The Odor and Aroma of Wine

Flavor (taste & smell) and Emotion

The chemical senses are the most primitive of the specialized sensory systems, with an evolutionary history of some 500 million years. It is fitting, then, that they deal with the most basic biological requirements: feeding, to preserve the organism, and reproduction, to preserve the species. While humans rely heavily on vision and hearing, our primary sensory legacy is taste and smell. We are unusual animals in this regard because of our recent ecological niches, aloft in trees and lifted up on two feet. Our sensory apparatus is clear of the taste- and odor-rich earth, mounted sufficiently high to offer a vantage that gives value to the straight lines demanded by vision. But chemical senses dominate the animal kingdom, and so should be expected to have pervasive, if subtle, effects on human evolution.

The sense of taste largely manages dietary selection, not only by its analysis of the quality and concentration of potential foods, but also through communication with the gut. Smell is used to identify predator and parent, and to find food, mate and home. Both chemical senses are intricately woven with two neural systems: those serving emotions and memories.

One rarely has a gustatory or olfactory experience without an accompanying emotional reaction. While we may use eyes and ears to survey our environment continuously and impassively, the chemical senses are engaged only occasionally, and always with passion. Odors and tastes carry emotional components of like or disgust, motivating the approach or withdrawal that determined which of our predecessors would survive to become our ancestors. We have inherited that hard-won and deeply ingrained knowledge. We call it body wisdom.

The chemical senses also generate extraordinarily acute and enduring memories. With taste, these have to do with the internal consequences of ingestion. Passionate preferences are created for those tastes that accompany nutrition. The Italian child with garlic on his pasta, the Japanese with soy beside her rice and the Mexican with pepper on his tortilla, each develops a preference for the taste identified with the accompanying carbohydrate load. From these preferences emerge the distinct cuisines that help characterize diverse human cultures.

The taste of Proust's madeleine transported him to a happy childhood, but not all gustatory memories are so kind. When a distinct and novel taste is followed even hours later by nausea, a powerful aversion is created and that taste is assiduously rejected thereafter. These learned aversions emerge from a single experience and may last a lifetime.

Odor perceptions are well known to evoke childhood memories, even in visually oriented humans. In lower animals, the memorial feats associated with smell are extraordinary. This might be expected from the anatomical structure of the olfactory system, which branches and reaches several brain areas thought to be involved in memory formation and maintenance.

Thus, smell and taste are the senses that have most shaped our evolutionary history. They guide our most primitive biological functions by evoking intense emotions of pleasure or revulsion that are stored for a lifetime.

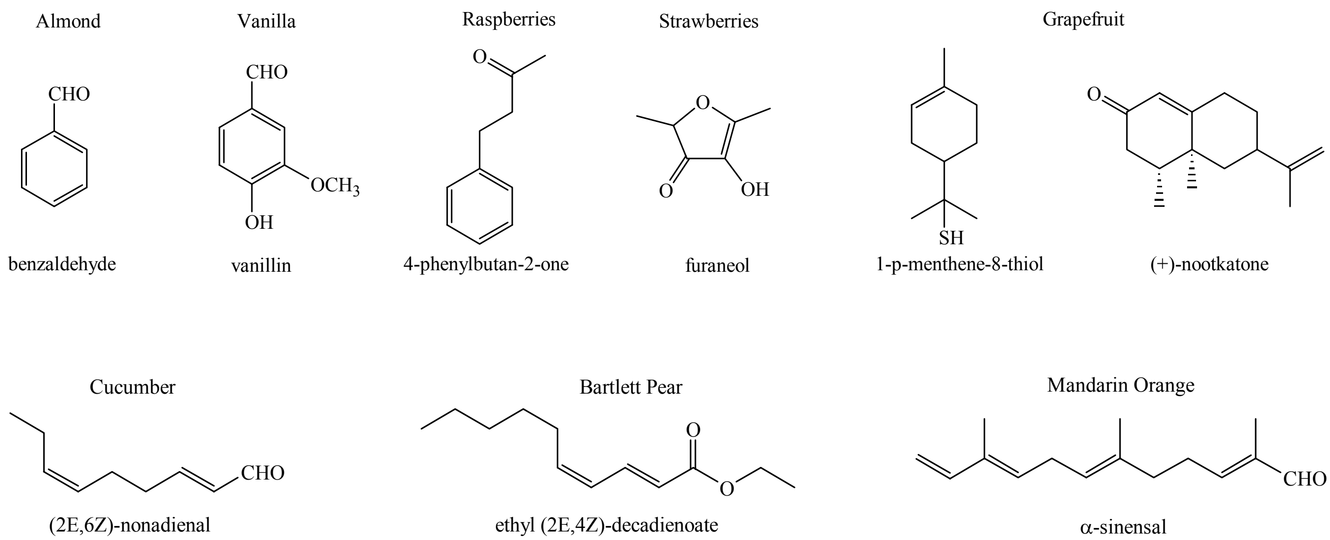
Flavor chemists are often preoccupied with the chemical characterization of flavor-active chemicals. Justifiably the study of humans and their responses to the chemicals that have been discovered are left to psychologists or sensory scientists.

