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Wine aroma

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Key words. Wine flavor; grape aroma; volatiles; fermentation aroma; wine bouquet; undesirable odors; off-odors.

Introduction

Among the various factors that contribute to the enjoyment of wine, its flavor is possibly the most important one. Flavor is the result of the interaction of chemical constituents with the sense of taste and smell of the consumer. Flavor is composed of volatile compounds, responsible for the odor, and nonvolatiles which cause taste sensations, such as sweetness, sourness, bitterness and saltiness. Compounds in wine that cause those limited flavor sensations experienced by the palate are sugars, organic acids, polymeric phenols and mineral substances. With a few exceptions those compounds need to be present in levels of 1% or more to influence taste.

Generally, the volatile components can be perceived in much lower concentrations, since our sense organs are extremely sensitive to certain aroma substances. Thresholds vary between 10^{-4} and 10^{-12} g/l[14,26]. As in many foods, the aroma of wine is caused by several hundred different compounds. Concentrations of individual components can range from 10^{-1} to 10^{-10} g/kg. Because there is no real character impact compound, wine aroma is formed by the balance of all those components.

The first studies on wine aroma were performed by Hennig and Villforth[30] in the mid forties. Using classical chemical methods they managed to identify a few compounds. In the late fifties Bayer et al.[9,10] were the first to apply gas chromatography in the field of wine aroma; they identified some higher alcohols and a few esters. Later on, applying gas chromatographic methods, many authors dealt with the aroma substances of grapes and wines, first using packed columns with low separation efficiencies, then employing high resolution capillary columns. Combined with sophisticated aroma enrichment techniques and spectroscopic methods, those separation techniques revolutionized wine aroma research.

It is beyond the scope of this paper to review the hundreds of papers on wine flavor in literature. Most of them are covered already in reviews[67,104] or surveys[100]. We rather intend to concentrate on compounds imparting characteristic odors to wines, their origin from various sources and the factors that influence wine aroma.

When dealing with wine aroma, a distinction is made between: 1) the aroma which originates from the grapes and the aroma due to modifications caused during grape processing, 2) the aroma produced by fermentation and 3) the bouquet which results from the transformation of the aroma during aging.

The amounts of the aroma components can be influenced by environmental factors (climate, soil), cultivar, the condition of the fruit, the conditions during the fermentation stage (pH, temperature, juice nutrients, microflora) and finally, the various postfermentation treatments (clarification, blending etc.).

The three groups into which the wine aroma is subdivided form the framework of the following essay. Additionally, some interesting off-odors are discussed in a separate chapter.

Grape aroma

The majority of volatiles of which grape aroma is composed are reported as constituents of many other fruits. Therefore, in the following we briefly discuss the neutral aroma of grapes, before we bring up grape varieties with a distinct aroma.

Besides the aliphatic n-alkanes and n-alkenes that are common grape surface waxes, some aromatic hydrocarbons like toluene, xylenes and alkylbenzenes have been detected[70, 89–91]. These compounds are largely insignificant in wine aroma because they precipitate with the must slurry during wine-making. Furthermore, their limited water solubility prevents their detection in wine. The same is true for sesquiterpene hydrocarbons that are trace constituents of grapes[70]. The contribution of the monoterpene hydrocarbons limonene, myrcene and p-cymene[67] to grape aroma has not been clarified yet.

Only a few esters, occurring in small quantities in grapes, contribute to the aroma of *V. vinifera* varieties. They are mainly acetate esters of short chain alcohols. The acetates of some monoterpene alcohols[57] and (E)-methyl geranoate[70] are esters found in muscat type grapes. Esters contribute mainly to the intense and characteristic aroma of *V. labrusca* and *V. rotundifolia* varieties growing in the United States. The importance of methyl anthranilate for the aroma of *V. labrusca* (Delaware, Niagara) has been pointed out by several authors[44, 88, 92].

Aldehydes form an interesting group of aroma substances in grapes or grape juice. At the moment of the grape cell destruction, C_6-aldehydes and alcohols[23] are formed enzymically. The aroma of grape juice could be determined in a high degree by those quantitatively dominating compounds. Trans-2-hexenal and n-hexanal are reported to occur in large amounts in grape juices of the varieties Grenache and Sultana[50, 90]. In experiments performed under conditions of enzyme inhibition various saturated and unsaturated aldehydes were identified, too[70]. Thus it is very difficult to decide to what extent those compounds belong to the original primary grape aroma.

Among the ketone fractions 2- and 3-n-alkanones are qualitatively dominating. The alcohol fraction is composed of n-alcohols of chain length C_4 to C_{11}, some branched and unsaturated short chain alcohols, aromatic compounds like benzyl alcohol, 1- and 2-phenylethanol and monoterpenols[67]. Welch et al.[105] attribute the flavor of the muscadine grape to the presence of isoamyl alcohol, hexanol, benzaldehyde and 2-phenylethanol and its derivatives. The only sesquiterpene alcohols that have been detected so far in grapes (wines) are α-cadinol and farnesol.

A key position is held by monoterpene alcohols and derivatives, especially for the aroma of muscat cultivars (Muscat d'Alexandrie, Morio-Muscat, Muscat blanc) and aroma related cultivars (Riesling, Scheurebe). At present more than 50 monoterpene compounds in grapes and wines are known. Figure 1 depicts some volatile alcohols and ethers of wine aroma. The most prominent terpene alcohols, generally occurring in muscat and related grape aromas, are linalool [**I**], geraniol [**II**], nerol [**III**], citronellol [**IV**], α-terpineol [**V**] and hotrienol [**VI**]. The alcohols [**I**]–[**IV**] are the most abundant naturally occurring oxygen-containing derivatives of the monoterpene series[47]. Together with their corresponding derivatives they constitute the base of many essential oils. In grapes, linalool is accompanied by the linalool oxides [**VII** a, b; **VIII** a, b]. The two grape constituents nerol oxide [**IX**] and rose oxide [**X**] are ingredients of Bulgarian rose oil, the ethers [**XI**] and [**XII** a, b] are constituents of other essential oils[47].

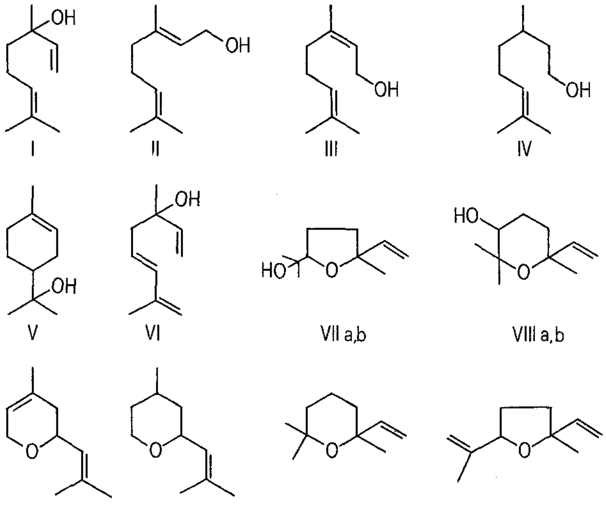

Figure 1. Volatile monoterpenes in wine.

