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Differentiation of the Four Major Species of Cinnamons (*C. burmannii*, *C. verum*, *C. cassia*, and *C. loureiroi*) Using a Flow Injection Mass Spectrometric (FIMS) Fingerprinting Method

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Supporting Information

ABSTRACT: A simple and efficient flow injection mass spectrometric (FIMS) method was developed to differentiate cinnamon (*Cinnamomum*) bark (CB) samples of the four major species (*C. burmannii*, *C. verum*, *C. aromaticum*, and *C. loureiroi*) of cinnamon. Fifty cinnamon samples collected from China, Vietnam, Indonesia, and Sri Lanka were studied using the developed FIMS fingerprinting method. The FIMS fingerprints of the cinnamon samples were analyzed using principal component analysis (PCA). The FIMS technique required only 1 min of analysis time per sample. The representative samples from each of the four major species of cinnamon were further examined using an ultrahigh-performance liquid chromatography–high-resolution mass spectrometry system, and the chemical differences between the four species were profiled. The results showed that the 1 min FIMS fingerprinting method successfully differentiated the four cinnamon species studied.

KEYWORDS: *cinnamon, mass spectrometer, fingerprinting, PCA*

INTRODUCTION

Cinnamon is one of the oldest known spices. The names "cinnamon" and "cassia" cause considerable confusion, as they are often used interchangeably in the United States. There are four main economically important species of cinnamon in the genus *Cinnamomum*. The first one is *Cinnamomum verum*, translation "true cinnamon". It is also called Sri Lankan or Ceylon cinnamon. Sri Lanka is the only regular supplier of true cinnamon bark and leaf oils. *C. verum*'s older botanical name,*Cinnamomum zeylanicum*, is derived from Sri Lanka's older name, Ceylon. The other three main species of cinnamon are *Cinnamomum cassia* (*C. aromaticaum*, also called Chinese cinnamon), *Cinnamomum burmannii* (also called Korintje, Java, or Indonesian cinnamon), and *Cinnamomum loureiroi* (also known as Vietnamese or Saigon cinnamon). In addition to these four species of common and economically valuable cinnamons, there are many other noncommercial or lesser known cinnamons used in local trade as a spice or an ingredient in medicinal preparations.[1]

The dried inner bark of the cinnamon plant has been used as a flavoring agent in foods, beverages, chewing gums, etc. *C. verum*'s flavor is often considered to be the most delicate and complex of the major species of cinnamons. For example, the special flavor of English and Mexican sweets comes from *C. verum*. *C. cassia* and *C. loureiroi* cinnamons have a strong, spicy-sweet flavor and aroma to which most Americans are accustomed. The characteristic flavor and aroma of cinnamon come from its aromatic essential oils. The strength of the flavor of cinnamon is often dependent upon the essential oil content: the higher the level, the stronger the flavor. *C. loureiroi* is usually considered stronger in flavor and routinely has high cinnamaldehyde and volatile oil contents. *C. burmannii*, although high in cinnamaldehyde, has a smoother taste with less bite than *C. cassia* and *C. loureiroi*.

Cinnamon and its extract, irrespective of the species, have been associated with a variety of beneficial health effects. In traditional medicine, cinnamon bark is reportedly used for the treatment of a wide range of conditions, including digestive disorders, diabetes, and respiratory tract infections. Over the past 20 years, cinnamon has been found to have potential antioxidant activity[2,3] and antimicrobial activity[4,5] and to play a role in glucose and lipid control.[6−11] Proanthocyanidins are believed to have potential health benefits due to their antioxidant activity.[12] Proanthocyanidins are various length polymers of flavanols (catechins and their ent-isomers) linked through a single C4→C8 or C4→C6 bond (B-type) or with an additional C2→O→C7 or C2→O→C5 bond (A-type). There are two main varieties of procyanidin oligomers that occur in plants. These can be distinguished from each other by mass spectrometric analysis. For example, the A-type procyanidin trimers and tetramers have molecular masses of 864 and 1152 Da, whereas the comparable B-type procyanidin trimers and tetramers have molecular masses of 866 and 1154 Da, respectively.[13]