Although the flavor reaction is simple, it represents a complex series of unknown biochemical events, and the visible consequence of these events is human behavior. Psychological processes such as awareness, emotion, memory, and cognition influence this behavior and complicate the task of observing and understanding a flavor reaction. Unfortunately, the precise nature of this stimulus-receptor interaction is not known, nor is the behavior that results from this interaction entirely predictable.

Chemical Compounds Responsible for Flavor

The majority of volatile compounds have no smell. An odor is usually elicited by a combination of volatile compounds each of which imparts its own smells. Differences in characteristics of certain aromas can be equated to the varying proportions of these volatiles. However, some substances contain trace amounts of a few volatile compounds that possess the characteristic essence of the odor. These are called character-impact compounds. The survey of character-impact compounds shown in Figure 1 is necessarily incomplete, but demonstrates the variety of chemical compound classes that elicit an aroma in the human nose.

Figure 1: Character Impact Compounds for some Foods

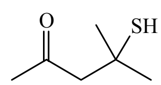


One must also realize that the chemicals of a single compound class can elicit many diverse flavors, especially as their concentrations vary.

Powerful Odorants

For some molecules, it has been estimated that as few as eight molecules are required to trigger one human olfactory neuron and that as few as 40 molecules can produce an identifiable sensation.

We can detect the smell of 1-p-menthene-8-thiol (grapefruit) at a concentration of 0.1 ppt (0.1 ng/L). This concentration corresponds to 0.1 μg in a metric ton of water. One of the major contributors to the aroma of Sauvignon blanc wines, 4-mercapto-4-methylpentan-2-one, can be detected at 0.8 ppt (0.8 ng/L).



4-mercapto-4-methylpentan-2-one

The odor threshold of a compound is the lowest concentration at which its smell can be detected. The **perception threshold** is the minimum detectable concentration for 50% of tasters while the **recognition threshold** is the minimum concentration for identification of the odor. The lower the odor threshold, the stronger the odorant will be.

The aroma of a compound is dependant on the partition coefficient for an odorant distributing between the aqueous solution and the vapor phase. For neutral compounds at dilute solute concentrations in pure water, this equilibrium partition constant is referred to as the Henry's constant (K_H). For real aqueous solutions (i.e. solutions that contain many other chemical species, such as grapefruit juice) it is usual to approximate the vapor phase – matrix solution (grapefruit juice) partition coefficient, K_{VW}, by the Henry's constant. Most thresholds are measured in water, where the nonpolar aroma compounds will be forced out into the vapor. In wine (13% ethanol) the odor compounds will be more soluble, less of the compound will be in the vapor and the threshold will be higher.

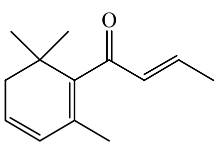
In a mixture of odorants we now need to assess which odorants are more important. This will depend on the threshold of an odorant and its concentration. A compound may have a high concentration but if its threshold is large (i.e. a high concentration of this compound is needed to smell it) it will not contribute significantly to the aroma. Conversely, a compound with a low threshold and large concentration will probably dominate the aroma.

The odor activity value (OAV) or as it is sometimes called the flavor activity is equal to the concentration of a component of the aroma divided by its detection threshold level.