In their studies on muscat aroma Ribéreau-Gayon et al.[65] found linalool and geraniol to be the most aromatic within the terpene fraction. Nerol and α-terpineol have perception threshold values three or four times higher than linalool (100 μg/l).

The oxides [**VII** a, b; **VIII** a,b] have perception thresholds of 3000–5000 μg/l. Because of additive or synergistic effects, the perception threshold of mixtures of these grape constituents is lower than the threshold of the most aromatic single component[65].

Terpene compounds may also contribute to the aroma of other non-muscat cultivars. In grapes of the Koshu cultivar, a native Japanese variety, terpinen-4-ol was a main volatile monoterpene and contributed most to the aroma of that cultivar[76].

Subtle differences in terpene profiles are responsible for the characteristic aroma of various muscat and aroma related cultivars. Figure 2 shows the terpene profiles of 'Muscat-type' (above) and 'Riesling-type' varieties (below). Terrier et al.[98] found that the terpene alcohols geraniol, nerol, α-terpineol and the linalool oxides occur in variety-typical distribution patterns in different white varieties of *V. vinifera*. The analytical differentiation of certain white wine varieties is based on this observation. It is noteworthy that the monoterpene alcohols are distributed differently in the grape skin and berry. 95% of geraniol and nerol are located in the skin of Muscat d'Alexandrie grapes, whereas linalool is almost equally distributed between juice and skin plus cellular debris[12, 18, 19]. Similar trends were observed in the case of Riesling grapes[101]. Since the aromatic profile of the skin differs considerably from that of the juice, the intensity and quality of the aroma might be influenced by different skin contact times which normally are geared to limit phenolic compounds as far as possible. Rapp et al.[54] however, proved that increasing skin contact time does not affect the amounts of the terpenes of the primary grape aroma. The most remarkable effect observed in these experiments was an increase of acetamide concentrations with extended skin contact times[27,54,66].

There are many compounds in grapes which are derived from terpene precursors. 2-Vinyl-2-methyl-tetrahydrofuran-5-on is regarded as an oxidation product of linalool and linalool oxides. Some norisoprenoids which are formed by biodegradation of higher molecular mass terpenoids, such as diterpenes and carotinoids, are depicted in figure 3. α- and β-ionone [**XIII**; **XIV**] have particularly low perception threshold values[16,31] and are used in the flavor industry to compound fruit flavors[42]. Only the spiroether [**XVII**], named vitispirane, was first found in aroma volatiles of grape juice[83]. Damascenone [**XV**], theaspirane **XVI** and dihydroactinidiolide [**XVIII**] were found in various other fruits, tobacco brands, tea and some essential oils[47]. The significance of these compounds for grape flavor is unknown.

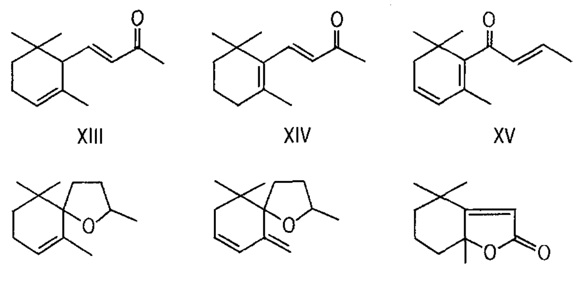

Figure 3. Metabolites from higher terpenes as grape aroma constituents[36,67,83].

The fungus *Botrytis cinerea* is responsible for the rotting of grapes. Under special climatic conditions it can cause noble rot which is a prerequisite for the production of botrytised wines having a distinct aroma. Only a few papers deal with the volatiles produced by this fungus. Boidron[15] observed decreases in monoterpenes of *Botrytis cinerea* infected Muscat varieties. Shimizu et al.[75] report that *B. cinerea* does not produce terpenoids in grapes without terpenes, but transforms linalool which has been added to grape must into some other monoterpenes. Apart from quantitative differences in the aroma composition of botrytised wines compared to normal

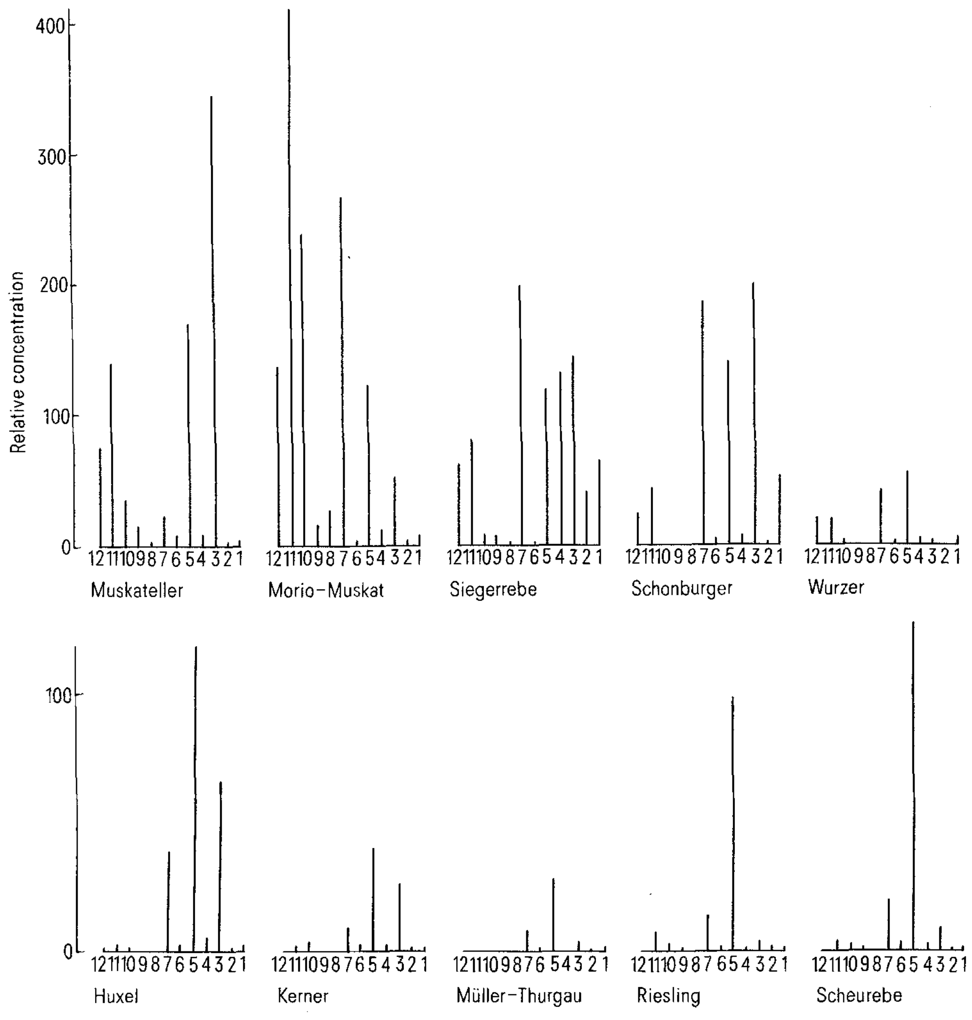

Figure 2. Terpene profiles of Muscat type and Riesling type varieties: 1 = trans-linalool oxide (f), 2 = cis-linalool oxide (f), 3 = linalool, 4 = hotrienol, 5 = trans-linalool oxide (p), 6 = cis-linalool oxide (p), 7 = 3,7-dimethylocta-1,5-diene-3,7-diol, 8 = nerol oxide, 9-citronellol, 10 = nerol, 11 = geraniol, 12 = (E)-geranoic acid.

