International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
www.chemijournal.com
IJCS 2024; 12(2): 01-03

Received: 02-01-2024
Accepted: 03-02-2024

Emily Pitonyak
Division of Natural Sciences and Mathematics, Keuka College, 141 Central Ave, Keuka Park, NY 14478, USA

Dr. Andrew J Robak
Professor, Division of Natural Sciences and Mathematics, Keuka College, 141 Central Ave, Keuka Park, NY 14478, USA

Corresponding Author:
Emily Pitonyak
Division of Natural Sciences and Mathematics, Keuka College, 141 Central Ave, Keuka Park, NY 14478, USA

Analysis of the ester composition of finger lakes wines using GC/MS and solid phase microextraction

Emily Pitonyak and Dr. Andrew J Robak

Abstract
The ester content of 7 New York Finger Lakes wines were determined using solid phase microextraction and gas chromatography/mass spectrometry. Wine samples were compared based on the grape varietal and type of yeast used during fermentation. It was found that the ester content of the wines was most similar when comparing similar varietals. Wines with the same yeast type and red vs white wines didn't have closely matching ester profiles.

Keywords: Gas chromatography, mass spectrometry, wine, esters, Finger Lakes

Introduction
The Finger Lakes wine region of New York is noted for being one of the best wine grape growing regions in the United States. Hundreds of wineries sit among the shores of these lakes, where grapes are grown, harvested, pressed, and transformed into wine that is sold and shipped across the United States. Among the most suitable grape varietals grown in this climate are Riesling and Pinot Noir which belong to the Vitis vinifera plant species. The large and diverse profile of wines from this region contain dynamic chemical compositions that influence both taste and smell. Wine aromatics, the vast array of scents derived from wine that are detected by the nose, consist of many different organic molecules existing in the gas phase.
The combination of esters and other small organic molecules play a significant role in creating the aromatic and flavor profile of a wine. While some fruits such as apples contain many esters, grapes do not contain very many. The esters occurring in wine are primarily formed during fermentation of grape juice [1, 2]. Hundreds of different molecules can be produced during this process [3] and then can be detected by the nose at varying concentrations and sensory thresholds. Over 160 esters have been identified in wine, although not all may be detectable by the nose. Fruity and floral aromas are among the most common scents associated with esters.
Winemakers can try to influence which type of esters are produced by controlling the temperature of fermentation and the yeast strain used [4]. While these are not the only factors influencing what aromatics will be produced, they do play a significant role. Fruity wine aromas are believed to be influenced by cooler fermentation temperatures at or near 50°F, floral aromas at or near 70°F, and a combination of the two at or near 60°F [1].
Solid phase microextraction (SPME) is a technique used to extract molecules from a vapor or liquid sample without using solvents. A small polymer fiber (usually nonpolar with high relative surface area) inserted into a sample will draw in organic molecules to adsorb to the surface. The fiber is housed within a syringe so that it can be put into the injector port for easy gas chromatography sampling. It has been used widely for high quality analysis of food and environmental samples [5].
The goal of our research was to compare the ester profiles found in several different wine varietals from the Finger Lakes wine region of New York. This helps us to attain a basic understanding of what kind of molecules may be most prevalent in wines and how their presence may or may not change across different varietals and with different yeasts used for fermentation. A combination of SPME and Gas chromatography/mass spectrometry (GC/MS) was used to extract and identify molecules in wine samples from the Finger Lakes region.

Materials and Methods

Sample Preparation

Wine samples from seven wineries on Keuka and Seneca Lake were collected and stored in the laboratory at 5°C.

Sample Extraction

Organic molecules present in the samples were extracted using the Restek PAL SPME Manual Injection Kit, with a Restek 100µm "red" polydimethylsiloxane fiber. The fiber was placed directly in each wine sample and suspended for 25 minutes at room temperature. After injection, The fiber was cleaned by suspension in ethanol for 2 minutes between runs and cleaned in an empty GC injector port at 200 °C at the end of the day.

