Food adulteration and counterfeiting continues to grow as a worldwide issue of food safety and economic concern. Spices are one of the most commonly adulterated and counterfeited agricultural products in the U.S. Our previous study determined extensive elemental and heavy metal contamination and adulteration in spices. Many of our spice products were identified as possibly being heavily adulterated or contaminated by heavy metals or other external contaminants. Our follow-up Organic study, on the other hand, focused on the organic markers and toxic organic compounds in common spices and botanicals. In our previous study, we showed that these products were not adulterated from an organic compound standpoint as well as an elemental standpoint.

Cryogenic grinding and microwave extraction were employed in sample processing. Samples were extracted for the primary and secondary marker compounds native to each spice group and for any potentially toxic organic compounds (dyes, preservatives, pesticides, and industrial residual (herbicides)). The concentration and identity of compounds were compared across the groups to cited concentration references for each market or compound. Low concentrations of critical markers were found in low-cost spice and botanical samples indicating potential adulteration. Samples that were previously suspect by ICP/MS examination were confirmed to be adulterated or economically compromised by reduced or absent concentration of these critical primary and secondary marker compounds. High levels of potentially toxic chemicals were also found in some of the previously suspected spice and spice product samples.

### RESULTS

**Black Pepper**

The primary marker compound for black pepper is piperine. Piperine and its isomers, chaenomeless, are alkaloid compounds responsible for the strong acid pepper odor and flavor. Piperine compounds are found naturally in black pepper in concentrations ranging from 5-10% by mass. The samples of black pepper analyzed contained between 1-15% piperine. The lower cost ground peppers purchased at the dollar stores and farmers markets contained the least amount of the primary marker compound (1-4%). The more expensive whole, retail, and organic black pepper samples contained between 4-10% of piperine.

![Figure 1. Piperine Content in Black Pepper Samples (Mass %)](image)

**Cinnamon**

The primary marker compound for cinnamon is cinnamaldehyde. Cinnamaldehyde is an unsaturated aldehyde responsible for the characteristic flavor and fragrance of cinnamon. Cinnamaldehyde is cited as being between 1-15% of the bark by mass and can be up to 90% of cinnamon essential oils. The samples of cinnamon contained between 0.5% and 2.1% cinnamaldehyde. The lowest concentrations were found in the low-cost dollar store and farmers brand. The highest concentrations were found in the organic ground cinnamon and the cinnamon tea. The cinnamon supplement contained just over 1% cinnamaldehyde.

![Figure 2. Cinnamon Terpene Markers](image)

**Organic Ground Cinnamon**

The secondary marker compounds in cinnamon include alpha and beta-pinenes, b-carophyllene and d-limones. These secondary marker compounds are terpenes which often provide fragrance or flavorful secondary notes to many natural products. Many of the secondary marker compounds were not detected in the samples. Only the whole stick samples retained the majority of the secondary marker compounds. Alpha and beta-pinenes were not detected at all in the ground samples except for the cinnamon supplement. The highest levels of b-carophyllene were found in the ground samples. The cinnamon tea did not contain any of the secondary marker compounds.

### CONCLUSION

The primary marker compound for black pepper is piperine, found in all samples of black pepper showing some component of the spice was actually the cited product. The lower cost ground spices, however, had a significantly lower level of the primary marker compound than the more expensive whole and ground pepper spices. In line with the lower levels of piperine in the less expensive spices, the secondary marker compounds show a lack of the fine flavor compounds which could be the result of loss through age and grinding or prove adulteration and counterfeiting of black pepper spices.

Cinnamon samples showed a similar pattern when it came to the concentration of the primary marker compound, cinnamaldehyde. The highest amounts of cinnamaldehyde were found in the more expensive spices and spice products. There was a general lack of the secondary marker compounds in all of the ground cinnamon spices and products. The whole cinnamon spices had the greatest variety of marker compounds native to each spice group and for any potentially toxic organic compounds (dyes, preservatives, pesticides, and industrial residual (herbicides)). The concentration and identity of compounds were compared across the groups to cited concentration references for each market or compound. Low concentrations of critical markers were found in low-cost spice and botanical samples indicating potential adulteration. Samples that were previously suspect by ICP/MS examination were confirmed to be adulterated or economically compromised by reduced or absent concentration of these critical primary and secondary marker compounds. High levels of potentially toxic chemicals were also found in some of the previously suspected spice and spice product samples.

### ABSTRACT

The primary marker compound for cinnamon is cinnamaldehyde. Cinnamaldehyde is an unsaturated aldehyde responsible for the characteristic flavor and fragrance of cinnamon. Cinnamaldehyde is cited as being between 1-15% of the bark by mass and can be up to 90% of cinnamon essential oils. The samples of cinnamon contained between 0.5% and 2.1% cinnamaldehyde. The lowest concentrations were found in the low-cost dollar store and farmers brand. The highest concentrations were found in the organic ground cinnamon and the cinnamon tea. The cinnamon supplement contained just over 1% cinnamaldehyde.