wines, Masuda et al.[39] found 2 compounds to be responsible for the flavor of botrytised wines. They are ethyl 9-hydroxynonanoate and 4,5-dimethyl-3-hydroxy-2(5H)-furanone (sotolone). The latter compound has a sweet, sugar- and caramel-like aroma and its threshold value is 2.5 ppb. The sotolone content in botrytised wine was about 5–20 ppb, in normal wines below 1 ppb[39]. This compound is also reported to contribute to the flavor of sugar molasses, aged rice wine and flor sherry[39]. Rapp et al.[51] observed a significantly higher amount of 1-octen-3-ol in *Botrytis*-infected grapes and wines. This alcohol is called 'mushroom alcohol' on account of its typical odor.

The fermentation aroma

The main part of the wine aroma arises during yeast fermentation. Figure 4 illustrates the changes in the aroma composition of a Morio-Muscat grape juice and the corresponding wine. The grapey odor of the juice is superimposed by the fermentation products which form the vinous flavor of the product. Ethanol and glycerol are quantitatively dominating alcohols, followed by diols, higher alcohols and esters which account for 0.2–1.2 g/l for white wines and 0.4–1.4 g/l for red wines[13]. 50% of these values are represented by n-propanol, n-butanol, 2-methylbutanol-1, 3-methylbutanol-1, phenylethanol, ethyl acetate and ethyl lactate.

Apart from its distinctive odor and its physiological effects on the central nervous system, ethanol determines viscosity (body) of wine, balances taste sensations and acts as a fixer for odors. The higher alcohols (fusel alcohols) are present in concentrations above their organoleptic perception threshold. At concentrations below 300 mg/l they certainly contribute to the desirable complexity of wine. When their concentrations exceed 400 mg/l, the fusel alcohols are regarded as a negative quality factor. In figure 5A the formation of fusel alcohols and ethyl acetate parallel to the ethanol content is illustrated. Methanol, arising from pectins, remains uninfluenced by yeast activity. The terpene alcohols and oxides of the grape aroma are also present in wine. During yeast fermentation there are small changes in the concentrations of monoterpene alcohols[33] which are related to nonvolatile monoterpene glycosides that have been found in

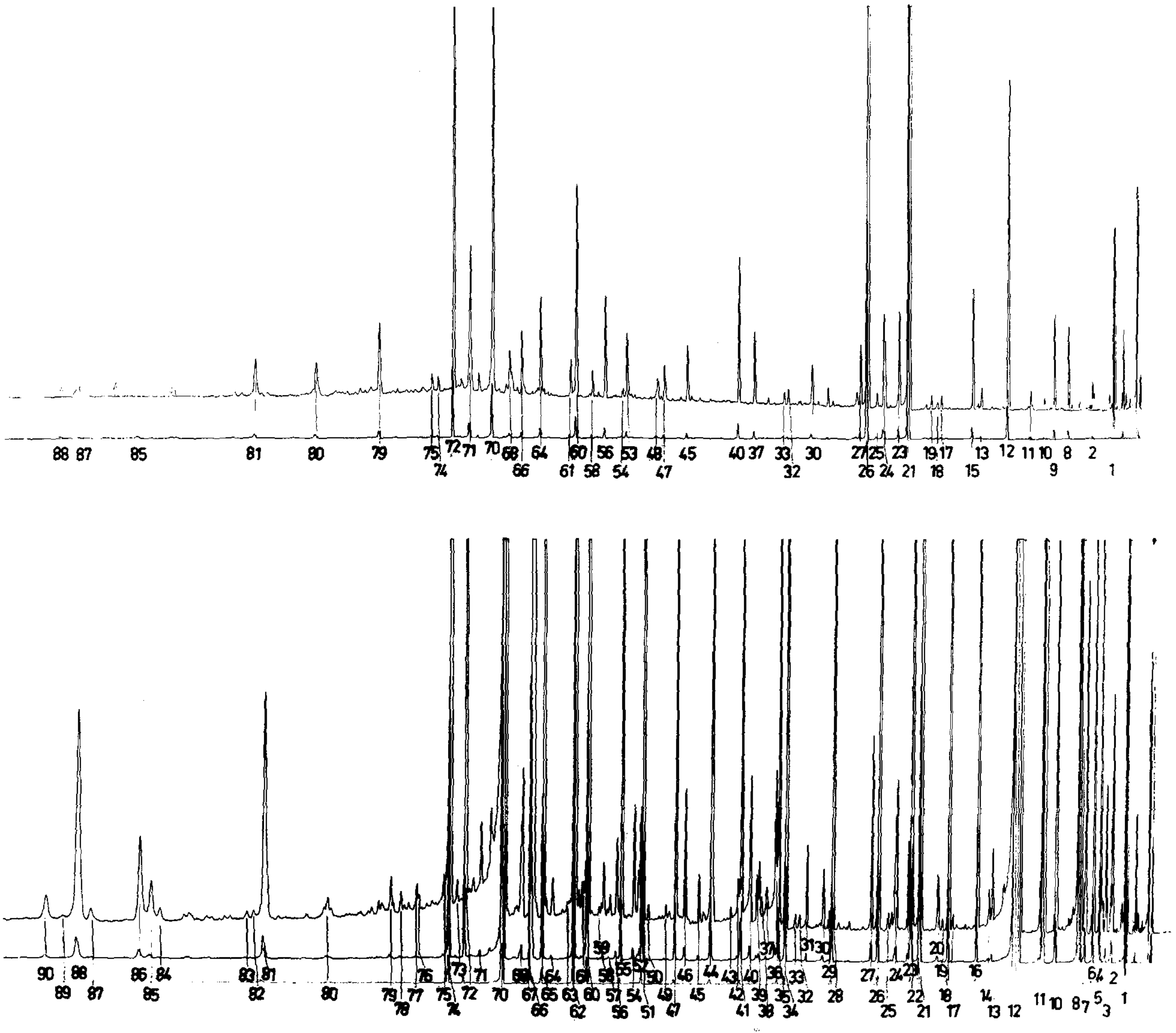

Figure 4. Aromagrams of grape must (above) and the corresponding wine (below), cultivar Morio-Muscat[60].

grapes and wines[108]. Although monoterpene ethers of the grape aroma can be derived via acid-catalyzed reactions from di- and tri-hydroxylated monoterpenes [61, 107], there is no remarkable change in the amount of monoterpene ethers during yeast fermentation[60] (fig. 5B).