The flow injection mass spectrometric (FIMS) fingerprinting technique combined with chemometric data analysis can be used to profile phytochemicals and discriminate between

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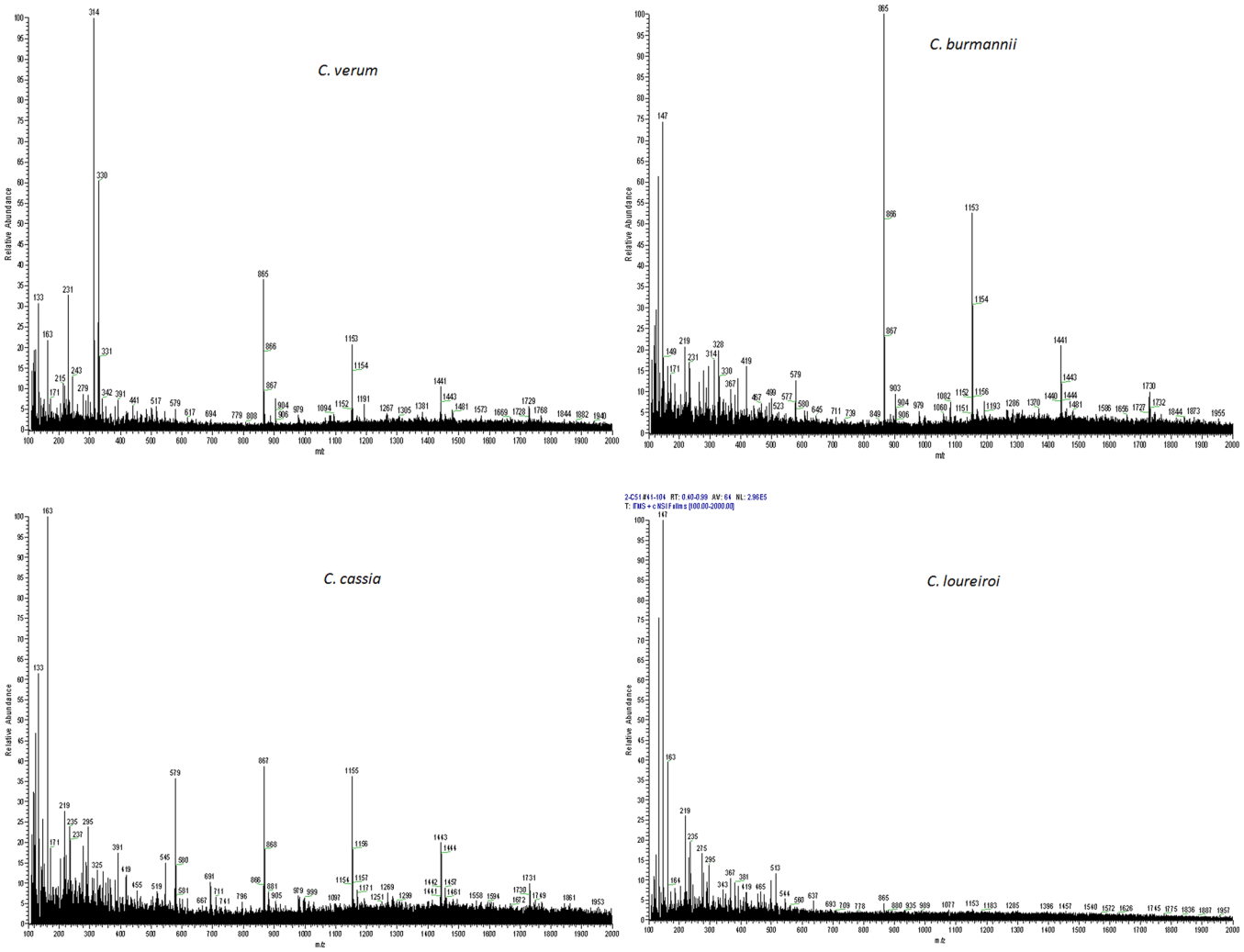