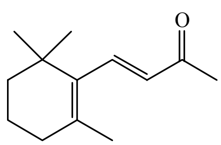
$$\text{OAV} = \frac{\text{Concentration}}{\text{Threshold}}$$

The more powerful odorants are very difficult to measure as they occur in very low concentrations, and as analytical techniques have improved so has our understanding of perfumes and bouquets. From the time of the Romans (and probably before) the aroma of the rose was valued for its fragrant perfume. Chemists have known for over 100 years that the main constituent of Rose oil is citronellol, but it wasn't until work in the 1960's & 70's that the trace constituents so essential to a rose fragrance were reported. Of the more than 275 constituents of Bulgarian rose oil, Ohloff calculated the relative odor contribution for the important aroma components.

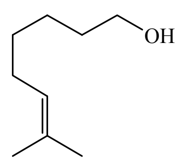
Rose Oil Component	% of Oil	Threshold in ppb	OAV's x 10^{-3}	Rel. % of OAV's
(-)-Citronellol	38	40	9500	4.3
C_{14} - C_{16} Paraffins	16	-	-	-
Geraniol	14	75	1860	0.8
Nerol	7	300	233	0.1
Phenethyl alcohol	2.8	750	37	0.016
Eugenol methyl ether	2.4	820	29	0.013
Eugenol	1.2	30	400	0.18
Farnesol	1.2	20	600	0.27
Linalool	1.4	6	2300	1
(-)-Rose oxide	0.46	0.5	9200	4.1
(-)-Carvone	0.41	50	82	0.036
Rose furan	0.16	200	8	0.003
β-Damascenone	0.14	0.002	156000	70
β-Ionone	0.03	0.007	42860	19.2



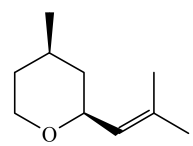
β-damascenone



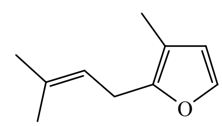
β-ionone



citronellol



rose oxide



rose furan

As you can see two components, β-damascenone and β-ionone with thresholds of 2 and 7 ppt, account for almost 90% of the aroma of Rose oil (using OAV's), while citronellol, the major constituent contributes 4.3%. β-Damascenone and β-ionone are C_{13}-norisoprenoids; citronellol, rose oxide, rose furan, carvone, linolool, nerol and geraniol are monoterpenes; farnesol is a sesquiterpene; and eugenol and eugenol methyl ether are phenolic guaiacyl derivatives (see Oak Barrel Aging).

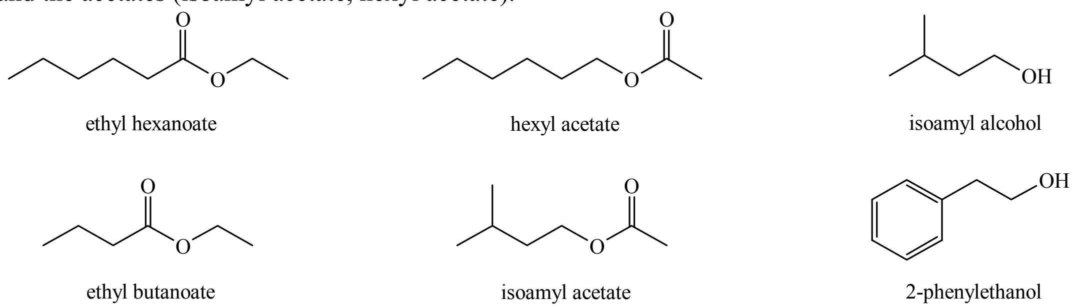
We will now look at a couple of wines; the first is an Okanagan Chardonnay, sampled from oak barrels before bottling, eight months after harvest.

