Investigations conducted during 2003 and 2004 into the nature and amelioration of taints in grapes and wine, caused by smoke resulting from bushfires

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During the 2003 vintage, Industry Services staff spent a very large amount of time dealing with the issue of 'smoky' taint in grapes and wine resulting from the bushfires that occurred in Victoria and southern New South Wales in January and February 2003. Some additional work was also conducted in 2004. The involvement of the Institute's Analytical Service in expediting the analysis of samples as part of these investigations is acknowledged, as is the input of other Institute staff particularly Dr Mark Sefton, Dr Alan Pollnitz, Dr Paul Henschke and Creina Stockley, and those who participated on the sensory panel.

The Industry Services team considers that this issue was the single largest problem dealt with since the inception of the team, both in terms of its value and the numbers of wine companies and grapegrowers affected. The investigations began with approaches from technical staff of several companies in Victoria and South Australia, who considered that there was a problem with 'smoke taint' in fruit that they had either processed or had contracted to purchase. Over subsequent days the number of approaches to the Institute became overwhelming, and it was clear that a dedicated trial was required to properly understand the nature and extent of the problem, rather than a 'scatter gun approach' of working with several companies concurrently. The Institute, therefore, supported a move by the *Alpine Valley Winemakers and Grapegrowers Association* to fund a researcher to conduct various trials. The Industry Services team helped to design targeted trials, much of this work necessarily being performed over a very short time frame. It is considered that the approach taken by the association's nominees and other affected parties was extremely thorough and professional, such that well controlled and executed replicated experiments were conducted, and well prepared samples delivered to the Institute for analysis. The fact that the affected regions contained declared phylloxera zones complicated the preparation and freighting of samples to Adelaide, and at all times phylloxera control protocols were followed. The Institute also acknowledges the valuable input and assistance provided by John Whiting of the Victorian *Department of Primary Industries,* Jill Kuchel of *Vignoble Monitoring Services,* Wendy Cameron and Terry Barnett of *Brown Brothers Milawa Vineyards*, and Shayne Cunningham of *Gapsted Wines*. As a result of various trials, it is considered that a high level of understanding of the problem has been achieved, unfortunately in spite of which, the problem has proved to be quite intractable in most cases.

The main conclusions of the initial investigations were:

- Various wines and juices submitted to the Institute were indeed considered to exhibit characters variously described by the Institute's sensory panel as *smoky, burnt, ash, ashtray, salami, smoked salmon* etc.

- It was established that guaiacol and 4-methylguaiacol were the most important compounds contributing to the sensory taint. Guaiacol and 4-methylguaiacol are compounds that commonly occur in wines that have been matured in contact with toasted oak products, and are formed during the toasting process from the degradation of lignin. Importantly, a back-palate *excessively drying* character and a lingering retro-nasal *ash* character appeared to be more pronounced in smoke-affected samples than in juices or wines spiked with similar concentrations of guaiacol. It is therefore considered likely that other compounds resulting from the smoke were present in the juices and wines at albeit very low concentrations. However, it was not possible with the resources available to identify the presence of such compounds, their possible concentrations, or their possible sensory or other impacts. As such, guaiacol and 4-methylguaiacol cannot be considered as solely responsible for the identified taint.

- Samples of a number of reference juices obtained from the University of Adelaide Hickinbotham Roseworthy Wine Science Laboratory, which had been sourced from various vineyards around Adelaide where there had not been bushfires during the growing season, were found to contain no detectable guaiacol or 4-methylguaiacol. The assistance of Mr Stephen Clarke in providing these samples is acknowledged. Mr Phil Spillman (pers. comm.) informed the team manager that in his trials previously conducted at the Institute using a Cabernet Sauvignon wine sourced from the 1993 vintage in Coonawarra, a control wine that was stored in stainless steel for 93 weeks contained 5 µg/L of guaiacol, which was attributed to the hydrolysis of fruit-derived precursors over time.

- The concentrations of guaiacol and 4-methylguaiacol in various sets of juice and wine samples were strongly correlated with the overall sensory panel rating of the intensity of the taint. It is important to note, however, that this does not imply that guaiacol and 4-methylguaiacol are solely responsible for the taint, and no work was performed to investigate any other compound that might be present in affected juices or wines.

