RESEARCH

EFFECT OF HYDROLYSABLE OAK ELLAGITANNIN DURING RED WINE FERMENTATION

OakWise
for beverages

PURPOSE

In a competitive wine market, enological tannins have become a popular tool used to increase the quality and value of what might be considered lower quality wine, or wine made from grapes with lower color intensity. Liquid ellagitannin products are easy to use and can increase the color intensity and stability of wines without imparting any oak aromatics, which may not be desired stylistically. These tannins can produce faster and more efficient binding with anthocyanins than traditional oak chips or other adjuncts, and do not add to bulky waste products after pressing.

This trial was conducted with the goal of showing the similarities between Oak Wise American Oak E Fresh with a popular competitor. The results show that the Oak Wise American Oak E Fresh offers similar or better impacts at a more competitive price.

INTRODUCTION

TANNINS

Tannins play a major role in red wine quality due to their contribution to color stability, flavor, and mouthfeel. The major source of tannins in grapes are seeds and skins, with an additional contribution from stems when whole cluster fermentations are performed. While the tannin content of grape seeds is generally higher than in the skins, seed tannins tend to be harder to extract into the wine matrix, so skin tannins tend to play a greater role in wine composition. In addition, seed tannins can have a bitter and distinctive "seedy" flavor, therefore most winemakers strive to avoid the extraction of seed tannins.

Tannins are the strongest antioxidant in red wine. Ellagitannins in particular protect against oxidation, in addition to their role in color stability. They also have the ability to precipitate proteins, in particular the proteins present in the saliva of wine drinkers. Tannins can mask green flavors and added tannins during fermentation can ameliorate the oxidative damage done to fruit caused by mold. Tannins may account for 50% of phenolics in wine and can increase with age.

COLOR

The color of red wine is a factor in perceived wine quality. Color extraction can depend on grape variety, growing region, maturity, and the physical condition of the fruit. For instance, grapes degraded by mold contain oxidative enzymes which may oxidize phenolic substrates causing browning in wine.

Anthocyanins are water soluble flavonoid pigments that accumulate in grape cell vacuoles and contribute to much of the color in red wine. Anthocyanins are generally extracted within the first 4-5 days of fermentation. Color stability can be improved through the use of oak adjuncts due to the fact that hydrolysable tannins participate in copigmentation reactions in addition to protecting wine anthocyanins from oxidation. The preferred ratio of anthocyanin to tannin is thought to be anywhere from 1:4 to 1:10, but the ideal ratio has not been elucidated. Maximum extraction of phenols from grapes is thought to be 60%. Polymeric pigments are formed when anthocyanins and tannins react to form more stable compounds. These reactions occur when anthocyanins and tannins act as nucleophiles and electrophiles to form linkages between the two molecules.

Many winemakers add enological tannins to grapes of lower quality, or which are from vineyards with a history of poor performance. The phenolic content in harvested grapes drops significantly during processing and fermentation, so the addition of enological tannins before or early in the fermentation will boost tannin content. Ellagitannins absorb dissolved oxygen and facilitates the hydroperoxidation of wine constituents. This reaction induces tannin/anthocyanin condensation via acetaldehyde, favoring stabilization and enhanced color development. Increased polymerization also serves to reduce the astringency of the final wine product. The addition of untoasted oak products reduces the amount of volatile organosulfur compounds in finished wine, which can contribute to vegetal aromas.

EXPERIMENTAL DESIGN

This trial was performed at a winery located in Lodi California during the 2019 harvest season. The grapes chosen for the trial were from a block of Cabernet Sauvignon with a history of being low to medium quality, with underdeveloped anthocyanins, tannins, and sugar levels.

TREATMENTS

Three oak products were used as treatments in this trial.

Oak adjunct:

- Oak Wise Untoasted American Oak Fine Chip - consists of quality untoasted American oak. American untoasted oak is commonly used since it offers fast extraction in a relatively short time.

  Dosage was determined by the winemaker at 12#/1000gal.

Two enological aqueous oak tannins:

- Oak Wise Premiere American Oak E Fresh - aqueous ellagitannins extracted from seasoned untoasted American oak chips.

  GAE 23g/L at 3°Brix or Specific Gravity at 1.012
  Dosage at 11.0L/4000L.
  A total of 140L of tannin was added to a 13,200 gal tank (~49,210 L crushed fruit).