Figure 1. Typical FIMS spectra of the four species of cinnamon.

botanical materials and, consequently, place the technique on a sound statistical base. The patterns of the FIMS fingerprints (spectra with no prior separation) have been successfully used to distinguish plant genera, species, and even farming methods.[14−17] Use of the FIMS fingerprints and principal component analysis (PCA) or analysis of variance (ANOVA) prevents undue reliance on one or two marker compounds, increases the robustness of the analysis, and provides for both visual display and statistical evaluation of the data. Another advantage of the method is the fast method development time (hours) and analysis time (1 min) compared to traditional liquid chromatography−mass spectrometry (LC-MS), which can take days to weeks for method development and up to 1 h or longer for sample analysis of various natural products. A shortcoming of the FIMS technique is that it may not provide all of the information available through a full LC-MS analysis. Therefore, the combination of using both the FIMS fingerprinting technique and LC-MS on selected samples (determined by FIMS) will often be the best approach.

EXPERIMENTAL PROCEDURES

Materials. Fifty authentic cinnamon samples (3 *C. verum*, CV; 2 *C. cassia*, CC; 40 *C. burmannii*, CB; and 5 *C. loureiroi*, CL) and 3 unknown cinnamon samples (CU) were obtained from the library of McCormick & Co., Inc. (Sparks, MD, USA). At the time of the study, cinnamon, typically in the form of bark or chips, was ethylene oxide (ETO) treated and dried if necessary to constant moisture (typically 10−14%) and stored. The samples (collected in 2009−2011) were sourced and vetted through the company's global sourcing division, and the identity of each sample was confirmed by McCormick's internal chemotaxonomic methods. Samples were ground in a Schutte Hammermill (model 24-15-301) or a Brinkman Restch ZM-1 centrifugal mill and passed through a 20 mesh sieve. The ground samples were stored at room temperature in sealed glass jars until use. An additional test cinnamon sample (label claim CL) was purchased in a local supermarket in Maryland.

Water, acetonitrile, and methanol were of Optima grade (Fisher Scientific, Pittsburgh, PA, USA). Formic acid was of mass spectrometry grade (Sigma-Aldrich, St. Louis, MO, USA).

Sample Preparation. All samples were first passed through a 20 mesh sieve. Next, 10 mg of each dried ground sample was mixed with 5 mL of methanol/water (6:4 by volume) in a 15 mL centrifuge tube. All samples were sonicated for 20 min at room temperature. The sample extract was centrifuged at 5000*g* for 15 min (IEC Clinical Centrifuge, Danon/IEC Division, Needham Heights, MA, USA). The supernatant was filtered through a 17 mm (0.45 μm) PVDF syringe filter (VWR Scientific, Seattle, WA, USA). The cinnamon samples were labeled CV01−CV04 for *C. verum*, CC01 and CC02 for *C. cassia*, CB01−CB 40 for *C. burmannii*, CL01−CL05 for *C. loureiroi*, and CU01−04 for unknown and test cinnamon samples.

To avoid errors arising from unexpected degradation of some phenolic compounds, the sample analysis was completed within 24 h of the extraction. The injection volume for all samples was 5 μL. Each

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sample was analyzed three times for the FIMS experiment. Representative samples from each species were analyzed one time for the UHPLC-HRMS experiment. Samples were run in randomized order.