- Little information is available in the literature concerning the sensory thresholds of guaiacol in juices and wines. The sensory difference threshold for guaiacol in white juice was established to be 6 µg/L or less, using a sensory panel comprised of tasters who had previously been exposed to albeit comparatively small numbers of affected samples. It is possible that tasters with more experience in the identification of the taint would have demonstrated a lower threshold. Using the same tasting panel, the sensory difference threshold in a red wine that contained a background level of 37 µg/L of guaiacol was established to be between approximately 15 and 25 µg/L. It is possible that in a wine with a lower background concentration of guaiacol the sensory threshold would also be lower. Some of the bushfire smoke affected red wines analysed contained in excess of 70 µg/L of guaiacol. The Institute's Analytical Service database contains results of several hundred guaiacol analyses. This sample-set must be considered as potentially heavily skewed towards wooded wines and wines that formed part of various

commercial cooperage trials. Approximately 60% of these samples contain guaiacol concentrations below 20 μg/L.

A trial was conducted to ascertain if it was possible to reduce the guaiacol concentration in grapes and wine by applying various 'vineyard-washing' treatments. The treatments examined were cold water, cold water plus wetting agent, warm water (approximately 25°C when contacting the fruit), cold water plus 5% ethanol, and milk. None of these treatments reduced the guaiacol concentration in either free run juice or crushed grapes that were macerated with skins for either one hour or 24 hours. Guaiacol concentrations were found to increase with increasing maceration time, and samples macerated with leaves contained higher guaiacol concentrations. This finding supported anecdotal observations made by winemakers, that machine harvested fruit was more badly affected than similar fruit that had been hand picked, and further anecdotal observations that the free-run juice from whole bunch pressing was less badly affected than the pressings, or juice from similar fruit that had been machine harvested. Samples of the liquids from each of the washing treatments were also collected and analysed. While it was obvious that some of them contained particulate matter, little or no guaiacol was detected in them. The Ovens Research Station (*Department of Primary Industries*, Victoria) examined bunches and leaves from the trial and ascertained that approximately 90% of ash and particulate matter had been washed off the grapes by the water washing treatments. As it is possible that this ash contained compounds with an undesirable sensory or oenological impact, it was deemed preferable to remove it before harvesting by applying a water spray in the vineyard. However, no guaiacol or 4-methylguaiacol were detected in samples of water used to wash ash from affected bunches.

These results from this initial vineyard washing trial were available within four days of the instigation of the trial, and based on them the following advice was developed:

- Leaf plucking followed by a high-volume, high-pressure cold water wash in the vineyard, followed by hand picking and whole bunch pressing with the separation of juice into several press fractions, was most likely to minimise the taint and allow maximum value to be salvaged.

- In the event that hand picking was not an option, then leaf plucking followed by a high-volume, high-pressure cold water wash in the vineyard, and minimisation of leaf matter entering the fruit during harvesting should be employed.

This advice was actively disseminated to growers and wine companies via various grower and winemaker associations, DPI Victoria, and many individual contacts made with the Institute by growers and media outlets.

Investigations were also conducted in order to ascertain if it was possible to reduce or ameliorate the taint during winemaking. A current Institute research project is examining the ability of various fining agents to 'scalp' or remove various flavour compounds from wine, and a preliminary summary of the results by Institute Senior Chemist Dr Alan Pollnitz, was published in *Technical Review* issue 142 (February 2003), and is also discussed elsewhere in this report. Guaiacol was one of the flavour compounds examined. Of the fining agents examined, only activated carbon was

found to remove any guaiacol, the concentration being reduced by approximately 5% with the addition of 300 mg/L of carbon. The effect of colloidal silica was not examined in the Pollnitz study, and consequently the action of this fining agent was tested on a smoke affected Sauvignon Blanc juice that had been found to contain 18 µg/L of guaiacol. Additions of 0.5 and 1 g/L colloidal silica were added using *Bakesol 30*, and the samples were shaken for two minutes, and then allowed to stand for one hour before being filtered and analysed for guaiacol concentration. The concentration of guaiacol was not affected by either fining rate. The intensity of *smoky* or *ashy* taint was not sensorially assessed in these samples.

