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Persistence of vegetal characters in winegrapes and wine

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Researchers have gained more insight, in the last several years, into one of the main categories of compounds responsible for vegetal or herbaceous characters in some wnes, chiefly the class of pyrazines that create the familiar green pepper/green bean aromas associated with many Bordeaux-type varieties.

Cabernet SAUVIGNON

Although these pyrazinaes, chiefly methoxypyrazines (MP), are not the only compounds responsible for many facets that define a grape or wine as "vegetal," they are the most common and the most well understood today. They may also act synergistically with other compounds to modify aroma and flavor in many different ways.

Below, we will summarize and present recent findings that will allow readers to gain a better understanding of what these pyrazines are and how they might be manipulated to meet specific quality standards or style considerations.

Sauvignon BLANC

We have reviewed pertinent literature on the methoxypyrazines of grapes and the influence of viticultural and enological practices on their formation and stability as a starting point to address the persistence of vegetal characters in winegrapes and wine. Some results of a preliminary nature reported from France, New Zealand, and Oakville in Napa Valley are included. Such findings need to be evaluated under the reader's local growing conditions to determine what role, if any, they might play in the characteristics that define a wine as "vegetal."

It is important to clarify if we are, indeed, actually seeing the persistence of vegetal characters rather than a change in the definition of enological ripeness. Perhaps those characters that defined winegrapes as mature in the past may not be included in the current definition of maturity, but instead, may be indicators of a lack of ripeness. The characters or their evolution did not change, but the definition of what they represent may have changed. This is likely the case with pyrazines.

MPs are one of a group of pyrazines that are widely distributed in nature. In winegrapes, they are present in such small quantities that, until recently, their chemical detection and enumeration has been difficult. Their threshold in red wine, especially Cabernet Sauvignon, Cabernet Franc, and Merlot, has been reported to be as low as 10 to 15 parts per trillion.[1] But within the range of their occurrence, their aroma can be overpowering and unpleasant.

MP concentrations in wines have always shown a consistent relationship between winegrape variety and grapegrowing conditions. Since MP concentrations are known to decrease during normal winegrape ripening, a high MP concentration in grapes at harvest has become commonly associated with a lack of ripeness and usually has a negative impact on wine aroma and flavor qualities.[2]

Because the fruit with vegetal characteristics is most often physiologically immature, there is often a corresponding lack of acceptable color development and an undesirable, harsh tannic quality in the wines produced from these grapes.

Winemaking decisions / methoxypyrazine content

It is important to understand how winemaking procedures may or may not impact the pyrazine content in a finished wine. In a recent published study, researchers in France were able to show that MP in grapes is highly extractable in the traditional winemaking process.[2]

MP concentration in Sauvignon Blanc wine was shown to be independent of pressing conditions of the juice. The final MP concentration in the Sauvignon Blanc wine, in this study, differed insignificantly from the first free run juice at pressing. Settling of the juice did, however, decrease MP content by almost half in the clarified portion. So, with white wines, settling may reduce grassy characters.

With Cabernet Sauvignon in the same study, all pyrazine, found in the wine after racking, had already been extracted from the grapes within 24 hours of crushing, before alcoholic fermentation began. This final pyrazine concentration in the wine was not affected by different cap management regimes or amount of time the wine spent on its skins.[2] This shows MP to be highly extractable in winegrape must.

Press wines, however, have been shown to contain higher levels of MP. This suggests that a fraction of MP remains in the skins and is extracted during rigorous pressing. In the same study, after ageing Cabernet Sauvignon for three years in a dark cellar, no significant change in MP content was recorded. Therefore, dependence on ageing or time in bottle to decrease vegetal character in wine is probably not an effective strategy.

An interesting observation from some researchers is that thermovinification of red grapes to promote extraction of phenolics and destroy oxidases also leads to a decrease in MP concentration in heat-treated wines.[1] The wines studied were heated to 60†C to 80†C for a short period of time. The resultant MP content was decreased to a concentration below the sensory threshold, so the original vegetal character was no longer perceptible.

In concurrent laboratory trials, MP was found to volatilize and dissipate into the headspace after heating to above 50†C. This could be useful in dealing with grapes that are harvested before optimal ripeness due to weather or growing conditions. Using thermovinification conservatively could, in certain cases, lead to more highly colored, fruity, less vegetal wines.

