

# Primer on Atypical Aging

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In the history of describing wine aromas accurately, atypical aging, commonly referred to as ATA, has come to the scene as a relatively recent aroma characterization. Its first documented appearance dates back to the 1980's in Germany. In the meantime, it has become one of the most serious quality problems in white wine making in nearly all wine producing countries. The US Mid-Atlantic growing areas are not excluded.

## A problem of sensory identification

In despite of the frequency in which ATA occurs in the global wine industry, producers are not always aware of the full extent of what is seen by many as the greatest challenge of white wine enology in modern times. Most frequently, it is incorrectly identified or mistaken for oxidative aging or, in the specific case of Riesling wines, the so-called "petrol flavor". Deficiencies in sensory discrimination bring about misleading technical advice when it comes to take enological measures against it. Indeed, oxidative aging has been known since forever as the typical kind of white wine aging, and the prevailing bulk of the enological literature dealing with wine aging focus upon it as if there were no other type of aging. Even though both kinds of aging may occur simultaneously in individual cases, their origins and pathways are totally different and, therefore, require very specific counter-measures.

Wines affected by ATA display an aroma profile variously described as reminiscent of mothballs, naphthalene, laundry detergent powder, soap, acacia and lemon blossom, damp towel, washing machine, or floor polish. Simultaneously, the desirable fruity, floral, or mineral aroma attributes are largely absent in a way that wines affected by this taint lose their varietal character very early. High levels of free SO<sub>2</sub> tend to reinforce that perception. In the aftertaste, these wines often come out meager and thin, displaying an increasing metallic bitterness which is not related to the presence of any tannins or metals. They have nothing in common with wines affected by oxidative degradation. White wines without any distinguishable aroma attributes during the first weeks or months after primary fermentation are not necessarily affected by ATA, but are often prone to develop it.

## Hormonal stress generates precursor

The direct cause of ATA is a hormonal stress in the vine. As a consequence, there is an accumulation of a phytohormone called 3-indol-acetic acid which undergoes further reactions in the wine. As much as to say, ATA is exclusively a problem associated with vineyard management. Viticultural factors promoting its appearance include:

- overcropping (5),
- nutrient deficiencies in the soil (14),
- premature harvest before aromatic ripeness is achieved (15),
- hydric stress (12, 16), and
- excessive UV radiation (7).

In the northern hemisphere, precipitation occurring between June and August has an important influence. Notably, water available 10 days before and 10 days after véraison has been shown to be decisive of the decrease of ATA potential. Under drought conditions, green cover reinforces the tendency towards ATA as it competes for the available water. In any case, the causes are complex and multifaceted. Reducing crop load, extending hang time until complete ripeness is achieved regardless of Brix or pH, and judicious irrigation are the most useful instruments for mitigating problems with ATA.

3-indol-acetic acid is the major precursor triggering ATA. It decreases during aromatic maturation. However, in times of global climate change, the discrepancy between grape sugar content and aromatic ripeness is increasingly accentuated. This means that aromatic ripeness does not run proportional to alcoholic ripeness, expressed as Brix. In extreme cases, that can cause a wine from 25 Brix or more to remind one of an aroma profile of 17 Brix grapes. Modern winemakers claim that they do not rely on numbers, but if they actually did not, the extent to which ATA affects white wines around the world would not be that impressive. Winemakers today should give less regard to traditional Brix and pH readings, and pay more attention to the sensory evaluation of aromatic ripeness of the fruit.

Fruit prone to develop ATA after fermentation tends to display low levels of yeast-assimilable nitrogen (YAN) (14). So far, YAN measurements before harvest may help to evaluate the potential for ATA. However, this connection is not a causal one. Therefore, improving deficient YAN levels by adding inorganic nitrogen or complex yeast nutrients to the fermenter is not a sufficient means to reduce any ATA potential.

### **SO<sub>2</sub> addition after fermentation triggers ATA formation**

Eventually, the compound primarily responsible for the olfactory perception of ATA is 2-aminoacetophenone (10), accompanied by some other compounds of minor importance. Higher contents of 2-aminoacetophenone have also been shown to contribute to the intrinsic flavor of hybrid varieties (1). For the purpose of sensory training, ATA can be produced by spiking a sound wine with 1 to 2 µg/L of 2-aminoacetophenone, the threshold being around 0.7 µg/L.