Chardonnay Component	Threshold (μg/L)	Concentration (μg/L)	OAV's
β-Damascenone	0.002	3	1500
Ethyl hexanoate	1	600	600
Isoamyl acetate	2	800	400
Ethyl butanoate	1	250	250
Isoamyl alcohol	300	50000	167
Hexyl acetate	2	300	150
2-Phenylethanol	750	50000	67
β-Ionone	0.007	0.08	11
Vanillin	20	150	8
Guaiacol	3	10	3
Oak lactone	200	300	2
Furfural	3000	100	0.03
Syringol	1860	50	0.03

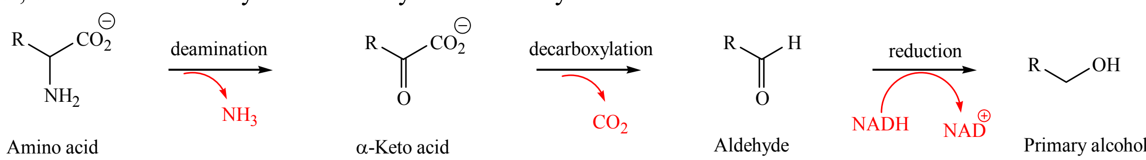
Furfural and syringol have OAV's less than one; their concentrations are less than their thresholds and they will not contribute to the aroma of this Chardonnay.

The aroma compounds can be divided into three groups: those arising from the fermentation; those coming from the oak barrels; and finally those arising from the grapes (varietal aroma).

Fermentation Aroma
These are the higher alcohols (2-phenylethanol, isoamyl alcohol), ethyl esters of fatty acids (ethyl butanoate, ethyl hexanoate) and the acetates (isoamyl acetate, hexyl acetate).

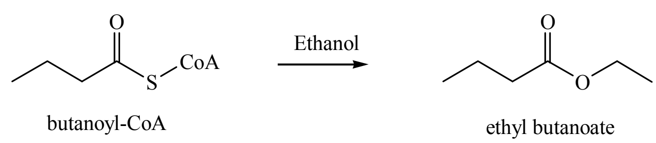


Yeasts excrete higher alcohols, synthesized from amino acids by the Ehrlich reaction. Amino acids are deaminated to the α-keto acids, which are decarboxylated to aldehydes and finally reduced to alcohols.

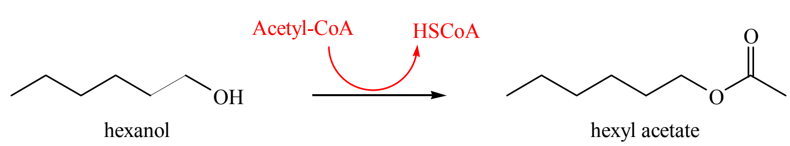


Isoamyl alcohol is formed from leucine and 2-phenylethanol from phenylalanine.

The fatty acid ethyl esters (e.g. ethyl butanoate, ethyl hexanoate and ethyl octanoate) are obtained by ethanolysis of the acylCoA that is formed during fatty acid synthesis or degradation.



