NEW TRICKS FOR AN OLD DOG: APPLICATION OF SILICONE AS A TREATMENT FOR CONTAMINATED WINES

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Abstract- Wine is a $300 billion global industry for which perceived quality is a key driver of purchase behaviour. Several odorant constituents of wine detract from this quality at elevated levels, and thus de-value the product. Important amongst these compounds are two alkyl-methoxypyrazines (isopropyl-(IPMP) and isobutyl-(IBMP) methoxypyrazine), and two ethylphenols (4-ethylgaiacol (4-EG) and 4-ethylphenol (4-EP)). In thisproject we investigated the capacity ofapolydimethylsiloxane (silicone) polymerto reduce concentrations of these fourtaint odorants. Red wine was spiked with either IPMP [20 ng/L]and IBMP[20 ng/L] (Study 1) or 4-EP [200 ug/L]and 4-EG[200 ug/L](Study 2) and then treated with silicone pieces[surface area 350 cm^2/L].Solid Phase Micro-Extraction Multi-Dimensional Gas Chromatography–Mass Spectrometry and Gas Chromatography-Mass Spectrometry was used to measure the methoxypyrazines and ethylphenols, respectively,both before and after treatment with silicone.Results showed significant reductions in the target odorants after 8hrs treatment, especially for methoxypyrazines: IPMP (82%), IBMP (94%), 4-EP (12%) and 4-EG (18%). 'Ladybug taint' is caused by elevated levels of IPMP in wine, and general 'greenness' is largely due to excessivegrape-derived IBMP concentrations; application of silicone would appear to offer considerable remediation benefits in addressing these common wine defects.

Keywords- 4-Ethylphenol, 4-Ethylguaiacol, Brettanomyces, Fining, Ladybug Taint, Methoxypyrazines

I. INTRODUCTION

Silicone is a molecule, usually polymeric, with chain segments of the general form $(R_nSiO_{(4-n)/2})_m$ where n is between 0 and 3, and m is 2 or higher [16]. It has been widely used in industrial applications and consumer goods for decades. Major uses include a sealant for airplanes and household goods,medical/dental implants and moulds, coatings for electronics, textiles and papers, electrical insulation, and drug delivery. Applications in the food industry are equally varied, reflective of its variable thermal and physical properties, including an emulsifying and anti-foaming agent, a rubber for baking tray coatings and spatulas, a resin for non-stick heat resistant coatings on bake ware, and an adhesive for pressure-sensitive labels [16].As silicone is available in food-grade form, is relatively non-toxic, and has been shown to be capable of scavenging odorants in food/beverage matrices, it has potential application with grape juice and wine. Indeed, it has recently beentrialled in juice and must, and found effective in reducing methoxypyrazine levels [15].

Wine is a widely consumed [2], high-value alcoholic beverage derived from fermented fruit. However, taints and off-flavors detract appreciably from its quality and acceptance, and can significantly reduce its value. Isopropyl- (IPMP), and isobutyl – (IBMP) methoxypyrazines are responsible for the off-flavour known as 'ladybug taint' [3], which is due to the inadvertent incorporation of Coccinellidae beetles into the winemaking process, and methoxypyrazinesalso contribute to the undesirable greenness in wine made from grapes that have not achieved desired ripeness levels[4]. One of the most common off-flavours in wine is known as 'Brett taint', and is caused by ethylphenols formed by Brettanomyces/Dekkera yeasts, specifically 4-ethylphenol (4-EP) and 4-ethylguaiacol (4-EG) [5]. These compounds form unpleasant 'barnyard' and 'Band-Aid' notes, typically in red wines. IPMP, IBMP, 4-EP and 4-EG are difficult to remove from wine,and winemakers have a limited portfolio of agents and materials that can be used to improve affected product.

Silicone, as a GRAS-certified and multi-functional polymer may offer some potential to improve the quality of faulted wine, particularly those tainted with methoxypyrazines, given its efficacy in lowering levels in grape juice[15], presumably facilitated by the non-polar nature of both silicone and methoxypyrazines. The short-term objective of this study is to assess the capacity of silicone to remediate wine containing elevated levels of IPMP, IBMP, 4-EP and 4-EG. The long-term goal is to develop polymer-based oenological treatments that will improve the quality and value of wines tainted with these odorants.

II. MATERIALS AND METHODS

A red, commercial Merlot sourced from a Niagara winery was used as the base wine in both studies described here.Table 1 shows the basic physico-chemical composition of the base wine. Isopropyl-, isobutyl– and secbutly-methoxypyrazines were all below the limit of quantitation (4 ng/L) for our

method (MD-GC-MS)). Silicone tubing (Tygon®, France) was cut into pieces to obtain a surface area of 350 cm^2 per liter of wine treated.

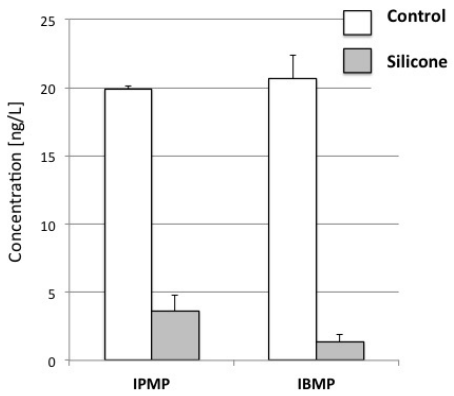
Table 1. Composition of the base red wine.

