Prevalence of Wildfire Smoke Exposure Markers in Oaked Commercial Wine

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Abstract

Background and goals
Grapes exposed to wildfire smoke and wine produced from contaminated grapes can be robustly identified through quantitative analysis of smoke exposure markers, volatile phenols, and phenolic glycosides (PGs). This assessment is based on comparison of data from suspect samples to concentrations of phenolic compounds typically found in non-smoke-exposed grapes and unoaked wines.

Oak products for winemaking are typically heat treated and represent a major source of guaiacol and other volatile phenols in wine. Although contact with oak products is thought to contribute negligible concentrations of PGs, the lack of data from oaked wines confounds the identification of a potential risk of smoke taint development in wine when assessing commercially produced, oaked wine. Therefore, this study aimed to determine the typical concentrations of smoke exposure markers in commercially produced, oaked wine.

Methods and key findings
Commercially produced wines (20 to 30 each) of Cabernet Sauvignon, Chardonnay, Pinot noir, and Shiraz cultivars were sourced from Australian regions and vintages free from known wildfire smoke exposure. Gas chromatography-mass spectrometry and high-performance liquid chromatography-mass spectrometry demonstrated that syringol and guaiacol were relatively abundant in oaked wine, reaching concentrations of 200 μg/L. In contrast, most PGs were <10 μg/L, and trace concentrations of cresols were infrequently found.

Conclusions and significance
The concentrations of established wildfire smoke marker compounds (guaiacol, 4-methylguaiacol, syringol, 4-methylsyringol, o-cresol, m-cresol, p-cresol, syringol gentiobioside, 4-methylsyringol gentiobioside, cresol rutinoside, phenol rutinoside, guaiacol rutinoside, and 4-methylguaiacol rutinoside) were determined in oaked Australian Cabernet Sauvignon, Chardonnay, Pinot noir, and Shiraz wines. The data enable confident identification of smoke-affected wine that has been in contact with oak.

Key words: oak, phenolic glycosides, smoke, volatile phenols, wine

Introduction

Since it was first reported in 2003, smoke taint caused by wildfire smoke has resulted in many millions of dollars in losses for wine producers worldwide, including in Australia, Canada, Chile, Greece and other Mediterranean countries, South Africa, and California (AWRI 2003, Krstic et al. 2021). Wine made from smoke-exposed grapes has been described as “smoky, burnt, ash, ashtray, salami, smoked salmon,” and notably, “lingering retro-nasal ash character” (AWRI 2003). Research over the last decade has established that smoke-exposed grapes and wines made from smoke-exposed vineyards can be reliably identified by measuring volatile phenols (VPs) and phenolic glycosides (PGs), and comparing these exposure markers to known concentrations typically found in non-smoke-exposed grapes and wines (Coulter et al. 2022). The concentration of smoke markers in grapes has recently been shown to predictively model smoke flavor intensity in wine (Parker et al. 2023).

The compounds utilized for identifying smoke-exposed grapes and wine include VPs: guaiacol; 4-methylguaiacol (MeGu); o-, m-, and p-cresol; syringol; and 4-methylsyringol (MeSyr), and glycosides: syringol gentiobioside (SyGG), methylsyringol gentiobioside (MSyGG), cresol rutinosides (CrRG), guaiacol rutinoside (GuRG), methylguaiacol rutinoside (MGuRG), and phenol rutinoside (PhRG).

VPs are formed from thermal lignin degradation during combustion, which can occur during toasting of oak products and barrels prior to their use in winemaking, and more generally, from generation of smoke by burning woody materials (Wittkowski et al. 1992, 1994, 1996, 2004, 2004; Wittkowski and Ternes 2006; Krstic et al. 2015).
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available for concentrations of PGs in oaked wine made in from grapes suspected of smoke exposure, and no data are tion of analytical data for VPs when assessing wine made al. (2003) did not detect any cresols in extracts of toasted of oak produced only trace levels of cresols, and Cadahía et 2010). By contrast, Chatonnet et al. (1999) found the toasting values of \( \mu g/L \) and 500 \( \mu g/L \) (Prida and Chatonnet maceutical data may have been reported in wine produced with heavily toasted oak. An aside, the formation of guaiacol as an artifact during gas chromatography-mass spectrometry analysis may have contributed to such high values, and true concentrations may have been much lower (Perez-Prieto et al. 2002, Pollnitz et al. 2004). Reported concentrations of cresols have generally been <5 \( \mu g/L \) (Prida and Chatonnet 2010, Chira and Teissedre 2013). Only one study of 79 wines reported higher concentrations of cresol, with an average concentration of 7 \( \mu g/L \) and a maximum value of 158 \( \mu g/L \) (Prida and Chatonnet 2010). By contrast, Chatonnet et al. (1999) found the toasting of oak produced only trace levels of cresols, and Cadahía et al. (2003) did not detect any cresols in extracts of toasted oak. Although contact with oak products is thought to contribute negligible concentrations of PGs, smoke marker data from oaked wine are currently lacking.