Flow Injection Mass Spectrometry. The FIMS system consisted of a LCQ DecaXP ion-trap mass spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) with an Agilent 1200 HPLC system (a quaternary pump with a vacuum degasser, a thermostated column compartment, an autosampler, and a diode array detector (DAD) (Agilent Technologies, Palo Alto, CA, USA). The flow injection was passed through a guard column (Adsorbosphere All-Guard Cartridge, C18, 5 μm, 4.6 × 7.5 mm, Alltech Associates, Inc., Deerfield, IL, USA) to minimize potential contamination for the MS system. Mobile phases consisted of 0.1% formic acid in H_2O (A) and 0.1% formic acid in acetonitrile (B) with isocratic elution at 60:40 (v/v) at a flow rate of 0.5 mL/min for 1.5 min. Electrospray ionization (ESI) was performed in positive ion mode from m/z 100 to 2000 to obtain the FIMS fingerprints. The acquisition mode was centroid. The following conditions were used for the DecaXP mass spectrometer: sheath gas flow rate, 80 (arbitrary units); auxiliary gas flow rate, 10 (arbitrary units); spray voltage, 4.50 kV; heated capillary temperature, 220 °C; capillary voltage, 4.0 V; tube lens offset, 25 V. Spectra were summed from 0.4 to 1.0 min interval required for the sample bolus to enter the MS. Three repeat analyses of the 54 different samples provided 162 spectra.

Data Processing for FIMS Fingerprint. The mass spectrum for each sample consisted of a one-dimensional matrix (ion counts versus mass for m/z 100−2000). The spectra were exported to Excel (Microsoft, Inc., Belleview, WA, USA) from Xcalibur for data preprocessing and then to SOLO (eigenvector Research, Inc., Wenatchee, WA, USA) for PCA. The preprocessing in Microsoft Excel involved combining the 162 spectra, sorting the data by sample names, deleting unnecessary and redundant information (headers, sample information, instrument information, etc.), and aligning the masses (each spectrum was a different length because not all masses appeared in each spectra) using a MS Excel macro written in house. The resulting two-dimensional 162 × 1901 matrix (162 samples versus 1901 masses) was then exported to SOLO for PCA. Preprocessing in SOLO, prior to PCA, consisted of normalization (sum of squares of the counts for a spectra was set to 1) and mean centering.

Ultrahigh-Performance Liquid Chromatography−High-Resolution Mass Spectrometry (UHPLC-HRMS). The UHPLC-HRMS system consists of a Thermo LTQ Orbitrap XL mass spectrometer with an Accela 1250 binary pump, a PAL-HTC-Accela1 autosampler, an Accela 1250 PDA detector, and an Agilent column compartment (G1316A). The separation was carried out on a Thermo Hypersil Gold C18 column (200 μm × 2.1 mm, 1.9 μm) with a flow rate of 0.35 mL/min. The column heater was kept at 50 °C. Mobile phase A consisted of 0.1% formic acid in water, and mobile phase B consisted of 0.1% formic acid in acetonitrile. The elution gradient ranged from 10 to 25% mobile phase B over 0−7 min, from 25 to 40% B over 7−10 min, from 40 to 95% B over 10−12 min, and was held at 95% B for an additional 6 min with subsequent return to initial conditions. Electrospray ionization (ESI) was performed in the positive ion mode to obtain the HRMS data. The HRMS conditions were as follows: sheath gas, 70 arbitrary units; auxiliary and sweep gas, 15 arbitrary units; spray voltage, 4.0 kV; capillary temperature, 300 °C; capillary voltage, 15 V; and tube lens offset voltage, −70 V. The mass range was from m/z 100 to 2000 with a resolution of 15000, isolation width of 1.5 amu, and maximum ion injection time of 500 ms. The most intense ion was selected for the data-dependent scan with a normalization collision energy at 35%.

RESULTS AND DISCUSSION

FIMS Fingerprints of the Cinnamon Samples. The first goal of this study was to differentiate the four different species of cinnamon samples without chromatography. No analytical column was used, only a C_{18} reverse-phase guard column as an online filter to protect the MS. The FIMS fingerprint for each sample was obtained as the average of all spectra between 0.4 and 1.0 min. Typical FIMS fingerprints of the four species of cinnamon samples are shown in Figure 1. The differences among the four species of cinnamon are quite obvious visually even though no chromatographic separation was performed. The most notable ions for CV are at m/z 314, 330, 865, and 1153; those for CB are at m/z 133, 147, 865, and 1153; those for CC are at m/z 163, 579, 867, and 1155; and those for CL are at m/z 133, 147, and 163. Some observations from inspection of the spectra are as follows: (1) the ions at m/z 314 and 320 dominate the CV spectrum; (2) the ions at m/z 147 and 865 dominate the CB spectrum; (3) the ion at m/z 163 dominates the CC spectrum; and (4) the CL spectrum has relatively low ion counts for the high atomic mass unit molecular ions.