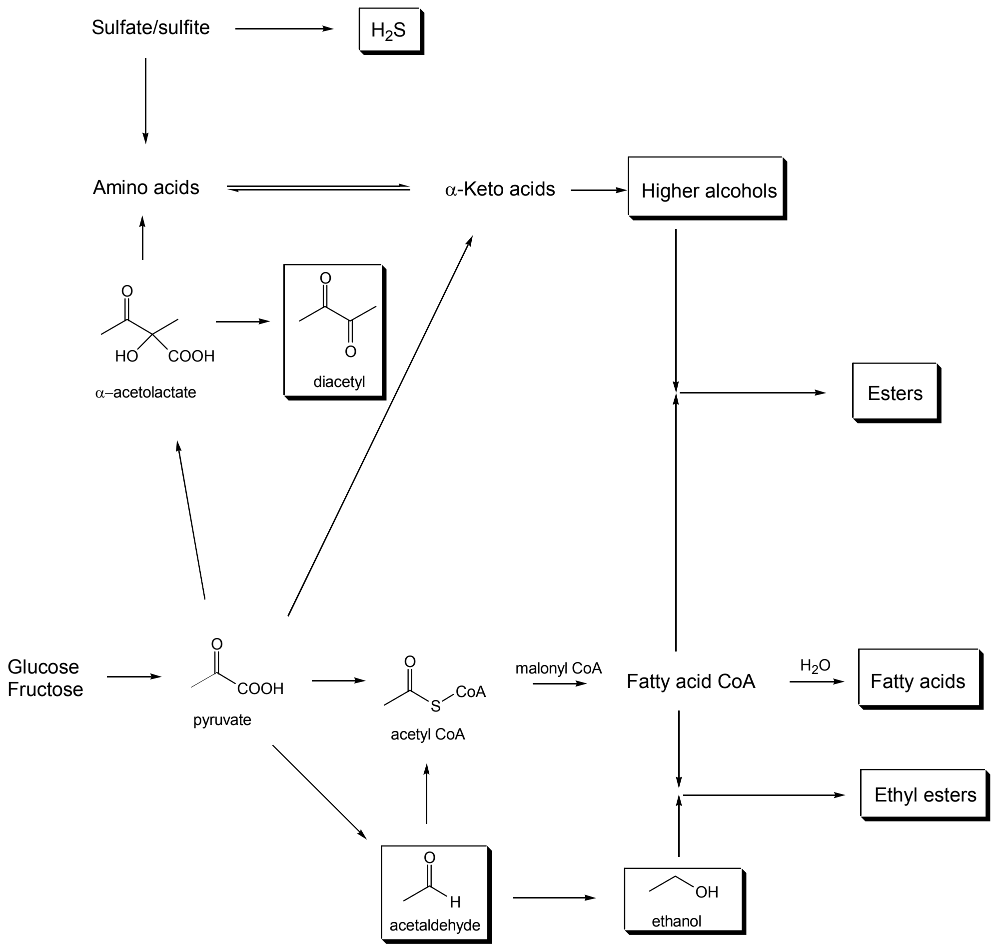
The acetate esters (e.g. isoamyl acetate, hexyl acetate) are the result of the reaction of acetylCoA with the higher alcohols. Hexanol probably arises from the oxidation of linoleic acid that occurs on crushing (see The Grape and Its Maturation; Green Odor)).



Both groups of esters reach a maximum concentration during fermentation; hexyl acetate and the fatty acid ethyl esters at the midpoint and the higher alcohol acetates towards the end. Enzymatic hydrolysis of esters also occurs during fermentation (via esterases) while chemical hydrolysis occurs during storage and aging.

Figure 1 provides a summary of how these compounds are formed during alcoholic fermentation with *Saccharomyces cerevisiae.* See Biochemistry of Yeast Fermentation - Fatty Acids; Esters and Biochemistry of Yeast Fermentation – Nitrogen; Formation of Higher Alcohols and Esters.

Figure 1: Derivation of Yeast Fermentation Flavor Compounds

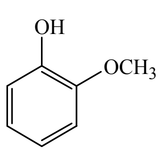


The fatty acid ethyl esters (ethyl butanoate, ethyl hexanoate and ethyl octanoate) have very pleasant odors of wax and honey which contribute to the aromatic finesse of white wines. Ethyl butanoate and ethyl hexanoate are described as fruity, apple peel and strawberry. The acetates have intense odors; isoamyl acetate has an aroma of fresh banana, hexyl acetate smells of fruit, herb and apples. Both groups of esters contribute to the fruitiness of wines and their concentrations slowly decline due to nonenzymic hydrolysis during conservation and aging of the wine.

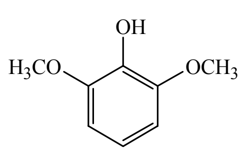
With the exception of 2-phenylethanol, which has a honey, spice, lilac and rose-like fragrance, higher alcohols do not have pleasant odors; isoamyl alcohol has an aroma described as bitter, burnt, whiskey and harsh, 2-methylpropan-1-ol is described as wine, solvent and bitter.

Oak Aroma

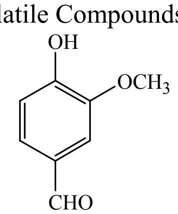
The compounds extracted into the Chardonnay wines from the oak barrels are: vanillin, guaiacol, oak lactone, furfural and syringol (See Oak Barrel Aging of Red Wines; Volatile Compounds and Toasting).



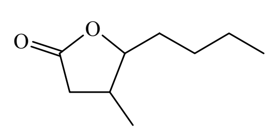
guaiacol



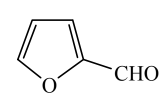
syringol



vanillin



β-methyl-γ-octalactone
or oak lactone



furfural

Toasting of the oak barrels leads to thermal degradation of lignin and produces the volatile phenols guaiacol and syringol.

