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Distinctive flavour or taint? The case of smoky characters in wine

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Abstract. Forest fires in the vicinity of vineyards have significantly increased in the last decade in many wine producing countries. The fires cause smoke drift throughout vineyards which cannot be avoided and may result in the production of wines described as 'smoky' or 'smoke tainted'. Such wines are characterised by undesirable aromas, and also by a lingering, unpleasant 'ashy' aftertaste. Notably, smoky aromas in wine and other beverages are not *a priori* quality defects, but are considered desirable in some styles of wines and deliberately introduced through ageing in toasted oak barrels. Compounds typically associated with smoky aromas in beverages are volatile phenols. In addition, glycosidic metabolites from volatile phenols are reliable markers for the detection of smoke exposure of grapes, important flavour precursors and also have a direct impact on the perceived 'smoky' aftertaste in wine. This paper provides a summary about 'smoky' flavours in wine and the contribution to wine aroma and flavour of volatile phenols and thiols, as well as glycoconjugates. In addition, approaches for managing environmental smoke exposure of grapes and undesirable 'smoky' flavours in wine will be presented, together with sensory data exploring what might represent unacceptable smoke taint.

1. Introduction

The severity and frequency of forest fires and wildfires have significantly increased since the early 2000s and exposure of vineyards and grapes to environmental smoke cannot be avoided. Uptake of volatile phenols from smoke by grapes during ripening can result in the production of wine with notable smoky notes. In severe cases, some wines are "smoke-tainted" because of excessive "smoky", "burnt", "ash", and "ash tray" aromas in combination with a lingering, unpleasant ashy aftertaste [1, 2].

Smoke taint in wine is not a new phenomenon and has already been described in 1892 by Giacomo Grazzi-Soncini in his classic textbook on wine classification, tasting, qualities, and defects: "With the smoky taste a wine.... changes into a liquid not to be tolerated by even the most uncritical palate." [3]. To date, smoke taint caused by wildfire smoke has resulted in billions of dollars in direct losses and extra cost to wine producers worldwide, including producers in Australia, Canada, Chile, Greece and other Mediterranean countries, South Africa, and California in the last two decades [1].

Once grapes have been exposed to smoke, limited options are available for remediation or amelioration [4]. At the same time, it is worth noting that smoky aromas in wine and other alcoholic beverages are not *a priori* quality defects; similar smoky characters are widely found and appreciated in spirits, particularly peat whiskeys and certain mezcals.

In wine, aromas such as "struck flint", "struck match", or "gun smoke", are considered desirable in some styles produced from grapes grown without any known smoke exposure, such as Burgundian Chablis and cooler climate barrel-fermented Australian Chardonnay [5-7]. Furthermore, the common practice of aging of wine in toasted oak barrels [8] deliberately introduces smoky characters [9-11]. Consequently, oak treatment complicates the interpretation of analytical and sensory data when assessing wine made from grapes suspected of smoke exposure [12].

As smoke exposure of grapes and smoke taint in wine is a common concern for grape growers and winemakers in many wine producing countries, this paper provides a summary about 'smoky' flavours in wine and the contributions of volatile phenols and thiols, as well as glycoconjugates (phenolic glycosides). In addition, approaches for managing environmental smoke exposure of grapes and undesirable 'smoky' flavours in wine will be discussed, together with sensory data to explore what represents unacceptable smoke taint.

2. Methods and materials

2.1. Grape and wine samples

Unoaked but smoke-affected wine was made in 2020 from grapes exposed to smoke prior to veraison [13] or from grapes that had experienced a range of smoke events during the 2019 to 2020 ripening season [14]. 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 volatile phenols and phenolic glycoside concentrations, as reported previously.

Small-scale fermentations were conducted on non-smoke-exposed grape berries collected from multiple regions across Australia over four vintages to produce 192 unoaked wines. Non-smoke-exposed and unoaked Cabernet Sauvignon (n = 32) wines were made over two vintages (2010 and 2011), Chardonnay (n = 52) and Shiraz (n = 66) 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. [15].

2.2. Analysis of volatile phenols, oak aroma compounds and phenolic glycosides

The concentrations of guaiacol, methyl guaiacol, *m*-cresol, *o*-cresol and *p*-cresol, syringol, methyl syringol, 5-methylfurfural, cis- and trans- oak lactone, eugenol, furfural, and vanillin in wine samples were determined by gas chromatography-mass spectrometry (GC-MS) using an Agilent 6890 GC coupled to an Agilent 5973 MS, as reported previously [16].