The GC/MS conditions were identical for all wine samples. The GC was a PerkinElmer Clarus 580 gas chromatograph with a 30.00 m column with a 250 µm diameter using a 10:1 split ratio and a He carrier gas flow rate of 1.00 mL/min. The injector port was set at 250 °C. The oven temperature started at 50°C held for 3.00 minutes followed by a 10°C/min increase to 250 °C and held for 15 minutes for a total run time of 30.0 minutes. The SPME fiber injection was done manually.

The conditions in the MS were identical in each experiment. The MS used was a Clarus SQ 8 S mass spectrometer with source and inlet line temperatures of 200°C. A solvent delay of 3.00 minutes was used with a total run time of 30.0 minutes. The mass scan was from 27 amu to 350 amu.

Each wine was extracted twice using the exact same wine sample. All peaks present on the resulting chromatogram were identified by taking an average of the mass spectra across the peak and subtracting the background. The NIST spectral library search was used to identify specific compounds. The structure was considered confirmed when there was a library match with an R value over 800 and the molecular ion was independently confirmed correct.

Results and Discussion

A total of 34 different ester compounds were identified in 7 different wine samples using our methods (Table 1). The number of unique esters in each wine ranged from 15-22 based on our detection methods, with Pinot Noir (sample 4) and Traminette (sample 5) having the smallest variety of esters with 15 each. There were nine esters that were common to every wine sample, which can be seen in the highlighted sections of Table 1. Examples include ethyl butanoate (ret time 4.4) which has a characteristic pineapple smell and isoamyl acetate (ret. time 5.85) which has a banana aroma.

Table 1: Esters detected in the wine samples by GC/MS.

Wine/Grape Type		**Pinot Gris**	**Concord Blend (red wine)**	**Lemberger (red wine)**	**Pinot Noir (red wine)**	**Traminette**	**Riesling**	**Riesling**
Yeast Type		Lalvin W-15	Epernay II	BRL97	Lalvin W-15	Epernay II	spontaneous	36% Lalvin W-15 and 64% Lalvin R2
Ret time:	**Ester Name:**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**
3.67	ethyl isobutyrate	X	X	X	X	X	X	X
4.4	ethyl butanoate	X	X	X	X	X	X	X
4.66	ethyl lactate	X		X	X			X
5.22	isopropyl butyrate		X					
5.25	ethyl 2-butenoate		X					
5.41	ethyl isovalerate	X		X				X
5.56	methyl 3-hydroxybutanoate		X					
5.85	isoamyl acetate	X	X	X	X	X	X	X
6.69	Butyrolactone	X		X	X		X	X
7.06	ethyl 3-hydroxybutyrate		X					
8.17	ethyl hexanoate	X	X	X	X	X	X	X
8.42	hexyl acetate		X			X	X	X
8.96	ethyl 2-hexenoate	X	X	X		X		X
9.87	ethyl heptanoate	X		X			X	X
10.11	heptyl acetate						X	
10.29	methyl octanoate		X				X	X
11.16	ethyl succinate	X	X	X	X	X	X	X
11.41	ethyl octanoate	X	X	X	X	X	X	X
12.19	ethyl phenacetate	X	X	X	X		X	
12.86	ethyl nonanoate		X	X				
14.19	ethyl decanoate	X	X	X	X	X	X	X
14.61	ethyl anthranilate		X					
14.64	ethyl isopentyl succinate	X		X	X			
14.87	isoamyl octanoate		X				X	X
16.66	ethyl dodecanoate	X	X	X	X	X	X	X
17.25	isoamyl decanoate	X					X	X
18.87	ethyl tetradecanoate	X	X			X	X	X
19.34	ethyl trans-4-methoxycinnamate		X	X				X
19.42	Isoamyl laurate					X		
20.18	2-(3-indolyl)ethyl acetate			X				
20.72	ethyl palmitoleate	X			X	X		
20.9	ethyl palmitate	X	X	X	X	X	X	X
22.49	ethyl linoleate	X						
22.74	ethyl stearate	X			X	X	X	X
24.45	Benzyl butyl phthalate (BBP)	X	X	X	X	X	X	X
24.76	bis(2-ethylhexyl) adipate (DEHA)	X		X		X		X

	Total number of unique esters	21	22	19	15	15	19	21

A cell marked with an X means that ester was identified in the wine sample.