The secondary marker compounds in cinnamon include alpha and beta-pinenes, b-carophyllene and d-limones. These secondary marker compounds are terpenes which often provide fragrance or flavorful secondary notes to many natural products. Many of the secondary marker compounds were not detected in the samples. Only the whole stick samples retained the majority of the secondary marker compounds. Alpha and beta-pinenes were not detected at all in the ground samples except for the cinnamon supplement. The highest levels of b-carophyllene were found in the ground samples. The cinnamon tea did not contain any of the secondary marker compounds.

The samples tested all contained measurable amounts of coumarin. The samples which contained the highest coumarin levels were the organic ground cinnamon, the retail whole cinnamon and the cinnamon tea. The cinnamon tea was reported to contain C. loureiroi, C. burmannii and "Indian cinnamon". These varieties of cinnamon contain the highest reported amounts of coumarin of all the species of cinnamon. The organic brand of cinnamon was reported to be C. loureiroi which has the highest cited amounts of coumarin of the cinnamon species. The retail whole spice did not report a species of cinnamon.

### METHOD & MATERIALS

#### Samples

Samples were purchased from several types of locations including online, health food stores, grocery stores, retail chain stores and discount or dollar stores. The samples ranged in price from a dollar per bottle to more than $20 per ounce. Some products were designated as “Organic.” The products represented seven different spice groups and a multitude of different products including supplements, teas, sauces, marinades, condiments, ground and whole spices. The sample breakdown was as follows:

- Black Pepper (pepper regrind) Whole & Ground Spices
- Cinnamon (Cinnamomum spec.) Whole & Ground Spices, Supplement, Tea
- Cinnamon species often used in the cinnamon spices include four different species from various geological locations around the world. The species are considered to be of varied qualities with the most expensive cinnamon species being C. verum or true cinnamon. The least expensive cinnamon species is C. cassia or ‘Chinese Cassia Cinnamon’. More than 70% of the cinnamon sold in the United States is the cheaper Chinese Cassia cinnamon.

#### Sample Preparation

**Initial Sample Preparation**

- Whole spices were ground using SPEX SamplePrep/FreezeMill
- Grind Conditions
  - 2 g of spice
  - Program
  - Process for 20 minutes
  - Ground for 5 cycles (2 minutes per cycle)
  - Each cycle = 2 minute cooling
  - Impact Rate: 16 impacts/second

- Powdered or ground spices were tested as purchased
- Support Aseptically were weighed and spread out
- Teas, sauces and condiments were tested as purchased

**Sample Digestion**

- Samples were extracted using a CEM Mars 5 Microwave
- Microwave conditions
  - Maxirapid Vessels
  - 1-1.5 g samples
  - 10 mL ECH
  - 15 minutes ramp to 100°C
  - 10 minutes hold
  - Stirring used

**Materials**

- SPEX CertiPrep Standards
- SPEX CLPS 870
- Marker Standards
- Can-Tep-Mix 1 & 6% 2

**Marker Compounds**

- Primary Marker Compounds
  - Piperine (Black Pepper)
  - Cinnamaldehyde (Cinnamon)
  - Secondary Marker Compounds
  - α & β-Pinenes
  - b-Carophyllene
  - D-3Carene
  - D-Limonene
  - Linalool
  - Eugenol
  - Coumarin

**Instruments**

- Agilent 6890 GC and 5973 MS
- Scan mode with EIC (54-450 m/z)
- CV-Sep capillary column (30 m x 0.25 mm x 0.25 μm)

**Method Design**

- The primary marker compound for black pepper was piperine, found in all samples of black pepper showing some component of the spice was actually the cited product. The lower cost ground spices, however, had a significantly lower level of the primary marker compound than the more expensive whole and ground pepper spices. In line with the lower levels of piperine in the less expensive spices, the secondary marker compounds show a lack of the fine flavor compounds which could be the result of loss through age and grinding or prove adulteration and counterfeiting of black pepper spices.

- Cinnamon samples showed a similar pattern when it came to the concentration of the primary marker compound, cinnamaldehyde. The highest amounts of cinnamaldehyde were found in the more expensive spices and spice products. There was a general lack of the secondary marker compounds in all of the ground cinnamon spices and products. The whole cinnamon spices had the greatest variety of marker compounds native to each spice group and for any potentially toxic organic compounds (dyes, preservatives, pesticides, and industrial residual (herbicides)). The concentration and identity of compounds were compared across the groups to cited concentration references for each market or compound. Low concentrations of critical markers were found in low-cost spice and botanical samples indicating potential adulteration. Samples that were previously suspect by ICP/MS examination were confirmed to be adulterated or economically compromised by reduced or absent concentration of these critical primary and secondary marker compounds. High levels of potentially toxic chemicals were also found in some of the previously suspected spice and spice product samples.