IMPACT OF FINING TREATMENTS ON JUICE QUALITY

Paul K. Bowyer[1], Marie-Laure Murat[2], Virginie Moine-Ledoux[3]

1 LAFFORT Australia, 5 Williams Circuit, Pooraka SA 5095, Australia. paul.bowyer@laffort.com.au - www.laffort.com

2 Manager Laboratoire SARCO, LAFFORT France research subsidiary, BP 40, 33072 Bordeaux. marielaure.murat@sarco.fr

3 Research Director, LAFFORT France, BP 40, 33072 Bordeaux. virginie.moine@sarco.fr

INTRODUCTION

In terms of juice handling, international winemaking practices vary significantly from country to country. In Australia, as in many other countries, it is typical to treat the free-run and pressings fractions of juice separately, whilst in India winemakers do not always take a pressings fraction. Since pressings fractions typically have elevated levels of phenolic compounds, a different management strategy is required to achieve similar juice quality to that of free-run fractions. This is the reason, for example, why fruit used in Champagne production is whole-bunch pressed: to minimize phenolic extraction, which would detract from the desired textural structure of the final product.

Studies on the impacts of various fining treatments on juice have been conducted by many of the larger wine companies, but usually only for internal benefit and to streamline their own specific processing regimes. Typically, phenolic extraction is the key focus of such studies, but recently another chemical of grape origin has become quite topical: glutathione (Lavigne et al. 2002). Glutathione is a grape-derived natural antioxidant, which is superior in action to both ascorbic acid and sulphur dioxide. This will be the subject of a future article, and will not be discussed in detail here, yet its function as an antioxidant in white wines and juice is clear: aroma preservation.

In order to gain some understanding of the impact of different typical fining treatments on juice quality, a series of trials were conducted in South Africa and France in 2008 and 2009 on Sauvignon blanc and other grape varieties containing volatile thiols. The results of these investigations were presented at the 2009 SASEV meeting in July, and are reproduced here.

JUICE QUALITY MARKERS

As mentioned, one of the key groups of compounds that is typically analysed when assessing juice quality is that of phenolic acids. The assay for these compounds can be as simple as measuring absorbance at 280 nm, which is where phenolic compounds absorb UV radiation. The data gained from this measurement are somewhat imprecise, however, so in this study HPLC with UV detection methodology was used. The phenolic acids measured are illustrated in figure 1. These phenolic compounds are of interest to winemakers for three main reasons: they can contribute to a sensation of tactile coarseness in wine; they can be metabolised by some organisms to generate volatile phenols, which detract from wine aromatic quality (Smit et al., 2003); and they can be oxidised to produce pinking.

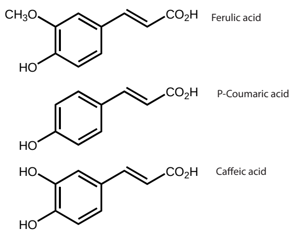

Fig. 1. The structures of the phenolic acids quantified in this study.

Glutathione (GSH) is a relatively newly discovered juice quality marker, and was measured by HPLC with fluorescence detection. It is a tripeptide with a sulphur functionality, and for this reason it, along with other sulphur-containing compounds like cysteine and N-acetyl cysteine (figure 2), is able to act as an antioxidant. Since the thiol group can be oxidised, the molecule is capable of absorbing oxygen, which is an informal definition of an antioxidant.

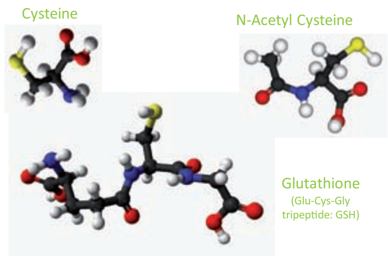

Fig. 2. Structures of redox-active molecules found in juice: cysteine, N-acetyl cysteine and the tripeptide glutathione.

As an adjunct to this study, isobutylmethoxypyrazine (IBMP) levels were measured by SBSE/GCMS. IBMP is found in some grape cultivars (notably the Sauvignons) and is negatively correlated both with the level of ripeness of the fruit with exposure of the fruit to sunlight during ripening. It is responsible for the dusty, capsicum characters sometimes found in wine made from these grapes. IBMP is thus a de facto measure of juice quality, and was included in this study.

The formation of the secondary structure is driven in large part by the hydrophobicity, or "water-fearing" sections of the protein chain. The hydrophobic sections tend to align or overlap in space to minimize contact with water molecules, thus generating shapes such as pleated sheets and helices (figure 1b).

