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 US. Our previous study determined there were extensive elemental and heavy metals contamination and adulteration in spices. Many of our spice products were identified being highly adulterated or contaminated by metals. In our follow-up Organic study, we focused on the organic markers and toxic organic compounds in our common spices and cinnamon. Black Pepper and Cinnamon in various forms (i.e. spices, teas, condiments and supplements) to determine if these products appeared to be 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 (toxins, preservatives & industrial medical chemicals). The concentration and identity of organic compounds were compared across the groups and to cited concentration references for each marker or compound. Low concentrations of critical markers were found in low-cost spices and botanical samples indicating potential adulteration. Samples that were previously suspect by ICM examination were confirmed to be adulterated or economically compromised by reduced or absent concentrations of these critical primary and secondary marker compounds. High levels of potentially toxic chemicals were also found in some of the previously suspect spices and spice products.

### Methods & 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, soaps, mixes, condiments, ground and whole spices. The samples breakdown was as follows:
  - **Black Pepper** (piper nigrum): Whole & Ground Spices
  - **Cinnamon** (Cinnamomum spp.): Whole & Ground Spices, Supplement, Tea

Cinnamon species often used in the cinnamon spices include four different species from different geological locations in the world. The different 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 often used in the cinnamon spices include four different species from different geological locations in the world. The different species represented seven different spice groups and a multitude of different products including supplements, teas, soaps, mixes, condiments, ground and whole spices. The samples ranged in price from a dollar per bottle to more than $20 per ounce. Some products were designated as "Organic". The products samples except for the cinnamon supplement. The highest levels of β-caryophyllene were found in the ground samples. The cinnamon tea did not contain any of the secondary marker compounds.

The secondary marker compounds for black pepper are a mix of common terpenes including: α & β-pinene, β-carophyllene, D-3-carene, and D-limonene. The largest concentration of the secondary marker compounds are found in the retail and organic samples. The less expensive dollar store and farmers brands have smaller amounts of these secondary compounds including α-pinene, β-carene, and D-limonene.

**Table 1. Species of Plants designated as Cinnamon**

<table>
<thead>
<tr>
<th>Species Type of Cinnamon</th>
<th>Avg. cited Coumarin</th>
<th>Retail Whole</th>
<th>Ground</th>
<th>Organic</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. verum True Cinnamon</td>
<td>0.017 g/kg</td>
<td>Retail Whole</td>
<td>Ground</td>
<td>Organic</td>
</tr>
<tr>
<td>C. cassia Chinese Cinnamon</td>
<td>0.005 g/kg</td>
<td>Ground</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C. loureiroi Vietnamese Cassia Cinnamon</td>
<td>0.017 g/kg</td>
<td>Ground</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2. Breakdown of Species of Cinnamon represented in the test Samples**

- **Sample Preparation**
  - Initial Sample Preparation:
    - Whole spices were ground using SPEX SamplePrep/Finezer Mill.
  - Grinding Conditions:
    - 2 g of Spices
    - Program:
      - Throws 1-28 minutes
      - 3 g of (1 g 2 min, 2 g 1 min, 1 g 2 min), 3 g of spice
      - Each cycle 2 min cooling.
    - Impact rate: 16 impacts/second
  - Whole and ground spices were tested as purchased.
  - Whole spices were ground using SPEX SamplePrep Freezer Mill.
  - Ground samples were oven dried and weighed out.
  - Teas, soaps and condiments were tested as purchased.
  - Materials:
    - SPEX Certiprep Standards:
      - SPEX CUTS-90
      - Marker Standards
        - Can/Tea 1-62
    - Microwaves
      - Microwave/Weigh:
        - 1-1.5 g sample
        - 10 min, SDS
        - 13.5 min ramp to 130 C
        - 30 min hold
        - Stringing used
    - Instruments:
      - Agilent 6890 GC with 5973 detector
        - GC-MS in scan mode with EIC (35-450 m/z)
        - CVI-2 quadrupole column (10 m @ 0.25 mm, 0.25 u)

**Results**

### Black Pepper

- The primary marker compound for black pepper is piperine. Piperine and its isomer, piperin, are the phthalides compounds responsible for the strong acid pepper odor and flavor. Piperine compounds are found naturally in black pepper in concentrations ranging from 3-10% by mass. The samples of black pepper analyzed contained between 1-10% piperine. The lower cost ground peppers purchased at the dollar stores and farmer's markets contained the lowest amount of the primary marker compound (1-4%). The more expensive retail and organic black pepper samples contained between 6-10% piperine.

**Figure 3. GC/MS Spectrum for Piperine (NIST Database)**

**Figure 4. Piperine Content in Black Pepper Samples (Percent)**

### Cinnamon

- The primary marker compound for cinnamon is cinnamaldehyde. Cinnamaldehyde is an unsaturated aldehyde responsible for the characteristic flavor and fragrance of cinnamon. Coumarin is cited as being between 1-3% of the bulk by mass and can be up to 9% of cinnamon essential oils. The second most common compound contained between 0.5% and 1.2%. Cinnamaldehyde in the lowest concentrations were found in the low-cost dollar store and farmer's brands. The highest concentrations were found in the organic ground cinnamon and the cinnamon tea. The cinnamon supplement contained just over 1% cinnamaldehyde.

**Figure 5. GC/MS Spectrum for Cinnamaldehyde (NIST Database)**

**Figure 6. Cinnamaldehyde Content in Black Pepper Samples (Percent)**

The samples tested all contained measurable amounts of coumarin. The sample which contained the highest coumarin levels were the organic ground cinnamon, the retail white cinnamon and the cinnamon tea. The cinnamon tea was reported to contain C. burmanii, C. biastreum and Indian cassia. 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 C. cassia which has the highest cited amounts of coumarin of the cinnamon species. The retail whole spice did not report species of cinnamon.

**Table 3. Average coumarin content**

<table>
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