- BRAND X - aqueous ellagitannins extracted from toasted French oak staves or chips.

  GAE 23g/L at 18°Brix or Specific Gravity at 1.074
  Dosage at 0.18L/4000L.
  A total of 2L of tannin was added to a 13,200 gal tank (~49,210 L crushed fruit).

Each oak product was added at the crusher. Samples from each treatment were collected after malolactic fermentation but prior to sulfur addition.

Due to recent social distancing restrictions, no tasting panels have been assembled at his time. Results will be collected at a later date.

MEASUREMENTS

All lab analysis for this study was performed at ETS Labs in St. Helena.

Red wine phenolic measurements include these parameters:

(1) Caffeic Acid - caffeic acid is a free hydroxycinnamic acid with phenolic and acrylic functional groups. In the presence of cinnamic esterase enzymes, free caffeic acid is formed through the cleavage of tartaric acid from caftaric acid molecules. These free caffeic acid molecules can be the precursors of aromatic compounds such as 4-ethylphenol and 4-ethylguaiacol. Caffeic acid reacts with malvidin-3-glucoside and produces a pyranonathocyanin which shows specific red color characteristics and shows more resistance to pH changes and SO2 additions during aging than malvidin-3-glucoside alone.

(2) Caftaric Acid - caftaric acid is a non-favonoid phenol compound and is formed through the esterification of caffeic acid and tartaric acid. Caftaric acid is found in the skins, pulp, and stems of grapes, but not in the seeds. Caftaric acid is readily oxidized during processing and can form highly reactive quinones which can cause browning over time.

(3) Catechin - catechins are flavonoids known as flavan-3-ols, the monomers of which are found in high concentrations in grape seeds and stems. Catechin is the trans isomer of the catechin molecule, with epicatechin being the cis isomer. Catechin in grape seeds combine with other compounds to form the seed coat, and this process in mature seeds make these phenolic compounds more difficult to extract. Catechin and epicatechin levels are generally lower in more mature grapes and can be an indicator of ripeness.

(4) Epicatechin - like catechins, epicatechins are primarily found in the seeds and stems of grapes. Epicatechins are the cis isomer of the catechin molecule. As with catechins, epicatechins can be used as an indicator of seed ripeness.

(5) Gallic Acid - gallic acid is found mainly in seeds and stems in grapes, in oak cooperage, and in many enological tannin products. Gallic acid can be present either as free gallic acid or as an ester attached to procyanidin polymers.

(6) Malvidin glucoside - Malvidin glucoside (more specifically, malvidin-3-glucoside) is a monomeric anthocyanin, anthocyanins being the primary red pigment found in red grape skins and young red wine. Of the 5-17 monomeric anthocyanins found in wine, malvidin glucoside is the most abundant, accounting for ~40-80% of the total anthocyanins.

(7) Monomeric Anthocyanins - monomeric anthocyanins are water soluble flavonoid pigments that accumulate in grape cell vacuoles and contribute to much of the color in red wine. The five most common anthocyanins found in grapes are malvidin, cyanidin, delphinidin, peonidin, and petunidin. Anthocyanins have several ionic forms which change depending on the pH of the wine matrix. The flavillium ion is the only one of these ionic forms which is a red pigment. At wine pH, ~10-15% of monomeric anthocyanins present are pigments. Monomeric anthocyanins are relatively unstable and are subject to SO2 bleaching, oxidation, hydrolysis, and polymerization. Anthocyanin concentrations are highest during fermentation and in young wines, with decreasing concentrations during aging. During fermentation, short term reactions include copigmentation through anthocyanin self-association or with other flavonoids. The formation of polymeric anthocyanins increases with wine age. In this report, the monomeric anthocyanin values are the total of all ionic forms, not just the pigmented forms.

(8) Polymeric Anthocyanins - polymeric anthocyanins form from the association of anthocyanins with flavan-3-ols and proanthocyanidins. The association with proanthocyanidins (condensed tannin) form pigmented tannin. These polymer complexes become significant contributors to color stability and color expression due to the fact that they are more resistant to SO2 bleaching and pH changes than monomeric forms and remain relatively stable over the life of a wine. Tannin concentrations in wine have more of an effect on the final concentrations of polymeric anthocyanins than monomeric anthocyanin.

