

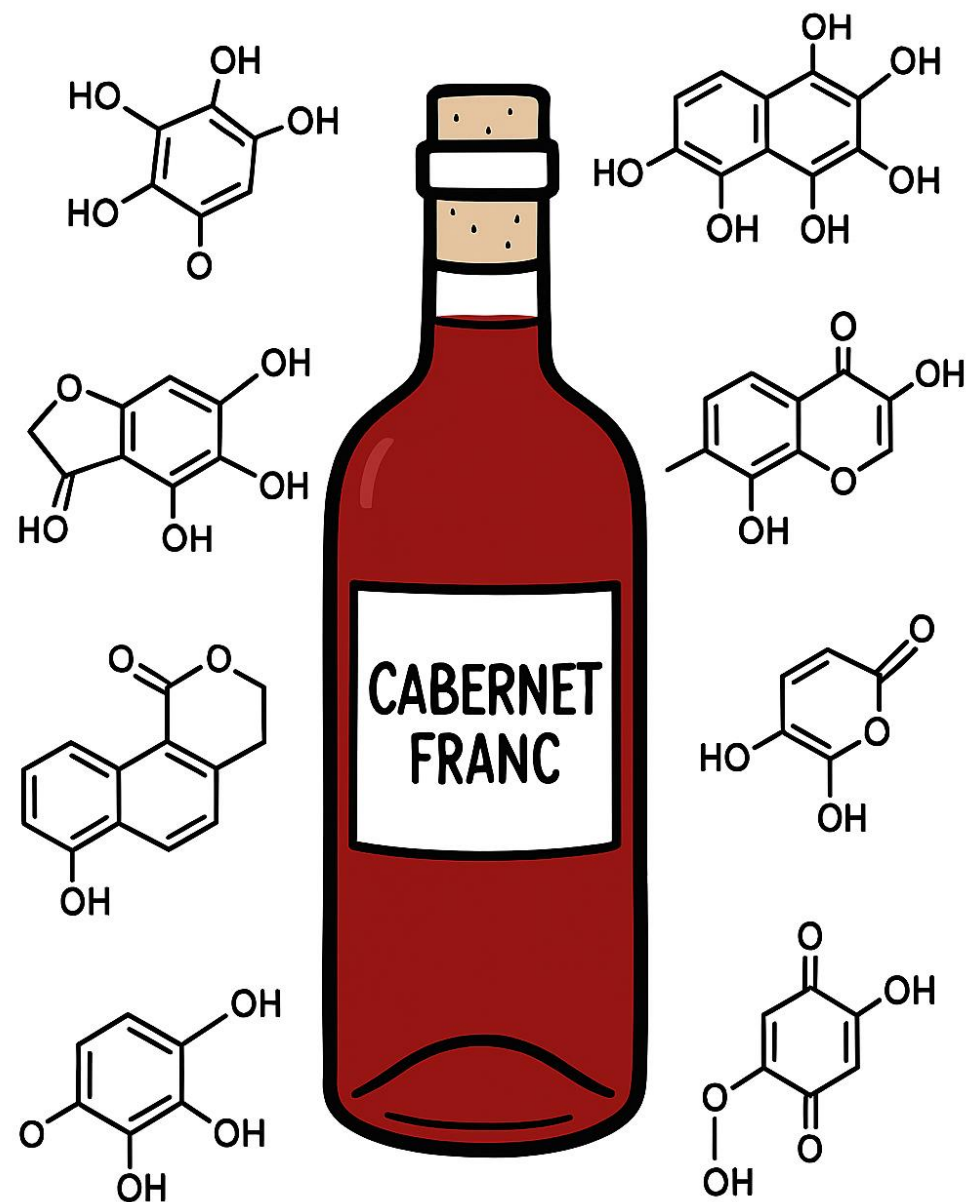
# 2024 Survey of Phenolic Compounds in Virginia Cabernet Franc Wines

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# Collection Strategy

Bottled Cabernet Franc wines made from 2019-2023 vintage grapes were collected for sample analysis.

All wines were made with 100% Virginia fruit and at least 75% Cabernet Franc (according to label laws).

79 samples included grapes from vineyards in 5 regions of Virginia: Northern (33), Central (31), the Shenandoah Valley (10), Southwest (3) and Eastern (2)

7 samples of Cabernet Franc from France, Italy & Argentina were also included in the analyses for comparison.

