

ATYPICAL AGING IN WINE:
HISTORY, DESCRIPTION AND ANALYSIS

A Thesis

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Christopher James Gerling

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ABSTRACT

Atypical aging (ATA) is a flavor defect in white wines, particularly but not limited to aromatic whites, where wine loses its varietal flavors very rapidly and atypical, waxy, furniture varnish, and dish rag like aromas appear when the wine is only 6 months to just over a year old. ATA is different from normal wine aging in both rate and flavor characteristics. This thesis is comprised of three papers: the first being a discussion of the history of research on the topic; next, a report on the process of describing ATA as a sensory phenomenon (taste panel results); the third paper describes research done to find ATA's causes and responsible compounds. Work done in Germany regarding ATA has focused primarily on ortho-aminoacetophenone (O-AP), a compound responsible for the 'foxy' note in American *labrusca* grapes. O-AP does not seem to be an important compound in New York wines with ATA, however. What is agreed upon is the oxidative nature of ATA and the need for antioxidants beyond SO₂, such as ascorbic acid, to protect at-risk wines. During the 2001-2003 growing seasons, trials were conducted in a Riesling vineyard in the Finger Lakes region of New York State to study the effects of irrigation and nitrogen fertilization on ATA development. Wines made from this fruit were then analyzed sensorially and chemically to determine any differences these treatments may have had on wine quality, particularly in relation to the atypical aging defect. We found that wines made from irrigated fruit tended to have both more varietal flavor character and less of the waxy, "dishrag" off-flavor than the wines made from the non-irrigated fruit. Nitrogen additions, or lack thereof, seemed to play a much smaller role in the sensory quality of the wines. Although attempts to chemically quantify this phenomenon have been inconclusive, results point toward effective management of water and nutrients in the vineyard being important steps in helping wines avoid ATA.

BIOGRAPHICAL SKETCH

Chris was born and raised in the Finger Lakes region. He grew up in Geneva, home of the New York State Agricultural Experiment Station (NYSAES), and worked in Barton Lab part time in high school. After high school he attended the College of Agriculture and Life Sciences at Cornell University, earning a BS in Communication in 1999. During summers between undergraduate years, he would return to the NYSAES and count mites on apple and grape leaves. After graduation he worked as a technician in the Enology and Viticulture labs in the Food Science and Horticultural Sciences departments, once again at the NYSAES. In 2002 he began splitting his years in half: fall was for winemaking and spring was for graduate work towards an MS. In early 2006, he left the NYSAES and joined Anthony Road Wine Company as assistant winemaker. He got married in June of 2007 and continues to be impressed every day by the extraordinary human being who he is so lucky to now have as his partner in all of this.

In loving memory of William Gerling Jr., Clarence Rea, John Witte, Kathy Hoch and Anne Acree. This work may not be worthy of you, but that doesn't mean you don't deserve a dedication.

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CHAPTER 1

A LITERATURE REVIEW

Aging is one of the most interesting, and perhaps least-understood, aspects of wine flavor development. A collector's second question after "which wine to buy?" is most likely "when to drink it?" Among the conventional wisdom most everyone carries about wine is the idea that wine can improve with age. The acceptance of this phenomenon means accepting a more fundamental notion, however, even if you do so unconsciously. To believe that wine improves with age, you must first agree it can change. Chemical and occasionally biological processes must be taking place in the bottle aging environment that may be essentially sterile and anaerobic. Of course, the word that throws all of this into even more disorder is the word "some." Sometimes wines improve as they age. Sometimes they don't. Some wines improve with age. Some don't. Every wine is different, from the variety and maturity of grapes used to the filtration (or lack thereof) method and closure applied to the bottle. The only universal truth of wine age is that improvement is temporary. Whether the process occurs over months or decades, time will eventually take its toll on every wine.

Red wines are most often associated with aging benefits, and there are a few reasons this idea is known to make sense. Reds undergo polymerizations of tannins and can have slight deacidification through chemical reactions such as crystallization and binding of acids with peptides and tannins. These changes can bring about a softer, mellower character that may be more appealing. White wines contain volatile terpenes, terpene alcohols, other esters derived from the fruit and fermentation that are produced in quantities too great for equilibrium to support (Jackson 2000). As these compounds become oxidized or otherwise disappear, the fresh, fruity fermentation character of the wine is lost. While the new flavors and aromas that form may be viewed as quite attractive to some, for the majority of people and the majority of white

wines, aging is viewed as a primarily harmful process. All wines, red and white, improve with aging of one to 2 years, some white wines such as Riesling can improve with 10 and more years of aging.

The idea that some wines age positively (for at least a certain amount of time) while others may not is accepted in the wine world. Not understood is why wines from the same cultivar and region can show drastically different aging trajectories. Why does a Riesling or Chardonnay from one vineyard have positive attributes 3-5 years down the road when a neighbor's is all but undrinkable within the first year? The wines may be somewhat different when going into the bottle, but they are not so different as they become in a few short months. Riesling is recognized as a white wine with better aging potential than most other white varieties (Simpson 1983). However, while some Rieslings go on to develop the unique and often sought after "bottle aged" character, others become very unattractive within a relatively short time after bottling. This phenomenon of rapid loss of varietal character accompanied by the increased appearance in old or dirty, off flavors is referred to as atypical aging (ATA).

Atypical aging (ATA) is a fault seen in white wines, especially aromatic whites. ATA was first identified in Germany in the late 1980s. Christoph, et al. traced the identification of the problem to the Franconia region in 1988. Atypical aging (ATA), in our definition, is a sensory problem where wine smells and tastes "old," even though it may have only a few months of bottle age. This character is distinct from mere oxidation. While some wines produce the aforementioned pleasant characteristic, wines afflicted with ATA have lost varietal character and developed unpleasant off-aromas and flavors that may be reminiscent of dish rag, furniture polish, floor wax, and even locust (acacia) blossom (Christoph et al. 2000). In Germany, the problem also describes vinifera wines taking on an American native

(*labrusca*) ‘foxy’ character (Rapp et al. 1993). A similar development has been noticed in some US Chardonnays; the wines tasted like they were blended with a *labrusca* wine (Henick-Kling personal communication).

Atypical aging (ATA) refers to a wine defect where wines with a few months of bottle age have lost most or all perceivable varietal character and gained descriptors like soapy, wet, foxy, acacia flower, Naphthalene, dirty underwear and others (Rapp 1998). These aromas will not have been perceptible before or at bottling. The problem was first recognized in Germany in 1988 and was eventually described as Untypische Alterungsnote, or UTA (Christoph et al. 1995). The compound responsible was assumed to be ortho-aminoacetophenone, or O-AP (Rapp et al. 1993). This compound is also responsible for the “foxy” character found in *labrusca* grapes native to the USA (Acree et al. 1990). In Germany, O-AP was traced back to indole acetic acid (IAA), a vine hormone whose production increases in times of vine stress (Rapp et al. 1993). IAA is then co-oxidized in the presence of sulfites (SO₂ added at bottling) to produce O-AP (Christoph et al. 2000). O-AP may also be created by yeast metabolism during fermentation (Ciolfi et al. 1995, Dollman et al. 1996).