(9) Quercetin Aglycone - quercetin aglycone is the de-glycosylated form of quercetin-3-glucoside and is commonly known simply as quercetin. Quercetin is a flavonol found in grape skins and stems and protects the berry from UV damage, and are in the greatest concentration in sun exposed fruit. Quercetin is very insoluble and its concentration in wine is usually controlled by solubility variables. Anthocyanins can help keep quercetin in solution, but quercetin can precipitate in bottled wines.

(10) Quercetin Glycosides - quercetin glycosides are flavonols found in grape skins and stems and have a protective effect on grape berries from UV radiation. These glycosides contribute a yellow color to wine and juice and can associate with anthocyanins in copigmentation reactions. These reactions aid in wine color stability.

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(11) Tannin - tannins are highly complex molecules and can be made up of both flavonoid and non-flavonoid phenols. Tannins have a major impact on wine flavor, color, and stability. Tannin polymers primarily consist of linked proanthocyanidin units (condensed tannins) such as catechin, epicatechin, epigallocatechin, and gallocatechin. These monomers are found in grape seeds, skins, and stems. In addition to these grape derived tannins, oak derived tannins (hydrolysable tannins) are formed by the esterification of gallic acid or ellagic acid usually with a glucose to form ellagitannin and gallotannins. These hydrolysable tannins can be increased by the use of enological tannins during or after fermentation. Tannin may account for 50% of the phenolic content of young wine and will generally increase with age. Tannin concentration and structure are responsible for much of the mouthfeel and body of red wine. Tannins are also strong antioxidants and can protect red wine from oxidative spoilage. Addition of enological tannin to lesser quality grapes can confer color stability and structure to the final wine product. The measurement performed by ETS and used in this study measures tannin based on molecular size (phenolic polymers with at least four linked proanthocyanidin units) and is expressed as mg/L of catechin equivalents. Tannin concentrations can range from 100mg/L in light reds to 2000mg/L in very tannic reds.

(12) Total Anthocyanin - total anthocyanin is the measurement of the sum of monomeric and polymeric anthocyanins. Lower measured anthocyanin could be attributed to the formation of large pigmented polymers, which can be due to the addition of ellagitannins.

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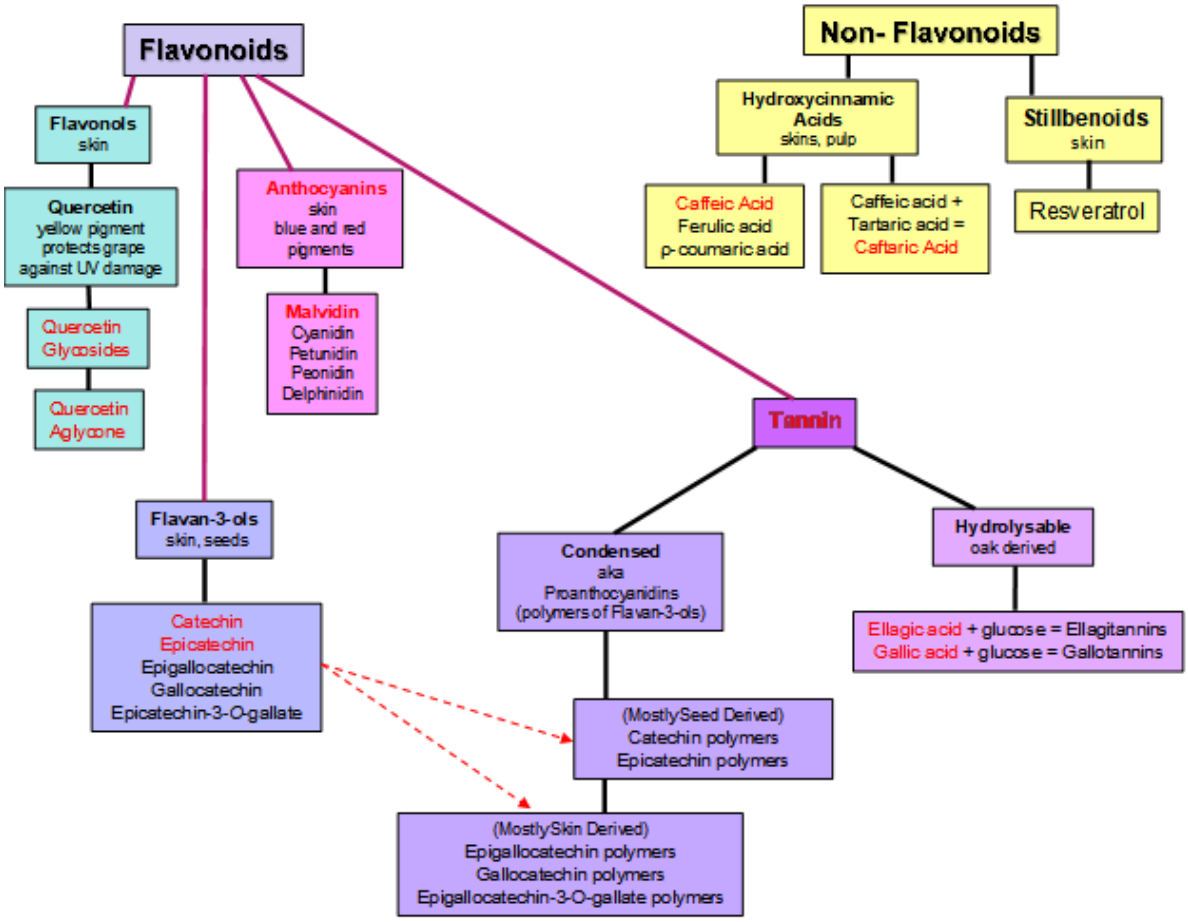