Since proteins are comprised of amino acids, and amino acids are responsive to pH changes (being acids), proteins too can alter their physical shape and chemistry as the pH of the medium changes. This is reflected in their solubility,

which changes according to pH as indicated in figure 2. The pH at which there is zero nett charge on the protein is called the protein's isoelectric point (pI) (Bowyer and Moine-Ledoux, 2007), and at this pH the protein is least soluble. Thus, the protein pI indicates its solubility in wine. As the medium pH moves away from the pI, solubility increases in concert with the increasing charge on the molecule, which aids aqueous dissolution.

CASE STUDIES

Case study 1: Durbanville, South Africa – reductive handling of all fractions

Sauvignon blanc grapes were handled thusly: hand harvest; fruit sprayed with 5 % SO_2 solution; pectolytic enzyme addition; fruit chilling to 10 °C; destemmed and crushed; free-run 1 h skin contact under N2 then cold-settled under N2 for 24 h; pressings fraction 12 h skin contact under N2 then pressed and settled for 24 h under N2. The following treatments were applied to the pressings fraction: bentonite 40 g/hL (**MICROCOL® CL**, LAFFORT); gelatine 40 mL/hL (**GECOLL® SUPRA**, LAFFORT); PVPP/casein blend 40 g/hL (**POLYLACT®**, LAFFORT). Juice chemical parameters are given in table 1.

	FREE -RUN	PRESSINGS FRACTION
Potential alcohol (% Vol.)	12.60	12.60
pH	3,19	3,47
Total Acidity (g/L tartaric acid)	8,12	6,43
Malic Acid (g/L)	3,24	3,06
Tartaric Acid (g/L)	4,83	4,26
YAN (mg/L)	320	360
SO_2 L (mg/L)	35	34
SO_2 T (mg/L)	63	71

Table 1: *Juice parameters for Case Study 1.*

Results

The glutathione content of both free-run and pressings fractions were equivalent, and were undiminished after treatment with the indicated fining agents (figure 3a). The phenolic acid content of the pressings fraction was close to double that of the free-run fraction, and the gelatine showed the greatest reduction in phenolic acid content after fining (figure 3b). IBMP was equally apportioned between the two juice fractions, and was unaffected by fining (figure 3c).

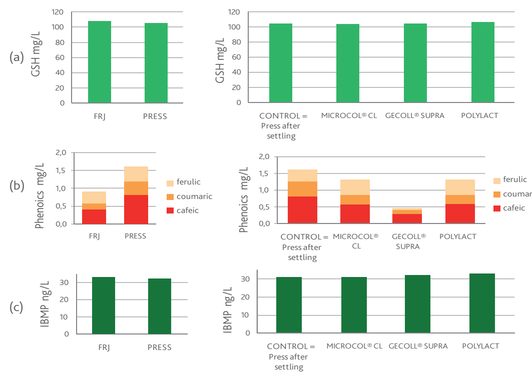

Fig. 3: *Case study 1 data: (a) Juice glutathione (GSH) content of free-run (FRJ) and pressings fractions (PRESS; left) and residual juice glutathione content of pressings fraction after treatment with indicated fining agents (right); (b) Juice phenolic acid content of free-run (FRJ) and pressings fractions (PRESS; left) and residual juice phenolic acid content of pressings fraction after treatment with indicated fining agents (right); (c) IBMP content of free-run (FRJ) and pressings fractions (PRESS; left) and residual juice IBMP content of pressings fraction after treatment with indicated fining agents (right).*

Discussion

As the juice for this trial was handled reductively, it was not surprising that preservation of glutathione was good. The glutathione content of this juice was found to be very high and is probably linked to the high juice YAN level, which bodes well for aroma preservation in the finished wine. The higher phenolic acid content of the pressings fraction was not unexpected, as more phenolic compounds are liberated from the skins and seeds under increased pressure. The strong impact of the gelatine in the fining of the press fraction was also expected, given that the main function of gelatine fining is to remove phenolics. The bentonite treatment was not expected to remove a large amount of phenolic acids. The PVPP/casein blend removed about the same amount of phenolic acid as the bentonite, which was somewhat unexpected. IBMP remained unaffected by any fining treatment, which suggests that unripe fruit characters in Sauvignon blanc cannot be simply removed from the juice by fining activity, hence viticultural control measures should be investigated.

