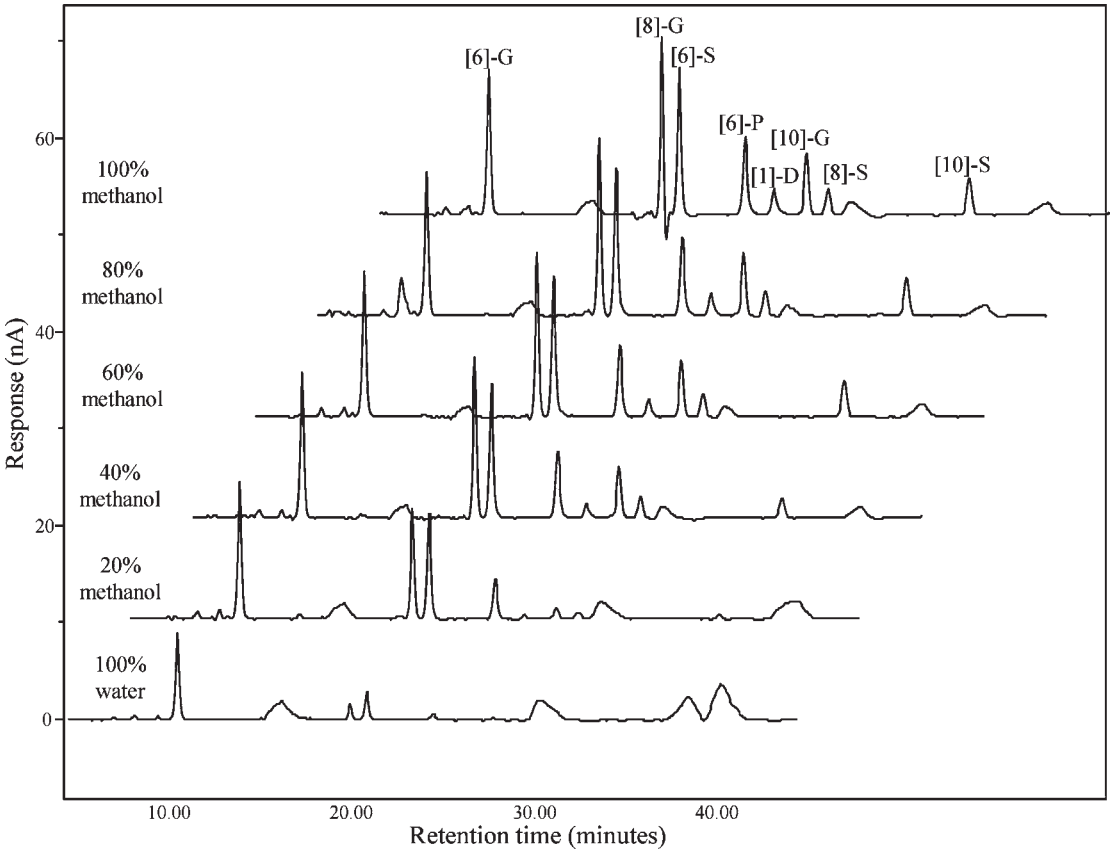

Figure 4. LC chromatograms of a mixed [6]-, [8]-, and [10]-gingerol, [6]-, [8]-, and [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione standard (100 ng/mL) dissolved in different solvent systems.

