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# Effect of early oxygen exposure on red wine colour and tannins

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ABSTRACT

Shiraz ferments were injected with different levels of oxygen (20% and 40% $O_2$ as gas mixtures) to assess the impact of early oxygen exposure on wine tannins and colour measures after fermentation, and after 2 and 12 months bottle-ageing under either Saranex™ or Saran Tin™ screw caps. The $O_2$-treated ferments contained lower concentrations of anthocyanins and tannins, and tannin composition showed lower molecular masses, conversion yields, and proportions of prodelphinidin subunits than those from the control ferments. The colour measures and tannin characteristics of the control wines after 12 months resembled those of the $O_2$-treated wines at 2 months bottle-ageing, and oxygen exposure during fermentation had a greater impact on tannin structure than closure type. Early oxygen exposure during winemaking may result in wines with phenolic compositions that are characteristic of more aged wines, which may reduce the need for extended wine ageing.



## 1. Introduction

Wine is a dynamic and complex system that is greatly influenced by the presence of $O_2$. Different levels of $O_2$ exposure can dramatically alter the colour and texture of red wines. Gradual exposure to $O_2$ over many months, for example, during barrel ageing, can impart a softer mouthfeel to the wine and a more reddish, rather than purple, hue.[13] Some $O_2$ exposure through the bottle closure is also considered beneficial to remove adverse sulphidic or 'reductive' aromas.[51] Too much $O_2$, on the other hand, can have deleterious impacts on overall wine sensory properties.[17,51] With $O_2$ exposure, the purple, monomeric anthocyanins become more stable and resistant to $SO_2$ bleaching by directly or indirectly forming polymers with condensed tannins as well as acetaldehyde-mediated derivatives such as pyranoanthocyanins.[2,21,47,4] This induces a change to red-orange hues[13] and can lower wine astringency, as anthocyanin-bound tannins are less astringent than non-pigmented tannins.[56] $O_2$ exposure also alters the structure of wine tannins by decreasing the proportion of acid-labile interflavan bonds, which is related to a decrease in percent conversion yield in depolymerisation reactions, as calculated from the molar mass of cleaved tannin subunits relative to the mass of tannin used in the reaction.[45,53] Lower percent tannin yield also decreases the extent of protein binding[22,37] and may lead to a less intense wine astringency.[22] Ageing of wines under bottle closures with high oxygen transfer rates (OTRs), such as cork or Saranex lined screw caps, can modify wine colour and tannin structures to a greater extent than closures with lower OTRs, such as Saran Tin screw caps. This effect is particularly enhanced for wines at lower pH.[38,22]

The importance of $O_2$ exposure on colour stability and mouthfeel without the use of extended barrel ageing has led to the development of microoxygenation (MOX) techniques in red wines.[49] Many reports have indicated that MOX can improve colour stability and some have suggested that such treatment softens wine astringency, particularly after subsequent bottle-ageing, although there is still significant debate about the best time to apply MOX and the ideal dosage rate.[22,11,46,49,43] The composition of the wine matrix such as wine pH and phenolic content can also impact the efficacy of MOX,[31,22,8] making a consistent prediction of the impact of MOX on wines difficult.

As an alternative to MOX, changing the level of $O_2$ exposure during fermentation may alter the colour and mouthfeel of the resulting wine by inducing chemical and enzymatic oxidation of polyphenols, including catechin and caffeic acid, and potentially modifying the extraction of tannin from grape cells. In the production of red wine, $O_2$ exposure may occur whenever the ferment is plunged or pumped over but the level of $O_2$ exposure can vary significantly, depending on the number, duration and modality of pump-overs. As an alternative to pump-overs or cap plunging, appropriate levels of grape skin contact during fermentation can be achieved during winemaking with the use of rotary fermenters. These fermenters are horizontal tanks that rotate axially and, while

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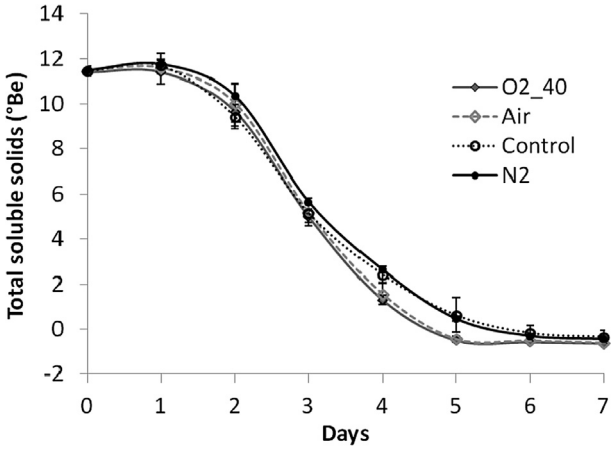


**Fig. 1.** Fermentation progress as measured by total soluble solids (°Be) per day of primary fermentation. Results are shown as the mean of triplicate fermentations±standard error.

effective in improving skin contact, the vessels are enclosed and can produce reductive conditions.[42] Grape tannins extracted from skins and seeds during winemaking[6] may be directly impacted by chemical oxidation, as well as enzymatic oxidation via such enzymes as laccase and polyphenol oxidases (PPO). PPO can polymerise flavan-3-ols and smaller phenolics such as caffeic acid,[41,23,29] which may react with tannin to form complex structures. The production of acetaldehyde as a fermentation product as well as from oxidation of ethanol may also increase with greater $O_2$ exposure during fermentation, changing the structures of extracted tannins.[57,18] Oxidation reactions at the grape cell surface (i.e., cell wall-bound PPO) may also potentially enhance the retention of tannins and anthocyanins by grape solids during winemaking.[32,7] This may reduce the amount of tannin extracted into the wine and thus the intensity of wine astringency.