The ester profiles of the wines as detected by SPME were evaluated by looking at each ester compound present when comparing 2 wines. If an ester was present in both wines, it was considered a match. If neither wine being compared had that particular ester, it was also a match. Simply taking the number of matches and dividing by the total number of esters in Table 1 gave us a percentage match for each wine compared to one another and can be seen in Table 2. The percent similarity was the lowest with a value of 44.1% between Pinot Gris sample 1 and Concord Blend sample 2. There was a high level of similarity between samples 1 and 4 (Pinot Gris and Pinot Noir) and samples 6 and 7 which were both Riesling wines.

When comparing the different yeasts used, identical yeast strains were used in wines 1 and 4 as well as wines 2 and 5. The similarity in ester profile for the concord blend (wine 2) and traminette (wine 5) both of which used epernay II yeast, was not a close match at 61.8%. Since the highest percentage of matching overall was between wines made from similar or the same grapes, it appears based on this data that the ester profile is most strongly influenced by the type of grape, and not the strain of yeast used in fermentation. No trend was apparent that showed any increased similarity between the red wines compared to other reds, nor the white wines. While the two Rieslings (samples 6 and 7, both white) were a very close match, Pinot gris (sample 1) is a white wine, while pinot noir (sample 4) is a red wine and also showed a close match.

There were two esters detected that were not considered in the data set, benzyl butyl phthalate (BBP) and bis(2-ethylhexyl) adipate (DEHA). Both are likely synthetic compounds that are commonly used as plasticizers in polymer manufacturing and it is unknown whether or not they are environmental contaminants in the wines or simply lab contamination. Since they were very likely not formed during fermentation, they were left out of the wine ester comparison calculation.

Table 2: Percent similarity of the seven wine types studied.

	Pinot Gris 1	**concord 2**	**Lemberger 3**	**Pinot Noir 4**	**Traminette 5**	**Reisling 6**	**Riesling 7**
Pinot Gris sample 1	Same wine	44.1%	76.5%	82.4%	70.6%	70.6%	76.5%
concord sample 2	44.1%		55.8%	50.0%	61.8%	61.8%	61.8%
Lemberger sample 3	76.5%	55.8%		76.5%	58.8%	58.8%	70.6%
Pinot Noir sample 4	82.4%	50.0%	76.5%		76.5%	70.6%	64.7%
Traminette sample 5	70.6%	61.8%	58.8%	76.5%		70.6%	70.6%
Reisling sample 6	70.6%	61.8%	58.8%	70.6%	70.6%		82.3%
Riesling sample 7	76.5%	61.8%	70.6%	64.7%	70.6%	82.3%	

The red wines are highlighted in red, wines using identical yeast strains are underlined (samples 2 and 5 match yeasts and 1 and 4 had the same yeast). The red and green percentages represent the lowest and highest ester profile matches, respectively.

Conclusion

Overall the results show that solid phase microextraction (SPME) is an effective way to study esters in wine. The data shows some correlation where similar wine grape varietals are likely to give a similar ester profile. For the 7 Finger Lakes wines that we measured, the ester profiles were very similar for wines made with the same grapes (Rielsing, Pinot), and there was no clear correlation between esters in wines that used the same yeasts but different grapes.

There were several limitations to this work, as we were unable to control for the fermentation temperature and the age of the wines. All samples were from the same season and were likely close. We also cannot make a direct connection to wine aromas since that would depend on having similar esters but also would require a way to look at the relative amounts of esters in each wine. Regardless of the limitations, the SPME method developed is a useful way to study the ester content in wines and future work will look to understand more clearly how grapes and growing and fermentation conditions affect esters and wine aromas. More examples would need to be tested before making any strong conclusions.

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