In the Finger Lakes region of New York, wines described as being ATA do not seem to have the ‘foxy’ character and are more often described as candle wax, dirty dish cloth, and/ or furniture varnish-like (See Chapter 3). Acree et al. added O-AP to Finger lakes wines and found no correlation between the compound and what we recognized as the ATA flavor defect (Kittel 2002). This is not too surprising given the different aromatic “symptoms” we find in the wines.

Many studies have looked at wine and wine flavors as related to aging. They have taken a variety of approaches reflecting the technology and knowledge of the time. Focus has been placed on both the loss of varietal aromas and flavors and the rise of unpleasant or off-flavors. Atypical aging may be a combination of these two

forces at work simultaneously. This article will discuss papers that have examined atypical aging and aspects of vineyard and winery treatments as they relate to flavor and aroma effects as seen in the bottle.

The compounds responsible for wine aroma come from precursors and organisms found in three primary sources: present in the grapes, introduced during processing and fermentation, and formed during aging (Rapp and Mandery 1986). When examining the primary source- the chemical make-up of the fruit before processing- the logical place to look is of course the vineyard conditions and viticultural treatments to which the grapes have been exposed. While the conclusion that grapes are products of their vineyards is a somewhat obvious one, work has been done to suggest that the vineyard may play a large role in all three of the wine aroma areas, especially wine aging. It may be the case, in fact, that the course a wine's flavors and aromas will travel is determined before it reaches the winery door.

Grapes, juice, and wine can all be affected by a wide array of environmental conditions. In the vineyard, soil type, vine health, weather, native microorganisms all play a role in determining the make-up of the fruit. What training system is used, the presence or absence of cover crops and the disease pressure that may be created by a combination of these earlier factors will also contribute (Reynolds and Wardle 1989). The application of fertilizers, herbicides, fungicides and pesticides will further affect the fruit. By the time the grapes reach the winery, they will have initial concentrations of microorganisms, flavor compounds and perhaps even chemical residues that will begin to shape what kind of wine is created.

Water

In the case of wine aging and atypical aging in particular, vineyard conditions may play a large role. One primary consideration when growing any plant is the

amount of water the plant receives, especially during the growing season. It is important to remember that water availability relates to timing versus need. It is not simply the total amount of water a vineyard receives throughout a season that's important, but instead the timing of irrigation or rainfall to coincide with the periods of greatest uptake that matters most. A vineyard may appear to have adequate water supply, therefore, but in fact suffer from drought stress (Lakso et al. 2002, Schultz 1995). Hühn et al. (2000) noted that "environmental stress can induce the formation of quality reducing substances in the wine." Water stress can also apparently affect the vine's ability to transport other nutrients. Without adequate water, additions of nitrogen will not be absorbed and used (Schultz et al. 2002). A strong connection between water availability and the appearance of ATA off-flavors is also suggested in later chapters of this thesis.

Nitrogen

Nitrogen content in grapes grown in NYS vineyards Finger Lakes vineyards tend to be fairly low, on average (Cheng et al. 2002, Edinger et. al. 1994 a and b, Henick-Kling 1996, Shively 2002) The amount of nitrogen in juice may not correlate with production of AAP (Schultz et al. 2002), but it does seem to correlate to ATA, with lower amounts of fermentable nitrogen leading to more (Löhnertz et al. 2002), (Rauhut et al. 2000). Low nitrogen levels can also cause higher levels of sulphur off-aromas (Rauhut et al, 2000) and glutathione which may lead to "aging defects" (DuBourdieu and Lavigne, 2002). Hydrogen disulfide, the source of an off-odor is also often seen simultaneously with ATA (Rauhut and Kürbel 2002). The answer to low nitrogen concentration in the must may seem easily fixable with winery additions of diammonium phosphate (DAP), Fermaid-K and the like. However, work has shown that the deficiency must be made up in the vineyard to be effective (Rauhut et

al, 2000, Sponholz 2002). Experience in NY confirms that nitrogen additions to the grape must can not avert the development of ATA. Increasing foliar additions of nitrogen, especially late in the season also seems like an effective way to increase assimilable nitrogen and reduce ATA (Hühn et al. 2002), Schultz et al. 2002). Other work has found that low nitrogen levels lead to lower glutathione amounts. The addition of glutathione tends to reduce “aging defects” (Dubourdieu and Lavigne-Cruege 2002). The relatively greater amount of fermentable nitrogen in red varieties is also a potential reason for lower incidence of ATA (Sponholz 2002), although the greater antioxidant potential in reds is also a potential explanation.

TDN & Heat

One compound that connects vineyard conditions and wine aging is 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN). TDN, a carbon 13 hydrocarbon formed by hydrolytic degradation of nonvolatile precursors that is described as “kerosene” or “petrol-like” (Winterhalter 1991), is an important part of the bottle-aged character of Riesling from warm, sunny climates (Simpson 1977). TDN is seen in higher concentrations with both increased vineyard heat accumulation (Marais et al. 1992, Sponholz and Hühn 1996) and increased storage temperatures of finished wines (Marais et al. 1992). Here we see vineyard conditions having both an initial and long-term chemical impact on wines. Since ATA is also thought to have vineyard origins and then after –bottling expression, TDN makes for an interesting substance to study in this context. The TDN precursors are thought to develop in fruit along with sugar accumulation (Winterhalter, 1991). TDN is therefore associated with riper grapes, but can also be associated with lower quality (Sponholz & Hühn 1996). Sponholz also noticed that the German classification system, based on sugar accumulation, should also see associated increases in TDN. He found this to be true until the beerenauslese

and trockenbeerenauslese levels, perhaps because *Botrytis cinerea* might be able to scavenge some of the TDN precursors or the botrytis derived flavor overpower the TDN flavor. Finally, it was noticed that while New York Rieslings had lower TDN concentrations than their German counterparts, they had more perceived TDN flavor (Sponholz and Hühn 1996). This finding may suggest that there are other as yet unknown factors contributing to aging potential and sensory character in wines.

Harvest timing is a factor that may play a role in ATA. More than one researcher has correlated early harvest with ATA occurrence (Schwab et al. 1999, Rapp and Versini 2002, Schultz et al. 2002). Early harvest will almost certainly mean lower pH fruit, as well, and pH 3 has been shown to be a more conducive environment for the chemical generation of TDN and linalool oxide than pH 4 (Ferreira et al. 2002). Early harvest also allows less time for flavor and flavor precursor accumulation, thus less flavor that can be lost in ATA. Terpene flavor accumulation is clearly linked to ripening (Girard et al. 2002) Later harvests will have a risk of more TDN through heat accumulation, however (Marais et al. 1992, Sponholz and Hühn 1996).

How the fruit is processed and vinified will also have a large impact on the compounds and organisms present in the wine. Grapes can be crushed and pressed in a variety of ways to maximize or minimize inclusion of compounds from skins, flesh and seeds. Enzymes may be added to further remove or extract certain compounds. It is important to remember that, assuming no additions of any external flavoring or concentrate, the winemaker must work with the initial compounds present in the fruit. There are still ways to modify various flavors with the choice of enzymes and yeast and bacteria cultures, however.