Case study 2: Stellenbosch, South Africa – reductive handling of all fractions

Sauvignon blanc grapes were handled thusly: hand harvest; SO_2 30 ppm; destemmed and crushed; fruit chilling to 8 °C; ascorbic acid added 5 g/100 kg; pectolytic enzyme addition (**LAFAZYM® EXTRACT**, LAFFORT); free-run 4 h skin contact under N2 (in press) then cold-settled under N2 for 24 – 48 h; pressings fraction 4 h skin contact under N2 then pressed and settled for 24 h under N2 with an addition of 40 ppm SO_2. The following treatments were applied to the pressings fraction: bentonite 40 g/hL (**MICROCOL® CL**, LAFFORT); gelatine 40 mL/hL (**GECOLL® SUPRA**, LAFFORT); PVPP/casein blend 40 g/hL (**POLYLACT®**, LAFFORT). Juice chemical parameters are given in table 2.

	FREE -RUN	PRESSINGS FRACTION
Potential alcohol (% Vol.)	12.60	12.60
pH	3,19	3,47
Total Acidity (g/L tartaric acid)	8,12	6,43
Malic Acid (g/L)	3,24	3,06
Tartaric Acid (g/L)	4,83	4,26
YAN (mg/L)	320	360
SO_2 L (mg/L)	35	34
SO_2 T (mg/L)	63	71

Table 2: *Juice parameters for Case Study 2.*

Results

Glutathione content of both free-run and pressings fractions was approximately equivalent, of about half the level of the Case Study 1 juice, and was undiminished after treatment with the indicated fining agents (figure 4a). The phenolic acid content of the pressings fraction was about 25 % more than that of the free-run fraction, and all fining treatments showed approximately equal reductions, with the PVPP/casein product performing the best (figure 4b). IBMP was equally apportioned between the two juice fractions, and no significant loss or differences were observed after the fining treatments (figure 4c).

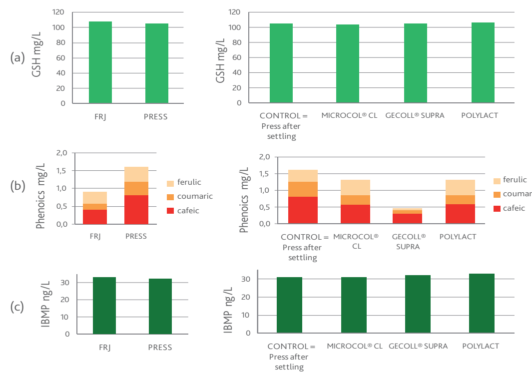

Fig. 4. *Case study 2 data: (a) Juice glutathione (GSH) content of free-run (FRJ) and pressings fractions (PRESS; left) and residual juice glutathione content of pressings fraction after treatment with indicated fining agents (right); (b) Juice phenolic acid content of free-run (FRJ) and pressings fractions (PRESS; left) and residual juice phenolic acid content of pressings fraction after treatment with indicated fining agents (right); (c) IBMP content of free-run (FRJ) and pressings fractions (PRESS; left) and residual juice IBMP content of pressings fraction after treatment with indicated fining agents (right).*

Discussion

The glutathione concentrations in both juice fractions was less than for the previous trial, yet were still quite high at around 50 ppm, again presumably linked with the high juice YAN value. As with the first trial, glutathione levels were unaffected by fining, which suggests that juice fining does not impair the natural antioxidant capacity of the juice. The phenolic acid content of the press fraction was only slightly higher than that of the free-run, perhaps a result of the fairly light pressing (only 60 L pressings juice was obtained per tonne). Curiously, no coumaric acid was detected in this juice sample. All fining treatments showed similar effectiveness with respect to the removal of phenolics, with marginally better performance observed with the PVPP/casein treatment. No significant decrease in IBMP was observed, again suggesting that pyrazine characters cannot be effectively managed through a fining treatment.

Case study 3: Stellenbosch, South Africa – oxidative handling of press fraction

This trial was conducted at the same winery as Case Study 2, but using the approach of oxidative handling of the pressings fraction whilst in the press. The theory associated with this practise is that exposing the juice of the pressings fraction to oxygen results in oxidation of the more oxidisable components of the juice (phenolics), so that once cleaned up, a juice that is somewhat "stabilised' with respect to oxidation is obtained. In effect, preliminary oxidation is used as a method of oxidation control, similar to the way in which malolactic fermentation is used to microbiologically stabilise red wines.