# Analyses

Sample analysis was completed at Virginia Tech in the lab of Dr. Dennis Cladis (Food Science & Technology)

Results of the following tests are included in this report:

**Total phenolic content (Folin-Ciocalteu assay)**

**Monomeric anthocyanins (pH differential assay)**

**Polymeric anthocyanins (bisulfite bleaching method)**

**Condensed tannin (methyl-cellulose precipitation)**

LC/MS-MS was used for quantification of individual compounds (results pending).



# 1. Total Phenolic Content

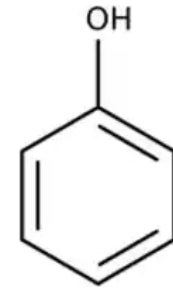
As a group, phenolic compounds affect the flavor, mouthfeel, astringency, and ageability of red wines, each of which is a hallmark of red wine quality.

The common thread in this complex group of compounds is that all phenolics are built on a backbone made up of one or more phenol groups (Figure 1a).

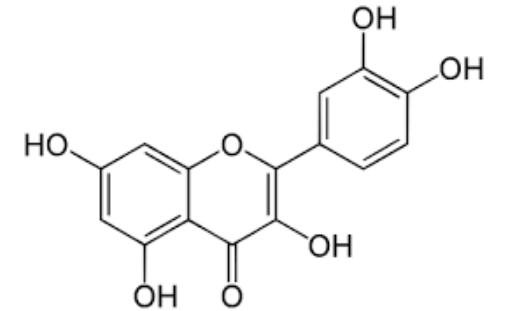
This simple structure can have many different substitutions around its ring and can bind with other rings to form molecules that have related but different chemical and sensory properties (Figure 1b-d give a few examples).

Phenolic compounds can be found as monomers (like those found in Figure 1), but these monomers can also bind together to form dimers (2 subunits), short chain polymers or very long chain polymers (more than 50 subunits long!). The subunits in the chain do not have to be the same, with mixing and matching leading to even more complexity.

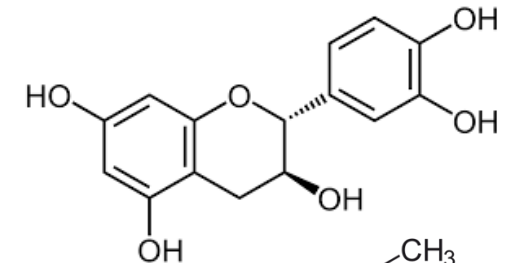
Total phenolic content is a general measurement that includes all the different phenolic compounds found in wine.



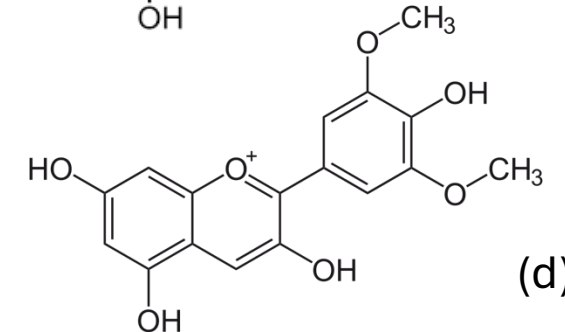
(a)



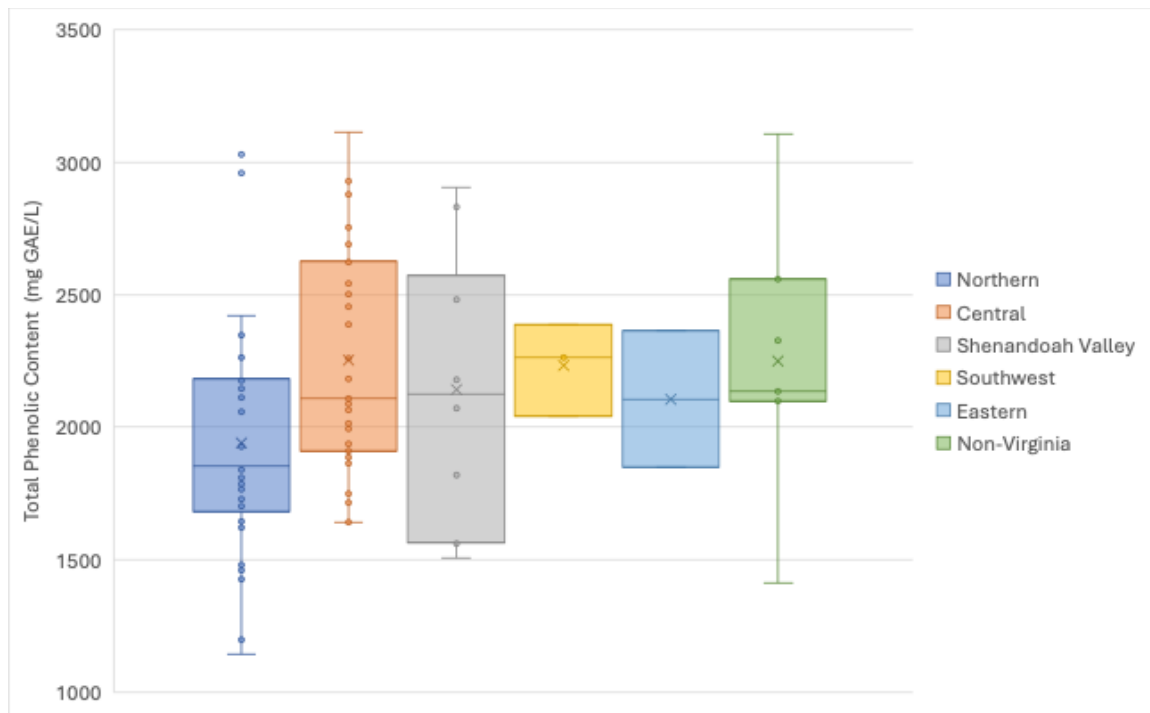
(b)



