Aroma Profiling of Commercial Poi Products in Fresh and Aged States Using Comprehensive Two-Dimensional Gas Chromatography

Sarah Foster[1], Cynthia Cheung[2], Laura Tipton[3,4], Jonathan D. Baker[3], Kahoalii K. Keahi-Wood[3], Katelynn A. Perrault Uptmor[1,2]

[1]*Nontargeted Separations Laboratory, Chemistry Department, William & Mary*
[2]*Laboratory of Forensic and Bioanalytical Chemistry/Forensic Sciences Unit, Chaminade University of Honolulu*
[3]*School of Natural Sciences and Mathematics, Chaminade University of Honolulu*
[4]*Departments of Biology and Mathematics & Statistics, James Madison University*

Introduction

Taro (Colocasia esculenta L.) is a tropical root from southeast Asia now found in tropical and subtropical regions around the world.

Poi is a food product prepared from steamed taro that has been macerated and allowed to ferment.

Investigating the profile of poi via GC×GC-qMS can enhance understanding of its unique qualities, historical context, and contemporary uses.

Volatile organic compounds (VOCs) produced during fermentation have traditionally been detected through gas chromatography-mass spectrometry (GC-MS).

Aim: observe changes in fresh to aged commercially purchased poi using comprehensive two-dimensional gas chromatography-quadrupole mass spectrometry with flame ionization detection (GC×GC-qMS), demonstrated to be a more effective tool in identifying the VOCs produced by fermentation[1,2,3].

Figure 1. Three commercially available brands of Poi from local grocery stores were surveyed.

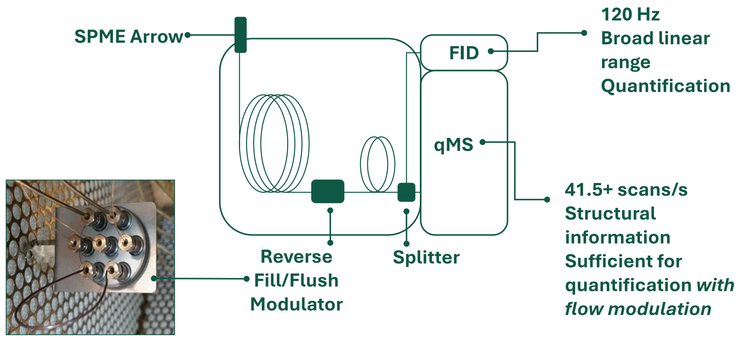

Figure 2. Schematic of GC×GC-qMS/FID with reverse fill/flush modulator.

Specifically, the three goals of the project were to:

1. establish the core VOC profile of poi
2. establish differences in commercial products
3. establish VOC changes that occur during fermentation

Conclusion

- Goal 1: Establish core VOC profile of poi
  - 56 compounds identified across all samples
  - 14 compounds present in fresh samples only and 18 compounds present in aged samples only
  - 24 core compounds found across all brands
- Goal 2: Establish differences in VOC profiles of commercial products
  - Each product had a unique set of 2-8 compounds that were not present in other products
- Goal 3: Establish changes that occur during fermentation of poi products
  - Presence of 1-pentanol, acetic acid, and 2,5-dimethylfuran indicated fermentation
  - Each brand also had unique markers to its fermentation process

References

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Method

Sample Preparation:

- Poi samples were prepared according to respective package instructions
- 5 g of poi was transferred into labelled 20 mL SPME headspace vials and analyzed on the GC×GC-qMS/FID immediately (fresh) and seven days after preparation (aged)
- Solid Phase Microextraction Arrow (SPME Arrow) sampling with a 1.50 mm wide sleeve divinylbenzene/carbon wide range (CWR) fiber was used

Quadrupole mass spectrometry data (albeit slower than time-of-flight) has been previously shown to be capable of sufficient data rate for integration[4]. The qMS data was analyzed using mass spectral data for peak integration though AnalyzerPro XD (Spectralworks Ltd.):

- Samples were input using group classes
  - Taro (Taro)
  - Hanalei (HA)
  - He Mea Ono (HMO)
- Data was visualized with principal component analysis (PCA) plots, box plots, and volcano plots
- Could "toggle" class comparisons by selecting/deselecting categories to answer different research questions
- Groups included: Hanalei (HA) aged and fresh, He Mea One (HMO) aged and fresh, Taro aged and fresh, Water, and Blanks.
- A threshold of 30% detection within class was used, leaving only compounds on the list which appeared in greater than 30% of the samples within each group.

Table 1. GC×GC-qMS/FID parameters on a TRACE1300 GC/FID and an ISQ 7000 Single Quadrupole Mass Spectrometer.