A winemaker's decisions can have a profound impact on the flavors present or absent in a wine. Chaptalization and nutrient additions such as diammonium phosphate (DAP) will contribute to the final alcohol and help yeast metabolism. The

choice of yeast strain can have a large bearing on many aspects of the wine, not least of which is flavor (Egli et al. 1998a, Henick-Kling 1998b). A winemaker can even choose not to inoculate with a specific yeast strain and allow the microbes present to carry out (spontaneous) fermentation. This decision will almost certainly have an impact on the flavor as well. As alcoholic fermentation ends, the winemaker can then decide whether or not to use bacteria to carry out malolactic fermentation, whether to use stainless steel tanks or oak barrels, whether to use fining agents and in what concentration, when and how to filter, etc. All of these decisions, as well as the pH, temperature and free SO₂ present in the wine, will impact the compounds present or absent in the wine.

SO₂

Another issue related to ATA and aging process in general is potassium metabisulfite (SO₂). Christoph et al. (2002) saw the addition of SO₂ at bottling as the potential point for IAA to be co-oxidized and form O-AP. The formation of O-AP is most likely after the SO₂ addition as opposed to during it, however (Hoenicke et al. 2002). It was found that free SO₂ quantities present and stable above 25 mg/ L prevent ATA (Gafner 2002). Adding ascorbic acid to wines with similar SO₂ also reduced O-AP production by 20% (Versini and Lunelli 2002). Adding 150 mg/L ascorbic is a method of preventing the oxidation of IAA and forming ATA (Christoph et al. 2000). Ascorbic additions may also limit methional, another compound that may be related to ATA (Rauhut and Kürbel 2002). While O-AP may not play a large role in ATA in NY, ascorbic acid additions still are recommended, and the model of some rapid oxidative process is probably similar. In fact, additions of ascorbic acid have been able to delay onset of ATA for 2 and more years. Oxidation can also potentially explain why ATA is seen almost exclusively in white wines as opposed to reds.

Wines with higher superoxide radical scavenger activity are less prone to UTA (Hoenicke et al. 2002). Red wines have higher contents of anthocyanins, and the antioxidant potential in these compounds may prevent ATA (Rapp and Versini 2002).

Finally, a wine will be bottled. A closure will be chosen, be it natural cork, synthetic cork, pilfer-proof screw cap or something else. At this point the winery has little to no control over what changes will take place in the wine. What is known for sure is that changes do occur. Wines will change, for better or for worse, and it is exceedingly difficult to predict how quickly and drastically these changes will happen. It would be useful indeed to know which of the decisions made in the vineyard and winery most affect what takes place when the cork goes in and control is effectively lost.

CHAPTER 2

DEFINING ATYPICAL AGING

Introduction

The New York wine industry is worth an estimated \$6 Billion to the state economy, according to the New York Wine & Grape Foundation. Riesling has proven to be the vinifera variety best suited to the region's climate and soils and numerous publications now describe Riesling as the area's "signature" grape. A "typical" varietal Riesling wine could be described as having a wide array of flavor characteristics. Depending on climate and soil, volatile terpenes and esters contribute to distinctive aromas that may be described as any citrus fruit, citrus peel, apple, mineral, flint, and others. Warmer climates can bring about a diesel, petrol or kerosene character that is associated with tri-methyl, di-hydronaphthalene (TDN) (Winterhalter 1991). Older Rieslings are also appreciated for their unique attributes, which tend to contain fewer of the volatile terpenes and esters and more TDN and vitispiranes (Simpson 1979). TDN may also be affected by storage time and temperature (Marais 1979). Wines as many as (10-15) years old can still exhibit pleasing flavors of honey, petrol and others that have replaced the fruity esters initially present (Simpson 1978, 1979a). Atypical aging (ATA), in our definition, is a sensory problem where wine smells and tastes "old," even though it may have only a few months of bottle age. This character is distinct from mere oxidation.

Flavor is a singular property of wine. Most food products (or any type of products for that matter), when it comes to taste and smell, are only evocative of themselves. An orange smells and tastes like: an orange, quite obviously. The same goes for cherries and chocolate and coffee and mint. These items would be considered suspicious if they began to smell or taste like each other. Of course coffee can have hazelnut flavor added and chocolate is made to hint of mint and with lots of vanilla,

but these are conscious choices made by people. Wine can smell and/ or taste like any of these flavors without any special ingredients or additives. The field of flavor chemistry has begun to unravel the compounds that cause things to smell and taste certain ways. We can now identify compounds that wine has in common with the foods and other products it resembles, but the fact that wine can contain this wide variety of flavorants is no less impressive. Gewürztraminer wines have long been thought to have a character that resembles the lychee fruit. Now we see that the two have important compounds, especially cis-rose oxide in common (Ong & Acree, 1999).

The downside to a wine's amazing capacity to evoke the aromas and flavors of fruits, vegetables, spices, and other foods is that this ability can reach beyond positives and contribute to unpleasant characteristics. These "off-flavors" can range from the simply unappealing ('green pepper') to fairly disgusting ('dirty underwear'). Off-flavors can develop from the metabolism of microorganisms allowed to thrive in a juice or wine, from chemical reactions involving existing precursors, or from accidental contamination from contact with flavor tainted wine treatment materials or tainted containers. Both of these spoilage sources occur in the presence of favorable environmental conditions. The temperature, pH, oxygen level and many other factors will dictate which organisms can survive and which reactions are favored. Decisions made in the cellar can help influence the environment created in the vineyard, where initial levels of constituent compounds are created.

Wine is a difficult entity to study because of its complexity. While many things are now understood about the chemical make-up including important odorants, spoilage organisms and more, it is still not fully understood what makes a Riesling a Riesling. No laboratory can synthesize what the vineyard and the fermentation naturally provide. It stands to reason that wine aging is such a challenging

phenomenon given that it is not exactly understood what is present to begin with. Many compounds can be measured, however, and measuring the change over time is an excellent place to start. Equally important is the ability to track the sensory changes since these are perhaps the most important aspect of aging. Eventually the responsible compounds, or more likely groups of compounds, that relate to aging (and flavor in general) will reveal themselves.

Researchers attempting to isolate flavor compounds can approach the problem from more than one way. In a laboratory, one complete wine can be analyzed with sensory and chemical techniques and perhaps find the compound responsible for the smell or taste. Or, selected wine components can be combined in various mixtures in natural wine or complete synthetic mixtures in order to understand how individual flavor compounds can affect the flavor mixture. Conversely, vineyard or winery trials can vary one aspect of production while making many wines in the hope of causing measurable sensory differences. These differences may then hopefully be seen through laboratory analysis.

Atypical aging (ATA) is a fault seen in white wines. ATA was first identified in Germany in the late 1980s. Christoph et al. (1995) traced the identification of the problem to the Franconia region in 1988. Atypical aging (ATA), in our definition, is a sensory problem where wine smells and tastes "old," even though it may have only a few months of bottle age. Wines afflicted with ATA have lost varietal character and developed unpleasant, atypical off-aromas and flavors that may be reminiscent of dish-rag, furniture polish, floor wax and even locust (acacia) blossom (Christoph et al. 2000). In Germany, the problem also describes vinifera wines taking on an American native (*labrusca*) 'foxy' character (Rapp et al. 1993).

ATA is an affliction that has proved difficult to characterize both chemically and sensorially. One often gets the impression that different people have different

ideas about what ATA is, or the problem has different expressions with time and with different flavor backgrounds. Obviously, different smells and tastes refer to the presence or absence of different compounds or at least different concentrations, so having a single working sensory definition of ATA aids researchers in attempting to find a chemical signature. Once specific compounds are identified, pathways and preventative measures can be found.