The phenolic aldehyde, vanillin is naturally present in oak, but toasting increases its concentration. It also arises from thermal degradation of lignin.

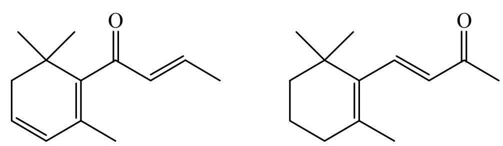
Toasting barrels also causes the thermal degradation of certain lipids or fatty acids, forming isomers of methyl-octalactone. This reaction increases in proportion to heating intensity (Table 5). The more odoriferous *cis* isomer, which already predominates in non-toasted wood, represents an even higher proportion of the isomers in toasted oak.

Furfural arises from themal degradation of hemicellulose, specifically a pentose. Degradation of hexoses yields 5-hydroxyfurfural.

Volatile phenols have smoky, medicinal odors. Guaiacol is described as smoke, sweet, medicine and syringol as smoke, phenol, medicine. Oak lactone is flowery, spice and coconut, and of course vanillin is vanilla. Furfural contributes to a caramel odor, it is described as bread, almond and sweet but is usually at concentrations below its threshold. In this wine we are unable to detect the aroma as its OAV < 1.

Varietal Aroma

The varietal aroma reslts from those compounds which arise from the grapes and in this case only two are important, β-damascenone and β-ionone. Both are C_{13}-norisoprenoids and very powerful odorants. β-Damascenone has a narcotic scent reminiscent of exotic flowers with a heavy fruity undertone and is described as apple, rose and honey, while β-ionone has a distinct aroma of violets. See Isoprenoid Metabolism in Higher Plants; Norisoprenoids and Figure 7. We will spend more time on these compounds later.



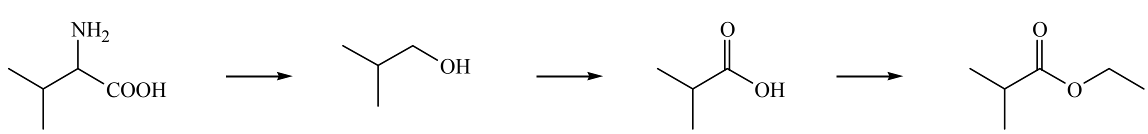
β-damascenone β-ionone

Now let us look at a second wine, a Gewürtztraminer taken form the literature (Guth, H. (1997). "Quantitation and sensory studies of character impact odorants of different white wine varieties." J. Agric. Food Chem. **45**: 3027-3032).

	Threshold (μg/L)	Concentration (μg/L)	OAV
ethyl octanoate	2	630	315
linalool	15	2040	136
rose oxide	0.2	21	105
ethyl hexanoate	5	490	98
isoamyl acetate	30	2900	97
damascenone	0.05	0.84	17
ethyl butanoate	20	210	11
ethyl isobutyrate	15	150	10
wine lactone	0.01	0.1	10

Fermentation Aroma

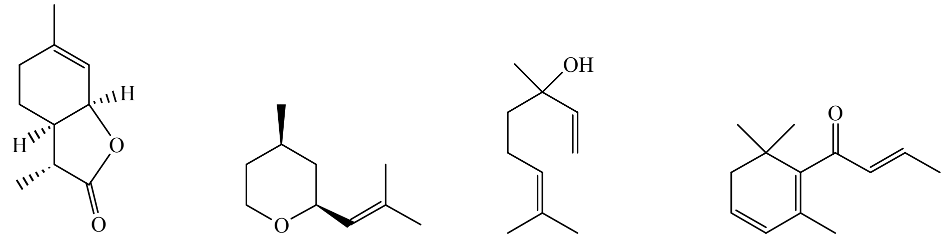
These are ethyl octanoate, ethyl hexanoate, isoamyl acetate, ethyl butanoate and one not important in the Chardonnay, ethyl isobutyrate. This latter compound has a strawberry aroma and probably arises from valine. An Ehrlich reaction yields the higher alcohol 2-methylpropan-1-ol (isobutyl alcohol), which is oxidized to isobutyric acid (2-methylpropanoic acid). Reaction of isobutyric acid with ethanol provides ethyl isobutyrate.