In this experiment, Shiraz wines were made in triplicate using rotary fermenters and treated with different levels of $O_2$ exposure during fermentation: air (containing approximately 20% $O_2$) and 40% $O_2$/60% $N_2$. The impact of the physical displacement of volatile compounds and mixing effects by gas was assessed using gas injections of pure $N_2$, and the controls were fermented without any gas addition. Wine colour and tannin characteristics were measured after fermentation (time 0), and after 2 and 12 months bottle-ageing under two different screw cap liners, Saran Tin (ST) and Saranex (Sx).

## 2. Results and discussion

### 2.1. Grape fermentation and wine matrix characteristics

To assess the impact of $O_2$ exposure during grape fermentation on the composition of the resulting wine, triplicate Shiraz grape ferments were injected twice per day with gas mixtures containing different concentrations of $O_2$. These gas mixtures included air (containing approximately 20% $O_2$) as representation of 'normal' $O_2$ concentrations, elevated $O_2$ concentrations with 40% $O_2$/$N_2$ (referred to as '$O_2$40') to counter the potential impact of yeast-produced $CO_2$ on the $O_2$ equilibrium concentration of the air-injected ferment,[48,40] and pure $N_2$ to assess the impact of the physical mixing process of the gas injections. The controls consisted of ferments without gas injections. The air and $O_2$40 treatments increased the rate of primary fermentation by one day (Fig. 1), however, for consistency all ferments were pressed off on the same day (day 7). Throughout the fermentation, the number of viable cells was similar across all treatments, suggesting that the observed chemical differences between treatments were not related to biomass differences. Secondary fermentation (malolactic fermentation, MLF) was also more rapid in the air/$O_2$40-treated wines than the control/$N_2$-treated wines (8 and 17 days, respectively), potentially due to the production of yeast fermentation products in the $O_2$-exposed wines or variations in metal concentrations that led to more favourable MLF conditions. Other factors that influence MLF, including fermentation temperature, wine pH and alcohol concentrations, did not vary significantly different between treatments (Table 1). Titratable acidity (TA) and volatile acidity (VA) were slightly yet significantly greater in the air/$O_2$40 wines compared with the control/$N_2$-treated wines. MOX treatment has also been shown to have a slight impact on the pH and TA of Cabernet Sauvignon wines[43] but the extent of MOX impacts on Monastrell wine matrices was shown to vary depending on phenolic concentration.[8]

The acetaldehyde concentrations (Table 1) in the $O_2$40 wines at time 0 were significantly higher ($p<0.05$) than the $N_2$-treated wines, which was consistent with the formation of acetaldehyde from the oxidation of ethanol as reported for wines treated with MOX after primary fermentation.[49] The air-treated and control

**Table 1**
Wine matrix composition and tannin composition of the finished wines (time 0) produced from each fermentation treatment. Results are shown as the mean of triplicate samples±one standard deviation, and results in the same row with different letters are significantly different ($p<0.05$)

| | $O_2$40 | Air | Control | $N_2$ |
|---|---|---|---|---|
| *Wine composition* | | | | |
| Wine pH | 3.72±0.05 | 3.71±0.02 | 3.85±0.16 | 3.74±0.03 |
| Alcohol (%v/v) | 12.07±0.25ab | 11.90±0.00b | 12.13±0.21a | 12.03±0.15ab |
| Titratable acidity (pH 8.2)[a] | 5.43±0.15a | 5.40±0.10a | 4.67±0.32b | 5.03±0.06b |
| Volatile acidity (g/L acetic acid)[b] | 0.20±0.00a | 0.19±0.02ab | 0.20±0.04ab | 0.17±0.01b |
| Acetaldehyde (mg/L) | 23.4±3.6a | 18.2±0.8b | 18.9±1.2b | 15.9±1.0c |
| *Tannin composition* | | | | |
| MM (g/mol)[a] | 1744±40b | 1743±24b | 1818±49a | 1881±27a |
| %$A_{520/280}$[b] | 6.8±0.5a | 6.4±0.1a | 5.4±0.2b | 5.1±0.3b |
| Mean degree of polymerisation (mDp)[c] | 8.7±0.2b | 8.8±0.3b | 10.3±0.5a | 11.1±0.4a |
| % Yield (EC equiv)[c,d] | 44.9±1.3b | 47.7±5.3b | 56.5±5.1a | 55.9±2.7a |
| % (−)-Epigallocatechin[c] | 20.9±1.3b | 22.3±0.5b | 29.3±0.1a | 29.7±0.1a |
| % (−)-Epicatechin gallate[c] | 5.4±0.8ab | 6.0±0.0a | 5.1±0.1b | 5.1±0.0b |
| % Skin tannin[e] | 57.5±6.7b | 61.1±2.0b | 78.7±0.7a | 79.1±0.6a |

[a] Average molecular mass at 50% GPC elution.
[b] Calculated from the relative GPC peak areas at 520 and 280 nm.
[c] Measured using phloroglucinolysis.
[d] Calculated from the molar mass of cleaved subunits relative to the amount of tannin used in the reaction (g/L epicatechin equivalents).
[e] Calculated based on the relative proportion of epigallocatechin extension subunits in extractable skin tannin compared with that of wine tannin.