Sauvignon blanc grapes were handled thusly: hand harvest; SO_2 30 ppm; destemmed and crushed; fruit chilling to 8 °C; free-run handled reductively with N2 cover, then cold-settled under N2 for 24 – 48 h; pressings fraction 4 h skin contact, then pressed with no N2 protection and cold settled under N2 for 24 h. The following treatments were applied to the pressings fraction: bentonite 40 g/hL (**MICROCOL® CL**, LAFFORT); gelatine 40 mL/hL (**GECOLL® SUPRA**, LAFFORT); PVPP/casein blend 40 g/hL (**POLYLACT®**, LAFFORT).

Discussion

Oxidative handling of the press juice had a significant impact on the glutathione content (figure 5a). The press fraction, which was exposed to oxygen in an attempt to oxidise the phenolic acids, suffered a large decrease in the glutathione content. This would have a strong impact on the inherent capacity of the wine made from this juice to age well, given that the natural antioxidant capacity of the wine would be severely reduced.

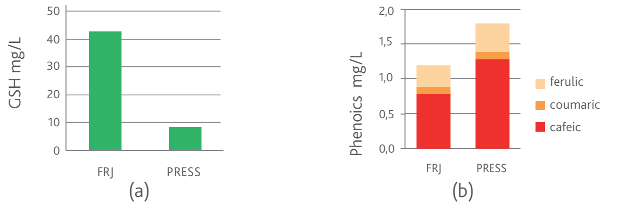

Fig. 5: *Case study 3 data: (a) Juice glutathione (GSH) content of free-run (FRJ) and pressings (PRESS) fractions with oxidative handling in-press. Note the significant loss of GSH with oxidative handling; (b) Juice phenolic acid content of free-run (FRJ) and pressings (PRESS) fractions with oxidative handling.*

The phenolic acid content of the press fraction was not decreased to the level of the free-run fraction (figure 5b). The biggest impact appeared to be on caffeic acid, which showed the greatest decline. Given that the phenolic acid content was not reduced to the same level as that of the free-run juice fraction, yet at the great expense of the glutathione content, the practice of handling juice oxidatively as a means of controlling phenolic acid content in juice appears somewhat dubious in terms of resultant potential wine quality.

Case study 4: Bordeaux, France – comparison between reductive and oxidative handling

As a means of illustrating the relative impacts of these different approaches on the level of phenolic acids in juice, a comparative trial was made using Sauvignon blanc in Bordeaux between the reductive handling of the free-run juice, reductive handling of the press fraction, oxidative handling of the press fraction and reductive handling of the press fraction and fining with **POLYMUST AF**® (LAFFORT), a combination of bentonite, PVPP and isinglass (figure 6).

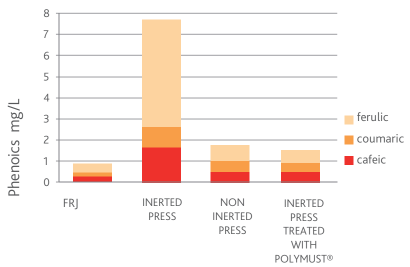

Fig. 6: *A comparison of the phenolic acid content of free-run juice (FRJ), pressings juice from an inert press (INERTED PRESS), pressings juice from an oxidatively-hanlded press (NON INERTED PRESS), and pressings juice from an inert press treated with Polymust (INERTED PRESS TREATED WITH POLYMUST, LAFFORT). Note that the same residual level of phenolic acids can be achieved with both oxidative handling of the juice and treatment with Polymust, except that the oxidative handling destroys much of the glutathione content of the juice (see figure 5) and thus greatly reduces inherent wine antioxidant capacity.*

The reductively-handled free-run and pressings juice fractions contained the lowest and highest levels of phenolic acids respectively, as anticipated. Oxidative handling of the same pressings fraction showed good reduction in the level of juice phenolic acids, and treatment of the juice with an appropriate fining agent yielded a slightly lower concentration of juice phenolics again.

Although oxidative handling of the pressings juice fraction lowered the phenolic acid content, this is achieved at a very high price in terms of juice (and therefore wine) quality: the significant loss of glutathione (figure 5a). This in turn has strong ramifications for the ageability of the wine made from oxidatively-handled juice, and is perhaps a factor in the phenomenon of "UTA", or "untypical ageing off-flavour" (Lavigne et al. 2002; Hoenicke et al., 2003) that has become a problem in parts of the global wine industry in recent years (Kalchschmidt, 2007).