Phenolic glycosides, namely syringol gentiobioside (SyGG), cresol rutinosides (CrRG), guaiacol rutinoside (GuRG), methyl guaiacol rutinoside (MGuRG), methyl syringol gentiobioside (MSyGG), and phenol rutinoside (PhRG), were quantified by HPLC-MS/MS [17].

2.3. Analysis of volatile sulfur compounds in wine

Volatile sulfur compounds, such as H_2S and methanethiol, were analysed by static HS-GC/SCD on an Agilent 7890B GC, coupled to an Agilent 8355 SCD and equipped with a Gerstel MPS2 XL [18, 19]

Trace concentrations of phenylmethanethiol (PMT) and 2-furylmethanethiol (FMT were quantified after derivatisation with 4,4′-dithiodipyridine by HPLC-MS/MS using an Exion UHPLC coupled to 6500 QTrap+ mass spectrometer (Sciex) [19, 20].

2.4. Sensory analysis of wine

Sensory assessments were conducted by trained panels with previous experience in wine smoke sensory evaluation and further training prior to quantitative descriptive analysis of wine and specialised smoke rating assessments [21].

Regular wine consumers aged 18 to 65 were recruited for consumer hedonic assessment [21]. Consumers were not linked to any marketing or wine industry organisation. All consumers were required to provide informed consent prior to commencing the study and were reminded that their participation was voluntary, and they could withdraw from the study at any point. All testing was conducted in isolated sensory booths with spittoons and water provided. For each assessment, expectoration and rinsing with water between wines was encouraged.

3. Smoky aromas in wine from thermally generated volatile phenols

The chemical basis of smoky characters in wine is complex, with a large number of compounds implicated. Volatile phenols are formed from thermal degradation of lignin, which occurs during wildfires as well as during toasting of oak products like barrels, chips and staves commonly used in winemaking. Key aroma compounds that confer smoky characters to wine and many beverages are volatile phenols, including guaiacol and syringol, together with 4-methylguaiacol and 4-methylsyringol, which contribute “smoky”, “sweet smoke”, and “smoky bacon” flavours. Cresol isomers are associated with nuanced smoky and some negative aromas (*o*-cresol, “phenol” and “plastic”; *m*-cresol, “smoky”, “phenolic”, “band-aid”, and “plastic”; and *p*-cresol, “faecal”, “horse stable-like”, and “medicinal”).

In a recent study of wines that had a wide range of smoke flavour intensities as rated by a trained sensory panel, the chemical composition of smoke-exposed grapes or wine was used to predict smoke flavour intensity in wine [14]. Guaiacol, which by itself is not necessarily a taint compound, was one of the most important predictors of smoke flavour for all samples included in this study. Furthermore, *o*-, *m*- and *p*-cresol were important to most samples. This is in line with previous observations that guaiacol and the cresols, in combination, are likely to drive the perception of smoke flavour in smoke-affected wines, due to their low sensory thresholds relative to the other volatile phenols [14].

Oak contact during wine production typically results in the presence of guaiacol, syringols, and cresols, with their concentrations varying by species and origin of oak wood and by the degree of toasting [8]. Concentrations of guaiacol and syringol up to 140 µg/L and 500 µg/L, respectively, have been reported in wine produced with heavily toasted oak. As a cautionary note, the formation of guaiacol as an artefact during GC-MS analysis has been reported, and true concentrations potentially can be much lower [9, 16]. Toasting of oak typically only produces trace levels of cresols [22] and reported concentrations of cresols in oaked wine have generally been below 5 µg/L [10].