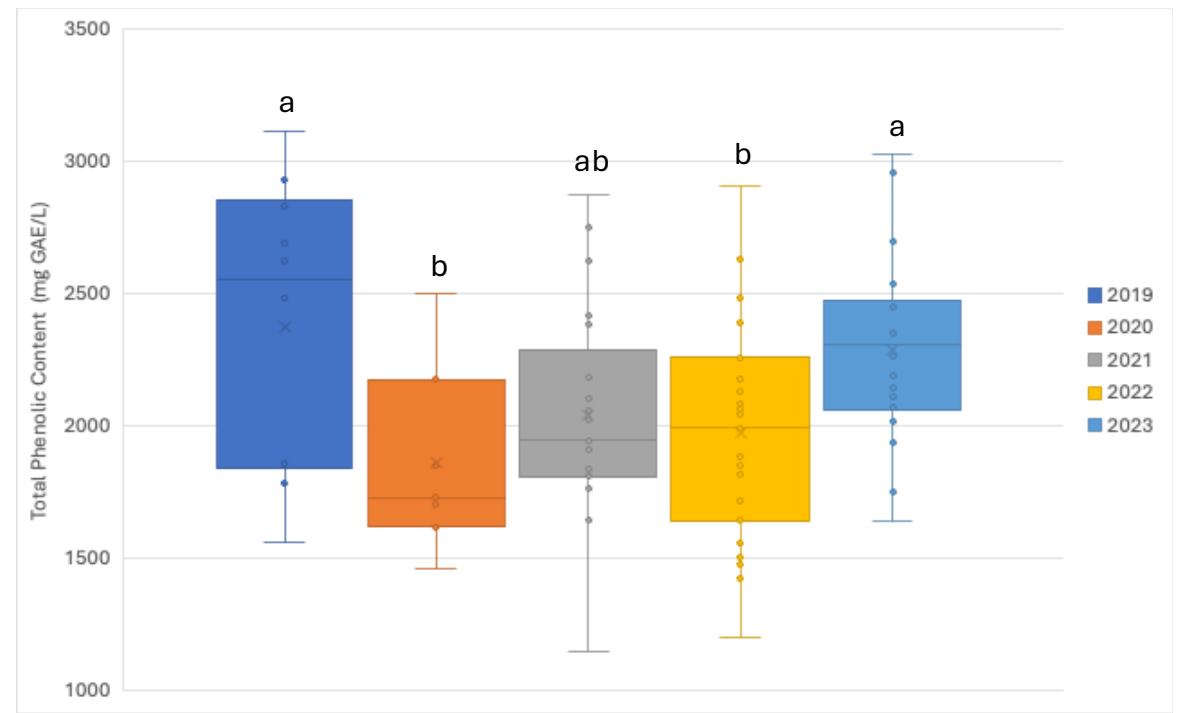
(c)



(d)



Wines from Virginia contained similar total phenolic content to the non-Virginia wines tested. Literature sources list average values for total phenolics from 1800 – 3000 mg GAE/L. Most Virginia samples were within that range. There was no significant difference in total phenolic content among wines from different regions within Virginia.



Total phenolic content was significantly different between vintages ( $p = 0.02$ ). Wines from 2019 and 2023 had significantly higher average total phenolic content than wines from 2020 and 2022 while wines from 2021 had intermediate values.

Total phenolic content includes many different compounds with different sensory qualities and impact on ageability of the wine. Some of the most important compounds in this group are anthocyanins and tannins, analyzed next.

