Final Technical Report

Nicole E Shriner, PhD

Department of Chemical Engineering and Materials Science

428 S Shaw Ln #2100, East Lansing, MI 48824

Email: shrinern@msu.edu

Phone: 517-896-4635

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Investigating Michigan Grain Terroir: Evaluation of Michigan Grain Varieties via Phenolic Acid Determination by HPLC

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1. Goals and Objectives

The overall goal of this project was to characterize Michigan-grown corn and rye varieties by their inherent phenolic acid content and profiles, thereby enabling a deeper understanding of grain terroir and its potential influence on flavor in craft beverages.

Specific objectives were to:

- Quantify the total phenolic acid (TPC) of each unique grain variety.
- Quantify individual phenolic acids present in each grain variety.
- Compare phenolic acid data to sensory evaluation results for each variety.
- Draw conclusions on the influence of location, soil composition, and climate on phenolic acid content.

This work aimed to remove process-related variables (e.g., mashing, fermentation, distillation, and aging) to allow evaluation of raw grain chemical composition at the source. Outcomes were intended to benefit Michigan farmers, brewers, and distillers by providing data to support grain selection, marketing, and further research on small grain terroir.

2. Results & Conclusions

Over the project period, significant progress was made toward characterizing phenolic acids in Michigan grain varieties.

Extraction and Analysis: All 2022 corn harvest samples underwent phenolic acid extraction. Individual phenolic acid profiles for these samples were completed using an HPLC method developed and optimized during the project.

Equipment and Standards: A gradient flow system was installed on the existing HPLC to allow multi-solvent analysis. Phenolic acid standards were sourced to ensure accurate identification and quantification.

Phenolic Profiling Method Development: An HPLC method was developed and optimized for individual phenolic acids present in the raw grain. The graphs at the end of this report (Figures 1-3) illustrate these results for the bloody butcher corn variety for years 2022 and 2023, as well as a comparison plot. For plots are available upon request.

Preliminary Findings: Total phenolic content and individual acid profiles varied significantly across corn varieties, suggesting strong potential for distinguishing varieties by chemical composition. Figure 3 illustrates the significant difference in ferulic acid content in the bloody butcher corn variety from 2022 to 2023.

Adaptation of Objectives: Sensory comparison was deferred due to challenges in assembling a trained panel and developing a robust lexicon within budget. GC-MS analysis of known aroma and flavor compounds was adopted as an alternative analytical approach.

Conclusions:

This work confirmed that Michigan-grown corn varieties exhibit measurable differences in phenolic acid content and composition, likely influenced by genetic and environmental factors. Like previous studies, ferulic acid was shown to vary between year and grain varietal. These differences support the concept of grain terroir and provide a foundation for linking raw grain chemistry to flavor potential in distilled products. Further analysis of additional harvest years and GC-MS data, combined with agronomic records, will enable stronger conclusions about the effects of location, soil, and climate.

3. Timeline

Project Period: February 12, 2024 – August 1, 2025

Research Context: This work builds on multi-year investigations by the Michigan State University Small Grains for Brewing and Distilling group. Previous projects (2019–2023) identified and distilled over 20 corn and rye varieties for sensory and chemical analysis.

Year 1 (2024-2025): Method development and optimization, installation of gradient flow HPLC system, procurement of standards, extraction of phenolic acids from 2022 corn harvest, preliminary total phenolic content (TPC) analysis, and initiation of individual phenolic acid profiling.

Year 2 (2025-2026): Completion of 2022 corn phenolic acid profiles, presentation of preliminary results at industry conferences, and continuation of extraction and analysis for subsequent harvest years. Second-year funding was awarded to complete corn and rye phenolic profiles of raw grain and complete GC-MS analyses. Integration of agronomic data from each harvest year will further enable terroir assessment.

4. Work Accomplished & Methods

Work Accomplished:

A reproducible and repeatable phenolic acid extraction procedure was established, optimized for cereal grains. The extraction method deciphers between free and bound phenolic acids. A gradient flow system was installed on the HPLC system for multi-solvent separation, enabling precise quantification of individual acids. Analytical-grade standards for target phenolic acids were sourced and used to develop and HPLC method. A HPLC-UV method was developed and optimized for separation and quantification of p-hydroxybenzoic acid, vanillic acid, caffeic acid, syringic acid, p-coumaric acid, ferulic acid, and o-coumaric acid. Extraction of phenolic acids is complete from all 2022 corn harvest samples. Complete phenolic acid profiles for all 2022 corn varieties have been generated, revealing significant varietal differences. Sensory testing was deferred due to challenges in budgeting for panel and lexicon development budget; GC-MS aroma and flavor analysis was adopted to complement chemical data. Use of GC-MS TOF requires training and method development. Training is complete and method development is

on-going. Once the GC/MS TOF method is developed, all previous distilled corn and rye samples will be analyzed.