Since the amounts of those compounds are little changed by the technological steps of must treatment[66], skin contact times[27, 54, 66] and yeast fermentation, and additionally are independant of the growing district[56], they have been used to differentiate varieties of Muscat and aroma related grapes and wines[22, 27, 53, 56, 72]. Figure 5 shows the differentiation of Riesling (R) and Morio-Muskat (M) wines by discriminant analysis based on selected monoterpenes[56].

Most of the aldehydes present in grapes or grape juice are only detectable in wines in the initial phase of fermentation[59]. Most probably they are reduced to alcohols. Except for acetaldehyde, the aldehydes in wine arise from carbohydrate degradation (furfural, 5-hydroxymethylfurfural), originate from lignins (vanilin, cinnamaldehyde) or are formed during wine aging. Most of the ketones reported in grapes are also found in wines, though in small amounts. The sensory impact on wine aroma of ketones, α-diketones and α-hydroxyketones that arise during yeast fermentation (e.g. acetone, acetoin, 2,3-pentanedione) seems to be very low. Diacetyl is reported to possess a buttery odor.

Like acetals, γ-lactones are reported to be important for the flavor of sherries[103] where they occur in relatively high concentrations. Because the threshold for γ-lactones is relatively low[2] their contribution to table wine aroma seems to be negligible. Most of the lactones found in sherries, have now also been reported as table wine constituents[27]. Among them are pantholactone, the sherry lactones and solerone which is described as having a typical wine-like aroma[5]. 4,5-dimethyl-tetrahydro-2,3-furandione seems to be important for Flor sherry type wine[25].

Relative few organic acids in wine are volatile enough to contribute to its odor. Odorous acids are acetic acid (vinegary), propanoic acid (goaty), butanoic acid (spoiled butter) and lactic acid. With the exception of acetic acid their amounts in wines are usually below perception threshold.

The volatile phenols which are found in wines are not present in grapes, except acetovanillone[67]. They result

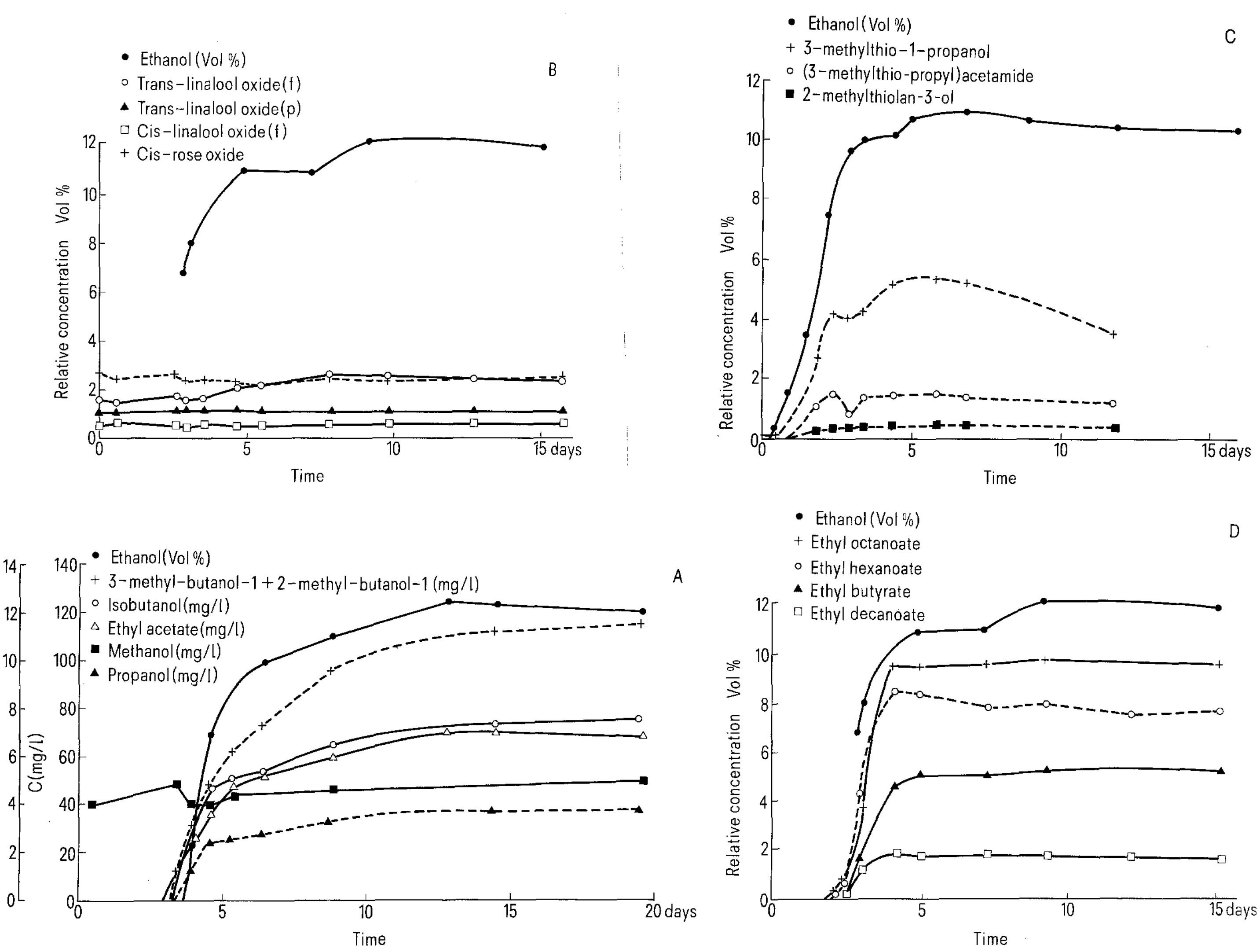

Figure 5. Formation of aroma compounds during yeast fermentation[59].

either from yeast or bacterial metabolism or from hydrolysis of higher phenols. For example, the volatile phenols 4-vinyl guajacol and 4-vinylphenol can originate from the cinnamic acids p-coumaric and ferulic acid[87] by enzymic or thermal decarboxylation[1,87]. These phenols can influence wine odor.

There is no evidence that N-containing compounds produced during fermentation (amines, N-alkyl acetymides) are of importance for the odor of wines. A sensory effect on wine taste cannot be excluded.