## 2. Monomeric and Polymeric Anthocyanins

Anthocyanins are pigmented phenolic compounds found in the skin cells of grapes that give red wine its color.

**Monomeric anthocyanins** are water soluble compounds extracted within the first 3-5 days of maceration, but many are lost during fermentation and aging due to interactions with other compounds, oxidation, and bleaching. They do not have aroma, flavor, or taste of their own, but they do influence human perception of flavor.

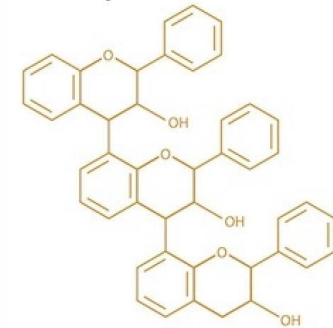
**Polymeric anthocyanins** form when monomeric anthocyanins bind to the end of tannin polymers during extended maceration and aging. These are partially resistant to bleaching and less dependent on pH for color expression than monomeric forms.

Formation of polymeric anthocyanins shifts the hue of the wine from blueish red to brick red. It also modulates the astringency of the wine by changing the interaction of tannin molecules with salivary proteins and may be a key mechanism of why wines become less astringent as they age.

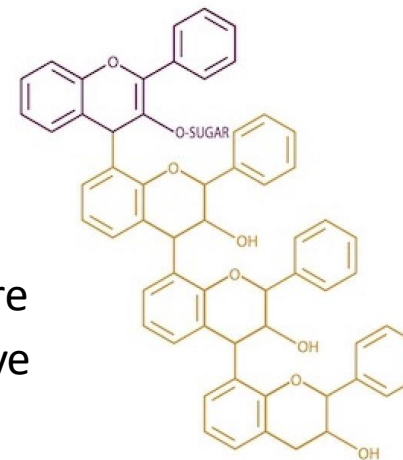
The rate of polymeric anthocyanin formation depends on the availability of tannin (more tannin = more polymeric anthocyanins), acetaldehyde for bridging, and time for bonds to form. Young wines may have 10-40% of total anthocyanins found as polymers while older wines may have 50-90% in this form.