Methods Summary:

Phenolic acids were extracted from 0.25 g of milled grain using alkaline hydrolysis (4 M NaOH, 90°C, 2 hours, inert atmosphere), followed by acidification (6 M HCl, pH 2), lipid removal (n-hexane), and phenolic acid recovery (ethyl acetate, three times). Extracts were evaporated to dryness and stored at −20°C in methanol suspension.

HPLC analysis was performed using a Shimadzu HPLC system with C18 column and UV detection at 25°C. The mobile phase comprised solvent A (1% aqueous formic acid) and solvent B (acetonitrile/methanol/water 8:1:1, v/v/v) with a gradient: 6% B for 34 min, 23% B for 10 min, 50% B for 4 min, and re-equilibration at 6% B for 9 min.

5. Communication Activities, Accomplishments, and Impact

Communication Activities:

Conference Presentations: Preliminary results presented at the University of Kentucky Beam Institute Conference (March 2025) and the American Craft Spirits Conference (March 2025).

Industry Engagement: Shared findings and provided sample tastings to farmers, distillers, retailers, and wholesalers visiting the MSU Fermented Beverage Lab.

Academic Dissemination: Preparing a peer-reviewed manuscript on total phenolic content (TPC) of 2022 corn harvest for submission by end of August 2025, to be followed by an article on phenolic acid profiles and GC-MS aroma data.

Accomplishments:

Developed a reproducible phenolic acid extraction method specific to Michigan corn and rye varieties.

Produced complete phenolic acid profiles for the 2022 corn harvest.

Identified significant compositional differences among varieties, supporting the concept of grain terroir in Michigan-grown grains.

Established a foundation for linking agronomic data, phenolic composition, and flavor potential.

Impacts:

For Farmers: Provides chemical data to help market grain based on flavor potential tied to location and variety.

For Distillers/Brewers: Enables informed grain selection to achieve desired flavor profiles and promote unique Michigan products.

For Research Capacity: Enhances MSU Fermented Beverage Lab capabilities for future terroir studies in small grains and potentially small fruits.

6. Budget Narrative

The project was conducted consistent with the budget proposed by the principal investigator and approved by the State of Michigan.