GC×GC Parameters	
Inlet	Split flow of 20 mL/min at 250 °C
Columns	[1]D: Rxi-624Sil MS column (30 m × 0.25 mm ID × 1.4 µm) [2]D: Stabilwax (5 m × 0.25 mm × 0.25 µm)
Modulator	Reverse Fill/Flush Modulator
Modulation Period	2.5 s
Oven Temperature Program	50 °C (hold 1 min) to 250 °C at 5 °C/min (hold 1 min)
Carrier Gas	Helium at 1.00 mL/min
qMS Parameters	
Ion Source Temperature	280 °C
Scan Range	40 to 300 *m/z*
Acquisition Rate	41.5 scans/s

Results and Discussion

Table 2. List of analytes and their compound class found in at least one aging state across every brand. Components highlighted in yellow have no documented natural sources, and may be associated with processing, packaging, and/or storage of the food product. "HA" refers to Hanalei brand poi, "HMO" refers to He Mea Ono brand poi, and "Taro" refers to Taro brand poi.

Components	HA Fresh	HA Aged	HMO Fresh	HMO Aged	Taro Fresh	Taro Aged	Class
1-prop-2-ynoxypropan-2-ol	x	x	x	x		x	Alcohol
2-methylbutanal	x			x	x	x	Aldehyde
acetaldehyde	x		x	x	x	x	Aldehyde
penta-1,4-diene	x		x			x	Alkene
2,5-dimethylfuran		x		x		x	Heteroaromatic
2,2,3,3-tetramethyloxirane	x		x	x	x		Epoxide
2-methylpropyl acetate	x	x	x	x		x	Carboxylic Acid Ester
3-methylbutyl acetate	x	x	x	x		x	Ester
butyl acetate	x	x	x	x	x		Carboxylic Acid Ester
ethyl acetate	x	x	x	x		x	Carboxylic Acid Ester
ethyl propanoate	x		x	x	x	x	Carboxylic Acid Ester
formyl acetate		x	x	x		x	Carboxylic Acid Ester
methyl acetate	x	x	x	x		x	Ester
n-propyl acetate	x	x	x	x		x	Ester
2-hydroxypentan-3-one	x	x	x	x	x		Ketone
4,4-dimethoxy-3-methylbutan-2-one	x		x		x		Ketone
urea		x		x	x	x	Nitrogen-containing

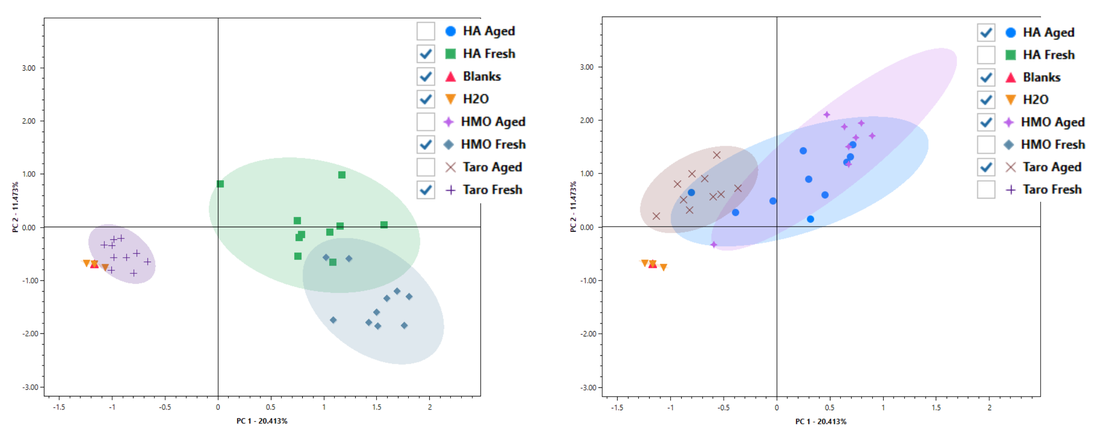

Figure 4. PCA scores plot for fresh samples across all brands (left) and PCA scores plot for aged samples across all brands (right). Pareto scaling with log transformation and 95% confidence ellipses in respective sample grouping colors.

- The PCA score plot for fresh samples demonstrates distinct aromatic profiles.
- After aging, fermentation profiles appear to converge for each brand.