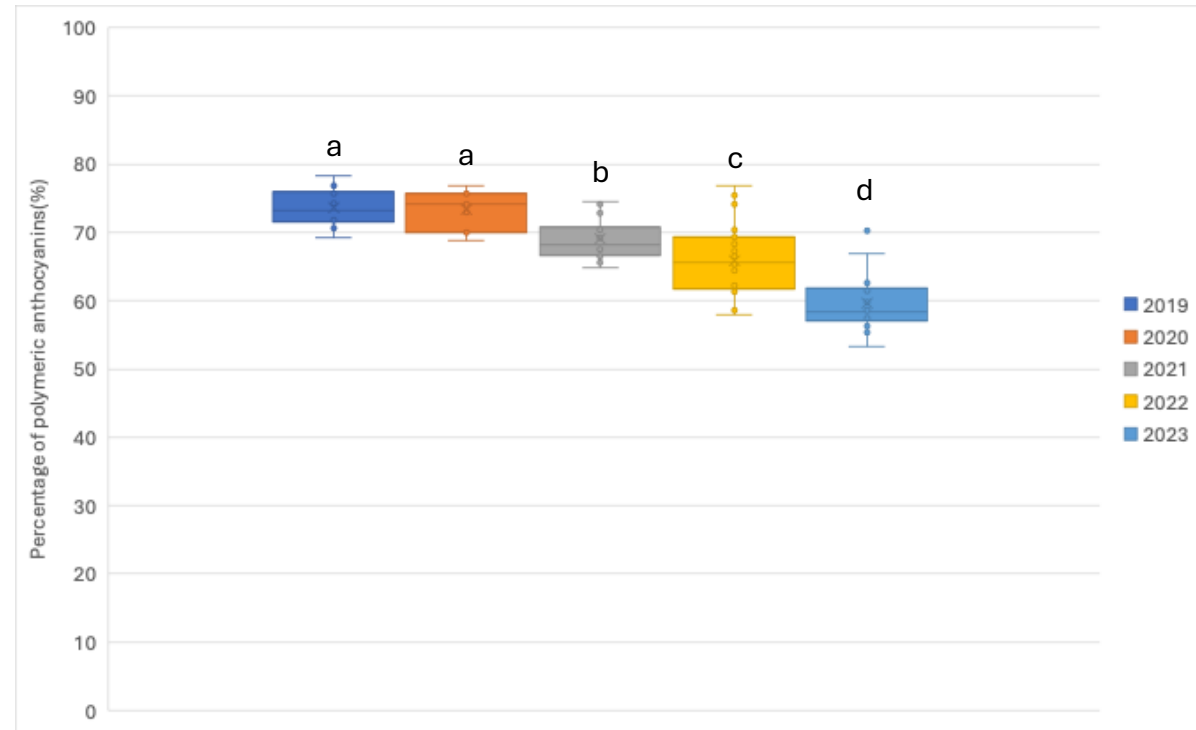
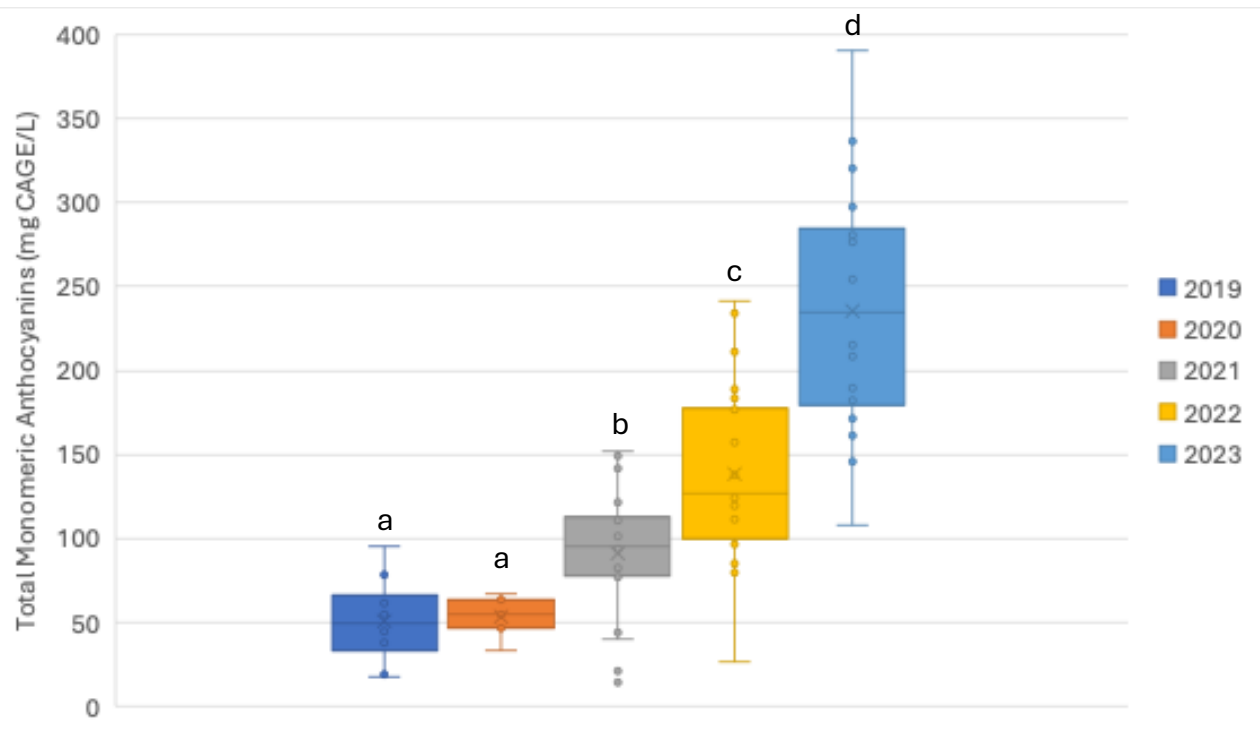


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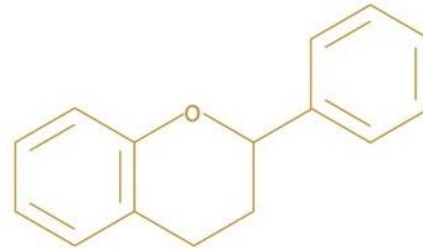
As expected, there was an inverse relationship between the concentration of monomeric and polymeric anthocyanins, with significantly higher concentration of monomeric anthocyanins in younger wines ( $p < 0.0001$ ) and significantly higher concentration of polymeric anthocyanins in older wines ( $p < 0.0001$ ). Monomeric anthocyanin concentration varies widely within a vintage year, especially in young wines. Literature sources report 200-800 mg/L in young red wines. Monomeric anthocyanin concentration reported here was on the lower end of that range (averaging 236 mg/L in Virginia wines from 2023). Cabernet Franc is a lighter colored wine than many other red varieties, so this relatively low concentration is expected in this variety. There were no significant differences in monomeric or polymeric anthocyanins among regions within Virginia or between Virginia and non-Virginia samples (data not shown).

