SPEX CertiPrep App Note

The Chemistry of Pumpkin Spice

Introduction

Taste and smell are two of our primary sensory systems in which humans perceive the world. The scent and taste we experience influence our moods, perceptions and memories. Both taste and smell are chemoreceptive senses, meaning that there are specialized sensory receptor cells that convert a chemical substance to a signal such as a neurotransmitter or an action potential in a nerve cell. There are two types of chemoreceptors; distance and direct. Distance chemoreceptors are in the olfactory system (smell) and allow the detection of chemicals in the air. Direct chemoreceptors are present in the gustatory system (taste).

Chemicals which produce flavor or fragrance contain functional groups which activate the corresponding taste receptors to perceive taste which combine with the other senses to produce familiar flavors. The most common functional group in flavors is carbonyls such as esters, aldehydes, ketones, etc. Other groups which produce flavors are carbohydrates, acids, salts, proteins, and terpenes. Terpenes are a diverse group of compounds responsible for characteristic flavors and fragrances such as citrus, florals, mints, and spices.

Many consumer products including perfume, flavorings, wine, and beer are dependent upon terpenes for the character, flavor and fragrances they impart upon products. In nature, terpenes are found in many common plants like roses and coniferous trees (see figure 1).

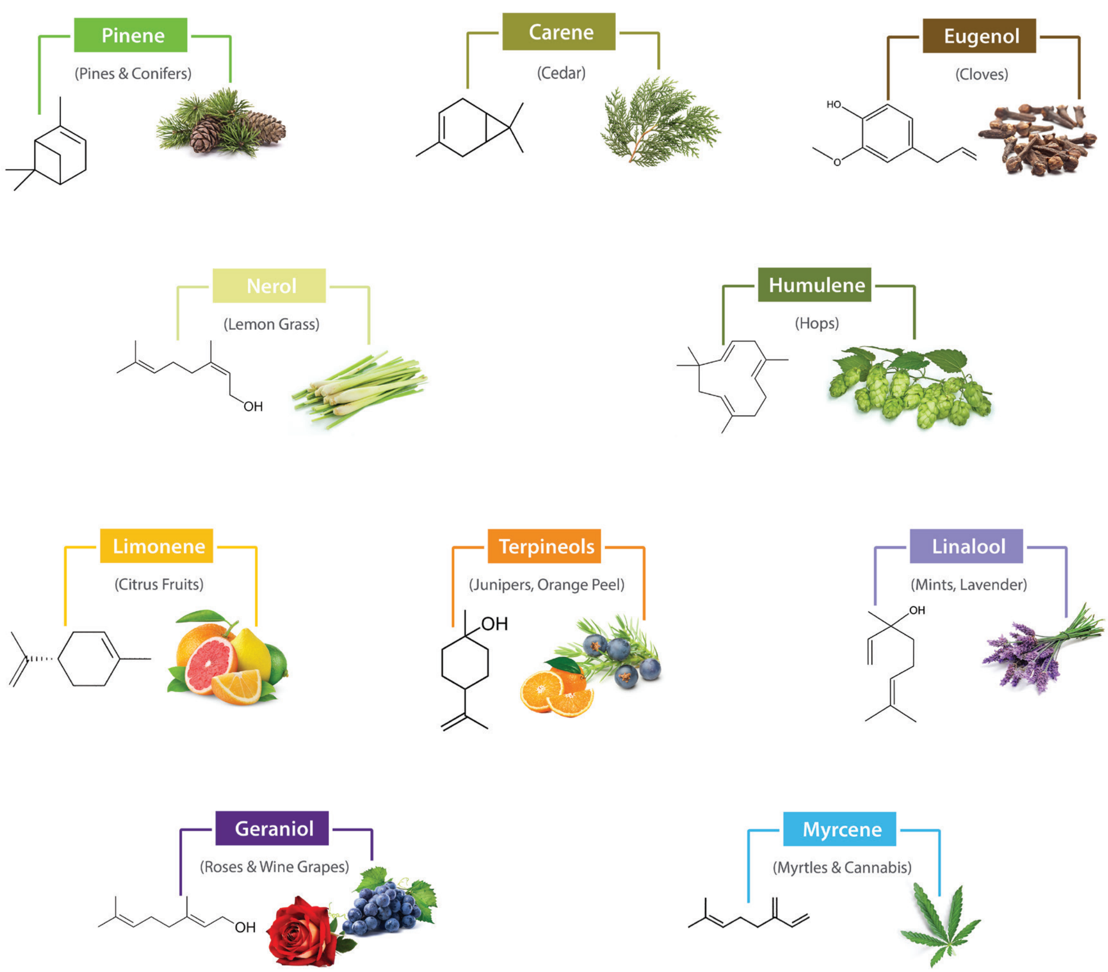

Figure 1. Common Terpenes and Terpenoids

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Terpene profiles are a way to characterize and fingerprint different varieties of botanicals so that they can be used in appropriate products or tested for adulteration. 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 as possibly being highly adulterated or contaminated by metals.

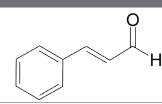
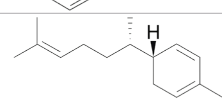
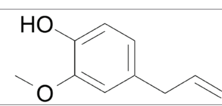
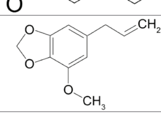