In Germany, such a process yielded ortho-aminoacetophenone (O-AP, 2-AAP) as a culprit (Rapp et al. 1993). O-AP has been shown to be one of the responsible compounds for the native ('foxy') character of American *labruscana* cultivars (Acree et al. 1990). The pathway was identified as the vine hormone indole-3-acetic acid's (IAA's) cooxidation in the presence of sulfite (SO₂) (Christoph et al. 2000). IAA may be present in greater amounts during times of vine stress and both IAA and O-AP can be produced or increased by specific yeast strain selection in model wines (Ciolfi et al. 1995; Dollman et al. 1996).

This proposed solution is a convenient one because it answers lots of questions about ATA and points toward somewhat specific solutions for prevention. The first problem is the anecdotal relationship between ATA and vineyard water stress. This stress might induce production of IAA and begin the ATA process. Furthermore, yeast strain selection and sulfite additions vary from winery to winery, so these factors could explain why ATA is seen in places it is not expected or not seen when it is expected. Finally, the activation by sulfite additions after bottling would explain the slight delay in the onset of the off-flavors, as ATA symptoms are usually not present at the time of bottling, although large amounts of fermentation esters still present may be masking these symptoms.

The problems with the IAA/ O-AP solution are twofold. First is the issue of concentrations. To make this theory work, and work all the time, one would expect

straightforward correlations between the amounts of all of the implicated substances and the occurrence of ATA. This does not seem to be the case, especially with IAA, where the amount in must or wine does not correlate to ATA (Hoenicke et al. 2002). Also, while nitrogen content in grape must have been found to correlate to ATA, they have not been found to correlate with IAA. And additions of yeast available nitrogen to deficient musts does not prevent ATA. Furthermore, O-AP is found in all wines, yet only certain wines in certain situations (besides *labrusca*) ever start to smell like it (Rapp and Versini 2002).

The second, and far more vexing, problem here in the Finger Lakes region of New York State is the problem of O-AP itself. Trials were made to spike normal Rieslings with O-AP to try to simulate ATA, and the aromas of the spiked wines did not correspond with our definition of ATA. Furthermore, an analysis of the O-AP levels in wines designated ATA did not seem to contain higher concentrations of O-AP than control wines (Kittel 2002). These findings are vexing to a point, but ‘foxy’ has never played a strong role in the definition of ATA. There exists the occasional wine with “old *labrusca*” character, but we see many, many more who have simply lost varietal character and gained dirty, waxy aromas after less than a year in the bottle.

Reluctantly discarding the ‘foxy’ character, we set out to develop a sensory definition of ATA and perhaps yield the chemical changes responsible for the off-aromas that are being seen. One danger of this definition is that, without the ‘foxy’ note, distinguishing between ATA and standard oxidation becomes more difficult. All wines are susceptible to the effects of time, and white wines in particular go through a process not totally unlike ATA where they lose their varietal character and begin to take on new “bottle-age bouquet” (Simpson 1979; Simpson 1983). Our major departure from ‘typical’ aging is the fact that while aged Riesling can have attractive

notes (honey, petrol, etc.), ATA wines become more reminiscent of ‘dirty dishrag,’ ‘floor wax,’ and even ‘dirty underwear’ (Rapp 1998; Christoph et al. 2000).

The other factor we used to differentiate ATA from standard aging is time. In an ideal situation, the aforementioned effects should take place over years as opposed to months. The gradual replacement of young, fruity and floral flavors would be replaced gradually by various oxidative products. We assumed that any wine that was a year or even two years old but had essentially no varietal aromas left was aging atypically. While the actual “lifespan” of a Riesling varies with region and vintage year, it is widely accepted that Riesling have a unique ability to age over many years and do not suddenly plummet after a one year or two of bottle age.

Materials and Methods

During the 2001-2003 growing seasons, trials were conducted in a Riesling vineyard in the Finger Lakes region to study the effects of irrigation and nitrogen additions. Wines made from this fruit were then analyzed sensorially and to determine any differences these treatments may have had on wine quality, particularly in relation to the atypical aging defect. Trained wine tasters were given each of the 12 wines twice in a random order and asked to rate them according to seven characteristics. Three of the characteristics were general wine criteria: varietal character, body/mouthfeel, and vegetative. The other four- dishcloth, linden/ waxy, furniture polish and bitterness-tended to be more specific to ATA. Panelists were asked to rate the intensity of each of these characteristics, the reasoning being that a “good” wine has strong varietal character and no dishcloth flavor, while an ATA wine will be the opposite. This rating system allowed us to measure the progression of the wines over time as aromas and flavors evolved.

One problem was the locust/ acacia blossom character that has been attached to the list of ATA descriptors (Christoph et al. 2000). It is a helpful criterion for those who are familiar with it, but it is not as well-known or evocative as ‘dishcloth’ or ‘floorwax.’ We brought blossoms from trees outside the laboratory and dried them in glass jars for panelists to sniff, but we rarely got significant results with the descriptor and later added ‘waxy’ alongside.

Once the first tastings had taken place and the data were available and analyzed statistically, we chose wines that had performed well and not well to compare with sensory and chemical techniques. Two wines that appeared to work particularly well were treatments #1 and #2 from the trial. These were simply the irrigated (1) and non-irrigated (2) controls (no nitrogen additions). What made these wines attractive for further investigation was the fact that they were very similar; they came from the same vineyard and were processed in the same way. Only irrigation separated their treatment, but they performed very differently in the tasting. While the irrigated treatment was rated among the best (the most varietal character mouthfeel and least of the ATA flavors), the non-irrigated treatment was rated among the worst.

After applying our sensory definition to these wines, we tried to analyze them for some chemical differences that might explain the aromas and flavors the panelists were experiencing. Juice samples from each treatment were thawed and analyzed for terpenes using the Brock University version of the method developed by Dimitriadis and Williams (Dimitriadis and Williams 1984). Unfortunately, no significant differences were found. On the one hand, this result could be surprising. On the other hand, keeping in mind that these wines may not show differences even at bottling, it may not be so surprising that the juices don’t look too chemically different. The question is whether there are precursors that might be different at the initial stage even if the main chemical change takes place after bottling.

One challenge of studying wine aging is the fact that wine is constantly changing chemically and sensorially. During fermentation, the aromas and flavors are changing by the hour if not the minute. In tanks and barrels post-fermentation, noticeable differences are now on the order of days and weeks. Once the wine has been bottled the rate of change slows, but is far from stopping. To keep a wine in relative stasis for long enough to study it, freon extracts were made. These snapshots allowed some time to attempt gas chromatography/ olfactometry (GC/O). The GC/O separates the various compounds by molecular weight and allows a researcher to sniff them individually over a 20-30 minute period. The sniffs can then be matched with the compounds that are causing them. Once again, there were no significant differences between the ATA wines and the control.

Not finding differences in the first methods, gas chromatography/ mass spectrometry (GCMS) was employed to see what chemical differences could be measured between ATA and non-ATA wines. GCMS revealed some differences that were not necessarily groundbreaking but may point toward what ATA may actually be. Analyses found lower amounts of linalool and isoamyl acetate in the ATA wines while also seeing higher concentrations of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN). These chemical differences would point towards less varietal character (first two compounds) and more aged flavors (TDN) being perceived in a wine. Instead of a new compound appearing, the problem may simply be a hyper-acceleration of typical aging, where very similar processes take place in the presence of free radicals and/ or other strong oxidizers.