valine 2-methylpropan-1-ol 2-methylpropanoic acid ethyl isobutyrate

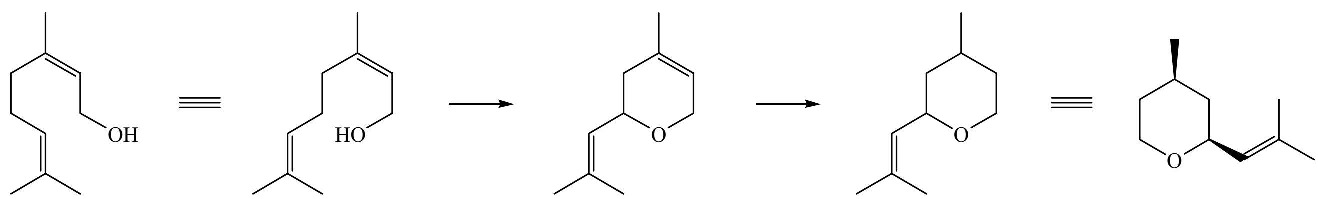
Oak Aroma
Gewürtztraminer wines are not aged in oak barrels so there are no oak aroma compounds.

Varietal Aroma
There are four important aroma compounds whose precursors were present in the grape berries: three monoterpenes; linalool, rose oxide and wine lactone and the C_{13}-norisoprenoid, damascenone.



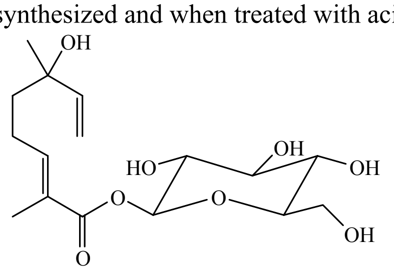
wine lactone   rose oxide   linalool   β-damascenone

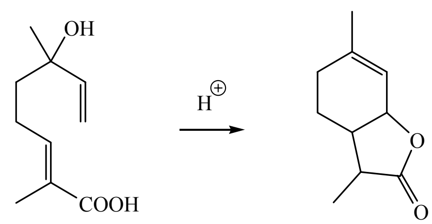
The biosynthesis of linalool and nerol is covered under Isoprenoid Metabolism in Higher Plants; Monoterpenoids. The aroma of linolool is described as flower, lavender and citrus. Rose oxide has a green, flower, sweet, rose-like odor and probably arises from nerol in the following manner:



nerol   nerol   nerol oxide   rose oxide   rose oxide

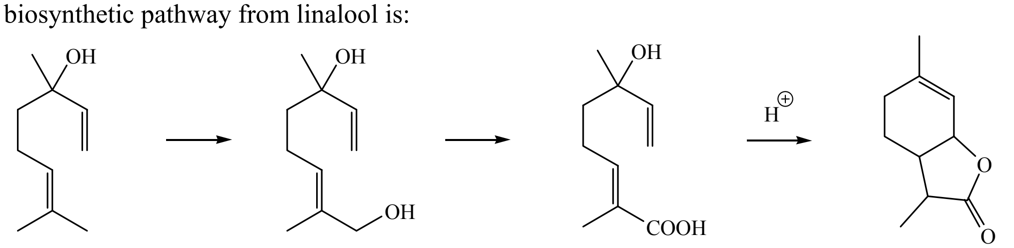
Wine lactone has an aroma described as coconut-like, woody and sweet; it was isolated from a Gewürtztraminer in 1997. In 1998 the following monoterpene glycoside was isolated from Riesling wines. (E)-2,6-dimethyl-6-hydroxyocta-2,7-dienoic acid was synthesized and when treated with acid (pH 3.2), wine lactone was formed.





wine lactone

It is presumed that (E)-2,6-dimethyl-6-hydroxyocta-2,7-dienoic acid 7-O-glucopyranoside is formed and stored in the grape. During the wine-making process β-glucosidase may hydrolyze this glucoside and the acidity converts it to wine lactone. The proposed biosynthetic pathway from linalool is:



linalool   wine lactone