In our follow-up organic studies, we focused on the organic markers and toxic organic compounds in our common spices and botanicals in various forms (i.e. spices, teas, condiments, and supplements) to determine if these products appeared to be adulterated from an organic compound standpoint as well as an elemental standpoint. For instance, a study by SPEX CertiPrep of black pepper found many black pepper samples lacked significant amounts of caryophylene and piperine which are the primary target terpenes in the flavor of black pepper (see SPEX App Note: *Elemental Content of Black Pepper to Determine Adulteration and Heavy Metal Contamination*). In this note we will look at the flavors of some important seasonal scent and flavor compounds.

Many consumer products including perfume, flavorings, wine, and beer are dependent upon terpenes for the character, flavor and fragrances they impart upon the products to make those products induce specific tastes, scents, feelings, emotions, and memories. How would Christmas be Christmas without the tastes and scents of pinene in our trees, and menthols in our candy canes? Would spring be the same without the scent of flowers? Summer scents are those of fruits , grasses and trees all courtesy of the scent and flavor chemicals. Finally, as fall begins the thoughts begin to drift towards the scents and flavors of pumpkin spice.

The components of pumpkin pie spices have been around for over a hundred years and was referenced in cookbooks from the 1890s. Pumpkin pie spice contains between four and five ingredients: cinnamon, ginger, nutmeg, clove, and sometimes allspice. The spice blend is added to everything from coffee to dinners. The sale of pumpkin pie spice products is half a billion dollars in sales annually. The fall season is the top selling time for pumpkin pie spice products and flavors.

Each of the spices has a large group of flavor and fragrance compounds with one or two being noted as characteristic for that particular spice. Cinnamon is characterized by cinnamaldehyde (see table 1), while other spices like cloves and allspice share high concentrations of eugenol.

Table 1. Pumpkin Pie Spice Compounds

Spice	Marker Compound	Structure
Cinnamon	Cinnamaldehyde	
Ginger	Zingiberne	
Clove & Allspice	Eugenol	
Nutmeg	Myristcin	

Methods & Materials

<u>*Samples:*</u>

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, mixes, condiments, ground, and whole spices. The sample breakdown was as follows:

Cinnamon (cinnamonium sp.): Whole & ground spices, supplements, tea.

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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 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 cinnamon.