*Phenols in red have measured values in this study

MEASUREMENTS

Color Profile:

The color profile provides a quantitative tool to measure the color of a wine. This test is especially useful for quality control monitoring, troubleshooting color problems, and for comparing two lots of wine. The results include a graphic depiction of the visible spectrum, absorbance at key wavelengths and CIELab color values.

(1) Color Analysis- CIELAB Color Space

The human eye can detect color in the 360- 780nm range. The CIE (Commission Internationale de l'Eclairage) system was developed to determine color matching functions for use in industry and was designed to approximate human vision. The current system, developed in 1976, expresses color in three values in a three-dimensional real number space:

L* is lightness from black (0) to white (100)
a* from green (-) to red (+)
b* from blue (-) to yellow (+)

The CIELab system has been proposed as the new OIV standard for wine color determination.

(2) Traditional Wine Color Measurement

Traditionally, wine color has been evaluated using a mathematical combination of absorbance values at multiple wavelengths. UV visible spectrophotometry is a simple technique for measuring color parameters in wine:

A420 - measures the yellow and brown hues
A520 - measures red hues

- Wine Color Intensity - this is the measurement of how dark the wine is and uses the sum of two or more measurements, in this case A420 + A520 = wine color intensity

- Wine Hue - a measurement of the appearance of the color of wine using the ratio of measurements, A420/A520 = wine color hue