PCA of the FIMS Fingerprints. The advantage of using PCA to process the MS fingerprints is automation and simplification. It is easy to visually compare the mass spectra of a few samples, but the comparison of hundreds of samples quickly overwhelms our ability to discriminate useful patterns. PCA provides visual patterns that are math-based but still aesthetically and statistically useful, avoiding subjective interpretations of the data.

The PCA score plot showed the 54 cinnamon samples in four different groups (Figure 2). The three CV samples (in triplicate) did not cluster very tightly, occupying a larger area from the right to the middle of the plot, but were still separated from the other groups. The PCA score plot also successfully categorized the unknown samples. For example, three samples were categorized as *C. cassia* (CC) and the remaining sample was identified as *C. loureiroi* (CL), confirming the label claim.

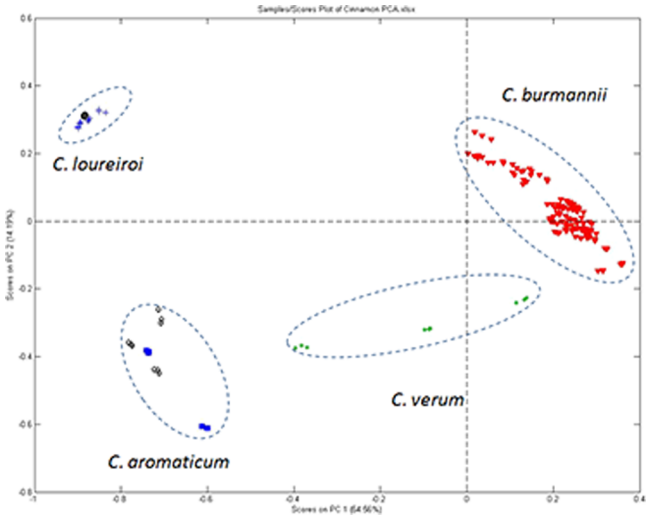

Figure 2. PCA score plot (for FIMS fingerprints) of the four species of cinnamon (▽, CB; ∗, CV; ■, CC; +, CL; ◇, unknown from McCormick; ●, unknown commercial, labeled CL).

PCA Loadings and UHPLC-HRMS Studies. The loading plot of a variable on a PCA reflects how much each of the variables contributed to that PC. The PC1 loading plot of the samples is shown in Figure 3. The plot indicates samples with higher ion counts at m/z 865, 903, 1154, and 1442 would yield a higher PC1 score, leading to positions toward the right of the PCA score plot. The important ions contributing to negative PC1 scores were m/z 133, 147, 275, 381, 465, and 513. This suggests the high molecular weight ions (m/z 865, 904, 1192,

