Optimizing Deacidification Methods for Cold Climate Cultivars

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Background and Rationale: Shorter growing seasons and cooler temperatures of northern climates can cause grapes grown in those regions to be high in total acidity, especially malic acid. New cold-hardy cultivars have the added challenge of being genetically predisposed to having very high levels of both tartaric and malic acid. The resulting wines can be harsh and astringent unless winemakers take actions to mitigate the sensory affects of high acidity. Enological treatments for reducing acidity include physical (blending and amelioration), biological, and chemical methods. While each of these treatments may positively impact a wine's acidity, they each may have drawbacks in terms of other sensory impacts to the wine.

Treatments:

1. **Yeast Biological Deacidification**
   - **Four wine grape cultivars:** La Crescent, Frontenac Gris, Frontenac, Marquette
   - One non-*saccharomyces* yeast strain was used in sequential inoculation trials in conjunction with a *Saccharomyces* yeast strain
   - Each Fermentation was replicated 5 times for each cultivar
   - Each malate-reducing yeast strain was replicated 10 times over two different cultivars.

2. Chemical Deacidification:
   - **Three wine grape cultivars:** La Crescent, Frontenac Gris, and Frontenac (produced as a rosé)
   - **Two chemical treatments:** Calcium carbonate vs. Sihadex (*Begerow, Langenlonsheim, Germany*)
     - Sihadex is a commercial product advertised as a "special lime developed…to precipitation tartaric acids and malic acids in equal parts." (*Sihadex Technical Sheet.)*

Methods:

1. Biological Deacidification:

Juice from the 2012 vintage, which had been previously frozen, was used for the trial. For each cold-hardy cultivar, we trialed three different yeast strains, and used a fourth yeast strain as a control. One lot of juice was divided into 20 micro-vinification lots of 500 mL each. Thus each yeast strain was replicated in 5 fermentation lots. We were mainly concerned with monitoring the reduction in malate of each lot. For white wines, Lalvin DV10 (*Lallemand*) was used as control, and for red wines we used ICV GRE (*Lallemand*) as a control yeast. Both are considered reliable fermenters with no reported malate degradation. The unusually hot weather in 2012 caused initial brix levels to be extremely elevated, so initial malate numbers reflect juice that had been diluted to bring the sugar concentration down to 25° Brix. Wines were fermented at ambient room temperature in 1.0 L

Erlenmeyer flasks with an airlock attached. When fermentation activity subsided, sugars were analyzed using Clinitest® reagent tablets. One of the treatment lots was unable to finish fermentation, so analysis was done on off-dry wines. Once dry according to Clinitest®, the wines were analyzed for total acidity (g/L tartaric acid), malate concentration, pH, and alcohol. Total residual sugar was also accurately measured enzymatically. Results were treated statistically by ANOVA and paired t-test.

	Lalvin C (Lalvin)	**Exotics (Anchor)**	**Opale (Lalvin)**	***Torulaspora delbrueckii*** (Lallemand)	**DV10**
Reported Malate Reduction	Up to 45%	Up to 17% observed	0.1 to 0.4 g/L	None Reported	Control
Yeast Type	*S. cerevisiae* var. *bayanus*	Hybrid yeast	*S. cerevisiae*	Non-Saccharomyces	*S. cerevisiae*

Table 1: Commercial yeast strains used for biological deacidification trial

2. Chemical Deacidification:

In the double-salt deacification method, 1-10% of the total juice to be treated is separated and treated with calcium carbonate, or a blend of calcium carbonate, calcium malate, and potassium bitartrate. In theory, this portion of the must is deacidified completely, removing both tartaric and malic acids, and achieving a pH near 5. Once clarified through filtration, this portion of juice is returned to the full lot with rapid stirring, and is alleged to effect either a preferential removal of malic acid, or a equivalent removal of tartaric and malic acid, depending on the source cited. Literature also suggests that malic acid removal is predicated on the formation of a double-salt formed of calcium-malate-tartrate, though the existence of this structure is currently under question.