In a recent study on the prevalence of volatile phenols in oaked commercial wine [12], syringol and methyl syringol were the most abundant compounds in the oaked wine, with median values in Shiraz wine ranging from 3 to 48 µg/L (Table 1) and reaching maximum concentrations of 187 µg/L for syringol and 96 µg/L methyl syringol. Notably these values are higher than those observed in smoke-affected wine [14] or unoaked wine made from grapes without known smoke exposure [15]. In the same study, concentrations of each of the cresols (*o*-, *m*-, and *p*-cresol) were below 5 µg/L in all oaked wines (Table 1). By contrast, values in smoke-affected wine reached 29 µg/L for *o*-cresol. Therefore, elevated cresol concentrations in wine could potentially indicate smoke exposure of grapes. Guaiacol median concentrations in the oaked wines ranged from 2 to 24 µg/L with a maximum concentration of 47 µg/L (Table 1). These values are in line with those previously reported for oaked wine [10, 11, 23] and higher than those found in unoaked experimental wines made from non-smoke-exposed grapes, in which the reported 99th percentile value was typically below 5 µg/L for most varieties and 13 µg/L for Shiraz [15].

In comparison to wine made from smoke-exposed grapes [14] the guaiacol concentrations in the commercial 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. This is clearly demonstrating that guaiacol concentrations in wine alone cannot be used to distinguish between oaked and smoke-affected wines.

Table 1. Median concentrations of volatile phenols in unoaked experimental wine (*unoaked*, [15]), commercial oaked wine (*oaked*, [12]) and wine made from grapes exposed to environmental smoke in the vineyard (*smoke*, [14]).

		Guaiacol µg/L [a]	*o*-Cresol µg/L	Syringol µg/L
Cabernet Sauvignon	unoaked	<1	<1	2.5
	oaked	8	<1	39
	smoke	nd [b]	nd	nd
Shiraz	unoaked	5.9	<1	2.4
	oaked	24	<1	48
	smoke	23	3	14
Pinot Noir	unoaked	<1	1.3	1.2
	oaked	8	<1	19
	smoke	16	11	6
Chardonnay	unoaked	<1	<1	<1
	oaked	2	<1	6
	smoke	2.5	2	<1

[a] Limit of quantification was 1 µg/L for all compounds in this table. [b] nd : not determined

4. Volatile sulfur compounds and smoky characters in wine

Volatile sulfur compounds are commonly present in many wines and contribute both desirable (e.g., 3-sulfanylhexanol, "passion fruit" and "tropical") and negative (e.g., H_2S and methanethiol, "rotten egg" and "rotten cabbage") characters. Phenylmethanethiol (PMT), also known as benzyl mercaptan or benzenemethanethiol, has an extremely low sensory aroma perception threshold of 0.3 ng/L in model hydroalcoholic solution, and addition studies confirmed that adding small concentrations of PMT to base wines can increase the intensity of "smoky" or "struck flint" aroma [24]. PMT is often detected in cool-climate Chardonnay and less frequently in Pinot Noir and Sauvignon Blanc table wines; it can be present in aged white or sparkling wines. Older, more expensive Chardonnay wines and wines from cooler regions are more likely to have higher concentrations of PMT, most likely reflecting lees contact and barrel fermentation [25].

In a recent study of commercial Chardonnay wine, the contribution of potent thiols PMT and 2-furylmethanethiol (FMT) to smoke-like "empyreumatic", struck-match aromas was assessed [7]. The term "empyreumatic" describes wines, often barrel- aged or barrel-fermented white wines, which display aromas reminiscent of smoke, gunpowder/gun flint, minerals, roasted coffee, toast, brioche, and the smoky/sulfidic aroma of a struck match [7]. This study showed that 2FMT (0.2 to 164.5 ng/L) and PMT (0.2 to 7.8 ng/L) were commonly present at concentrations of sensory significance in most commercially produced Chardonnay wines from Australia. Notably, PMT and 2FMT were confirmed to be associated with 'empyreumatic' nuances, with 2FMT in these wines most strongly related to 'flint', 'struck-match', 'mineral' aromas rather than ‘roasted coffee’ as suggested by previous reports [7]. A separate study of bottle-aged Bordeaux red wine blends (matured in oak barrels prior to bottling) also found that 2FMT was associated with the “empyreumatic” attribute [26]. Importantly, these observations indicate an association between ng/L concentrations of the volatile thiol, PMT, and smoke-like “empyreumatic” aromas in Chardonnay wine made from grapes without a known history of smoke exposure in vineyards; hence smoky characters in these wines are most likely the consequence of barrel fermentation and -aging.

Notably, additional volatile thiols, such as disulfanes [27] and thia-analogues of volatile phenols described above [28], might be implicated in the expression of “smoky” aromas in wine. The latter thiols evoked an enhanced “ashy” flavour when spiked in combination with volatile phenols into red wine [28]. The formation of “smoky” thiols through pyrolysis of plant material [28], or from precursors in oak wood and their presence in aged red wine [29] is a focus of active research.