How vineyard decisions

affect wine MP content

Since it can be shown that winemaking procedures probably have a minimal impact on pyrazine concentrations, it is most appropriate to focus on recent viticultural research for clarification on pyrazine management. This research seems to confirm that grape ripening conditions in the vineyard are primarily responsible for the methoxypyrazine content in wines.[1] This means that if your target wine style does not include a vegetal component, you will have to start your winemaking process very early by understanding what happens in the vineyard and how these compounds can be manipulated before harvest.

A very significant study, recently completed at the University of California, Davis, investigated the effects of yield manipulation through vine pruning and cluster thinning on the resultant sensory attributes and actual MP concentrations of Cabernet Sauvignon wines.[3] Researchers subjected vines to six different winter-pruning treatments and eight different cluster-thinning treatments; thinning being imposed at veraison.

This research is particularly significant because the large number of treatments resulted in an equally broad range of vine yields. In 2000 and 2001, vines were pruned to 12, 18, 24, 30, 36, or 48 buds per vine, with 24 buds per vine as the control. Separately, in 2001, vines were pruned to 24 or 48 buds per vine and clusters were removed at veraison to leave 12, 24, 36, or 48 clusters for the 24-bud vines and 48, 64, 72, and 96 clusters per vine for the 48-bud vines.

Yields ranged from 1.75 tons per acre to 9 tons per acre. In both experiments, treatments were imposed in a randomized complete block design with six replications. All wines were made in triplicate. Also, lending to importance of this research is the fact that researchers used trained judges employing descriptive analysis techniques to determine the sensory attributes of resultant wines.

Analysis of variance and principal component analysis showed that pruning vines to a very low bud number, produced wines that were perceived by the panel of judges to be higher in vegetal aroma and flavor, bell pepper aroma, bitterness, and astringency than wines from “high yield” vines.

Wines from vines that carried more crop (higher bud numbers) were consistently rated as higher in red/black berry aroma, jam aroma, fresh fruit aroma, and fruity flavor. Regression analysis showed that, in general, vegetal attributes decreased in intensity and fruity attributes increased in intensity as bud number and yield increased.

In contrast, there were few differences detected in wines made from various cluster-thinning treatments, though the yield range was greater. They concluded that Cabernet Sauvignon aromas and flavors respond to yield manipulation, but do so significantly only when yield is manipulated early in fruit development (winter pruning, in this experiment).

This sensory evaluation was substantiated by a newly developed chemical analysis using a rapid and automated solid phase micro-extraction (SPME) stable isotope dilution gas chromatography/mass spectrometry (GC-MS) method for quantifying 2-methoxy-3-isobutylpyrazine (MP) concentrations in red wine. This assay showed that MP concentrations in wines studied were significantly negatively-correlated with number of buds per vine.[5] As bud numbers increased, MP concentrations decreased and, alternately, as bud numbers decreased, MP concentrations increased. In addition, MP concentration determined by GC-MS was directly related to sensory vegetal intensity ratings obtained by descriptive analysis.

The same study showed that crop thinning had a very limited effect on wine quality, though it obviously impacted yield significantly. These data are significant because they seem to challenge the paradigm that as winegrape yield increases, resultant Cabernet Sauvignon wine quality decreases. They further suggest that how the crop yield is attained, rather than the exact yield itself, is significant for resultant wine quality. This underscores the importance of determining proper balance for a given set of growing conditions as a function of the varietal, rather than having a pre-determined crop level that ignores vine performance at the site and overall grape composition.

Although the actual MP precursors have not been definitively determined, some

important features of their synthesis and degradation are more clearly understood today. MP synthesis in grapes seems to occur between fruit set and two to three weeks prior to veraison.[2] This phenomenon seems to be related to grapevine water status before veraison, as initial pyrazine concentrations were less in drier years in France. At this pre-veraison stage, its concentration is highest in the stems. It is also found in the berry pre-veraison, but it is not known if it is actually synthesized in the berry or if it is synthesized elsewhere and transported to the berry.

MP has also been identified in Cabernet Sauvignon leaves, with basal leaves having the highest concentration, much higher than in clusters. About three weeks before veraison, MP content in berries decreases through to harvest.