7. Tables & Figures

Figure 1: Bloody Butcher Phenolic Profile 2022 Harvest

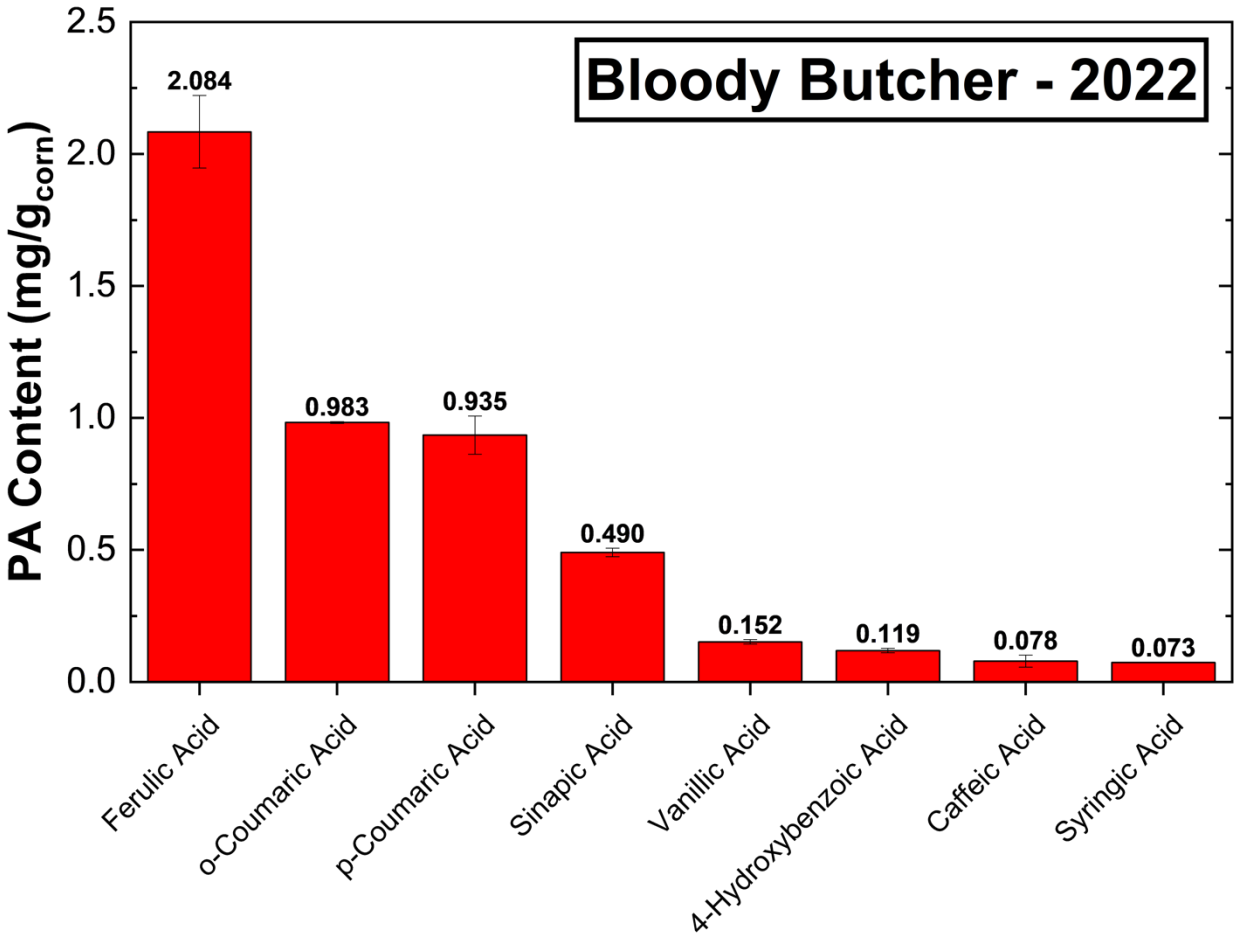

Figure 2: Bloody Butcher Phenolic Profile 2023 Harvest

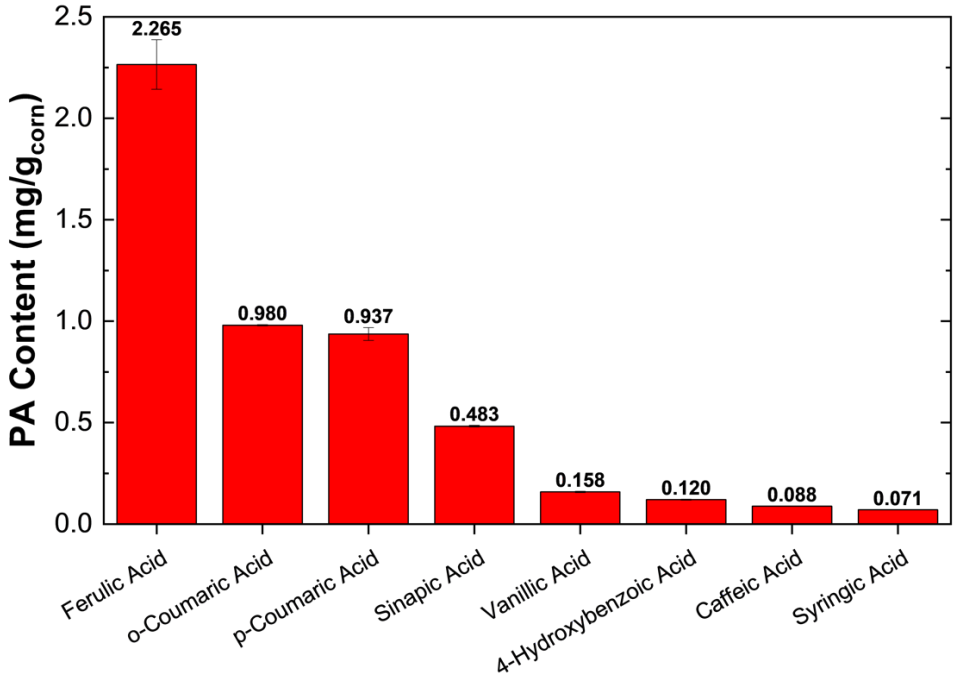

Figure 3: Bloody Butcher Phenolic Profile 2022 and 2023 Harvest Comparison