In summary, oak treatment complicates the interpretation of analytical data for VPs when assessing wine made from grapes suspected of smoke exposure, and no data are available for concentrations of PGs in oaked wine made in years without smoke exposure of vineyards. Therefore, this study was initiated to determine the concentrations of VPs and PGs in commercial oaked wine, with the aim of providing information critical for identifying smoke-affected wine that has been in contact with oak. The concentrations of key smoke marker compounds, VPs, and PGs were determined in 88 commercial oaked wines from four cultivars and compared to concentrations found in unoaked, non-smoke- exposed wine and unoaked, smoke-affected wine. Overall, the results establish which markers are suitable indicators of smoke exposure when assessing oaked wine.

Materials and Methods

Oaked wine selection

A total of 88 wines from four different cultivars (Cabernet Sauvignon, Chardonnay, Pinot noir, and Shiraz \( [n = 28, 20, 20, \) and 20, respectively]) were purchased from local wine stores in Adelaide, Australia, in 2022. All wine was selected from Australian wine regions. Due to the occurrence of multiple wildfire events across Australia in the 2019 to 2020 growing season, wines from vintage 2020 and 2021 were avoided, considering that up to 15% of wine from the 2020 vintage may have been included in the final wine blend, under current label integrity rules (Wine Australia 2020). Three Shiraz wines from vintage 2020 had been made from grapes from the McLaren Vale and Barossa wine regions, which were not exposed to wildfire smoke (Wine Australia 2020). The aim of the wine selection was to achieve a broad distribution of samples across price points, regions, and vintages. Details of the wine selection can be found in Supplemental Table 1.

The winemaking details of all selected wine were found on producers’ websites, and to the authors’ knowledge, all wine was oak treated. The oak treatments included grapes fermented in French barrels, maturation in French or American barrels (old or new), and wine in contact with oak chips or staves after fermentation, for various periods of time. In summary, all wine was selected from various subregions in Australia and made from grapes without apparent exposure to wildfire smoke, but had undergone varied oak treatment during vinification.

Smoke-affected wine

Unoaked but smoke-affected wine was made in 2020 from grapes exposed to smoke prior to veraison (Jiang et al. 2022) or from grapes that had experienced a range of smoke events during the 2019 to 2020 ripening season (Parker et al. 2023). A total of 49 smoke-exposed wines were used from the cultivars Chardonnay, Pinot noir, and Shiraz \( [n = 16, 14, \) and 19, respectively), with a broad range of VP and PG concentrations, as reported previously.

Unoaked small-scale wine made from non-smoke-exposed grapes

Small-scale fermentations were conducted on non-smoke-exposed grape berries collected from multiple regions across Australia over four vintages to produce 192
Results and Discussion

Concentrations of oak-specific volatiles (cis-oak lactone, trans-oak lactone, vanillin, 5-methylfurfural, eugenol, and furfural) are summarized in Table 1. The LoQ for PGs was 1 µg/L. The concentrations of smoke exposure markers, VPs, and PGs in the commercial oaked wines are summarized by cultivar in Table 2. To illustrate how key smoke marker compounds distinguish smoke-exposed wine from oaked wine, the results from oaked wine were compared with data from wine made from smoke-exposed grapes and from unoaked small-lot wine made from non-smoke-exposed grapes (Figure 1).

Syringol and MeSyrr were the most abundant compounds in the oaked wine, with median values in Shiraz wine ranging from 3 to 47 µg/L and reaching maximum concentrations of 187 µg/L and 96 µg/L, respectively (Table 2). These values are higher than those observed in smoke-affected wine (Parker et al. 2023). Syringol and MeSyrr were rarely detected in smoke-affected unoaked Chardonnay. Median values in smoke-affected red wine ranged from 6 to 12 µg/L for syringol and <1.0 to 4 µg/L for MeSyrr; maximum concentrations were 65 µg/L and 25 µg/L, respectively. MeGu was also present in many of the oaked wines, reaching a maximum of 35 µg/L, which is in line with previously reported values (Ribéreau-Gayon et al. 2006, Prida and Chatonnet 2010) and higher than the maximum value of 25 µg/L observed in smoke-affected wine (Parker et al. 2023). Overall, MeGu, syringol, and MeSyrr had similar abundance in oaked and smoke-affected wine and are not suitable markers to distinguish oaked from smoke-affected wine.