5. Sensory characterisation of smoky grape and wine samples

As discussed above, smoky aromas are common in many wines and sought after in oaked red wines and certain white wine styles, such as barrel-fermented Chardonnay. On the other hand, wines made from smoke-affected grapes, particularly wines made with skin contact, can have unpleasant smoky aromas, flavours, and an “ashy” aftertaste. Such excessive “smoke” flavours have for many years been recognised as undesirable quality defects by many in the wine industry [3]. Sensory evaluation of wines produced from potentially smoke-exposed grapes is challenging: the response of individuals to smoke volatile compounds, such as guaiacol, is known to be variable, and recent research has shown a large degree of interindividual variation in sensitivity to guaiacol and guaiacol glucoside [30]. Therefore, individuals who are sensitive to volatile phenols and glycosides experience a lengthy smoky aftertaste, and as a consequence, carry-over effects are a concern in smoke sensory assessments [31]. While chemical models for predicting smoky sensory characters in wine, based on grape or wine compositional analysis, are available and can be used to better define the risk of quality defects [14], the substantial matrix effects between wines of different styles and interindividual variability hamper generalization of such predictive models. Furthermore, using sensory thresholds to define a problematic level of smoke taint in wine is largely impractical as a result of the large number of compounds involved that would need to be evaluated in a broad range of different wine styles, the fact that compounds like guaiacol are not taint compounds as such but widely present in fault-less wines produced from grapes with no known smoke exposure, and the large degree of interindividual variation, especially with regard to recognizing retronasal flavour release from flavour precursors.

As alternative to expert sensory assessments, consumer responses can provide better guidance as to whether and at what level smoky attributes in wine are likely to be perceived negatively by the market. Results from a recent consumer sensory study clearly demonstrated that smoke flavour was a strong negative driver of consumer liking for the three wine styles assessed, namely Pinot Noir rosé, Chardonnay, and unoaked Shiraz wines [21]. Notably, the sensitivity of consumers to smoke-affected wines correlated highly with “smoke” flavour ratings from a screened and trained smoke-sensitive panel for each wine type. In the same consumer sensory study, it was observed that the mean “smoke” flavour score that significantly affected consumer liking was different among the three different wine styles, which suggests that the involvement of matrix effects can influence the absolute magnitude of the “smoke” flavour rating and consumer liking. Detailed data analysis revealed that consumers (who were wine drinkers) fell into one of three categories: highly responsive to “smoke” characters, moderately responsive, and a smaller group of non-responders; the size of each of these clusters was different between each consumer group and wine style.

In summary, what constitutes objectionable smoke taint for consumers and experts and cannot be generalised to date, given the interindividual differences, observed clusters of consumer liking and influences of wine style on the absolute magnitude of “smoke” flavour ratings and consumer liking.

6. Making wine from potentially smoke-exposed grapes

Given the increasing number of wildfires and smoke events, wine producers seek to understand the probability of producing an unacceptable smoke-tainted wine from mildly smoke-affected grapes when making grape harvesting or purchasing decisions. Objectively defining robust sensory boundaries for what represent unacceptable or excessive ‘smoky’ characters is difficult, and reliable sensory data from rapid mini-ferments of suspect grapes ahead of harvest are not always available. These factors make it difficult to make informed decisions about harvesting and winemaking practices when dealing with larger smoke events.

When vineyards are exposed to smoke, volatile phenols are taken up by grape berries and leaves and rapidly metabolised to form phenolic glycoconjugates. Following initial exposure, phenolic glycosides accumulate in grapes during ripening; subsequently volatile phenols and phenolic glycosides are readily extracted into must and wine during winemaking. As a consequence, wine made from heavily smoke-exposed grapes may contain higher concentrations of volatile phenols, particularly cresols and phenolic glycosides, when compared to wine made with oak contact [12, 14]. Notably, the smoke-related phenolic glycosides are not found in oak barrels but are unique to smoke-exposed grapes and key contributors to the “lingering ashy aftertaste” that is typical for wine made from smoke-exposed grapes [12, 32].