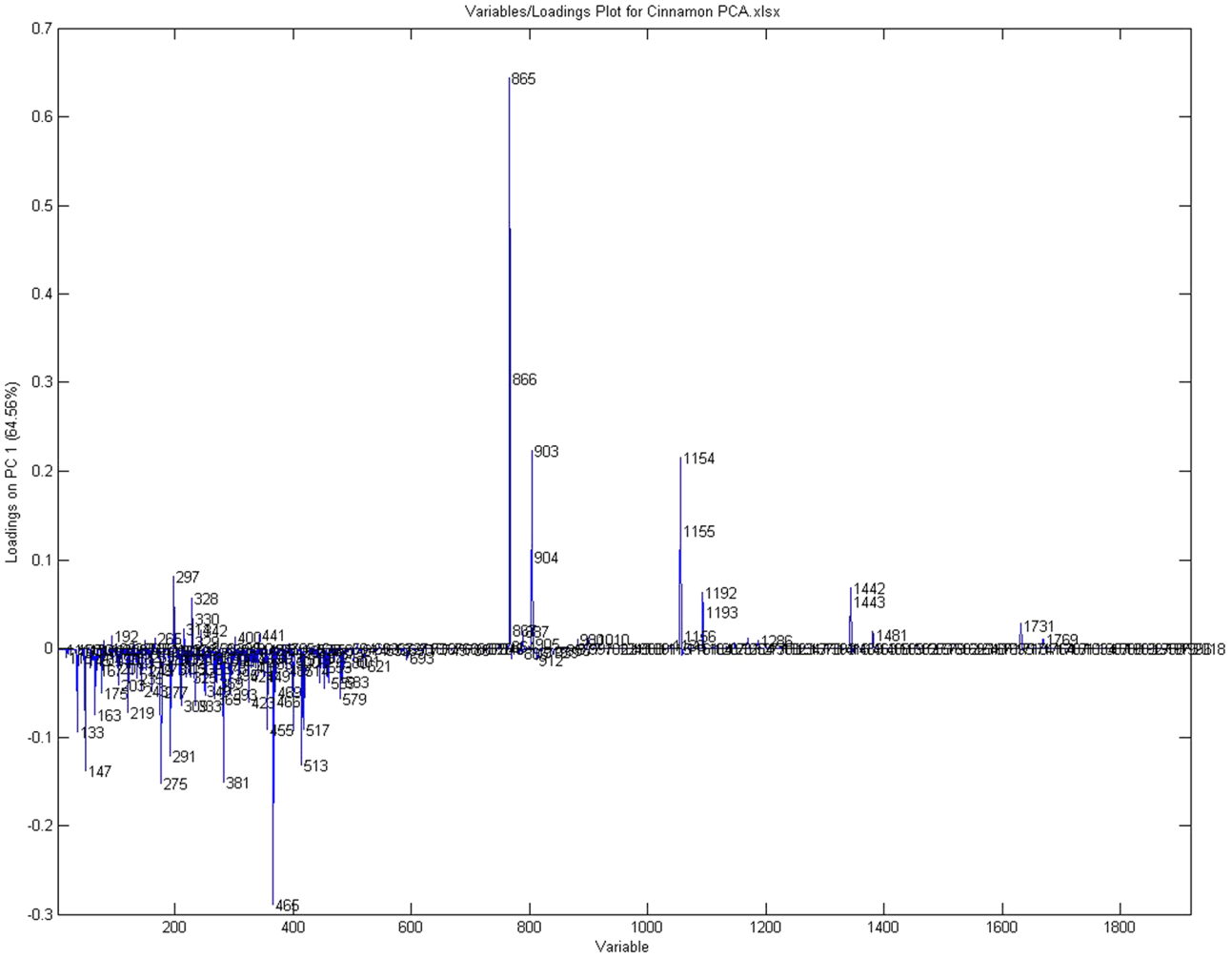

Figure 3. PCA loading plot of PC1 for FIMS fingerprints.

and 1442) tend to position the samples to the right of the PCA score plot, whereas the low molecular weight ions shifted sample positions more to the left side of the plots.

The above-mentioned ions from the PCA loading plot were further studied using UHPLC-HRMS. The HRMS measurements of the ion at *m/z* 865, 1154, and 1442 gave accurate masses of 865.1981 ($C_{45}H_{37}O_{18}$, 0.785 ppm), 1153.2629 ($C_{60}H_{49}O_{24}$, 1.796 ppm), and 1441.3259 ($C_{75}H_{61}O_{30}$, 0.785 ppm). MS^2 and MS^3 experiments were performed on these ions (spectra shown in the Supporting Information). The occurrence of an ion at *m/z* 287 in the MS^2 or MS^3 spectrum is an indication of the doubly linked A-type catechin/epicatechin oligomers, which contain $C_4 \rightarrow C_8$ carbon and $C_2 \rightarrow O \rightarrow C_7$ ether bonds. For example, the ion at *m/z* 865 had MS^2 fragments at *m/z* 533, 713, 453, and 287, in addition to the neutral losses of 286, 288, and 290, indicating it is an A-type trimer proanthocyanin, which has been previously reported.[18,19] Similarly, ions at *m/z* 1153.2629 and 1441.3259 were identified as A-type tetramers and pentamers, respectively. The HRMS measurements of the ions at *m/z* 133 and 147 gave accurate masses of 133.0646 (C_9H_9O, −1.061 ppm) and 147.0439 ($C_9H_7O_2$, −1.061 ppm). A literature paper[20] and our own data from the MS^2 studies (Supporting Information) confirmed these two ions represent the cinnamon components cinnamaldehyde and coumarin.