Guaiacol concentrations in the oaked wine had median values ranging from 2 to 24 µg/L and a maximum concentration of 47 µg/L (Table 2). These values are in line with those previously reported for oaked wine (Spillman et al. 2004, Ribéreau-Gayon et al. 2006, Prida and Chatonnet 2010). The guaiacol concentrations in the oaked wine were similar but generally lower than values observed in smoke-affected wine, which had median values ranging from 2 to 55 µg/L and maximum concentrations up to 125 µg/L, clearly demonstrating that guaiacol concentration alone cannot be used to distinguish between oaked and smoke-affected wines (Figure 1). The values are higher than those found in wine made from non-smoke-exposed grapes, in which the reported 99th percentile value is typically <5

The concentrations of smoke exposure markers, VPs, and PGs in the commercial oaked wines were made over two vintages (2010 and 2011), Chardonnay and Shiraz (n = 52 and 66, respectively) wines were produced over three vintages (2010, 2011, and 2016), and Pinot noir (n = 42) wines were produced over four vintages (2010, 2011, 2016, and 2017). Details of sample collection, winemaking, and analysis results are described and presented by Coulter et al. (2022).

### Table 1 Concentrations of oak-derived volatiles in commercial oaked wine. Limit of quantification (LoQ) for all compounds is 10 µg/L.

<table>
<thead>
<tr>
<th></th>
<th>5-Methylfurfural (µg/L)</th>
<th>cis-Oak lactone (µg/L)</th>
<th>Eugenol (µg/L)</th>
<th>Furfural (µg/L)</th>
<th>trans-Oak lactone (µg/L)</th>
<th>Vanillin (µg/L)</th>
</tr>
</thead>
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<tr>
<td>Cabernet Sauvignon</td>
<td>Min</td>
<td>&lt;LoQ</td>
<td>77</td>
<td>&lt;LoQ</td>
<td>67</td>
<td>39</td>
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<tr>
<td></td>
<td>Max</td>
<td>18</td>
<td>294</td>
<td>34</td>
<td>329</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td>Median</td>
<td>&lt;LoQ</td>
<td>134</td>
<td>20</td>
<td>109</td>
<td>119</td>
</tr>
<tr>
<td>Chardonnay</td>
<td>Min</td>
<td>&lt;LoQ</td>
<td>15</td>
<td>&lt;LoQ</td>
<td>31</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>326</td>
<td>172</td>
<td>19</td>
<td>1709</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Median</td>
<td>98</td>
<td>88</td>
<td>11</td>
<td>473</td>
<td>56</td>
</tr>
<tr>
<td>Pinot noir</td>
<td>Min</td>
<td>&lt;LoQ</td>
<td>&lt;LoQ</td>
<td>&lt;LoQ</td>
<td>62</td>
<td>&lt;LoQ</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>60</td>
<td>155</td>
<td>23</td>
<td>369</td>
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</tr>
<tr>
<td></td>
<td>Median</td>
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<td>52</td>
<td>&lt;LoQ</td>
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<tr>
<td>Shiraz</td>
<td>Min</td>
<td>&lt;LoQ</td>
<td>&lt;LoQ</td>
<td>&lt;LoQ</td>
<td>79</td>
<td>&lt;LoQ</td>
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<tr>
<td></td>
<td>Max</td>
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<td>488</td>
<td>37</td>
<td>508</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>Median</td>
<td>18</td>
<td>54</td>
<td>&lt;LoQ</td>
<td>170</td>
<td>30</td>
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</tbody>
</table>
Figure 1 Smoke exposure markers guaiacol (A), o-cresol (B), and syringol gentiobioside (C; SyGG) in commercial oaked, smoke-affected, and control unoaked small-scale wines made from non-smoke-exposed grapes. CS, Cabernet Sauvignon; C, Chardonnay; P, Pinot noir; S, Shiraz. Control, unoaked small-lot wines from grapes with no smoke exposure (n = 192), published previously (Coulter et al. 2022); Oak, wines described in this study; Smoke, wines made from Chardonnay, Pinot noir, and Shiraz grapes exposed to smoke while ripening in the vineyard (n = 49), published previously (Jiang et al. 2022, Parker et al. 2023). No data on smoke-affected Cabernet Sauvignon wine were available for comparison.
μg/L for most varieties and 13 μg/L for Shiraz. The values are also higher than the maximum value (2.3 μg/L) reported by Merrell et al. (2021) for Pinot noir wine from the 2019 vintage.