Conversely, there still may be one compound that has to this point evaded detection with current GCO and GCMS techniques. The compound(s) might not be extracted with our extraction methods and it might co-elude with other more abundant substances and thus be overlooked. Our trials showed that simply irrigation (avoiding

water stress) could make a big difference in ATA development in the wines. This single variable approach might seem to negate the previous paragraph. The fact of the matter was that none of the wines in the study aged particularly well, however. By the third tasting, most all of the wines had lost their varietal character. One could argue that they were all succumbing to ATA, and some cases were more acute than others. This is likely due to the limited understanding of best irrigation management for white grape varieties. Irrigation management for white wines is a critical area to be studied further. Such studies are currently underway in Australia, Germany, and Washington State.

Further work will have to magnify the small differences already detected and also search for new differences and indicator chemicals. First and foremost, the complete chemical signature of Riesling should be explored. Next, the natural aging process Riesling passes through should be understood. Knowing these two fundamental pieces should make ATA much easier to understand. We are confident that ATA will eventually give up all of its secrets.

CHAPTER 3

RESULTS

Materials and Methods: Vineyard Experiment: Treatments

A vineyard trial was conducted in the seasons of 2001, 2002, and 2003 in a Riesling block in a Finger Lakes vineyard on Seneca Lake in New York State. Random, replicated panels were given 1 of 6 possible treatments (Table 1). The trial varied irrigation and nitrogen additions in an attempt to see what differences could be brought out in fruit and wine flavors. Berry samples were taken periodically and measured for sugar content (soluble solids by refractometer) and titratable acidity (Zoecklein et al. 1995) as harvest approached. The fruit from all treatments was harvested at the same time each year.

Table 1 Treatments

Treatment 1 Irrigation, No N	Treatment 2 No Irrigation, No N
Treatment 3 Irrigation, 30 lbs. foliar N in 4 pre-veraison applications.	Treatment 4 No Irrigation, 30 lbs. foliar N in 4 pre-veraison applications.
Treatment 5 Irrigation, 30 lbs. soil N in pre-veraison application.	Treatment 6 No Irrigation, 30 lbs. soil N in pre-veraison application.

Materials and Methods: Preparation of Experimental Wines and Wine Analyses

This trial was conducted exclusively with *Vitis vinifera* cv. Riesling. All fruit was sourced from a single vineyard belonging to Prejean Winery on the West shore of Seneca Lake and was harvested by hand. Harvest dates were determined by a

combination of brix, TA and availability of harvest labor. Grapes were taken directly to Cornell University's experimental winemaking facility at Geneva, NY, where they were crushed the same day or put into a cold room (2 degrees C) overnight and crushed the next day. The grapes were de-stemmed at 60 RPM (Rossi e Cama, Italy) and then pressed at approximately 20 PSI in a small custom-made hydraulic basket press (2 press loads per lot). Each lot contained approximately 60 kg of crushed fruit and yielded an average of approximately 18 kg of juice after crushing, pressing, settling overnight and racking the following day.

In order to have sufficient wine from each treatment, the fruit from the three vineyard replicates from each treatment was combined and then split in half then crushed, pressed and the juice racked. Two fermentation replicates were made from each treatment for a total of 12 wines. The fermentations were carried out in 19 L glass carboys fitted with fermentation locks. Two juice samples were taken from the pressed juice of each lot and frozen for later analysis. 50 mg/L SO₂ was added after pressing. If necessary, the juices were chaptalized to achieve the same final alcohol content in the finished wines from all treatments (Table 2 and 3). Before inoculation, 1.0 g/Kg of diammonium phosphate (DAP) and 0.2 g/Kg of Fermaid-K were added. All musts were inoculated with yeast EC1118 (Lallemand Inc.) and fermentations were carried out in a constant temperature room at 16°C. Wines were fermented to dryness (less than 2 g/L residual glucose + fructose). After completion of alcoholic fermentation each wine was racked into an 11 L glass carboy, 80 mg/L SO₂ was added and the carboy was filled to the top and closed with a silicon bung. The wines were then placed in a room at 5°C for cold stabilization. After cold stabilization the free SO₂ was adjusted to 40 mg/L and the titratable acidity adjusted if necessary to keep it all wines as similar as possible while also trying to avoid manipulating the wines unnecessarily. Free SO₂ was tested again and if necessary adjusted.

Table 2 Harvest Data 2002

<i>Treatments</i>		<i>Brix</i>	<i>Yield</i>	<i>Berry Wt</i>	<i>Berry#</i>	<i>Cluster Wt</i>	<i>Cluster #</i>
<i>Irrigation</i>	<i>N</i>	<i>(%)</i>	<i>(kg/vine)</i>	<i>(g)</i>	<i>(#/cluster)</i>	<i>(g)</i>	<i>(#/vine)</i>
No	0	18.9	5.04	1.31	58.1	76.3	65.9
	Foliar N	18.5	5.42	1.36	56.5	77.0	70.1
	Soil N	18.4	5.78	1.33	56.5	74.9	76.5
Yes	0	21.7	5.57	1.82	42.8	77.9	72.1
	Foliar N	21.2	5.91	1.74	43.2	75.4	78.6
	Soil N	21.6	5.13	1.70	43.7	73.3	70.1
Significance (P)							
Irrigation		0.0001	ns	0.0001	0.0001	ns	ns
N		ns	ns	ns	ns	ns	ns

P VALUES INDICATE THE SIGNIFICANCE LEVEL. NS: NON-SIGNIFICANT.

Table 3 Juice Measurements

				Brix		TA	Total Phenolics	Ammonia	1° Amino Nitrogen	YANC*
Yr	Lot	Treatment	Rep		pH	(g/L)	OD ₂₈₀ - 4	mg/L	mg/L	
01	100	1	A	23.0	3.23	9.9	3.47	87.31	144.37	231.68
01	101	1	B	22.6	3.24	10.3	1.35	103.96	153.76	257.71
01	102	2	A	20.2	3.16	8.6	1.96	88.05	108.22	196.27
01	103	2	B	20.4	3.19	8.5	2.06	74.85	90.73	165.58
01	104	3	A	22.2	3.26	9.6	4.79	114.69	186.62	301.31
01	105	3	B	22.0	3.25	10	1.86	123.44	233.57	357.01
01	106	4	A	19.6	3.22	8.9	1.35	116.78	163.03	279.81
01	107	4	B	20.4	3.20	8.8	4.48	106.18	168.19	274.37
01	108	5	A	23.0	3.22	9.3	4.18	77.94	150.47	228.41
01	109	5	B	22.4	3.20	9.6	4.38	102.72	158.45	261.17
01	110	6	A	20.4	3.16	8.8	3.68	76.83	90.49	167.32
01	111	6	B	20.0	3.13	8.6	5.29	80.77	89.67	170.44

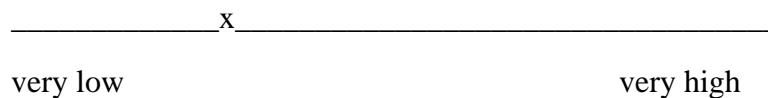
*Yeast assimilable nitrogen compounds = Ammonia + Primary Amino Nitrogen
 Ammonia and Primary Amino Nitrogen were determined using analysis kits from UNITECH
 SCIENTIFIC- Lakewood, CA