Table 2. Species of plants designated as cinnamon

Species	Type of Cinnamon
C. cassia	Chinese Cassia Cinnamon
C. burmannii	Indonesian Cassia Cinnamon
C. loureiroi	Vietnamese Cassia Cinnamon
C. verum	True Cinnamon

Table 3. Breakdown of species of cinnamon represented in the test samples

Sample	Type of Cinnamon
Dollar E Ground	Cinnamon unknown type
Dollar 5 Ground	Cinnamon unknown type
Farmers Whole	Cinnamon unknown type
Chain GV Ground	Cinnamon unknown type
Retail Ground	Cinnamon unknown type
Organic Ground	Cinnamon (cinnamomum loureirii)
Retail Whole	Cinnamon unknown type
Supplement	Cinnamon cassia
Tea	Cinnamon (60% Vietnam, 16% Indonesia, 10% Indian)

Sample Preparation

Initial Sample Preparation:

- Whole spices were ground using SPEX SamplePrep Freezer Mill
  - Grinding conditions:
    - 2 g of spice
    - Program
      - Pre-cool = 20 miniutes
      - Grind for 5 cycles (2 minutes/cycle)
      - Each cycle = 2 minute cooling
      - Impact rate = 16 impacts/second
- Powdered or ground spices were tested as purchased
- Supplement capsules were opened and weighed out
- Teas, sauces and condiments were tested as purchased

Sample Extraction

- Samples were extracted using a CEM Mars 5 microwave
  - Microwave conditions
    - MarsXPress Vessels
    - 1-1.5 g sample
    - 10 mL EtOH
      - 15 minute ramp to 130 °C
      - 30 minute hold
      - Stirring used

Materials:

- SPEX CertiPrep Standards
  - SPEX CLPS-I90
  - Marker Standards
  - CAN-TERP-MIX1 and CAN-TERP-MIX2
  - Marker Compounds
    - Primary Marker Compounds
      - Cinnamaldehyde (cinnamon)
    - Secondary Marker Compounds
      - a & b-Pinene
      - beta-Carophyllene
      - d-3-Carene
      - d-Limonene
      - Linalool
      - Eugenol
      - Coumarin

Instrumentation:

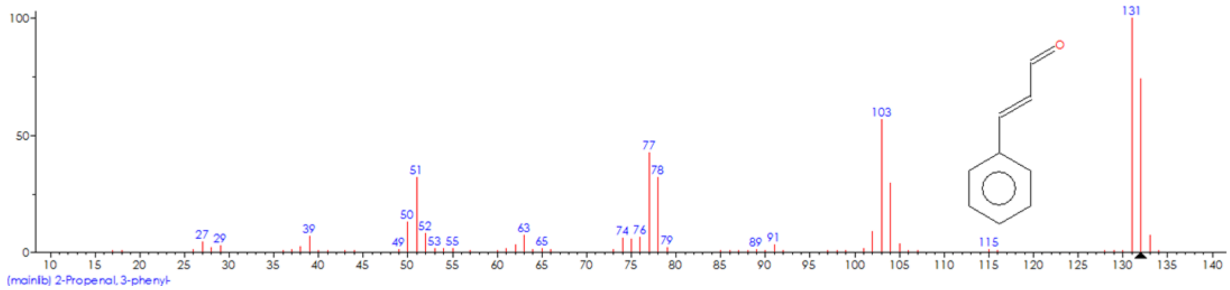
- Agilent 5890 GC with 5973
- GM/MS in scan mode with EIC (35-450 m/z)
- CV-5 capillary column (30 m x 0.25 mm x 0.25 µm)

Method Design

Our previous study of spices was designed to evaluate the metal content in the spices for evidence of contamination by heavy metals or for adulteration and counterfeiting by notable concentrations of wear or additive metals. This study targeted the same spice samples to quantify the characteristic primary and secondary market compounds for each spice group.