Concentrations of each of the cresols (α-, m-, and p-cresol) were <5 μg/L in all oaked wine and below the LoQ of 1 μg/L in many of the wines (Table 2 and Figure 1). The maximum concentration of any isomer was 3 μg/L of α-cresol in six of the Pinot noir wines. These values are comparable to those found in non-smoke-exposed small-scale ferments (controls) (Coult et al. 2022), the maximum value (2.8 μg/L) reported by Merrell et al. (2021) for non-smoke-exposed Pinot noir wine from the 2019 vintage, and previous reported concentrations in oaked wine (Ribéreau-Gayon et al. 2006, Prida and Chatonnet 2010). By contrast, values in smoke-affected wine reached 29 μg/L (α-cresol). Therefore, cresol concentrations >3 μg/L in wine could potentially indicate smoke exposure.

PGs were all <20 μg/L in the oaked wine. All PGs were below the LoQ (1.0 μg/L) in all oaked Chardonnay wine, and many PGs were below the LoQ (1.0 μg/L) in most of the Pinot noir wine. The oaked Shiraz and Cabernet Sauvignon wines had higher concentrations of PGs, a trend also seen in the non-smoke-exposed wine. GuRG and SyGG were the most abundant PGs in the oaked wine and the only PGs that exceeded 10 μg/L. Shiraz wine generally had higher concentrations of SyGG and GuRG than the other cultivars, with median values of 8 μg/L and 7 μg/L and maximum concentrations of 18 μg/L and 20 μg/L, respectively.

Surprisingly, some of the red wine had concentrations of SyGG and GuRG that exceeded those typically observed in small-scale wine made from non-smoke-exposed grapes under controlled conditions, which are generally <13 μg/L (Coult et al. 2022). Nonetheless, the concentrations of PGs in both control and oaked wine were very low compared to the values observed in wine made from smoke-exposed grapes (Figure 1). In smoke-exposed Shiraz wine, SyGG was commonly detected in the range of 13 to 123 μg/L and reached a maximum of 690 μg/L, and GuRG was detected in the range of 11 to 85 μg/L (Parker et al. 2023).

To our knowledge, this is the most comprehensive survey of PGs in commercially produced wine. In many cases, concentrations of PGs allow for reliable differentiation between wine made from grapes with and without smoke exposure, even after the wine was in contact with oak products. Still, certain limitations should be considered. The smoke-exposed wines in this study were all sourced from one vintage in Australia and generally had similar patterns of smoke exposure markers, with SyGG being the most abundant smoke marker. However, other patterns are possible, such as the recently reported higher relative abundance of PhRG in California wine (Wilkinson and Ristic 2020, Crews et al. 2022). Variations in the relative abundance of smoke exposure markers likely reflect differences in fire behavior, environmental conditions, and/or the type of fuel from which smoke was generated; for example, pyrolysis of angiosperms such as hardwood Eucalyptus trees yields syringols, guaiacols, and cresols, whereas syringol is absent in smoke from burning gymnosperms such as Pinus woods (Simoneit et al. 1993, Kelly et al. 2012). Therefore, the authors recommend considering the whole suite of VPs and PGs when attempting to identify wine made from smoke-exposed grapes after future smoke events.
Conclusion
This study determined the concentrations of known smoke marker compounds in commercial oaked wines of Cabernet Sauvignon, Chardonnay, Pinot noir, and Shiraz cultivars. Comparing smoke marker data from commercial oaked wine with concentrations previously reported in unoaked small-scale wine made from non-smoke-exposed grapes and with unoaked wine made from grapes exposed to wildfire smoke enabled a selection of phenolic compounds that can be used to identify smoke exposure when evaluating a suspect sample. Specifically, SyGG; other phenolic glycosides; and the VPs o-, m-, and p-cresol are suitable to distinguish smoke-affected wine from oaked and unoaked wines made from non-smoke-exposed grapes. By contrast, VPs guaiacol, MeGu, syringol, and MeSyr are clearly not suitable for distinguishing smoke-affected wine from oaked wine because their concentrations found in oaked wine were similar and, in some cases, exceeded concentrations in smoke-affected wine.

Further research is needed to establish the concentrations of smoke markers in oaked wine made from other cultivars and to include oaked and smoke-affected wines from other vintages, regions, and countries. Further validation of these results can be gained by testing the effect of known amounts and duration of oak treatments on smoke-related marker compounds. Despite these limitations, this study allows producers and researchers to assess smoke marker concentrations in wine to indicate wildfire smoke exposure of grapes used for commercial wine.

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Supplemental Data
The following supplemental materials are available for this article at ajevonline.org:

Supplemental Table 1 Commercial wine included in the study.