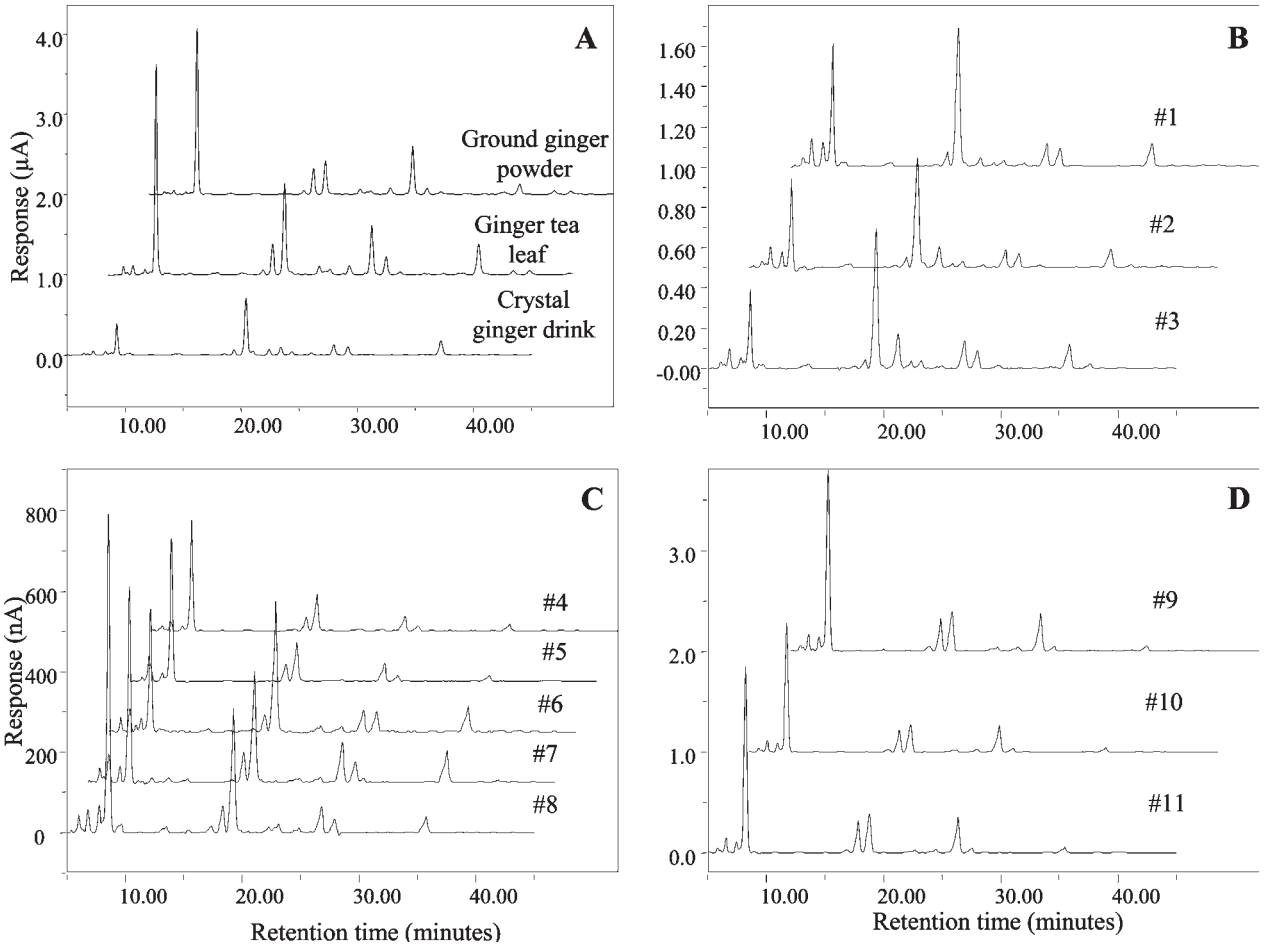

Figure 5. LC chromatograms of ginger-related commercial products: (**A**) selected ground ginger powder, ginger tea leaf, and crystal ginger drink; (**B**) three crystal ginger drink samples (samples 1−3); (**C**) five ginger tea leaf samples (samples 4−8); (**D**) three ground ginger powder samples (samples 9−11).

Table 4. Concentrations of [6]-, [8]-, and [10]-Gingerol, [6]-, [8]-, and [10]-Shogaol, [6]-Paradol, and [1]-Dehydrogingerdione in 11 Commercially Available Ginger Products: Ginger Crystal Drink (Samples 1−3), Ginger Tea Leaf (Samples 4−8), and Ground Ginger Powder (Samples 9−11)