The first step in understanding the mechanism of double-salt deacidification in high malic wines is to determine whether complete deacidification of the juice aliquot occurs, and the relative rates at which malic and tartaric acid are removed from solution. Previous work in model wine solutions suggests that the majority of acid precipitation occurs in the first 30 minutes after the deacidification agent (calcium carbonate or proprietary blends of calcium carbonate, calcium malate, and potassium bitartrate) is added, and that tartaric acid is removed preferentially. Some fraction of malic acid was removed after the tartaric acid in the system was exhausted. To test this under real-world conditions, juice from three cold-hardy wine grape cultivars was treated with XX amount of either calcium carbonate or the commercial Sihadex lime blend, and samples were taken at various time points (0, 30, and 120 min; also at 60 min, 480 min, and 960 min for calcium carbonate additions.) Samples were analyzed via HPLC for malic and tartaric acid concentrations.

Results:

1. Biological Deacidification:

Frontenac Gris Fermentation Lots

The juice used in the yeast trials with Frontenac Gris was ameliorated to 25ºBrix, had a total acidity of 9.92 g/L, a pH of 3.00, and 5.1 g/L of malic acid. We found that all the yeast strains used lowered the malate concentration significantly over the control yeast strain (DV10). However, the non-*Saccharomyces* yeast in sequential inoculation with the *Exotics®* did not lower the acidity more than using *Exotics®* alone.

Frontenac Gris Fermentation Lots				
	Lalvin DV10 (Lallemand)	Lalvin C (Lallemand)	Exotics (Anchor)	TD + Exotics
Avg. Malate (g/L) of wine	**4.28** ±0.002 a	**3.48** ±0.002 b	**3.74** ±0.003 c	**3.56** ±0.003 c

Table 2: Average malate reduction in Frontenac Gris. Different letters indicate statistically significant differences ($p < 0.05$).

La Crescent Fermentation Lots

The La Crescent juice that we divided up for the micro-vinification trials was ameliorated to 25 Brix, which left the starting malate levels at 5.3 g/L. The decrease in malic acid during fermentation was less pronounced than what we saw during the Frontenac Gris trials. Only the vinification lot in which *Exotics*® was used showed a statistically significant drop in malic acid ($p < 0.05$). ICV Opale is advertised to lower malate levels by 0.1 to 0.4 g/L. Our trials show that it exceeded this level in high malate juice, however, this decrease was not significantly lower than our control yeast which has no reported malate reducing properties.

La Crescent Fermentation Lots				
	Lalvin DV10 (Lallemand)	ICV Opale (Lallemand)	Exotics (Anchor)	TD + ICV Opale
Avg. Malate (g/L) of wine	**4.78** ±0.05 a	**4.74** ±0.02 a	**4.26** ±0.03 b	**4.70** ±0.02 a

Table 3: Average malate concentration for La Crescent Fermentation lots. Different letters indicate statistically significant differences ($p < 0.05$).

Marquette Fermentation Lots

Marquette grapes were pressed immediately after harvest and the juice was fermented as a rosé. The ameliorated juice had an initial malic acid concentration of 4.1 g/L. Exotics and VRB showed identical malate reduction capabilities, and even though the difference between these two yeasts and the control (ICV GRE) was only slight, the difference is statistically significant ($p=0.046$). Nonetheless, a decrease in acidity of 0.10 g/L is probably not practically significant for wineries. It is worth noting that all of these lots showed a large decrease in malate from the juice concentration. Once again, Lalvin C proved to have the greatest potential for malate reduction, with a 1.10 g/L decrease in malic acid concentration from the juice.

Marquette Fermentation Lots				
	ICV GRE (Lallemand)	Exotics (Anchor)	ICV VRB (Lallemand)	TD + Lalvin C
Avg. Malate (g/L) of wine	**3.38** ±0.002 **a**	**3.28** ±0.007 **b**	**3.28** ±0.017 **b**	**3.00** ±0.00 **c**

Table 4: Average malate concentration for Marquette Fermentation lots. Different letters indicate statistically significant differences ($p < 0.05$).

Frontenac Fermentation Lots

Frontenac grapes were pressed and fermented as a rosé. Again, it was necessary to ameliorate to reduce the initial sugar concentration. Nonetheless, the initial malate concentration of the juice was still relatively high at 4.6 g/L. All yeast used for this trial caused a decrease in the final malic acid concentration of the wine. All observed differences in malate reduction were statistically significant ($p<0.05$), except for the two lots that were fermented with Lalvin C. There is no statistical difference between the observed malate reduction when using Lalvin C in conjunction with *T. delbrueckii* yeast. This, along with the other results seen when using *T. delbrueckii,* suggests that any impact on the perception of acidity due to this yeast is likely not related to malate degradation.