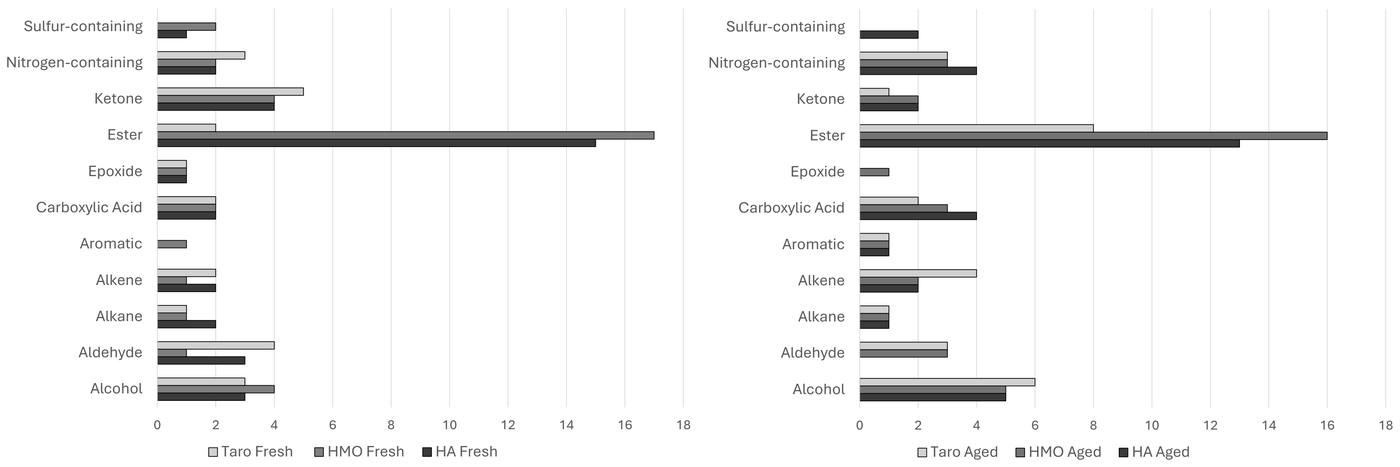

Figure 5. Chemical classes across sample classifications. **A)** all fresh samples across Hanalei (HA) brand poi, He Mea Ono (HMO) brand poi, and Taro brand poi and **B)** all aged samples across HA, HMO, and Taro.

- The number of compounds in each class differed between fresh samples and aged samples for each brand.
- Esters and carboxylic acids were prominent in HMO and HA
- Organic acids and alcohols were found in greater numbers across all three brands when fermented
- The number of ketones decreased across all three brands when fermented.

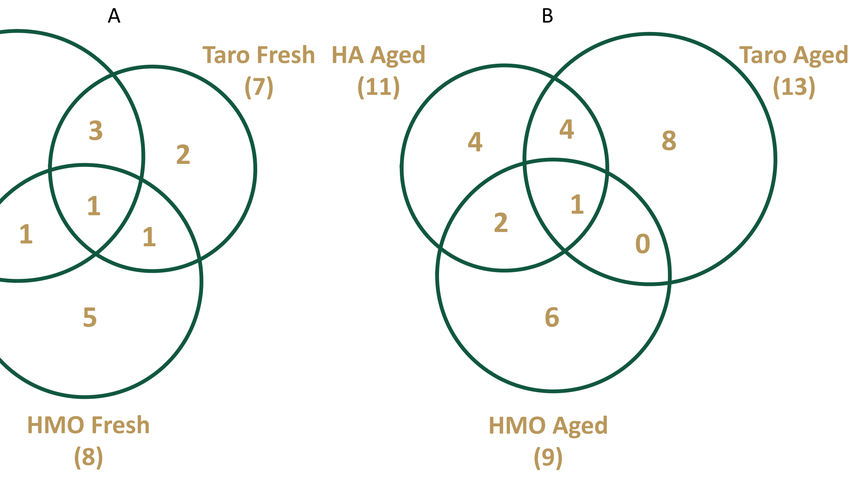

Figure 3. Multiple intersection Venn diagram illustrating the relationship between Hanalei (HA) brand poi, He Mea Ono (HMO) brand poi, and Taro brand poi for (A) fresh samples and (B) aged samples

- Considering analytes only found in the "fresh" state, each brand of poi contained more unique VOCs than shared ones, resulting in a distinct flavor profile for each brand when "fresh".
- As aging occurred, Taro brand poi became more similar to Hanalei brand poi and less similar to He Mea Ono brand poi. Similarly, He Mea Ono brand poi became more like Hanalei brand poi.

Table 3. Aroma descriptors highlighting the differences in the flavor profile of fresh and aged samples across Hanalei brand poi, He Me Ono brand poi, and Taro brand poi.

	Hanalei		He Me Ono		Taro	
Fresh	Fruity Nutty Floral Sweet	Earthy Creamy Vegetal Cocoa	Fruity Floral Green Savory	Sweet Earthy Creamy Caramel	Fruity Nutty Caramel Dairy	Floral Green Savory Earthy
Aged	Fruity Nutty Floral Sweet	Savory Creamy Tangy Sour	Fruity Floral Nutty Sweet	Dairy Alcoholic Sour Acidic	Fruity Floral Sweet Nutty	Creamy Malt Acidic Alcoholic

- Fermentation descriptors associated: tangy, sour, floral, acidic, and alcoholic.
- Aged samples consistently exhibited 1-pentanol, acetic acid, and 2,5-dimethylfuran.