It was considered that an explanation was required as to why the vineyard washing treatments had no effect on guaiacol and 4-methylguaiacol, compounds that are reported to be very soluble in water. It was considered important to understand the location of the guaiacol within or on the grape, in order to assist the minimisation of its extraction during processing. Therefore, various samples of grapes were peeled, and the skins and pulp were analysed separately. The results of this experiment were as follows:

- Guaiacol and 4-methylguaiacol were detected in all of the skin samples, but were not detected in any of the pulp samples.

- In subsequent experiments, washing bunches in 95% ethanol for 30 seconds had no effect on the concentration of guaiacol in crushed grape samples that were macerated with skins for 24 hours. The ethanol that had been used for washing subsequently contained a very low concentration of guaiacol equivalent to approximately 4 µg per bunch. Similar results were obtained from an experiment using hexane as the solvent, rather than ethanol.

One purpose of this experiment was to ascertain if the guaiacol was located within the wax bloom on the grapes, or whether it was partitioned in the skin. Based on the assumption that the ethanol and hexane did remove the wax bloom from the grapes, the results suggest that the guaiacol had permeated the grape skin, but that it had not passed through the skins into the grape pulp. It is suggested that this experiment should be repeated using chloroform, as previous workers have used this solvent in experiments to elucidate the composition of the wax cuticle on grape skins (Martin, 1960, and Radler 1965).

Based on the knowledge that the guaiacol appeared to be located in the grape skin, it was considered reasonable to predict that the maximum extraction of the compound would occur during red wine maceration in the presence of ethanol. Whilst this did indeed prove to be the case, the concentrations of guaiacol that were extracted during fermentation were perhaps surprising considering the concentrations that had been observed in the previous experiments.

A number of batches of red grapes were analysed for guaiacol concentration pre-crushing, using the 24-hour maceration treatment that had been used in earlier experiments. Additionally, samples were homogenized in a 10% ethanol solution in order to ascertain if this treatment could be used to predict, pre-processing, the total amount of guaiacol that would subsequently be extracted during fermentation. Fermentations were sampled daily and at pressing, where free run and light and heavy

press fractions were sampled. Samples of marc ex-pressing were also analysed. The following results were obtained from these various red wine fermentation experiments:

- The concentration of guaiacol increased in a near linear manner for the first three to four days of fermentation, and increased only slightly thereafter.

- Free run, light and heavy press fractions all contained the same concentration of guaiacol and 4-methylguaiacol.

- Approximately 25-33% of the total guaiacol present in grapes was apparently extracted when grapes were crushed and macerated with skins for approximately 24 hours before guaiacol analysis was conducted.

- Approximately 75% of the total guaiacol present was apparently extracted from grape skins when they were homogenised in a 10% ethanol solution.

- A small amount of guaiacol and 4-methylguaiacol remained in the marc after pressing.

Work conducted in late 2003 and in 2004 included investigations of fruit from a vineyard that had been exposed to "high intensity" smoke for approximately six to eight hours. The fire occurred in December 2003, approximately three to four weeks prior to veraison for the Cabernet Sauvignon grapes involved. The fruit was sampled in the days immediately following the fire, and then approximately four-weekly until harvest. The resulting wine was also analysed a number of times over the next year. The fruit was found to contain relatively high concentrations of guaiacol and 4-methylguaiacol when compared to fruit from North Eastern Victoria that had been exposed to albeit lower concentrations of smoke for up to six weeks continuously. The concentration of guaiacol and 4-methylguaiacol in the fruit was seen to fall marginally during the following three months up to harvest, possibly due to a dilution effect as the berries increased in volume. The resulting wine was rated as being badly tainted during sensory analysis, and was considered to have little commercial value by the winemaker concerned.

Further work was conducted during 2004 which provided further evidence that the smoke-tainting compounds were somehow partitioned within the grape skin and not on the surface, or incorporated into the wax coating on the skins. Whole bunches were dipped for approximately two seconds into a variety of solvents. The wax residues obtained were subsequently analysed for of guaiacol and 4-methylguaiacol, but none was detected in any of the samples. Samples of grapes from those bunches were then homogenised and were also analysed for guaiacol and 4-methylguaiacol. In all cases the concentrations of guaiacol and 4-methylguaiacol obtained were higher than from similar bunces from the same vineyard which had not been subjected to dipping in solvents. It is possible that the solvents helped to break down the grape skins and release extra guaiacol and 4-methylguaiacol into the homogenate.