Breakdown of malic acid and pyrazines seems to occur simultaneously in winegrapes, irrespective of soil type, grape variety, or vintage.[7] This very strong correlation in their respective concentrations may allow MP content to be considered a marker of grape immaturity. MPs may serve as a biological deterrent to consumption of the fruit before the seeds have attained sufficient ripeness to survive, and may indeed be directly linked to ripening. However, other explanations for the function of MPs have also been proposed.

Because the shape of the MP content-curve during ripening does not change as a function of how the units are expressed, it can be inferred that the decrease in MP content seen from about three weeks before veraison through to harvest is independent of the dilution that occurs during berry enlargement.[1] Therefore, unlike tartaric acid, MP is actually broken down as the berry swells and ripens.

Several studies have revealed a strong relationship between exposure to light and decrease in MP content to explain this decrease after mid-veraison. It is known that MP is broken down in the laboratory by light.[6] More work needs to be done in the vineyard on intact berries and clusters to determine if light is actually the chief agent of MP degradation. Regardless of phenological stage, the pulp contains very little MP while stems and older leaves contain a lot.[2]

At harvest in the cluster, MP is found mainly in the stems or rachis. It has been shown that, under identical environmental conditions, MP accumulates in leaves simultaneously with its degradation in grapes during ripening. All data, so far, suggests that metabolism of this pyrazine is completely different in grapes, stems, and leaves.[1]

Although actual quantification of MP content in grapes is not practical for most wineries today, it may be possible to track the curve of its degradation by monitoring the concurrent decrease in malic acid during ripening.

Recent research from France has shown that there is a significant correlation between degradation of MP content during grape ripening and loss of malic acid during the same period.[17] For the two years studied, Cabernet Sauvignon and Merlot grapes grown under different environmental and cultural conditions, were tested for both malic acid content and MP content from veraison to harvest. These data show that the breakdown of malic acid and MP occurred simultaneously, irrespective of soil type, grape variety, or vintage. The determination coefficient (r2) between the breakdown of these two compounds was 0.90 and 0.96 in 1996 and 0.91 and 0.99 in 1997. They are, therefore, highly correlated.

Knowing that many products that are synthesized in the leaves are transported to the berries, in a preliminary study (not yet published), researchers treated grape leaves with a solution of a marked analogue of MP by putting the solution on leaf blades, then analyzing its movement after several days.[1] This was done between the small pea stage and beginning of veraison.

Researchers observed a redistribution (movement) of the marked compound to petioles and other growing parts of the vine, including clusters. Amounts of MP confirmed the fact that, at this stage of ripeness, metabolites are preferentially routed to clusters. They found the marked MP in the rachis and berries, demonstrating that this compound is transported by the phloem from leaves to berries. Since it can be shown that MP is moved from leaves to the berries, this fact underscores the importance of managing vegetative growth to decrease the production of pyrazines. It is still unknown whether the berry actually synthesizes

pyrazines itself or whether they are transported to the berry from the vine's vegetative structures.

These results confirm the advantages of leaf removal to decrease the perception of vegetal/green pepper characteristics. Another aspect of this research measured the effects of various canopy manipulation practices and their timing on the pyrazine content of Cabernet Sauvignon and Merlot grapes. Summer thinning of laterals, leaves, and clusters all had a direct effect on decreasing MP concentration in these two varieties.[1] The light-sensitive nature of MP may partially explain this result.

Wines made from cluster-thinned or leaf-thinned groups had higher alcohol, more color, and a lower MP content than those of the control. But timing of the vineyard work was also shown to be an important determinant of final MP content in the resultant wines.

Leaf thinning between fruit set and before veraison leads to grapes with a higher sugar content, smaller size, and less green pepper character at harvest. It is interesting to note that one year of the study in France, there was significant rainfall during veraison that greatly slowed the usual MP breakdown that occurs in this phase of berry ripening. This also resulted in an unusual heterogeneity in berry ripeness. The vineyard had been leaf-thinned after fruit set, prior to the rains, so MP synthesis had already been inhibited somewhat.

Due to these lower levels of MP synthesis after leaf thinning and decreased breakdown due to rainfall during veraison, MP levels at harvest were close to zero. Comparing those results to a more typical year with less dramatic rainfall, the typical season showed much higher levels of MP at mid-veraison. These levels held through to harvest. This highlights the assertion that it is weather conditions just prior to and during veraison that most impact the final MP concentration in grapes, rather than the period between veraison and harvest.