# 3. Condensed Tannins

Condensed tannins (AKA proanthocyanidins) are a complex group of polymerized phenolic compounds made up of subunits primarily from the flavonoid group of phenolics (catechin, epicatechin, epigallocatechin, and epicatechin-3-o-gallate). Tannins can range from very few (2-5) to very many (>100) subunits in the chain.



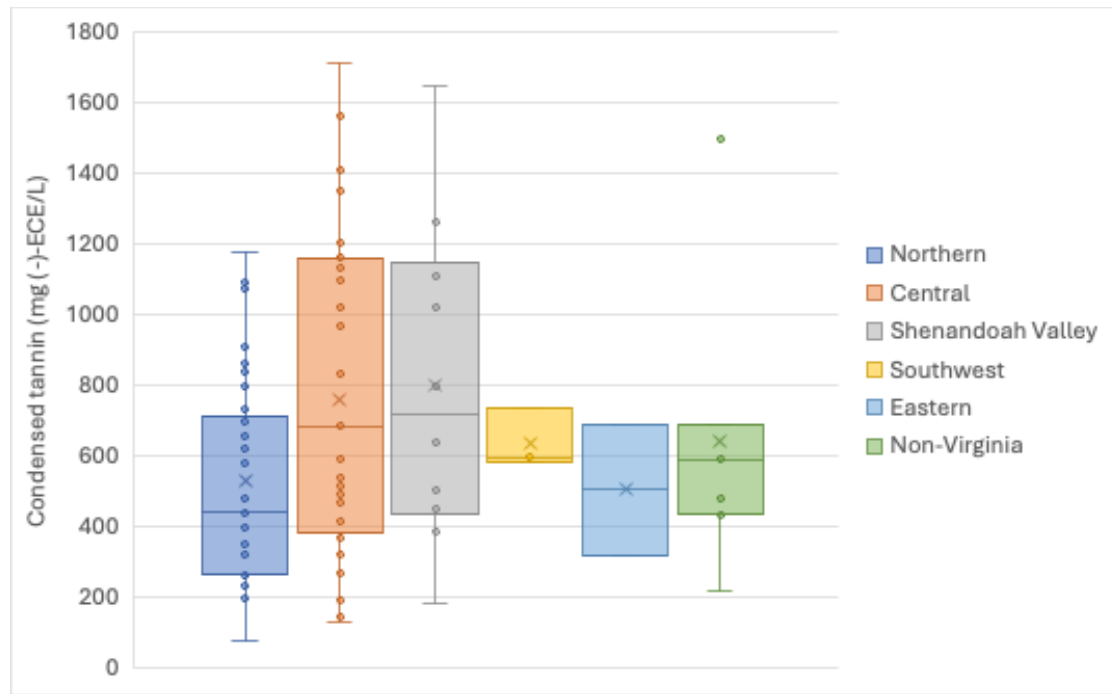
Phenol



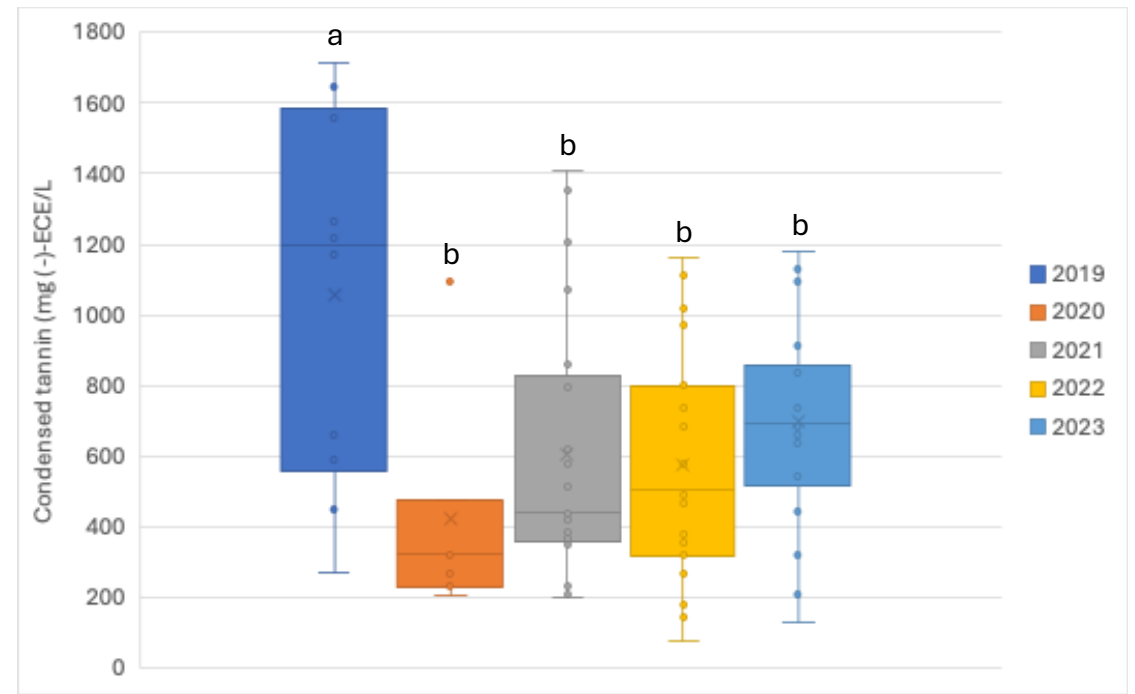
Flavanoid

Tannins originate from grape skins, seeds, and stems (if included in maceration) as well as oak from barrels. They are extracted from grapes during maceration at a pace slower than anthocyanins. Skin tannins are extracted faster and enter the wine sooner than seed tannins. In the wine, all tannins are in dynamic balance, forming new structures as they complex with other compounds in the wine.

Tannins are primarily responsible for the astringency in the wine based on interactions with lubricating proteins in the saliva. Both the number of subunits and the identity of the subunits impact sensory attributes. The source of the tannin (skin vs. seed) may influence sensory aspects such as the grain of the tannin (silky vs. coarse) based on different number of subunits (degree of polymerization) and the proportion of individual flavanols (catechin vs. epicatechin).



Virginia Cabernet Franc had a comparable average tannin concentration to Cabernet Franc from other regions. Literature sources report a range of 200-2000 mg/L of catechin units for red wines, with Cabernet Sauvignon and Merlot averages from 500-1500 mg/L. Virginia Cabernet Franc averaged 652 mg/L, well within this reported range. There were no significant differences in condensed tannin concentration between regions within Virginia.