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RESULTS

Figure 1 - Phenolic Panel

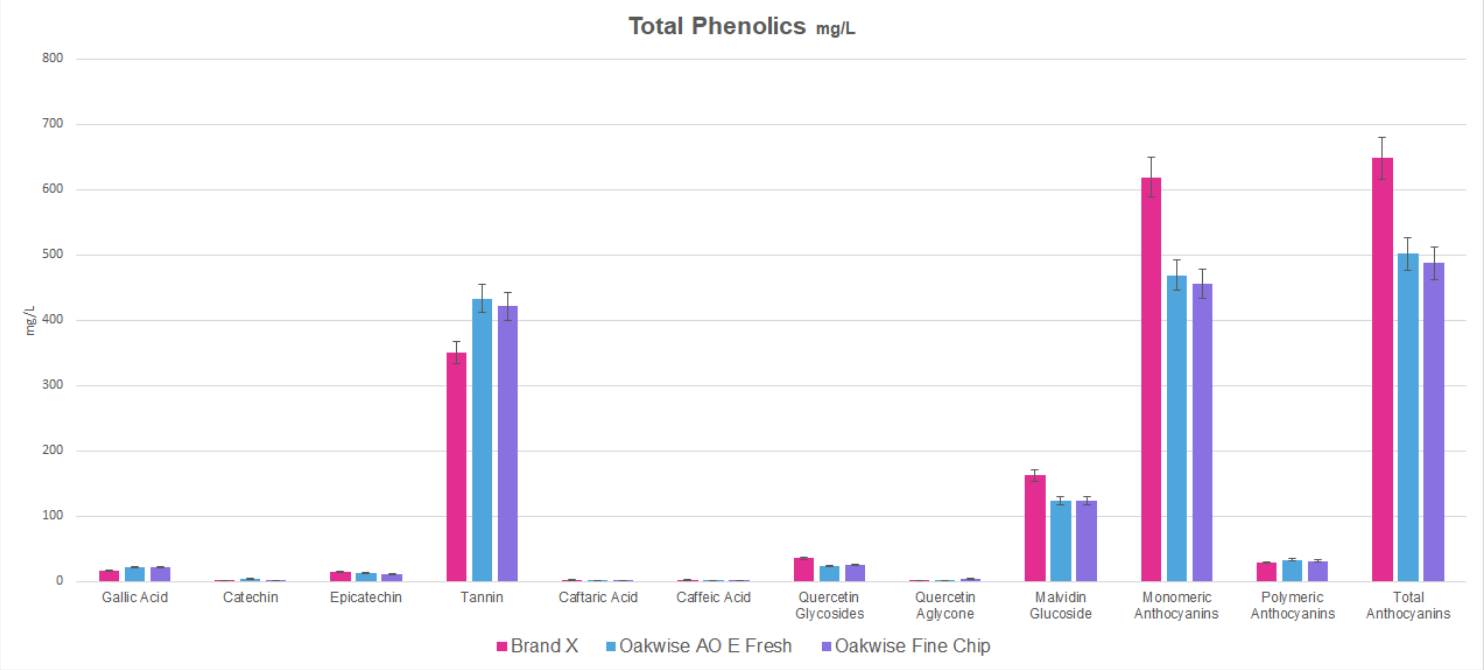


Figure 1 shows the phenolic panel results for the three wine treatments. Note the similarity in the polymeric (bound) anthocyanins, which are responsible for the stability of color in a red wine. Also note the higher tannin levels in the Oak Wise treated wines. Also, lower measured total anthocyanins can often be attributed to the formation of large pigmented polymers, which can be due to the addition of ellagitannins.

Figure 2 - Color Intensity

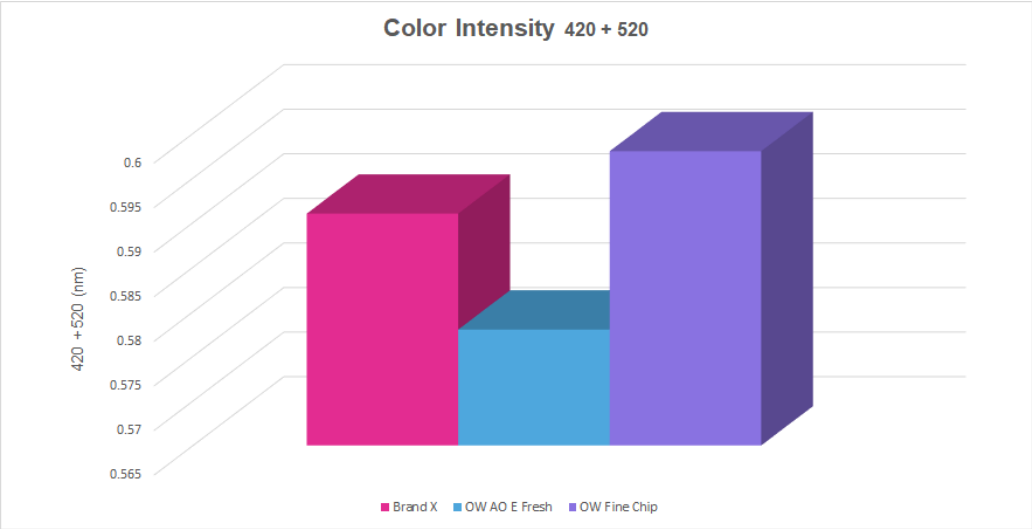
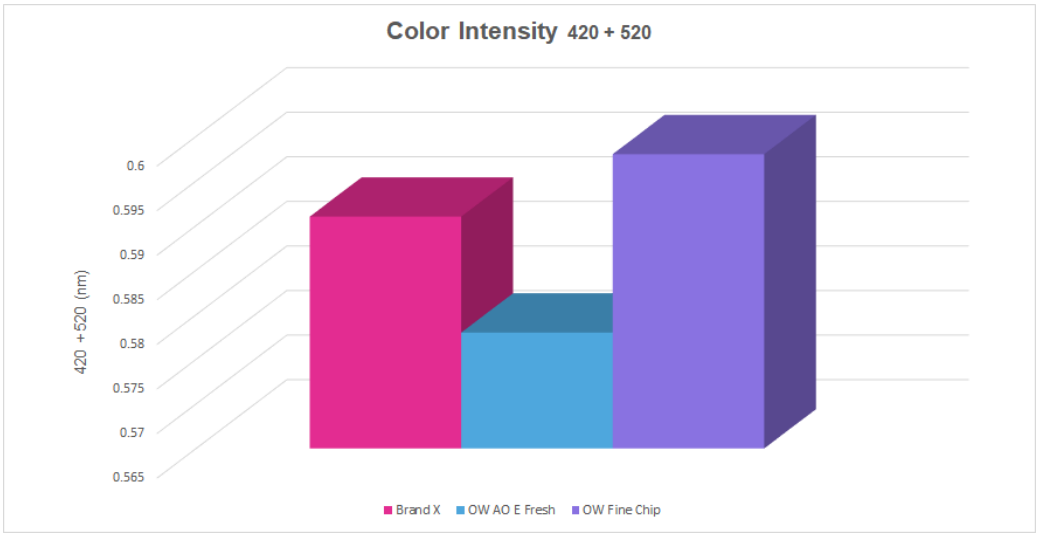