Research over the past decade has established that volatile phenols can be detected in grapes within hours or a few days after exposure to smoke, and well ahead of commercial maturity and harvest. Similarly, HPLC−MS/MS analysis can demonstrate presence of significantly elevated concentrations of a range of phenolic glycosides in grapes from smoke-exposed vineyards; these glycosidic grape metabolites are specific biomarkers for smoke exposure of grapes but also for wine, even after oak contact during winemaking [17]. These phenolic glycosides can also contribute to the flavour and lingering aftertaste of smoke-affected wines, by releasing odorants in the mouth during consumption, whereby the released odorant is perceived retronasally [33].

Phenolic markers typically used to identify smoke-exposed grapes prior to harvest include volatile phenols (guaiacol, 4-methylguaiacol, *o*-, *m*-, and *p*-cresol, syringol, and 4-methylsyringol), together with some of their grape metabolites, i.e. syringol gentiobioside (SyGG), 4-methylsyringol gentiobioside, cresol rutinosides, guaiacol rutinoside, 4- methylguaiacol rutinoside, and phenol rutinoside. These measurements enable the reliable identification of grapes that have not been affected by smoke despite being sourced from vineyards located in regions exposed to wildfire activity or smoke haze; and they allow identification of substantially contaminated grapes that are likely to produce smoke-tainted wine, thereby eliminating smoke-damaged grapes from the supply chain [15]. Being able to verify ‘at-risk’ grapes and vineyards through chemical analysis of grape composition prior to harvest is particularly valuable because recent research has demonstrated that considerable smoke haze can originate from well outside the local area where a vineyard might be located, with smoke regularly traveling hundreds of kilometres [34].

During large-scale testing in Australia of grape samples from the 2020 vintage, which was significantly affected by wildfires, no verified cases of false-positive classifications of grapes were reported. At the same time, it was recognised that a substantial proportion of moderately smoke-exposed grape samples, especially from white varieties, will not inevitably give tainted wine [2]. In this context, a recent study has established critical concentrations of volatile phenols and phenolic glycosides in grapes likely to produce smoky wines [14]. Based on analytical data for a large number of Chardonnay, Pinot Noir, and Shiraz grape and wine samples, threshold concepts from exposure risk assessment, ‘no observed adverse effect levels’ (NOAELs) and ‘lowest observed adverse effect levels’ (LOAELs), were adapted empirically based on measurement of smoke markers such as SyGG in grapes. Effectively, grapes with SyGG *concentrations below the NOAEL are unlikely to give notable smoke taint in wine*, while above is a moderate risk for some wines to be rated smoky. Similarly, the LOAEL serves as *lower boundary for a high risk of smoke taint in wine* because at concentrations of smoke exposure markers in grapes above the LOAEL there was a demonstrated ‘smoky’ sensory effect in all wines made from such grapes [2].

Such moderately smoke-exposed grapes, with smoke exposure marker concentrations above NOAELs and below LOAELs, if identified early during harvest or winemaking, can be handled separately using optimised winemaking practices to reduce the risk for smoke taint developing in wine, for example through minimising skin contact of grapes, gentle pressing, use of fining agents and blending [4, 35, 36].

7. Summary and outlook

Smoke exposure of vineyards and grapes is an ongoing problem for many wine producers, and can cause significant wine quality defects and substantial economic losses through the development of excessive smoky characters and an unpleasant “ashy” aftertaste, that is referred to as ‘smoke taint’. Smoke exposure markers in grapes are well established and essential for identifying grapes affected by smoke from grass and forest fires.

Because prevention is much preferable to the limited remediation options currently available, the development of low-cost and field-deployable analytical techniques for rapid assessment of large sample numbers ahead of harvest of grapes should complement the existing testing of proven phenolic exposure markers.

Notwithstanding that further smoke- related aroma and taste compounds, including modulating and masking compounds, might be discovered in grapes or wine by future research, greater efforts are required to inhibit uptake of volatile phenols by grapes, invest into breeding of varieties resilient to smoke-exposure and/or achieve the selective and full removal from wine of aroma compounds and glycosidic precursors that contribute to excessive smoky characters.

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The authors declare no competing financial interest. The employer of the authors, AWRI, is a not-for-profit research organization and provides smoke marker analysis as a commercial service through Affinity Laboratories, where clients cover the cost. The analytical methods have been published; relevant standards are commercially available; and other commercial laboratories within Australia and internationally also offer this service.

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