In vinifera varieties, sensorially detectable amounts of 2-aminoacetophenone are the result of the breakdown of 3-indol-acetic acid. This conversion can take place following two pathways:

- A microbiological degradation by some indigenous non-Saccharomyces yeast strains borne on the grapes which are stressed by nutrient deficiency during fermentation. Yeast strains from *Saccharomyces cerevisiae* and active dry yeast are not able to perform that degradation (3, 4, 8). Hence, the production of 2-aminoacetophenone during fermentation is restricted in current winemaking practice by the prompt initiation of fermentation with active dry yeast.
- A chemical breakdown of 3-indolacetic acid through a chain reaction triggered by oxygen radicals. These radicals are generated when sulfites oxidize (2, 5, 6). In technical and sensory terms, this pathway is of crucial importance because it explains why ATA appears most frequently when young white wines are sulfited for the first time after fermentation. In the worst case, this may happen within a few days. Hence, ATA is not necessarily an aging flavor produced with some delay, but may also occur as a premature aroma defect in young wines. It can be masked temporarily by short-lived fermentation-derived aromatics, emerging only when these aromatics break down or are expelled by inappropriate cellar operations.

It should be noted that contrary to some popular belief, oxidative degradation must be ruled out as the cause of ATA since it occurs particularly in sulfited and topped-up wines carefully protected from oxygen uptake. ATA formation is not affected by any storage conditions other than SO<sub>2</sub>, nor by other winery operations capable of shifting the oxidation-reduction equilibrium. The oxygen radicals mentioned in the context of ATA formation are not related to the well known wine oxidation phenomenon as generated by the ingress of atmospheric oxygen. Generally, oxidation means that the oxidizable compound donates electrons; the combination with oxygen is a very special form of oxidation. Oxygen radicals are also generated when wine constituents are reduced by sulfites, inducing the oxidation of the latter.

### **Enological measures mitigating ATA**

In red wines, the oxygen radicals involved in ATA formation are scavenged by tannins. Therefore, red wines cannot develop any ATA. Its occurrence is limited to white and rosé wines which, by their intrinsic characteristics, do not contain significant amounts of phenols.

In certain marginal cases, some enological tools can prevent or delay the formation of ATA, or reduce its olfactory intensity. To some extent, prolonged skin contact or the addition of commercial tannins may act in this way. Either of these measures enhance the total phenol content in white wines but are incapable of achieving levels that even begin to compare with those found in red wines. Accordingly, they are of limited efficiency (11). Rather one obtains bitter and harsh wines with a stronger inclination to produce oxidative aging and astringency while the original problem is not securely resolved.

On the other hand, oxidative juice processing, since it lowers total phenols by precipitation, can to some extent enhance any existing ATA potential. Such an effect has been observed especially when flotation with air is used for juice clarification. This effect may be mitigated, however, by the quantity of ATA precursor removed during clarification. Inversely, the traditional juice processing with sulfur dioxide, which retains phenols, may slightly reduce the ATA potential. Hence, oxidation-reduction conditions during vinification have some impact on ATA formation insofar as they affect the phenol content.

When juice solids are fermented separately after racking, the resulting wine has a higher ATA potential than the wine produced from clarified juice. Obviously, a fraction of the ATA precursor is bound to juice solids and is therefore removed with them at racking. Thus, a severe juice clarification is a further, but insufficient step to reduce ATA formation.

During storage of young wines, the production of 2-aminoacetophenone has been claimed to decrease when the unfiltered wine is stored on the lees. This effect was attributed to the glutathione released by yeast (9). Practical experience, however, demonstrates that the presence of residual yeast post fermentation is generally not sufficient a means to protect a wine against ATA. Filtration is without any influence.

All in all, it has to be stated that current vinification procedures do not offer reliable means to produce clean wines on the long-term when ATA-affected fruit is harvested. Only the deliberate addition of ascorbic acid is able to prevent the formation of ATA in wines prone to it.

### **Ascorbic acid prevents ATA**

In the context of ATA, ascorbic acid shows an effect comparable to that of the tannin in red wines. It is able to scavenge the oxygen radicals resulting from the oxidation of sulfites and, thereby, prevent the appearance of ATA to a large extent. However, it can definitely not remove any ATA already produced. Its action is merely preventive. Its prophylactic addition is recommended to all young white wines suspected to produce ATA.