Case study 5: Bordeaux, France – comparison between fining agents with reductive handling

Given that the importance of glutathione retention in juice is now understood and linked with wine quality and ageability, a similar comparison was made between blended proprietary products and gelatine/silica sol applications. This comparison is pertinent given that gelatine is most commonly used for removing phenolics yet it is not an innocuous fining agent (Bowyer, 2008). The trial was conducted using Gros Manseng with reductive handling of all treatments. 600 L/tonne of free-run juice were taken and the pressings fraction (60-70 L/tonne) had 4 h skin contact under N2. Applied treatments were: PVPP/casein (**POLYLACT**® , LAFFORT) 40 g/hL; PVPP/bentonite/isinglass (**POLYMUST AF**®, LAFFORT) 40 g/hL; gelatine/silica sol (Gelarom/Siligel, LAFFORT) each 20 mL/hL; and gelatine/silica sol (**GECOLL**® **SUPRA**/Siligel, LAFFORT) each 20 mL/hL The data are presented in figure 7.

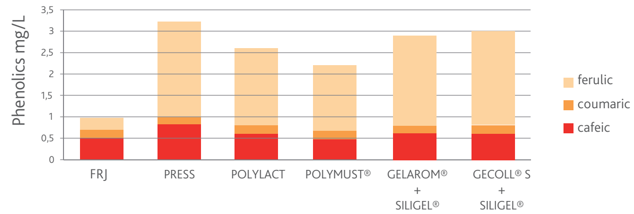

Fig. 7: *A comparative analysis of the reduction in phenolic acid content of free-run and pressings juice fractions with various treatments. FRJ = free-run juice; PRESS = pressings juice; POLYLACT = casein/PVPP blend (LAFFORT), POLYMUST = bentonite/PVPP/isinglass blend (LAFFORT); GELAROM = gelatine (LAFFORT); SILIGEL = silica sol solution (LAFFORT); GECOLL S = gelatine (LAFFORT).*

In this trial the greatest reduction in phenolic acid content was after treatment with Polymust AF, followed by Polylact and then the two co-fined gelatine treatments. Comparing these results with those obtained from the preceding trials suggests that different juices respond differently to different fining agents, so it is a matter of trial and error to find the most appropriate treatment for a given juice. In time this could presumably be built up into an historical fining programme for a given parcel of fruit to ensure the best and most consistent results.

Summary

While there are no "right" or "wrong" approaches to juice handling, there are clearly different processing methods available to the winemaker, with correspondingly different outcomes in terms of juice and, ultimately, wine quality. Given the large impact that glutathione has on juice and wine quality, it is pertinent to remember that oxidative handling, while capable of reducing juice phenolic load, is also highly destructive towards this precious antioxidant. In the event that oxidative handling methods are employed, or to maximise juice antioxidant capacity overall, it would appear prudent that glutathione be supplemented. Glutathione management for increased wine quality will be the subject of a future article.

REFERENCES

Bowyer, P. K. (2008) "Proteinaceous fining agents", The Australian and New Zealand Grapegrower and Winemaker, June 2008, 55-63.

Hoenicke, K., Borchert, O., Gruening, K and Simat, T. J. (2002) "Untypical aging off-flavor in wine: synthesis of potential degradation compounds of indole-3-acetic acid and kynurenine and their evaluation as precursors of 2-aminoacetophenone", J. Agric. Food Chem., 50, pp 4303–4309.

Kalchschmidt, E. (2007), Kalchschmidt Oenologie, personal communication.

Lavigne V., Pons A., and Dubourdieu D. (2002) "Role of glutathione on development of aroma defects in dry white wines" In the 13th International Enology Symposium, 331-347, Montpellier.

Smit, A., Cordero Otero, R. R., Lambrechts, M. G., Pretorius, I. S., and van Rensburg, P. (2003) Enhancing volatile phenol concentrations in wine by expressing various phenolic acid decarboxylase genes in Saccharomyces cerevisiae, J. Agric. Food Chem., 51, pp 4909–4915.

Products discussed in this article are available in Australia through LAFFORT, phone 08 8260 7974 and in New Zealand from Oenological Resources (Greg Wilkin: greg@oenological.co.nz), phone 0213 22290. www.laffort.com

Dr Paul Bowyer is the Technical Manager for LAFFORT, and in that role he provides technical information and advice to the wine industry in the Australasian region. He can be contacted on 08 8260 7974 or by email at paul.bowyer@laffort.com