Parameter	Method	Value
pH	pH meter	3.58
Ethanol [% v/v]	GC-FID	12.6
Titratable acidity [g/L]	Titration	5.2
Acetic acid [g/L]	Enzymatic	0.68
Total reducing sugars [g/L]	Enzymatic	1.3
4-Ethylphenol (ug/L)	GC-MS	198
4-Ethylguaiacol (ug/L)	GC-MS	164

Study 1. The base wine was spiked with 20 ng/L of secbutylmethoxypyrazine (SBMP), IPMP and IBMP (all Sigma Aldrich, MO, USA) (= 'Control' wine) which, for the latter two compounds, approximates concentrations commonly found in wines affected by ladybug taint or wines produced from under- ripe grapes. Only data for IPMP and IBMP are reported here. Wines were distributed into 200 ml Schott bottlesand triplicate treatments, and the silicone was added and submerged in the wine for 8hrs. After 8hrs, MP concentrations were determined in duplicate for both the Control and silicone-treated wines using Solid Phase Micro-Extraction Multi-Dimensional Gas Chromatography–Mass Spectrometry (MD-GC-MS) [6]. Study 2.In a separate study, the same base wine was spiked with4-EP and 4-EG ('Control' wine) and the same protocols as described in Study 1 were employed. Analysis of these ethylphenols was made in triplicate using Gas Chromatography-Mass Spectrometry (GC-MS).

III. RESULTS

Fig. 1a shows the change in IPMP and IBMP concentrations after treatment with silicone for 8 hrs. As can be seen, both IPMP and IBMP showed substantial reductions after treatment: 82% and 94%, respectively. Fig.1b,shows the reduction in levels of 4-EP and 4-EG; they were smaller than for the methoxypyrazines, reducing by 12% for 4-EP and 18% for 4-EG.



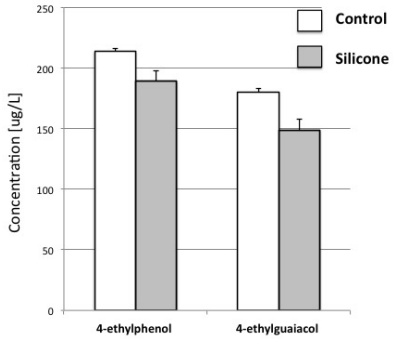


Fig. 1. Change in alkyl-methoxypyrazine (1a) and ethylphenol (1b) levels in red wine after treatment with silicone. IPMP: isopropyl- methoxypyrazine; IBMP: isobutyl-methoxypyrazine. Data represent the mean values of replicate treatments and measurements +/- SD.

IV. DISCUSSION AND CONCLUSION

This preliminary data demonstrates the abilityof silicone to decreaselevels of these important taint compounds in red wine, particularly IPMP and IBMP. Similar decreases were reported in grape juice and must [15]. Treatment of juice rather than wine is likely optimal with respect to unintended scavenging of desirable odorants in wine, many of which are formed during the alcoholic fermentation. However, methoxypyrazines can take several days to be fully extracted from grapes during red wine fermentation[15], as is likely the case with their extraction from Coccinellidaein the case of ladybug taint; thus application of silicone to finished or partially-finished winesrather than juice may be necessary. This consideration does not preclude fining with silicone at multiple stages during the winemaking process, depending on the rate of IPMP and IBMP extraction and other compositional changes that occur. Nor does it preclude treatment with other fining agents or interventions. For instance, in the case of white wines affected by Coccinellidae, juice clarification [7,8] or a highly-selective protein-based fining system [12] may reduce initial IPMP loads, and treatment with silicone could be employed after alcoholic fermentation to scavengeany residual methoxypyrazines.

With respect to ethylphenols,the reduction from silicone fining observed here is modest. However, the ultimate goal is to reduce concentrations to below sensory threshold rather than complete elimination, therefore other treatments could also be considered in tandem with silicone. Activated charcoal may also reduce 4-EP and 4-EG by modest amounts[13],however it is very non-selective, stripping out many desirable odorants in the process[13], and thus is unlikely to improve wine quality significantly[14].Of more promise for use in conjunction with silicone is cellulose acetate propionate, which canreduce both ethylphenols by 31-32%, andmay lead to better sensory outcomes [5], although this remains to be fully determined.

Therefore, even the relatively modest reduction in 4-EP and 4-EG demonstrated withsiliconeprovides wine makers with some promisingoptions for remediating Brett-affected wines.

Silicone can be manufactured in a variety of molecular weights and forms with differing physical and thermal properties, which allows for some potential flexibility when incorporating it into juice and wine processing. It could, for instance, be integrated into existing filtration systems or fermentation vessels, or added directly as a fining agent that can laterbe removed when taint compounds have been reduced to target levels.However, before use of silicone can be recommendedcommercially, determination of its effects on non-target odorants and non-volatile wine constituents is needed, and this work is currently underway in our lab. In the case of non-target odorants, the results from [15]for silicone treatment of juice are encouraging. We are also currently determining the potential to regenerate silicone to facilitate multiple applications. As with all wine faults, prevention is better than remediation; adoption of best practises with respect to winery hygiene (Brett taint) and viticultural practises (methoxypyrazines) are recommended.

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