Sensory Evaluation

Three structured tastings were carried out for each vintage. One tasting happened within six months of bottling, the next occurred approximately one year from bottling, and the last tasting was performed between one and a half and two years post-bottling. Trained panelists were asked to rate the wines for perceived intensity of seven characteristics (Figure 1). The wines were served blind in random order, with each wine poured twice at each tasting. The panelists had a 10 cm line on which to mark the intensity of each flavor characteristic. The marks were then measured (in cm) and recorded for statistical analysis.

e.g. Mark a line according to intensity of perception:

Dish Cloth



Varietal fruit intensity, Vegetative, Linden blossom/ Black Locust/
Acacia, Furniture varnish/ Floor polish, Dish cloth, Body/ Mouthfeel, Bitterness

Figure 1 Tasting Characteristics & Sample Line

Results & Discussion

Keeping in mind that our definition of ATA is a loss of varietal character combined with an increase in off-flavors that range from “furniture polish” to “dishrag,” we monitored the tasters’ impressions over time. We found that the irrigated treatments tended to have significantly stronger varietal flavors and body,

and significantly less dishrag and furniture polish flavors in 2001 and 2002 (Christoph, Bauer-Christoph et al. 1998). Despite the possibility that perceived bitterness might be higher in the irrigated treatments (Schultz, Löhnertz et al. 2002), there seemed to be no strong correlation between these two factors, and in fact perceived bitterness tended to be lower in the irrigated treatments in the first two years with no significant differences in the third. We also noticed that in the first two years the treatment with irrigation but no nitrogen seemed to be rated as much lower in ATA flavors and higher in varietal character than the treatments with nitrogen but no irrigation. Furthermore, while nitrogen additions, especially foliar additions, resulted in higher the nitrogen content (ammonia and free amino nitrogen) in the must, this did not translate into preventing ATA flavors in wine, at least without irrigation. This phenomenon may be explained by the fact that, even in the presence of nutrients, vines can't transport without water (Schultz, Löhnertz et al. 2002). Throughout the trial, the Linden blossom/ acacia characteristic, another ATA descriptor sometimes used by other investigators, failed to show significant differences. Panelists were trained by smelling dried Linden blossoms, but seemed unable to detect a similar character in the wines.

2001

The 2001 wines showed some strong differences in the tasters' perceptions. When comparing the irrigated vs. non-irrigated treatments, the irrigated treatments were perceived to have stronger varietal flavors and more body/ mouthfeel (Table 4). They also had lower perceived intensity of dish cloth and furniture varnish (Table 5). Treatment 1, the treatment with just irrigation but no N, was the "highest" (high varietal character and mouthfeel, low dish cloth, low wax and bitterness) rated wine in many categories. By comparison, the wines made from treatments that saw

fertilization but not irrigation were rated less favorably. These trends held throughout the three tastings, although it should be noted that none of the wines “improved” with age (Figure 2). By the time of the third tasting-when the wines had now spent roughly 24 months in the bottle- all wines were receiving lower values for perceived varietal character and body/mouthfeel and higher values for the ATA characteristics and bitterness. While some statistically significant differences remained by the third tasting, they were now fewer and less extreme as the wines all succumbed to aging, typical or not.

Table 4 Tasting 1, 2001, Varietal Character

		Varietal Character	
		<i>2001</i>	
		Irrigation	No Irrigation
No N	5.15 A	2.88 D	
Foliar N	4.38 B	3.75 BC	
Soil N	4.15 B	3.09 BC	

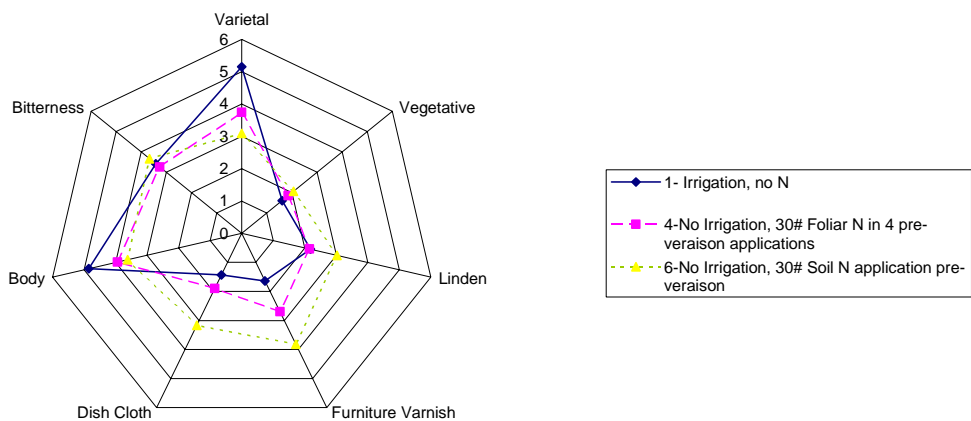
*Significant at .05
(May 16, 2002)*

Table 5 Tasting 1, 2001, Dish Cloth

	Irrigation	No Irrigation
No N	1.43 B	3.1 A
Foliar N	1.91 B	1.89 B
Soil N	2.06 B	3.16 A

*Significant at .05
(May 16, 2002)*

2001



(March 18, 2003)

Figure 2 Tasting 2, 2001, Comparison of Three Treatments

2002

The wines made in 2002 followed a pattern much like the wines from the 2001 season in terms of how the treatments were rated for ATA character (Tables 6 and 7). The wines made from irrigated treatments were again perceived to have more intense positive wine attributes and less of the negative, ATA, descriptors (Figures 3 and 4). The progression of the pattern over time differed from 2001, however. While in 2001 many significant differences appeared after the first tasting, in 2002 the first tasting showed less variation among treatments. The third tasting, conversely, seems to have kept the treatments even a little more distinct in the views of the tasters than 2001. In spite of the differences, all wines were rated as lower in varietal character and higher in dish cloth by the third tasting. Once again, as in 2001, the treatment with irrigation and no N was perceived as being much less ATA-affected than any treatment without irrigation, regardless of N application.

Table 6 Tasting 2, 2002, Varietal Character

		Varietal Character	
		2002	
		Irrigation	No Irrigation
No N		4.81 A	3.09 B
Foliar N		4.45 A	3.48 B
Soil N		4.29 A	3.21 B

*Significant at .05
(November 30, 2004)*

Table 7 Tasting 2, 2002, Varnish

Varnish
2002

	Irrigation	No Irrigation
No N	2.15 C	3.50 A
Foliar N	2.18 C	3.03 AB
Soil N	2.5 BC	3.16 AB