Virginia Cabernet Franc from 2019 had a significantly higher average concentration of condensed tannins than wines from the other four vintages ( $p=0.003$ ). Growing conditions in 2019 were characterized by warm, dry conditions with low disease pressure, all of which increase condensed tannins. The 2020-2022 vintages had cooler, wetter conditions which likely limited tannin development. Growing conditions in 2023 were closer to 2019; it is not clear why tannin concentration was not as high in this vintage as 2019.

## 4. Ongoing Analyses

Within each group of phenolic compounds examined in this study, multiple individual compounds contribute differently to wine quality. For example, while 2019 Cabernet Franc wines show higher concentrations of condensed tannin relative to other vintages, it is not yet clear whether this increase reflects greater extraction of desirable skin tannins or harsher seed tannins. Skin tannins become more extractable as grapes mature but also depend on factors such as berry processing (higher extraction in crushed vs. whole berries), maceration time, temperature, and alcohol content. By contrast, seed tannins become less extractable as grapes mature, but more prevalent during extended maceration. The elevated tannin content measured in 2019 wines may arise from either source, with very different implications for sensory quality.

Additional LC-MS analysis is underway to quantify these compounds and provide deeper insight into phenolic composition in Virginia Cabernet Franc. LC-MS quantification of catechin, epicatechin, epigallocatechin, and epicatechin-3-O-gallate, key tannin subunits, will allow calculation of skin- and seed-derived tannin proportions and help clarify their contributions to wine structure and mouthfeel. Likewise, subunits of other groups will be compared to provide additional insights into the phenolic chemistry of Virginia Cabernet Franc wines.

A full list of compounds analyzed by LC-MS is provided in the next slide.