Conclusions

It is unfortunate that these investigations, while by no means definitive in nature, indicate that exposure of grapes to bushfire smoke as early as veraison may cause levels of taint in the resulting wine which substantially reduces its commercial value. It is apparent that the taint compounds are present within the grape skin, and thus their extraction is difficult to avoid during winemaking, especially red-winemaking where extended skin contact is necessary. For white wines, winemaking treatments that minimise contact between juice and skin may be beneficial in reducing the intensity of any taint.

The Institute had previously been asked to consider if smoke resulting from controlled burning of bushland might result in a taint occurring in grapes in nearby vineyards, and had provided advice that there was a possibility that such a taint could arise. The results of these investigations provide conclusive evidence that tainting of grapes and wine by bushfire smoke can occur, and potentially have a major economic impact. Many affected white juices, wines and especially sparkling base wines, were deemed to be 'unfit for purpose' and were consequently severely downgraded in terms of value.

As Australian viticulture continues to spread into locations that might be considered as more bushfire-prone than many established grape growing areas, there is a possibility that smoke taint might become a sporadic but more common occurrence in the future. It is evident that few vineyards were actually damaged by the 2003 fires, but damage caused by smoke taint was widespread. It is therefore apparent that, in this situation, insurance cover for smoke damage would have been of greater benefit than for fire damage. However, while it appears that few growers had insurance cover for smoke damage, many do maintain insurance against contamination, and in the Institute's view guaiacol in grapes and wines resulting from the bushfire smoke, is a contaminant.

In spite of the fact that these investigations have greatly increased understanding of the nature of this problem, solutions remain elusive. However, the Institute has analysed a number of commercial samples that were purported to originate from reverse osmosis treatment of red wines, which was being applied with a view to reducing the intensity of the taint, and the concentration of guaiacol in the wines. The results demonstrated an apparent reduction in guaiacol concentration of approximately one third, in the two wines tested. Sensory analysis was conduced on pre and post-treatment samples of one of the wines, with the Institute's sensory panel rating samples that contained lower guaiacol concentrations as lower in *smoke taint*. It is possible that the process may also remove compounds other than guaiacol that may contribute to the perception of the taint. However, there were no significant differences between the panel's ratings of *preference* for the samples pre or post treatment. While the results of this trial are encouraging, the Institute advises persons who are considering the use of this technology commercially to conduct their own trials, conducting rigorous sensory evaluation on samples pre and post-treatment, and to have the samples independently analysed for guaiacol concentration.

References

Martin, J.T. (1960) Determination of the components of plant cuticles. J. Sci. Food Agr. 11, 635-640.

Radler, F. (1965) The main constituents of the surface waxes of varieties and species of the genus *Vitis.* Am. J. Enol. Vitic. 16, 159-167.

The AWRI does offer an analytical service for measurement of key compounds responsible for smoke taints.

Guaiacol and **4-methylguaiacol** are the most important compounds contributing to 'smoky' taint in juice and wines, attributed to bushfire smoke. The AWRI Analytical Service has an inexpensive and rapid method to accurately measure these compounds in grapes, juice and wine, with sensitivity to levels less than the sensory threshold, approximated at 6 µg/L.

If you suspect your fruit has been affected by smoke taint, please contact Randell Taylor, Trace Analysis Laboratory Supervisor or our Customer Service on **telephone 08 8303 6600** or email randell.taylor@awri.com.au or analyticalservice@awri.com.au

Please refer to the AWRI website www.awri.com.au/analytical_service for more information including pricing and response time.

Submission of samples:

Berries:
Package min. 200 g of berries in suitable berry containers. It is preferable to **freeze** the berries prior to dispatch and to pack them so that they will remain frozen during the journey.

Juice:
Juice should be submitted in **plastic** vessel. You will need to freeze the juice prior to dispatch and it is advisable to add a protective amount of SO_2 (~ 200mg/L) to prevent fermentation.

For advice or sample containers contact the Analytical Service prior to submission of samples.

Quarantine requirements regarding the importation of grapevine material from phylloxera infested areas to South Australia are available through Plant Health Operations, Primary Industries and Resources SA (PIRSA), contact Bruce Baker 1300 666 010.

The Analytical Service will be closed between 23 December and 2 January 2007 and we will not be able to receive samples in this period.