Generally speaking, volatile organic sulphur compounds are of outstanding importance for aromas because for the most part they have extremely low perception thresholds. The most important S-containing representative in wine is hydrogen sulphide which has a recognition threshold below 1 μg/l. It appears predominantly in high amounts during the fermentation of grapes with free elemental sulphur and causes the horrible 'rotten egg' odor. Other odor intensive sulphur compounds in wine are thioethers (dimethylsulphide, diethylsulphide), thiols (ethanthiol, 4-methylthio-1-butanol), thiolanes (2-methylthiolane-3-one, 2-methylthiolane-3-ols), esters of sulphur-containing acids (methyl and ethyl-3-methylthiopropionate), thiazols, a mercaptal and an acetamide[27,52,67,71]. The odor of trans-2-methylthiolane-3-ol is onionlike, that of ethanthiol is fecal and formic aldehyde methyl-2-hydroxyethyl mercaptal has a smell reminiscent of cauliflower[52]. The formation of sulphur compounds is closely linked with yeast metabolism (fig. 5C). Only for a few compounds has the genesis been clarified: 3-methylthio-1-propanol is formed via the 'Ehrlich pathway' out of the amino acid methionine[71].

Significant components in young wines are esters, formed during yeast fermentation. Although present in small amounts in grapes already, the bulk of acetate esters and fatty acid ethyl esters parallels ethanol formation (fig. 5D). The main ester is ethyl acetate. Other esters of fusel alcohols and short chain fatty acids, termed 'fruit esters' because of their pleasing aroma, also appear. Especially in white wines the fatty acid ethyl esters (ethyl butanoate, caproate, caprylate, caprate, laurate) are important. Their amount is below 10 mg/l[1], but this value is approximately 10 times their perception threshold. The odor of ethyl caproate is of a fruity quality. As the acid carbon number increases, the odor of the esters tends to become soft, then soaplike and finally stearic.

The type of yeast has a great influence on the production of esters, but even more important are the fermentation conditions. There is a large positive effect of low fermentation temperatures on the total quantity of higher esters[86]. The aroma of such wines is distinctively characterized by a fruity and soaplike odor typical of these esters. Avakyants et al.[6] attribute the basic odor of wines to the four esters ethyl acetate, isoamyl acetate, ethyl caproate and caprylate, two alcohols (isobutyl, isoamyl) and acetaldehyde. The other compounds are considered to modify the basic odor.

Wine bouquet

Depending on the storage conditions, several chemical reactions influence the composition of volatile constituents in wine and transform the aroma into the bouquet. Two types of bouquet are distinguished: The bouquet of oxidation which is due to the presence of aldehydes and acetals, and the bouquet of reduction which is formed after aging in bottles[64].

Particularly the flavor of fine red wines benefits from storage in wooden barrels, when various aromatic elements of wood are extracted into the wine without dominating the wine character afterwards. Phenolic compounds from lignin degradation belong to that category of wood extracted compounds as well as the diastereomers of 3-methyl-γ octalactone which are found in oak wood[38]. Those compounds have been detected in wines which were aged in wooden casks[32,73], and also in whiskey[45] and brandy[28,48,74]. The cis-lactone is more fragrant than the trans-lactone, which is probably responsible for the typical whiskey odor, together with isopentyl and isobutyl alcohols[48]. The presence of 3-methyl-γ-octalactone in some German white wines[68] which are normally not stored in wooden barrels, requires another explanation for the origin or formation of these compounds.

Apart from the extraction of wood components and reactions of wood with the aging wine, oxygen penetrates through the wood and causes drastic flavor changes.

Reazin et al.[62] proved that in aging whiskey distillates acetaldehyde, acetic acid and ethylacetate are produced from ethanol by oxidation and esterification reactions. Although similar investigations with specifically labeled ethanol added to aging wine are still lacking, the results obtained by other researchers clearly indicate that similar reactions take place in wine aged in wooden barrels; among other modifications in wine composition, Ribéreau-Gayon[63] found variable increases in the levels of volatile acidity and ethyl acetate accompanying the storage of wine in wooden barrels.

Increases in the concentration of acetaldehyde[8] and some other, higher aldehydes[7,106] during storage of wine were observed by other authors.

Aldehydes and the alcohols in wine form a variety of acetals of which only a few were detected[27,33,69,73]. They are mostly acetaldehyde acetals with alcohols present in high concentrations in wine. So far the flavor character of these compounds is still undetermined.

In contrast to the bouquet of oxidation, acetals are relatively unimportant for the bouquet of reduction. A detailed investigation on changes in aroma substances of Riesling wines during storage in bottles showed that there is no rise in acetal concentration during bottle aging[27]. Table 1 details changes in the concentration of Riesling aroma constituents that are affected most by bottle aging. The investigated material were Riesling wines from 10 different vintages (1964, 1973–1975, 1977–1982) from the same estate. Section II of table 1 compares the aroma compounds of a Riesling wine which was frozen for 6 years, with the corresponding normally seasoned (cellar stored) product. The first conspicuous fact is the decrease of acetates and the increase of ethylesters of diprotic acids.

Contributing to the pleasant fruit-like aroma of new wines, the acetates are produced enzymically in excess of their equilibrium concentrations. During storage they gradually hydrolyze until they approach equilibrium with their corresponding acids and alcohols. Table 1 shows that only acetates occurring initially in high postfermentation concentrations are detectable in fair amounts after nearly 20 years of bottle storage. Similar results were obtained by Marais[34,35,37], Simpson[78,80,82], Shinohara and Watanabe[77] who mainly simulated the aging process by exposing wines to higher temperatures. The decrease in concentration of these acetates could be responsible for the loss of freshness and fruitiness especially of white wines. Unlike the acetates, the concentrations of the straight chain fatty acid ethyl esters remain fairly constant during storage. This can be explained by the fact that ethyl esters hydrolyze more slowly than acetate esters[49], considering the high concentrations of the hydrolysis product ethanol. Most probably those compounds are produced by the yeasts in concentrations which are very close to the equilibrium concentrations of ester, fatty acid and ethanol.

The group of ethyl esters of diprotic acids show constant concentration increases caused by chemical esterification during the course of aging.

Some components, resulting from carotinoid degradation, are of particular interest with reference to wine aging. The amounts of the vitispiranes were found to increase with storage[79,81,83]. Those compounds are of camphoraceous eucalyptus-like odor[79].

A hydrocarbon that develops on storage is 1,1,6-trimethyl-1,2-dehydro-naphthaline[27,55,69,79,81]. It is supposed to impart wine flavor of a bottle-aged or kerosene character. Table 1 clearly shows the increase of that compound during storage. Damascenone is an example of a compound originating from carotene metabolism, which shows a concentration decline during storage[27]. The furane derivatives of table 1 are regarded as carbohydrate degradation products. In all young wines of the investigated series, furfural and ethyl furoate were formed. Additionally, 2-acetylfuran, furfuryl alcohol, 2-ethoxymethyl-5-furfural, 2-hydroxymethyl-5-furfural and levulinic acid ethyl ester were detected after a few years of storage. Remarkable is the increase of furfural (table 1) during bottle aging. Similar results of furfural increases with extended storage time or with thermal abuse are reported from orange juice. For this reason furfural has been proposed as an index of storage time[40,41].