Frontenac Fermentation Lots				
	ICV GRE (Lallemand)	Exotics (Anchor)	Lalvin C (Lallemand)	TD + Lalvin C
Avg. Malate (g/L) of wine	**3.40** ±0.05 a	**3.18** ±0.02 b	**3.02** ±0.02 c	**2.98** ±0.07 c

Table 5: Average malate concentration for Frontenac Fermentation lots. Different letters indicate statistically significant differences ($p < 0.05$).

2. Chemical Deacidification:

In all three cultivars tested, addition of calcium carbonate and Sihadex reduced tartaric acid concentrations to nearly non-detectable levels within 30 minutes. (Table 1.) While acid reduction was not significantly different between the two methods, Sihadex precipitated slightly more malic acid, likely due to increased pH. Subsequent trials suggested that, with similar pH adjustment, calcium carbonate additions effect equivalent reductions in malic acid (data not shown.)

Table 1: Deacidification in La Crescent, Frontenac gris and Frontenac rosé through addition of calcium carbonate or Sihadex.

	Averages (SD)				% Remaining				pH	
	Sihadex		CaCO3		Sihadex		CaCO3		Sihadex	CaCO3
	Tartaric	Malic	Tartaric	Malic	Tartaric	Malic	Tartaric	Malic	pH (SD)	pH (SD)
La Crescent										
0 min	2.8 (0.04)	6.3 (0.06)	3.0 (0.04)	6.2 (0.07)	100	100	100	100	3.12 (0.01)	3.08 (0.01)
30 min	0.1 (0.00)	5.5 (0.13)	0.1 (0.00)	5.9 (0.03)	0	87.9	0	94.9	5.35 (0.01)	5.00 (0.00)
120 min	0.1 (0.00)	4.8 (0.23)	0.1 (0.00)	5.4 (0.21)	0	76.2	0	88.0	5.53 (0.00)	5.18 (0.01)
Frontenac gris										
0 min	3.8 (0.20)	5.0 (0.05)	4.0 (0.03)	5.0 (0.01)	100	100	100	100	3.05 (0.01)	3.01 (0.01)
30 min	0.1 (0.00)	4.5 (0.06)	0.1 (0.00)	4.7 (0.11)	0	90.2	0	93.8	5.50 (0.01)	5.13 (0.00)
120 min	0.1 (0.00)	4.4 (0.08)	0.1 (0.00)	4.6 (0.01)	0	88.2	0	92.8	5.69 (0.00)	5.32 (0.00)
Frontenac rose										
0 min	1.7 (0.60)	3.8 (0.15)	1.7 (0.02)	3.9 (0.04)	100	100	100	100	3.41 (0.00)	3.36 (0.01)
30 min	0.1 (0.00)	3.4 (0.16)	0.1 (0.00)	3.6 (0.10)	0	89.6	0	90.2	5.26 (0.01)	5.01 (0.01)
120 min	0.1 (0.00)	3.3 (0.27)	0.1 (0.00)	3.4 (0.12)	0	85.0	0	87.0	5.39 (0.00)	5.14 (0.01)

Notably, neither addition protocol resulted in preferential removal of malic acid, or in equivalent removal of tartaric and malic acids, such that post-addition juices retained as much as 92% of their original malic acid content. While we have not yet performed trials in which this juice aliquot is blended back into the larger wine lot to assess actual acid reduction, chemical modeling suggests that it is improbable for significant malic acid reduction to occur.

What the results mean:

- Neither preferential removal of malic acid, or equitable removal of malic and tartaric acid, was achieved under trial conditions. Further modeling, testing additional wine matrix variables, are necessary to fully understand the mechanism and potential of chemical deacidification.
- Up to 35% reduction in malate concentration was observed using selected commercial yeast strains.
- Observed reduction in malate was lower than reported malate reduction for Lalvin C (*Lallemand*), though this yeast out-performed other commercial strains used in the trial
- High initial malate levels can be reduced during alcoholic fermentation, which may hasten Malolactic fermentation