The PC2 loading plot of the samples is shown in Figure 4. The plot indicates samples with high ion counts at*m/z* 147, 465, 499, 513, and 865 yield a higher PC2 score, which would lead to positioning at the top of the PCA score plot. The ions contributing the most to the negative PC1 score were at *m/z* 579, 867, and 1156. The HRMS measurements of these ions indicate the formulas $C_{30}H_{27}O_{12}$ (*m/z* 579.1501, 0.447 ppm), $C_{45}H_{39}O_{18}$ (*m/z* 867.2134, 0.349 ppm), and $C_{60}H_{51}O_{24}$ (*m/z*1155.2782, 1.721 ppm). Using the *m/z* 579.1501 ion as an example, it fragmented into *m/z* 451, 427, 409, and 291 (17−26%), consistent with the report of procyanidins B_1. Similarly, ions *m/z* 867.2134 and 1155.2782 were identified as a B-type trimer and tetramer, respectively (Figure S2 in the Supporting Information).

These ions were ultimately identified as the dimer, trimer, and tetramers of B-type proanthocyanidins in cinnamon.[13]

To summarize, the coumarin and A-type proanthocyanidins give higher PC2 scores, whereas the B-type proanthocyanidins give lower PC2 scores, thus demonstrating different PCA groupings for the samples containing these profiles.

The ions at *m/z* 465, 499, and 513 are all very small peaks in the UHPLC-HRMS chromatograms. They are only visible using extracted ion mode. Regardless, it is not unusual for a relatively minor component that plays a significant role in PCA to be more visible in the FIMS spectrum than in an UHPLC-HRMS chromatogram.[17]