*Significant at .05
(November 30, 2004)*

2002 Tasting 2 Irr. vs. Non

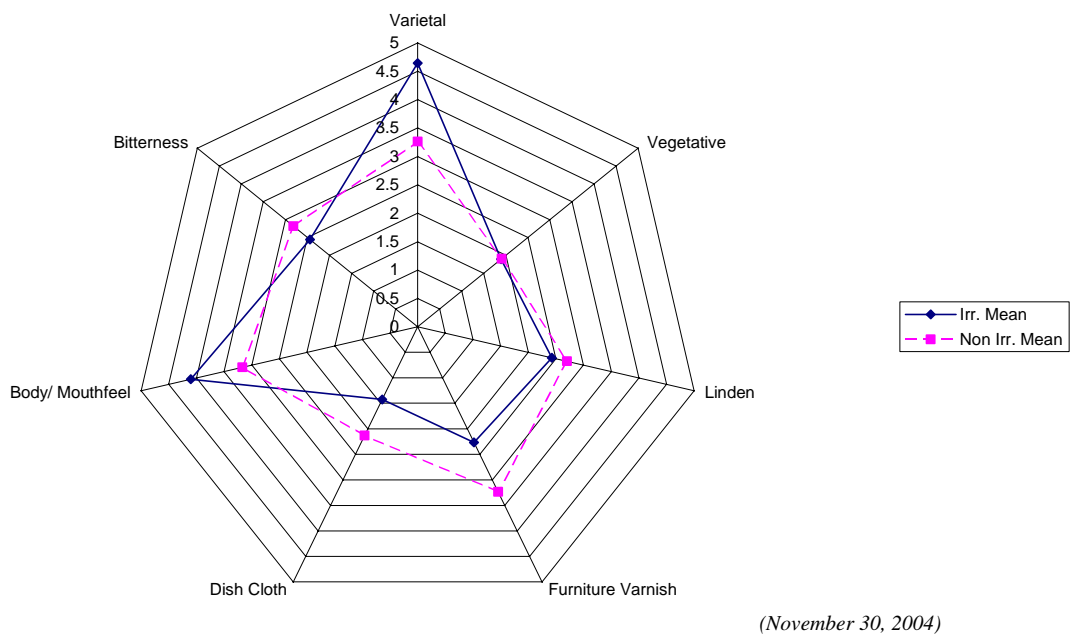


Figure 3 Tasting 2, 2002, Comparison of Irrigated Versus Non-Irrigated Treatments

2002 Tasting 2 N vs. No N

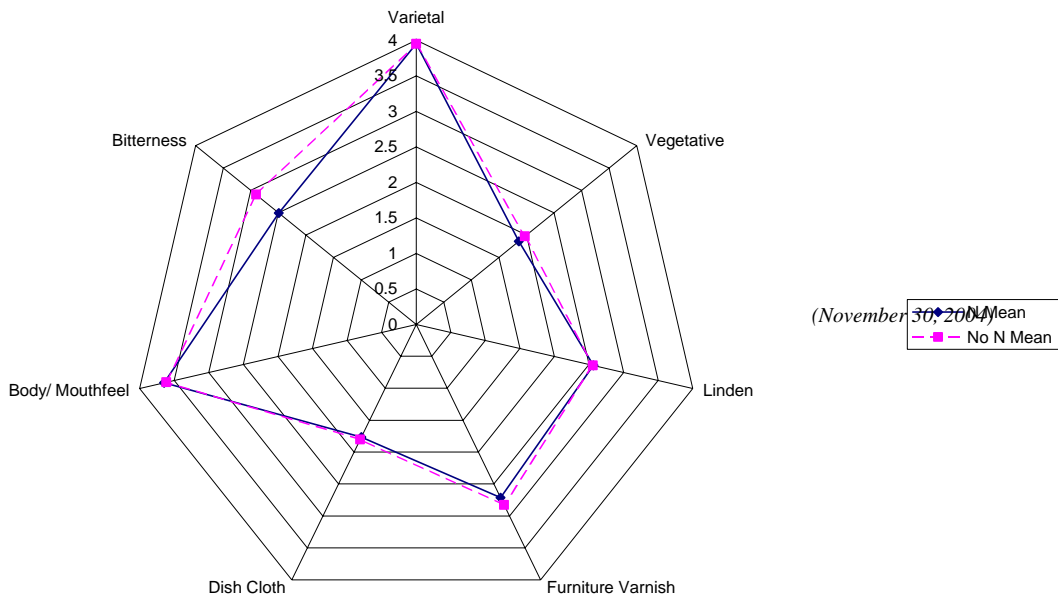


Figure 4 Tasting 2, 2002, Comparison of Nitrogen Versus No Nitrogen Treatments

2003

The third year provided a change from the treatment rankings of the first two years. While water (or lack thereof) had been the strongest predictor of how a wine might be rated for ATA character in 2001 and in 2002, N addition was more important in 2003 (Figures 5 and 6). Wines made from the treatments with nitrogen additions were rated as having more intense varietal flavors and more body/ mouthfeel, while having lower perceived amounts of dish cloth, wax and varnish (Table 8). Treatment #1, irrigation but no N, which often was described as having the strongest varietal flavors and lowest perceived off-flavors for 2001-2002, was rated near the bottom in 2003 (Figure 7). However, the treatments with both irrigation and N additions were still rated marginally better than those with N additions alone. Our idea about what could have brought about the role reversal in 2003 is discussed below.

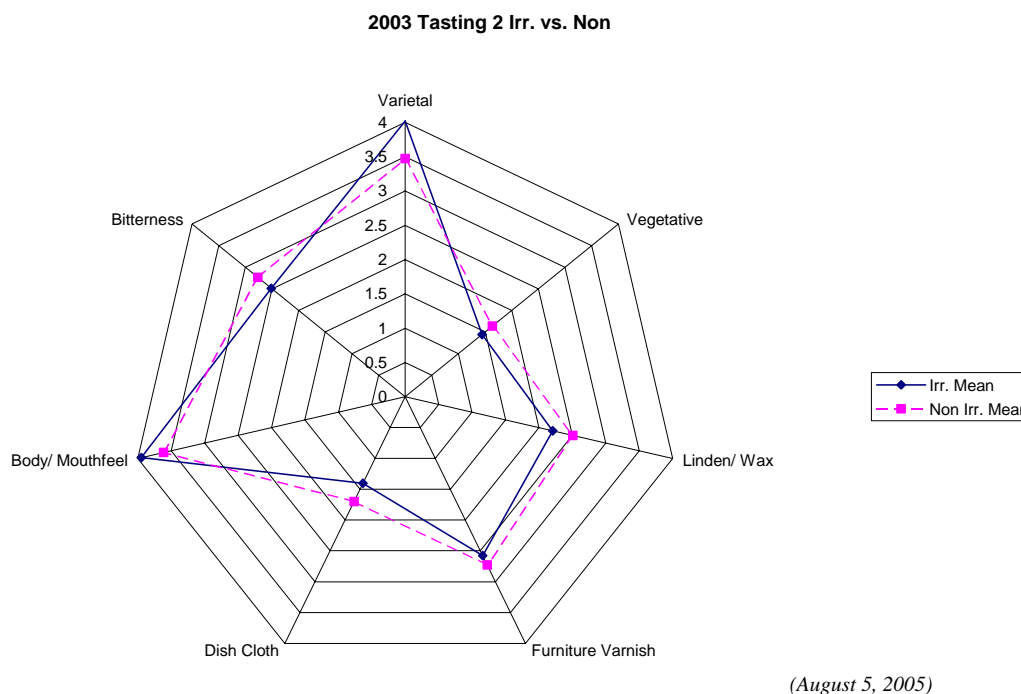
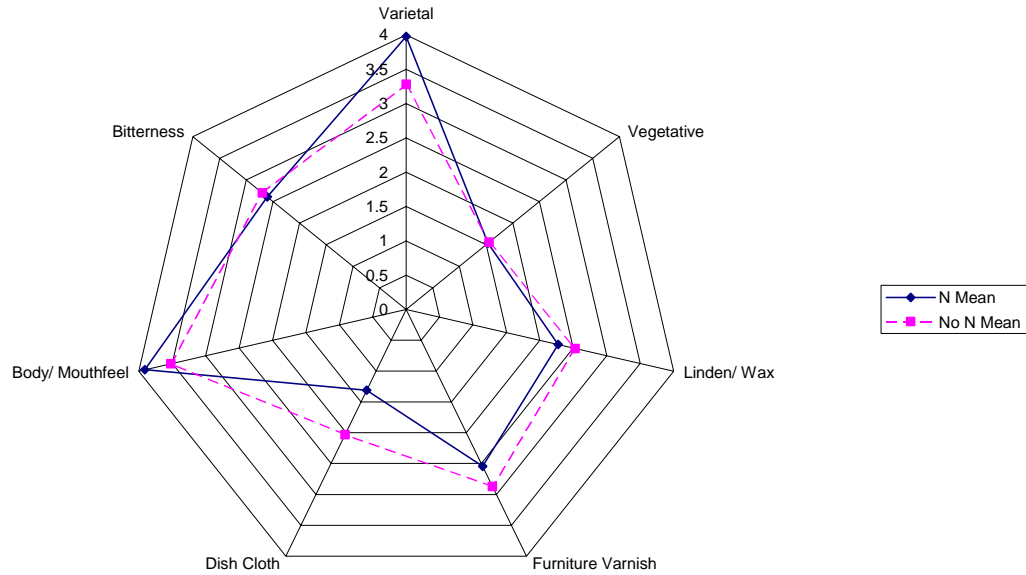