The monoterpenes of white wine show considerable changes during the aging of wine. They can be categorized as followed:

- monoterpene alcohols like linalool, geraniol and citronellol decrease,
- the linalool oxides as well as nerol oxide, hotrienol, hydroxylinalool and hydroxycitronellol increase,
- and 2,6,6-trimethyl-2-vinyl-tetrahydropyran, the anhydrolinalool oxides, 2,2-dimethyl-5 (1-methylpropyl)-tetrahydrofuran and cis-1,8-menthandiol are formed[16,30]. Figure 7 explains the decreases of the 4 monoterpene alcohols nerol [III], linalool [I], geraniol [II] and citronellol [IV] and the increase of α-terpineol [V] cis-1,8-menthandiol [XXIII] and the corresponding diols [XIV–XXII].

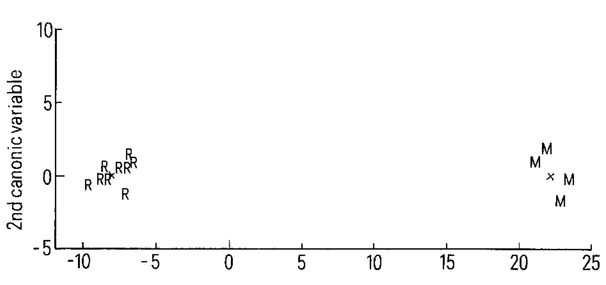

Figure 6. Differentiation of the varieties Riesling (R) and Morio-Muscat (M) by discriminant analysis[56].

Table 1. Changes of Riesling aroma constituents during bottle aging* (relative concentration)[27,55]

Vintage	1982	1978	1973	1964	Frozen in	Cellar stored
Acetates						
n-propyl acetate	2.3	1.8	1.1	1.9	9.4	2.9
isobutyl acetate	16.7	4.2	2.8	3.1	32.1	6.0
isoamyl acetate	107	58.4	5.9	10.9	243	27.1
n-hexyl acetate	6.9	5.4	–	–	7.3	–
3-(methylthio)propyl acetate	–	–	–	–	0.5	–
1,3-propandiol-mono-acetate	30.7	4.5	1.6	0.5	22.3	1.7
2-phenylethyl acetate	38.7	25.1	1.9	5.7	27.2	3.2
Ethyl esters of diprotic acids						
diethyl succinate	41	384	656	738	117	407
diethyl malate	96	640	1375	969	262	729
monoethyl succinate	128	338	438	415	152	339
Carotinoid degradation products						
1,1,6-trimethyl-1,2-dihydronaphthaline (1,1,6-TDN)	–	0.5	3.0	3.4	–	1.0
Damascenone	0.9	–	–	–	0.7	–
Carbohydrate degradation products						
furfural	4.1	13.9	39.1	44.6	2.2	27.1
2-acetylfuran	–	–	0.5	0.6	0.1	0.5
ethyl furoate	0.4	0.6	2.4	2.8	0.7	2.0
furfurylalcohol	–	0.3	1.0	1.3	–	–
2-ethoxymethyl-5-furfural	–	–	4.6	7.1	0.8	1.7
2-formyl-pyrrol	–	2.4	7.5	5.2	0.4	1.9
2-hydroxymethyl-5-furfural	–	–	1.0	2.2	–	0.5
Monoterpenes						
2,6,6-trimethyl-2-vinyl-tetrahydropyran	–	0.8	1.9	3.2	–	1.0
cis-5-i-propenyl-2-methyl-2-vinyl-tetrahydrofuran (anhydro linalool oxide)	–	0.5	0.5	0.7	–	0.8
trans linalool oxide (furanoid)	1.5	1.6	7.3	14.3	2.2	8.8
cis linalool oxide (furanoid)	0.5	0.7	3.1	6.4	0.9	3.5
nerol oxide	0.8	1.0	4.4	7.2	1.0	5.0
linalool	16.8	1.0	–	–	19.4	2.8
3,7-dimethyl-1,5,7-octatrien-3-ol (hotrienol)	5.1	3.3	4.6	7.0	6.0	14.7
α-terpineol	8.4	3.2	7.0	8.3	10.8	16.6
trans linalool oxide (pyranoid)	1.6	1.3	2.2	3.0	2.5	4.0
cis linalool oxide (pyranoid)	0.7	0.3	0.8	0.8	0.5	0.5
citronellol	0.4	–	–	–	1.0	–
geraniol	3.2	0.8	0.9	1.0	3.0	1.6
3,7-dimethyl-1,5-octadien-3,7-diol	33.3	12.6	9.2	15.1	28.6	28.3
3,7-dimethyl-1-octen-3,7-diol (hydroxylinalool)	1.4	0.4	5.2	6.9	1.4	7.5
cis-1,8-methandiol	–	0.3	3.4	6.2	–	2.0
3,7-dimethyl-octan-1,7-diol (hydroxycitronellol)	0.5	–	0.3	0.6	0.7	1.0

* All wines were analyzed in 1983; –: not evaluated due to low concentration.

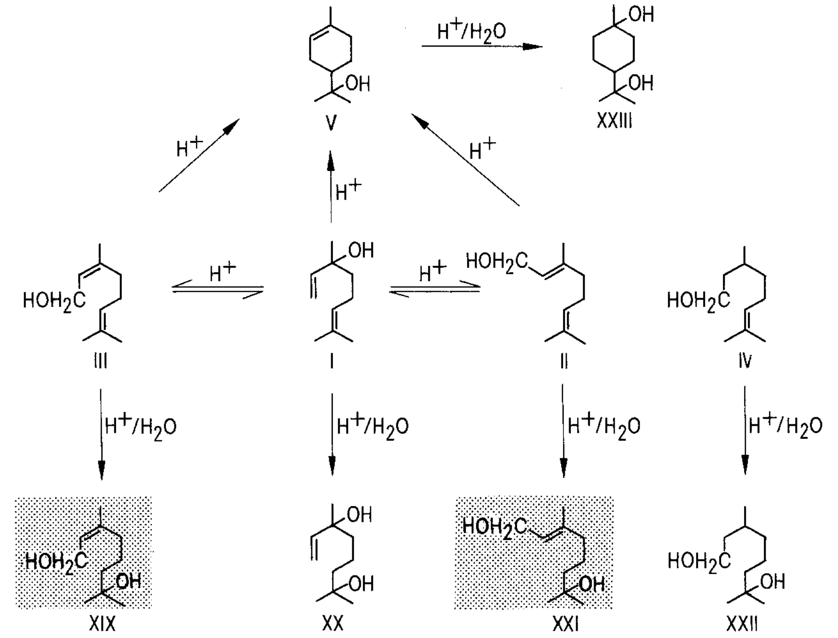

Figure 7. Proposed reaction scheme of monoterpene alcohols during bottle aging of white wine[27, 55].