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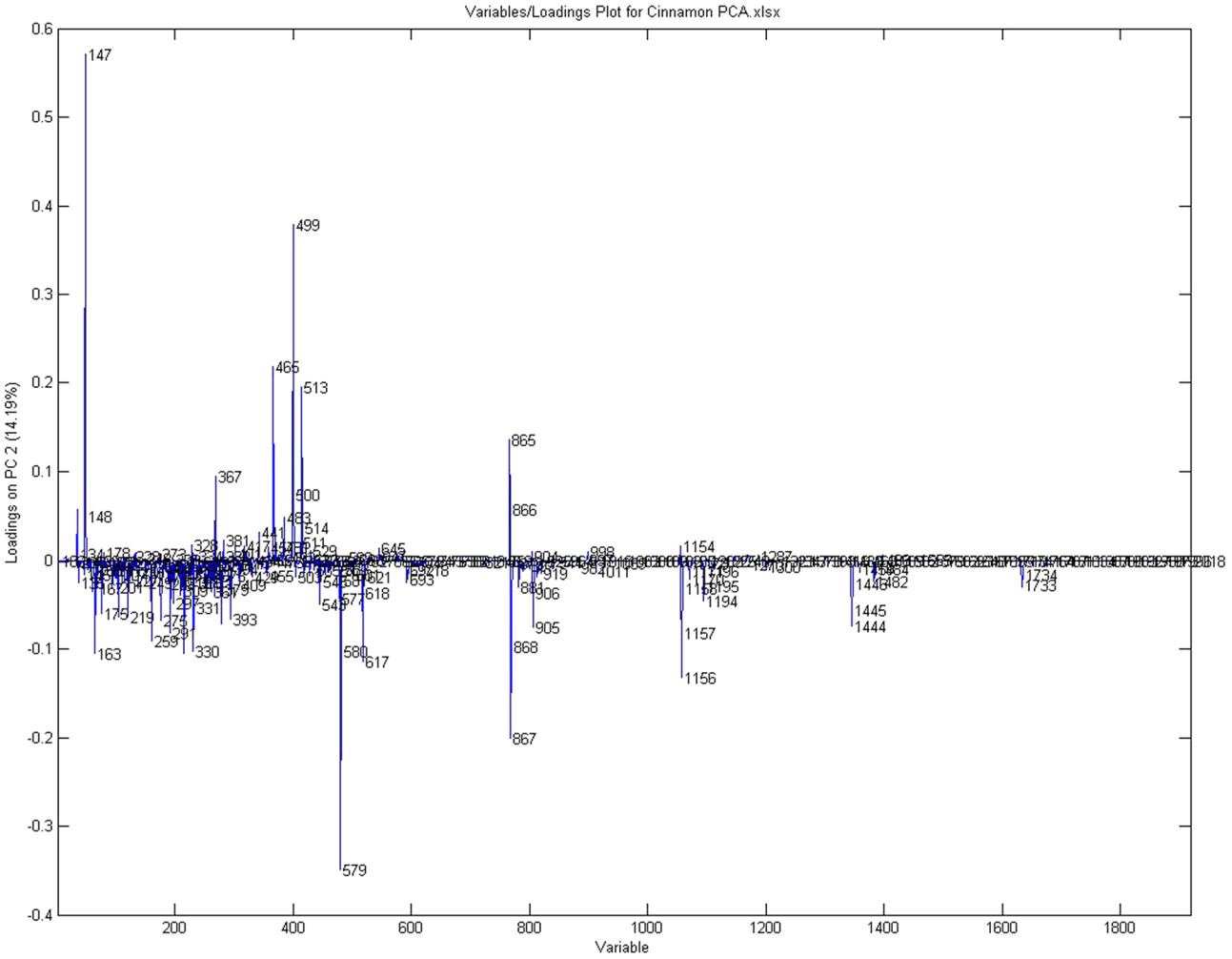

Figure 4. PCA loading plot of PC2 for FIMS fingerprints.

On a further note, it is common to observe that feeding studies and clinical trials involving natural products and their extracts give different or inconsistent test results. Cinnamon studies are no exception. Khan et al. found that cinnamon improves glucose and lipid levels of people with type 2 diabetes.[10] However, Loon's group did not reach this same conclusion.[21] Both groups claimed to use CC in their studies, but neither group attempted to identify the cinnamon samples by source or characterize the composition of the cinnamon samples before administering their respective studies. Thus, it is impossible to tell how different their respective samples are chemically and if the cinnamon used was actually CC or not. Another interesting observation is that the type-A proanthocyanidins isolated from CB were speculated to have insulin-like biological activity.[11] Yet both of the human feeding studies used CC, which contained more type-B than type-A proanthocyanidins. There was no explanation of why CC was chosen for both studies instead of CB or CV, nor were there any reports on the comparison of different cinnamon samples in human studies. The results from the present study clearly show the chemical composition differences between the four species of cinnamon samples. If the assumption is type-A proanthocyanidins have more insulin-like activity, then clearly CB or CV should be expected to perform better in human studies or biological assays, and CL would be the least effective. The results from this study show the importance of analytically determining the chemical composition of the samples when feeding studies are designed.

This study demonstrates a simple, fast, and reliable analytical method that can be used to differentiate four different species of cinnamons. Not only can the method be used for botanical authentication in food supply chains, it also can be used to help design better, more meaningful, and insightful feeding studies or assays, especially when combined with the UHPLC-HRMS method. The data suggested a model system in which the FIMS fingerprinting method is used to screen many samples quickly, whereas representative samples from a group and outlier samples are analyzed using the UHPLC-HRMS method to provide detailed information about a sample's unique chemical composition.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1−S9. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

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