The propensity of a given wine for generating ATA can be assessed by a simple screening test within a few days. This test works as an accelerated aging test: The wine is adjusted to 40 to 50 mg/L free SO<sub>2</sub>, clarified, poured into two flasks so that they are completely full, and sealed. One of the flasks is treated with 150 mg/L ascorbic acid, the other serves as a control. Both samples are stored for three to four days in an incubator set at 60 to 70° C. After removing and cooling the flasks, a sensory evaluation is run, comparing the control to the treated sample. If the treated sample smells significantly better or even displays ATA, the test is positive, and the best course of action is to add ascorbic acid to the wine.

As mentioned above, the reactions giving rise to ATA are triggered by the first addition of sulfur dioxide to the wine after fermentations are completed. Therefore, it is important to add ascorbic acid (150 to 200 mg/L) as soon as possible, be it at the moment of adding SO<sub>2</sub> or within a time window of one week after that. In individual cases, the addition of ascorbic acid at a later time can also prevent the formation of ATA or the sensory intensification of ATA already detectable.

There is no way to remove ATA with ascorbic acid or any other enological means. The molecules underlying this off-flavor are chemically inert and do not react with any fining agents. Thus, the fining procedures advertised by the winery supply industry for removing these molecules are useless. The outcome is an even stronger perception of ATA since all these treatments diminish beneficial aroma compounds which are able to mask it partially.

At this time, other than the use of ascorbic acid, there are no enological tools able to prevent effectively the appearance of ATA in wines made from affected fruit. However, wines treated in this way for that purpose will never become great wines exceeding the quality level of simple, fruity, and non-distinctive wines for easy consumption. Therefore, for wineries suffering from a chronic ATA problem, the addition of ascorbic acid can only be a transitory solution. Since ATA has its ultimate and definitive cause in the vineyard, the long-term solution has to be found in improved viticultural management.

Ascorbic acid reacts spontaneously with dissolved oxygen to yield its oxidized, inactive form. Simultaneously, sulfur dioxide diminishes. As a consequence, its use in wine requires some peculiar precautions:

- Prior to its addition, free SO<sub>2</sub> should be adjusted and stabilized at approximately 50 mg/L. Thereafter, the determination of sulfur dioxide using current iodine titration is no longer feasible because ascorbic acid interferes and causes falsely higher SO<sub>2</sub> readings. An amount of 100 mg/L of ascorbic acid resembles 37 mg/L SO<sub>2</sub>. As a consequence, SO<sub>2</sub> readings have to be corrected for ascorbic acid, or other methods than iodine titration must be used.
- During further storage and cellar operations, oxygen uptake must be in order to preserve both ascorbic acid and free sulfur dioxide in their active, reduced state. Thereof results the need of careful topping of the containers, filling them from the bottom, and avoiding barrel aging.
- Frequently, the formation of ATA goes along with a higher propensity for reduction flavor. This is not surprising because both of them trace their origin back to stress in the vineyard and nitrogen deficiency. Not uncommonly, ATA is only fully recognized by smell after the reduction flavor has been removed. Depending on the wine, ascorbic acid can decrease or, more often, increase the propensity for reduction flavor.
- Reduction odors are currently removed by copper ions, added as copper sulfate. On the other hand, ascorbic acid lowers copper solubility by approximately 30 %. Hence, wines to be bottled with ascorbic acid should not display more than 0.3 mg/L of copper (13) in order to remain stable. Precise copper measurements may be required to make sure that this concentration limit is not exceeded.

## **Summary**

ATA is induced by a hormonal stress in the vines prompting the berries to store elevated amounts of 3-indolacetic acid which is converted into the odor-active 2-aminoacetophenone after SO<sub>2</sub> is added to white wines post fermentation. The typical off-flavor can develop as a premature aroma defect that has no connection with oxygen uptake or oxidative degradation. However, the addition of ascorbic acid is the only useful enological means to prevent its appearance in wines made from affected fruit. Long-term solutions must be sought in the vineyard. The sensory identification and discrimination of ATA from other forms of aging, including oxidative spoilage or petrol flavor, is crucial in order to avoid inappropriate counter-measures.

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