Early lateral removal and leaf thinning also facilitate later season vineyard work by eliminating some vegetation in the fruiting zone. These practices improve vine balance, allow better light penetration , lead to better aeration around clusters, and remove vegetative structures requiring additional nutrients, which, in turn, promotes better distribution of photosynthates for improved ripening.[1]

Enological ripeness

Another aspect of the role of methoxypyrazines in wine production concerns the relatively recent practice of extended hang time of winegrapes to achieve more ripe flavors. There has been a great deal of speculation about the reasons and ramifications of this practice.

It is true that, from a winemaking perspective, the fruit of some varietals in some regions simply does continue to improve with extended ripening. In a study of Sauvignon Blanc in New Zealand, fruit grown in a warmer region (2100 heat summation units) had pyrazine levels below the threshold of detection while fruit from a much cooler region (1430 heat summation units) had a pyrazine level four-fold greater than the detection threshold at harvest.[5] This study is consistent with much earlier work stating that the loss of such "unripe" characters was the basis of recommendations of how varietals performed, or how they reached enological ripeness, as a function of degree day summation units.

As mentioned earlier, pyrazine characters have been shown to decrease with ripening, allowing a winemaker to time harvest to the appropriate level of vegetal character for the wine style being produced.

Some wine writers and consumers do not appreciate vegetal characters in wines, preferring instead wines of concentrated fruitiness. This preference has resulted in a trend towards extended ripening in an effort to further reduce vegetal character in winegrapes and to enhance wine fruit aroma profile. The efficacy of a particular grower or manager's program of extended ripening is predicated on the assumption that grapes are grown in an area that allows proper ripening.

Today, such errors in judgment are rare, yet there is a belief that vegetal characters are persisting in the fruit much longer than they should based on other indices of ripeness or based on historical data obtained when most vines were planted to AxR1 rootstock. Many new vineyard practices were introduced simultaneously with

extensive replanting of vines to rootstock other than AxR1.

Some of these practices resulted from extensive wine quality evaluation, although not necessarily broadly applicable beyond the region in which they were initially studied. But most studies simply evaluated vine growth parameters without benefit of accurate sensory evaluation of wines produced. Indeed, few were evaluated in combination, and changes in ripening of the scion varieties could simply reflect changes in vineyard practices.

However, it is also apparent that the definition of enological ripeness has changed and planting recommendations based on a historical target fruit composition may no longer be valid.

Should degree day summation recommendations be revisited in terms of changes in consumer tastes, viticultural practices, and definitions of enological ripeness?

Are some varietals simply not able to ripen to new standards demanded in the marketplace in regions in which they have been planted? Or are other forces in play? These are important questions that need to be addressed.

Summary
Winemakers and grapegrowers know a lot more about methoxypyrazines today than several years ago. A lot of that information can be put to work almost immediately to help grow better grapes and make better wine. The data clearly shows that MP content of a wine depends mainly on the content in the grapes it was made from, and that it is only very marginally affected by winemaking techniques. The one exception appears to be thermovinification, or heating the must or wine to approximately 60†C to 80†C for a short period, which has been shown to greatly decrease MP and could be a solution in some cases.

Winegrowers need to focus on how to manipulate methoxypyrazines to the preferred level in the vineyard. Vine balance is key to this. Vines that are undercropped produce wines with high levels of green pepper attributes, as do vines that are overly vigorous and cropped too heavily.

Because the maximum MP content is achieved prior to veraison, the period between set and veraison is when a grower can employ practices that have the most impact on the vegetal concentration of winegrapes There are significant data to show that early shoot and leaf removal are beneficial in decreasing these vegetal characters in grapes. Early season deficit irrigation, prior to veraison, can also be used to decrease vegetal characters.

It appears that MP synthesis is related to vegetative growth of grapevines, so any early intervention that decreases canopy size/leaf area also decreases pyrazine content in berries. There may be growing areas where some varietals can’t achieve enological “ripeness,” if the definition of ripeness includes absence of vegetal characters. But in most areas, manipulation of pyrazines in the vineyard is key to their expression in a resultant wine.

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