Figure 5 Tasting 2, 2003, Comparison of Irrigated Versus Non-Irrigated Treatments

2003 Tasting 2 N vs. No N



(August 5, 2005)

Figure 6 Tasting 2, 2003, Comparison of Nitrogen Versus No Nitrogen Treatments

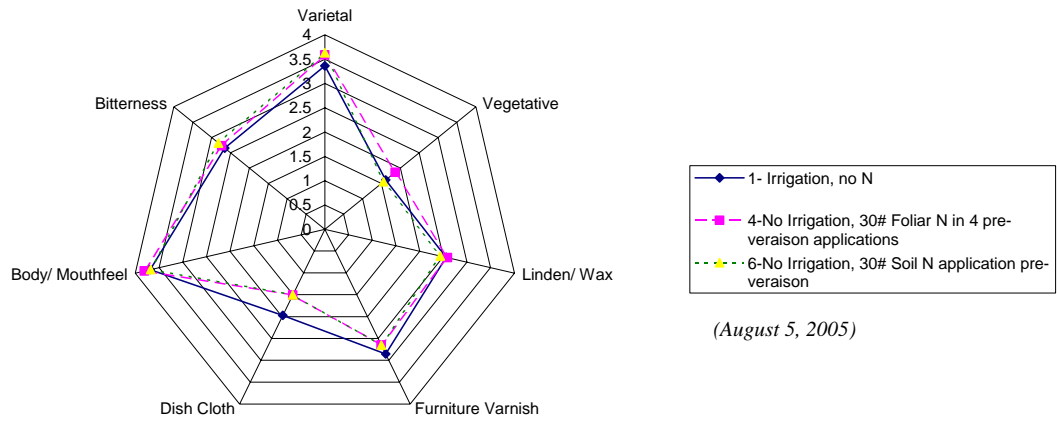
Table 8 Tasting 2, 2003, Dish Cloth

Dish Cloth 2003

	Irrigation	No Irrigation
No N	1.97 A	2.09 A
Foliar N	1.22 B	1.51 AB
Soil N	1.01 B	1.5 AB

Significant at .05
(August 5, 2005)

2003



(August 5, 2005)

Figure 7 Tasting 2, 2003, Comparison of Three Treatments

Weather Differences

When comparing the observed results with the vineyard conditions over the three growing seasons, our data show a very clear correlative relationship of drought stress to the appearance and intensity of ATA off-flavors in the dry years of 2001 and 2002. Table 4 shows how the combined irrigated treatments were rated as compared to the treatments that received no irrigation. The 2001 and 2002 results were practically identical for illustrative purposes, so only 2002 is shown and compared with 2003. Table 5 shows the mean performance of the treatments that received nitrogen compared with those that received none. In 2001 and 2002, the irrigated treatments received noticeably better ratings than the non-irrigated counterparts; all 6 treatments tracked much more closely when nitrogen is compared. In 2003, however, the irrigated treatments and the treatments with nitrogen added both led to comparably better ratings. One possible explanation for the difference in first two years from the third is weather. 2001 and 2002 were relatively dry years. Water availability was definitely a limiting factor for these two years. This was not the case in 2003. For all intents and purposes no irrigation took place for any treatment in 2003 since, in the words of one researcher, “the drip tubes were all under water.” In a wet year like 2003, with no apparent drought stress, the flavor impact on the wines might be more affected by the available nitrogen. There might also be effects to some degree from the conditions in the previous year. Such a carry over effect was noticed in the vines in vine size and in cold hardiness. This might also explain why the wines from irrigated treatments still marginally outperformed their non-irrigated counterparts in a year when water was not necessarily a variable. It is also important to remember that water availability can vary even in a year where there is “enough” natural rainfall (Lakso & Pool, 2002). A trial similar to this trial was conducted for the following three-year span using only the N differences and removing irrigation as a variable.

Chemical Analyses

With the sensory differences in hand, several chemical analyses were made to determine whether these perceptions could be linked to specific compounds. Ideally the presence or absence of some marker compound could be identified that might correspond to the sensory differences. In this way a pathway for ATA could be located and we might find vineyard or winery practices to counteract ATA formation. Gas chromatography - olfactory (GC-O) was employed to try to compare wines rated as different by the sensory panel and relate these to specific chemical differences. Unfortunately, the presence or absence of no single compound (that could be measured) seemed to relate to the sensory findings. Possible conclusions are that the chemical difference is either not measurable at this time or, more likely, there is a complex interaction of multiple elements and compounds.

Conclusion

In this study, wines made from fruit with six vineyard management treatments showed some significant sensory differences. In the first two, dryer growing seasons, we saw a clear link between lack of water and appearance of ATA off-flavors. The 2001 wines showed differences sooner, and the 2002 wines seemed to stay significant longer than 2001. In the wet year of 2003, when water was not a limiting factor, the flavor differences might have been principally due to different nitrogen availability. The root cause of the flavor difference and the appearance of ATA off-flavors remain, for the most part, unknown. Clearly drought stress during fruit ripening is a major factor. Additional work is necessary to further define the conditions under which ATA are caused. Studies by European researchers and our own experience have shown that early addition of ascorbic acid (at the end of alcoholic fermentation) can prevent the appearance of ATA off-flavors for 2 years and sometimes longer. Unfortunately,

many wines are still aging poorly in the bottle, and this premature collapse of varietal character can only be harmful to both the economics and enjoyment of these wines. It is probably safe to say that both wine producers and consumers are less concerned with the question of whether this is a new problem or a combination of old ones and more concerned with wines that smell and taste the way they should. As we press forward with further investigations, it's important to remember that good wine is always the ultimate goal.

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