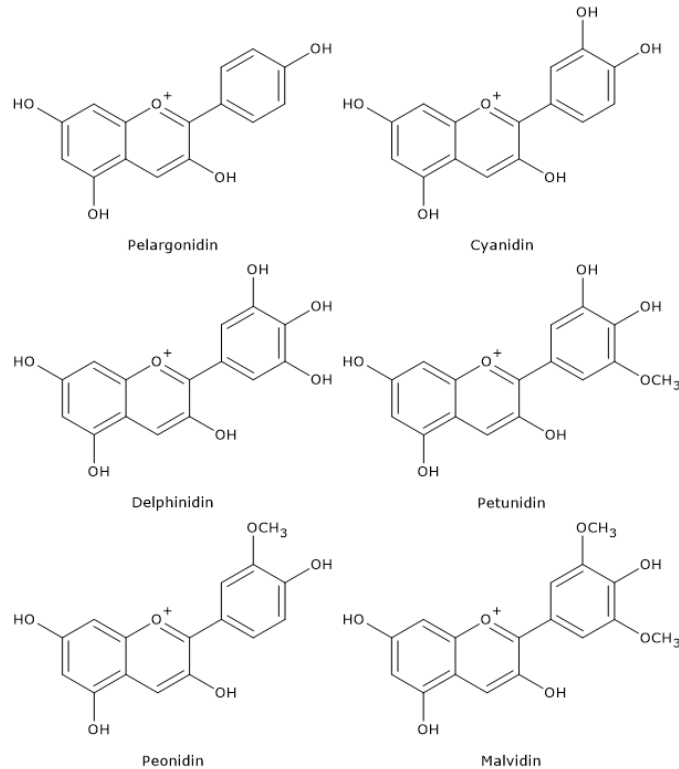
# Ongoing LC-MS Analysis

## Anthocyanins

Malvidin-3-glucoside (oenin)  
Malvidin-3,5-diglucoside  
Cyanidin-3-glucoside  
Cyanidin-3-(6-acetylglucoside)  
Malvidin-3-(6-acetylglucoside)  
Delphinidin-3-glucoside (myrtillin)  
Delphinidin-3-(6-acetylglucoside)  
Delphinidin glucuronide  
Petunidin-3-glucoside  
Petunidin-3-(6-acetylglucoside)  
Pelargonidin-3-glucoside  
Peonidin-3-glucoside  
Peonidin-3-(6-acetylglucoside)

## Other flavonoids

Quercetin  
Quercetin-3-glucoside  
Kaempferol-3-glucoside  
Myricetin



## Phenolic acids

Gallic acid  
Catechin and epicatechin  
Epigallocatechin (EGC)  
Gallocatechin (GC)  
Caffeic acid  
Caftaric acid  
Vanillin acid  
Ferulic acid  
p-coumaric acid  
p-coumaric acid glucoside  
Chlorogenic acid  
Resveratrol  
Syringic acid  
Salicylic acid  
Gentisic acid

# 5. Summary

The analyses reported here (total phenolics, monomeric & polymeric anthocyanins, condensed tannins) provide a snapshot of phenolic content in Virginia Cabernet Franc across five regions and five vintages.

- In all cases, Virginia Cabernet Franc contained similar concentration of phenolic compounds as reference wines from Italy, France and Argentina.
- Wines from 2019 and 2023 had significantly higher total phenolic content than wines from 2020-2022, but for different reasons.
- Cabernet Franc from 2019 had a significantly higher average concentration of condensed tannin, consistent with a long growing season (no spring frost), warm conditions (ample GDD), low rainfall (moderate but not severe water stress post veraison) and low disease pressure (limiting oxidation by laccase).
- Cabernet Franc from 2023 had significantly higher monomeric anthocyanin concentration than the other vintages. This may have been simply due to the younger age of the wine (anthocyanins are lost over time) or due to higher anthocyanin production that year.

LC-MS analysis, currently underway, will allow further elucidation of compounds to better understand differences between the wines.

# References

**Adams, D.O.** Phenolics and ripening in grape berries. *Am. J. Enol. Vitic.* 2006, 57, 249–256

**Casassa, L.F.; Harbertson, J.F.** Extraction, evolution, and sensory impact of phenolic compounds during red wine maceration. *Annu. Rev. Food Sci. Technol.* 2014, 5, 83–109

**Granato, D. et al.** Phenolic composition of South American red wines. *Food Chem.* 2011, 129, 366–373

**Gutiérrez-Escobar, R. et al.** Wine polyphenol content and its influence on wine quality and health. *Molecules* 2021, 26, 718

**Harbertson, J.F.; Spayd, S.** Measuring phenolics in the winery. *Am. J. Enol. Vitic.* 2006, 57, 280–288

**Kennedy, J.A.** Grape and wine phenolics: observations and recent findings. *Cienc. Investig. Agrar.* 2008, 35, 107–120

**Nemzer, B. et al.** Chemical composition and polyphenolic compounds of red wine. *Beverages* 2021, 7(1), 1

**Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D.** *Handbook of Enology, Volume 2: The Chemistry of Wine.* 2nd ed., Wiley, 2006

**Waterhouse, A.L.; Sacks, G.L.; Jeffery, D.W.** *Understanding Wine Chemistry.* Wiley, 2016 (and 2nd ed. 2024)