	concn (mg/100 g of product)							
sample	[6]-gingerol	[8]-gingerol	[10]-gingerol	[6]-shogaol	[8]-shogaol	[10]-shogaol	[6]-paradol	[1]-dehydrogingerdione
1	11.58 ± 0.39	1.52 ± 0.10	2.78 ± 0.07	16.23 ± 0.07	1.90 ± 0.01	6.09 ± 0.17	0.80 ± 0.18	0.58 ± 0.03
2	15.70 ± 0.30	1.92 ± 0.11	3.42 ± 0.38	19.68 ± 1.13	2.50 ± 0.27	7.12 ± 1.08	0.21 ± 0.07	0.59 ± 0.16
3	9.74 ± 0.24	1.29 ± 0.05	4.66 ± 0.22	20.07 ± 0.34	2.52 ± 0.10	7.76 ± 0.41	0.90 ± 0.09	0.30 ± 0.01
4	60.87 ± 7.02	9.32 ± 0.30	10.22 ± 1.44	25.75 ± 2.51	0.74 ± 0.10	10.33 ± 1.70	nd[a]	nd
5	123.07 ± 10.47	17.75 ± 1.92	17.94 ± 1.00	35.08 ± 2.12	1.70 ± 0.10	11.24 ± 0.93	nd	nd
6	78.59 ± 8.73	14.87 ± 1.04	18.90 ± 2.36	111.64 ± 12.34	16.21 ± 0.96	51.90 ± 7.34	0.19 ± 0.02	4.48 ± 0.87
7	148.34 ± 18.76	27.45 ± 3.85	38.13 ± 5.27	96.54 ± 9.58	16.30 ± 1.86	65.37 ± 8.11	nd	2.90 ± 0.54
8	277.51 ± 25.60	24.15 ± 2.82	23.44 ± 2.14	111.00 ± 8.66	8.72 ± 0.43	31.13 ± 2.38	4.73 ± 1.27	6.89 ± 7.10
9	767.40 ± 14.78	131.29 ± 3.04	157.38 ± 7.47	145.62 ± 2.71	11.56 ± 2.36	47.22 ± 4.15	4.85 ± 0.11	19.42 ± 8.70
10	554.87 ± 49.77	104.37 ± 11.34	136.54 ± 15.29	115.67 ± 13.76	8.58 ± 1.71	41.02 ± 4.54	2.95 ± 0.67	15.36 ± 1.41
11	772.33 ± 47.74	140.04 ± 10.00	173.40 ± 11.78	149.54 ± 8.47	10.91 ± 1.52	45.58 ± 7.52	6.56 ± 2.34	nd

[a] nd, not detected.

and ginger crystal); panels **B**, **C**, and **D** of **Figure 5** represent three crystal products, five tea leaf products, and three ground ginger powder products, respectively. All ginger products have such high levels of [6]-, [8]-, and [10]-gingerol and [6]-, [8]-, and [10]-shogaol that they are easily detected by the CoulArray ECD. The detailed levels of the 8 ginger components in the 11 commercial products are listed in **Table 4**. The [6]-gingerol concentration in different ginger products was found to be higher than that of [8]- or [10]-gingerol concentration, but not always higher than that of [6]-shogaol, especially in crystallized products. For instance, the concentrations of [6]-shogaol were around 1.25−2.06 times higher than those of [6]-gingerol in all three crystal products. Possible reasons may be granulation, drying, or the crystallization process in which generated heat caused conversion from gingerols to shogaols (*22*). The concentration of all eight components in the different commercial products varied greatly. For instance, the levels of [6]-gingerol in ground powder are almost 35−80 times higher than those in crystallized products. Meanwhile, the level of each component varies a lot even in the same type of product. For example, the concentration of [6]-gingerol in sample 4 is almost 4.5 times higher than the concentration in sample 8. Similarly, the level of [6]-shogaol in sample 8 is much lower than

in the sample 4. The levels of both [6]-paradol and [1]-dehydrogingerdione are significantly lower than those of the other six components in all commercial products, even too low to be detected in certain products, mostly in ginger tea products.

In conclusion, a new HPLC-ECD array method has been developed allowing for the determination and quantification of 8 ginger components, [6]-, [8]-, [10]-gingerol, [6]-, [8]-, [10]-shogaol, [6]-paradol, and [1]-dehydrogingerdione, in 11 commercial products with higher accuracy than previously reported. The method resulted in clearly increased chromatographic separation as well as higher detection sensitivity compared to traditional UV detection. The peak areas detected by ECD were around 19−120 times higher than those detected by UV in the same run. Very low LODs and LOQs at the picogram level were obtained, enabling the detection of the eight ginger components from complex commercial samples, indicating the potential of applying this method to analyze ginger components and their metabolites in biofluids collected in future animal and human studies.

It has been reported that gingerols are the major pungent components in fresh ginger and that they are not stable during storage or thermal processing as they generate the dehydration products, shogaols, which are predominant pungent constituents in the ginger oleoresin from dried ginger (*7*, *8*). This is the potential reason that the levels of gingerols and shogaols in commercial ginger products vary significantly. Therefore, it is important to standardize ginger products used in in vivo study using both gingerols and shogaols as marker compounds.

ABBREVIATIONS USED

ECD, electrochemical detection; [6]-G, [6]-gingerol; [8]-G, [8]-gingerol; [10]-G, [10]-gingerol; [6]-S, [6]-shogaol; [8]-S, [8]-shogaol; [10]-S, [10]-shogaol; [6]-P, [6]-paradol; [1]-D, [1]-dehydrogingerdione.

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