III	nerol	**XXIII**	cis-1,8-terpine
I	linalool	**XIX**	hydroxynerol
II	geraniol	**XX**	hydroxylinalool
IV	citronellol	**XXI**	hydroxygeraniol
V	α-terpineol	**XXII**	hydroxycitronellol

The hatched diols [**XIX, XXI**] were only found recently in wines with muscat character[66] and thus complete the proposed reaction scheme. By heating grape must from the cultivar Muscat of Alexandrie, Williams et al.[107] made similar observations concerning the formation of monoterpene ethers, hotrienol and α-terpineol.

One can expect that these changes in terpene composition would influence the character of the wine. Let us consider the example of linalool, which is one of the chief monoterpene alcohols in young Riesling wines. After a few years of storage the linalool content decreased to about 10% of its original amount. Starting from an estimated average concentration of 400 μg/l linalool in young Riesling wines, the remaining amount after a few years of storage will clearly be below the perception threshold of 100 μg/l[27, 55]. The increases in linalool oxides are not such that they drastically exceed the approximate perception threshold as published by Terrier and Ribéreau-Gayon et al.[65, 97].

On the other hand, the increase in α-terpineol probably affects wine flavor in a negative sense. In orange juice, for example, this compound is known to impart a stale, musty or piney odor to the juice[96]. As its concentration increases linearly with storage time, it was suggested as an indicator for predicting storage time of orange juice[3]. Since the olfactory perception threshold for the monoterpenes in wine vary, ranging from 100 μg/l to 700 μg/l, and additive effects lower the olfactory threshold[64], it is very difficult to predict exactly the aroma changes during aging. However, the insight into the monoterpene composition during aging explains why wines of Muscat-type cultivars, which are strongly formed by the fragrant monoterpene alcohols, seldom improve with bottle storage, whereas Riesling-type wines are not that negatively affected by aging.

For most of the red wines, which have almost no monoterpenes contributing to the flavor, this problem does not exist. Decreases in acetate amounts will affect both red and white wines during storage.

Foreign and undesirable odors in wines

One of the major problems with wines is that of foreign or undesirable odors. They are classified as those derived from the cultivar, from fermentation and processing or from microbial spoilage. To produce wines of good organoleptic quality it is necessary to identify the chemical nature of the compound(s) responsible for the off-odor and trace them back to their origin.

Very often those unpleasant odors are due to components present in micro concentrations. Therefore sophisticated aroma enrichment and separation techniques are required to solve the problem. The off-odor is pinpointed during gas chromatographic separation of the complex aroma mixture by effluent sniffing. Once allocated, the chemical nature of the off-odor is elucidated by spectroscopic methods. From the long list of possible undesirable odors in wines only a few are mentioned in table 2.

The green pepper taint of some white and Cabernet wines is due to 3-alkyl-2-methoxypyrazines[4, 11]. 3-isobutyl-2-methoxypyrazine is claimed to be characteristic of the cultivar Cabernet Sauvignon. However, it could not be identified in the wine[85]. Wines made from unripe grapes usually possess a green odor. Drawert[21] attributes it to hexanal and hexenals, Webb and Berg[102] connect it with leaf alcohol and aldehyde. Many fruit names are used in wine aroma terminology to describe foreign aroma notes[46]. The black currant-like aroma of Cabernet Sauvignon wines, the guava taint of some South African

Chenin blanc and Colombard wines and the strawberry aroma of grapes and wines of some German interspecific grapevine breedings are interesting examples. (It goes without saying that those aroma notes cannot be put on the same level with evil-smelling aromas).

Rapp et al.[58] identified the compounds that caused the strawberry-like aroma in wines: 2,5-dimethyl-4-hydroxy-2,3-dihydro-3-furanone (furaneol) and 2,5-dimethyl-4-methoxy-2,3-dihydro-3-furanone. They were only found in hybrids with *V. labrusca.* Since both compounds usually occur together in those hybrids, the analytical detection of the major compound furaneol indicates a potential for strawberry-note properties.

Figure 8 shows the furaneol concentrations of wines from different varieties and vintages. All Castor samples had the strawberry-like aroma, whereas in the variety Pollux the strawberry note was perceivable only in the year 1976. In the other years the furaneol amount was below the perception threshold of 30–50 ppb, but above the analytical detection threshold of 2 ppb. Wines of *V. vinifera* varieties do not contain furaneol in detectable amounts (e.g. Riesling; fig. 8).

The foxy flavor of native American grape cultivars was correlated with methyl anthranilate which has not been found in European *V. vinifera* grapes and wines. Recent investigations demonstrated that the foxy flavor is not solely due to the presence of this ester[43].

The geranium-like odor is highly undesirable. It results from bacterial activity in wines containing the preservative sorbic acid. 2-ethoxy-hexa-3,5-diene accounts for that defect[20].

Mousiness is an undesirable flavor of wines infected by certain spoilage microorganisms. Tucknott[99] claims that 2-ethyl-3,4,5,6-tetrahydropyridine is responsible for that off-flavor. Strauss and Heresztyn[93] identified 2-acetyl-3,4,5,6-tetrahydropyridine and 2-acetyl-1,4,5,6-tetrahydropyridine as the compounds producing a strong mousy off-flavor in wines.

Not fully understood are the off-flavors arising during fermentation which are caused by hydrogen sulphide and other organic sulphur compounds. Hydrogen sulphide is blamed for the rotten egg smell. The chemical nature of the mercaptan odor is still an analytical challenge.

The odor of acetic acid and ethyl acetate is described as vinegary. In concentrations below 50 mg/l ethyl acetate has a pleasant odor, which turns into a vinegary one at levels above 150 mg/l. Between these levels the ester contributes to the hard characater of the wine[64].

The sauerkraut or lactic odor is either a sign of bacterially spoiled wines or active malolactic fermentation. Compounds involved are, amongst others, lactic acid and diacetyl.

Corkiness is an off-odor that is very often encountered. In about 2% of all German wines this odor reveals itself and causes immense economic damage. There are various theories which try to explain this off-odor. The problem seems to be very complex and one gets the impression that scientists are talking about different phenomena which are described by the same term, but are not of the same origin or nature.