Figure 3 - Color Hue



Figures 2 and 3 show traditional wine color intensity and wine hue values.

Figure 4 - Wine Spectra

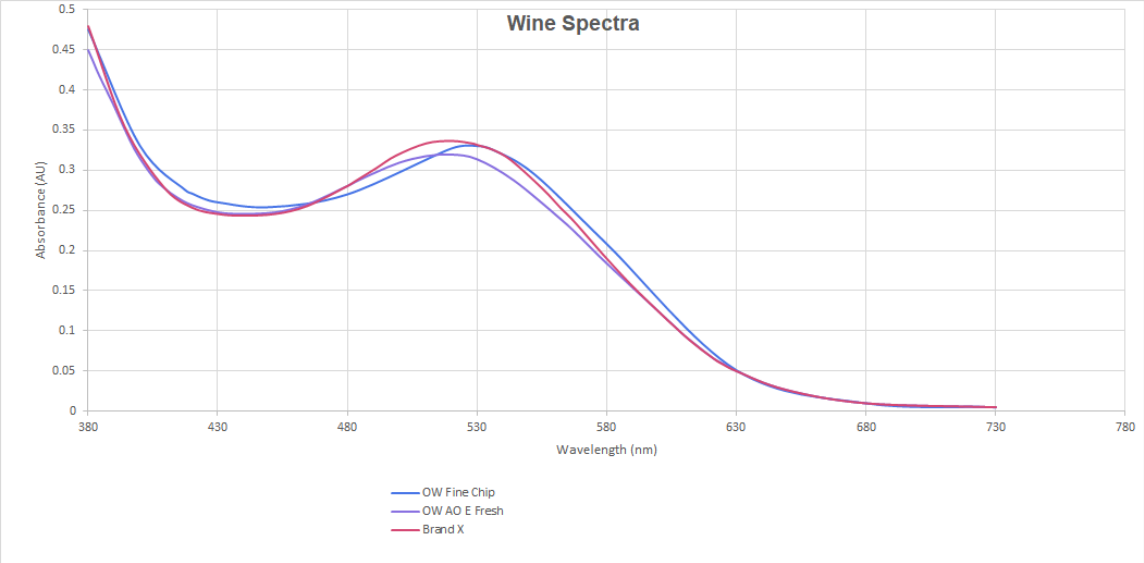


Figure 4 is the full wine spectra measurement from 380-730nm. Note the similarities between all of the treatments.