Results

Cinnamon



GC/MS Spectrum for Cinnamaldehyde (NIST database)

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 1-3% 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 brands. The highest concentrations were found in the organic ground cinnamon and the cinnamon tea. The cinnamon supplement contained just over 1% cinnamaldehyde.

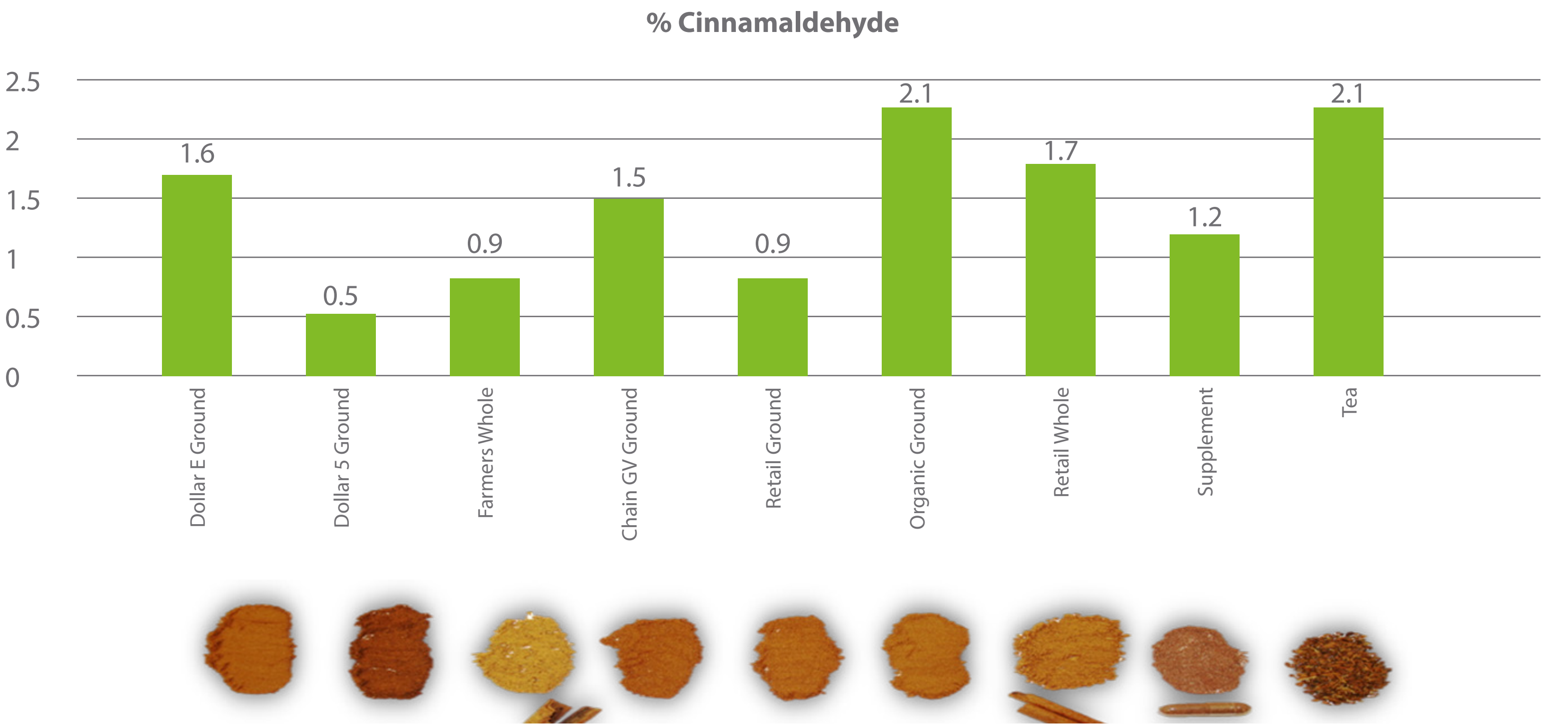
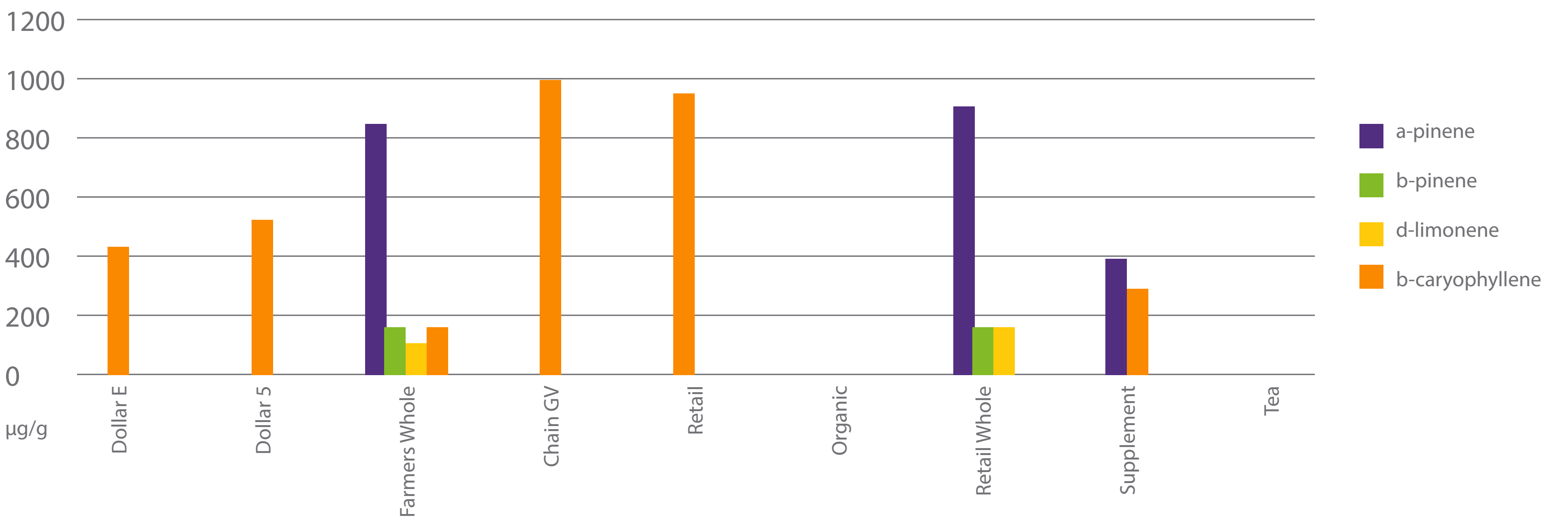


Figure 2. Cinnamaldehyde in cinnamon samples

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



There are two marker compounds, eugenol and coumarin, present in certain species of cinnamon that could be used to identify the different species of cinnamon. While eugenol is a compound which can give products added flavor and fragrance, coumarin is potentially toxic.

Table 4. Average coumarin content

Species	Type of Cinnamon	Average Coumarin Content
C. cassia	Chinese Cassia Cinnamon	0.31 g/kg
C. burmannii	Indonesian Cassia Cinnamon	2.15 g/kg
C. loureiroi	Vietnamese Cassia Cinnamon	6.97 g/kg
C. verum	True Cinnamon	0.017 g/kg

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 varities of cinnamon contain the highest reported amounts of coumarin of all of 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.

Conclusions

Cinnamon samples showed a 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 secondary marker compounds suggesting that the grinding of the spices was possibly responsible for the loss of secondary flavor and fragrance notes.

The results suggest that the cheaper spice samples obtained from the dollar store and farmers markets contained the least amount of all of the marker compounds. This reduction of marker compounds suggest some of these products could possibly be adulterated in some way which reduced the marker compounds. It is also possible that the age and grinding of the samples caused a reduction of the marker compounds.

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