Dubois and Rigaud[24] reported methyl tetrahydronaphthalene to be responsible for corkiness. Tanner and Zanier[94, 95] identified 2,4,6-trichloroanisole in bottled and

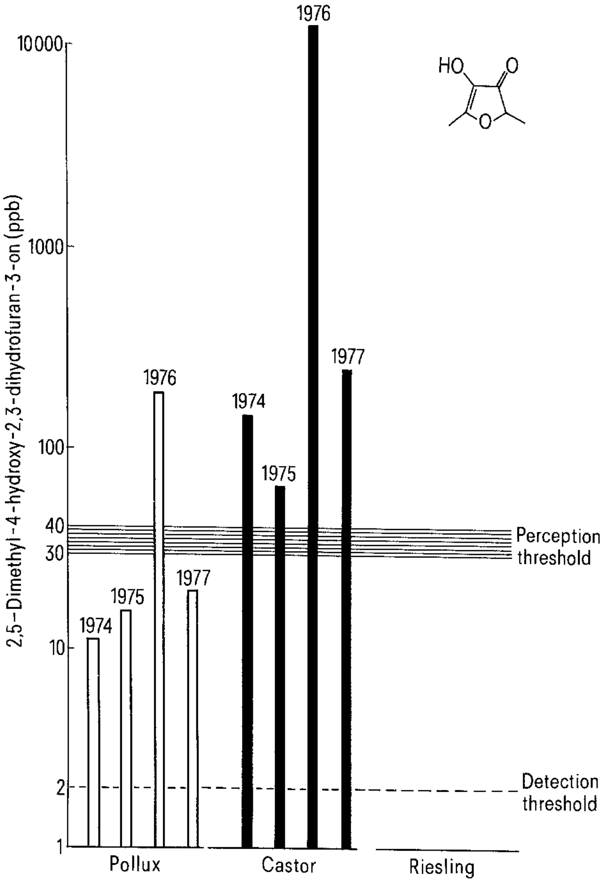

Figure 8. Furaneol in wines of the cultivars Pollux (B-6-18), Castor (B-7-2) and Riesling.

Table 2. Foreign and undesirable odors in wines

Odor description	Compound(s) responsible for the odor	Literature
Green pepper, grassy	3-isobutyl-2-methoxypyrazine	Bayonove et al.[11]
	3-isopropyl-2-methoxypyrazine	
	3-ethyl-2-methoxypyrazine	Augustyn et al.[4]
Green	hexanal, hexenals	Drawert[21]
Strawberry	2,5-dimethyl-4-methoxy-2,3-dihydro-3-furanone	Rapp et al.[58]
	2,5-dimethyl-4-hydroxy-2,3-dihydro-3-furanone	
Geranium-like	2-ethoxy-hexa-3,5-diene	Crowell and Gujmon[20]
Mousy	2-ethyl-3,4,5,6-tetrahydro-pyridine	Tucknott[99]
	2-acetyl-3,4,5,6-tetrahydro-pyridine	Strauss and Heresztyn[93],
	2-acetyl-1,4,5,6-tetrahydro-pyridine	Rapp et al., unpubl.
Rotten eggs	hydrogen sulfide	
Onion-like/ garlic-like	mercaptans	
Vinegary	ethyl acetate, acetic acid	
Sauerkraut	lactic acid, diacetyl + other components	
Corky	methyl tetrahydronaphthalene	Dubois and Rigaud[24]
	2,4,6-trichloroanisole	Tanner and Zannier[94,95]
	sesquiterpenes produced by *P. roquefortii*	Heimann, Rapp et al.[29]
	2,3,4,6-tetrachloroanisole and pentachloroanisole	Tanner et al.[95]
Woody	3-methyl-γ-octalactone	Kepner et al.[32]
	phenols of oak wood	Singleton and Noble[84]

corked European wines as the chief component responsible for the musty cork taint.

Wines with that distinct off-odor contained 2,4,6-trichloroanisole concentrations ranging from 20 to 370 ppt. In sound wines this compound was not detectable (< 2–8 ppt). Together with other chlorinated anisoles[95] this compound could originate from the chlorination of lignin-related substances during cork bleaching, which is involved in the processing of cork. Later on these compounds are extracted into the wine. Heimann and co-workers[29] managed to isolate *P. roquefortii* from corks which were used for wine bottling, where that off-odor was observed. Growing on cork-wood containing culture mediums, this fungus produced a typical corky off-odor. The corky-smelling compounds were identified by effluent sniffing and GCMS-analysis as sesquiterpenes.

Conclusions

The progress made in the analysis of volatile wine constituents has led to a better understanding of the complexity of wine aroma.

Now many factors influencing wine aroma are not only characterized by their sensory impact, but also by chemical data which in many cases allow a more differentiated approach. By correlating sensory and analytical data headway has been made, especially in the field of wine off-odors. Successful analytical cultivar differentiation based on wine volatiles indicates the importance and possibilities of wine aroma for quality control.

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Microbial biochemistry

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Key words. Yeasts; malate; succinate; pyruvate.

1. Introduction

The process of making wine from grapes can be seen from a technological point of view (which encompasses the handling, treatment, transport and storage of the grapes and the liquids[87]) or also, for example, from a biochemical point of view. Only this latter aspect will be considered in this review. The final product, wine, is the result of a vast series of biochemical reactions that have been gradually recognized over the last century. These reactions are catalyzed by enzymes that are produced either by the grape itself or by microorganisms (i.e. yeasts, filamentous molds, bacteria). Of course, the main reactions that eventually turn grape must into wine are those of the well-known alcoholic fermentation of the hexoses by the enzymes of yeasts. Even this rather simple alcoholic fermentation requires the growth of the yeast cells and thus a plethora of biochemical reactions is involved in the overall process. As it is impossible to cover even the main aspects of the microbial biochemistry involved in wine-making this review article will be devoted to some catabolic reactions, mainly the metabolism of carboxylic acids by yeasts and lactic acid bacteria, the biochemistry of killer-proteins from yeasts, and some metabolic activities of the mold *Botrytis cinerea*. For more detailed information on this and on other topics such as the metabolism of nitrogen, sulfur, aromatic or flavor compounds recent textbooks or reviews should be consulted[1,3,19,42,43,53,72].

2. Fermentative metabolism of carboxylic acids

Grape must and wine contain a variety of carboxylic acids. Their concentration varies greatly and depends on the condition and maturity of the grapes. The main acids and some of the minor acids are listed in table 1. The main acids of must are malate and tartrate that are produced by the grape. Many of the acids of wine are of microbial origin.

Malate

The metabolism of malate has been studied intensively. The usual wine yeasts of the genus *Saccharomyces* are capable of metabolizing malate during the fermentation, but generally only about one fifth of the acid that is present in the must is fermented[28,69,90]. Therefore the change in total acidity is small. The biochemical mechanism for the decomposition of malate is the same for the yeasts of the genera *Saccharomyces*[29] and *Schizosaccharomyces*[18,83]. Malate is first oxidatively decarboxylated to pyruvate by an NAD-dependent malic enzyme. Pyruvate is decarboxylated to acetaldehyde which is reduced to ethanol. These reactions are catalyzed by two enzymes that are involved in the alcoholic fermentation. The overall result is that one molecule of malate yields two molecules of carbon dioxide and one molecule of ethanol. In addition, part of the malate is probably transformed to succinate via fumarate[40]. So far the attempts to employ