Figure 5 - CIELAB Plots

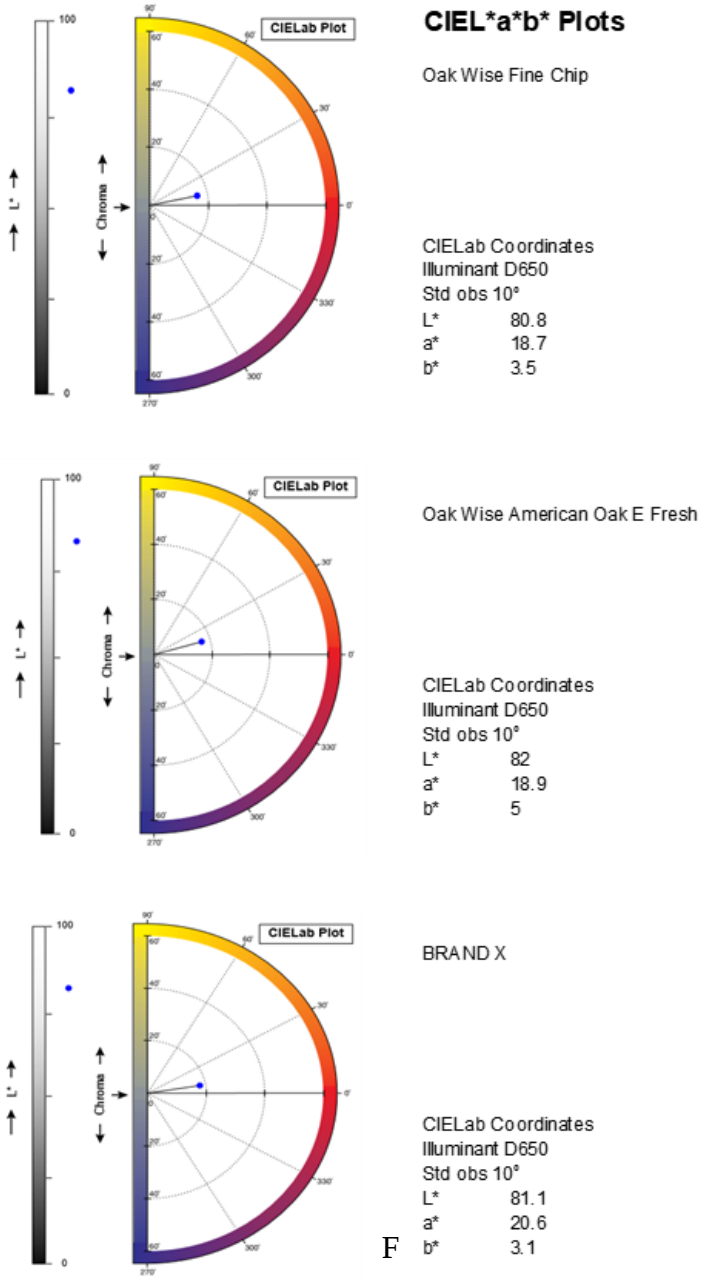


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Figure 5 The above plots are a two-dimensional representation of the three-dimensional real number space that is generated using the CIEL∗a∗b∗ system. Also shown to the right are representations of the colors produced using the CIELab data. These color samples were produced using the Nix Color Sensor Color Converter https://www.nixsensor.com/free-color-converter/

DISCUSSION

When producing wine from grapes of lesser quality or varieties that are notorious for lacking color, the use of enological tannins can be an effective way to boost and stabilize color in the finished wine product. In low tannin grapes, the addition of enological tannins will provide binding sites and promote reactions between anthocyanins and tannins, providing color fixation and stability. It is important to add these tannins early due to the fact that most anthocyanins are extracted during the first 4-5 days of fermentation.

As the analysis performed on these trials show, Oak Wise American Oak E Fresh enological tannin, as well as the Oak Wise Untoasted Fine Chip show comparable levels of Flavonols, Flavan-3-ols, and Non-flavonoids. Although the Oak Wise anthocyanin levels were lower than the competitor, this is most likely due to the formation of large pigmented polymers, which can be due to the addition of ellagitannins. Also, in both Oak Wise products the tannin levels measured were substantially higher than that of the competitor. In visual color comparison, the wine produced in this trial using the Oak Wise products compare well with the competitor.

Enological tannins are recommended when color and mouthfeel need improvement without the resultant oak aromatics imparted by toasted oak products. Oak Wise American Oak E Fresh is an economical and easy to use product that yields great results and can improve the quality and value of treated wine. The Oak Wise Untoasted Fine Chip is also a viable option for color and mouthfeel impact. If oak aromatics are a desired attribute, this product can offer similar color and stability to the enological tannin.

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