Aromatic and Phenolic Ripeness

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Everyone knows it: As the yield increases, quality declines. The quantity-quality-law is not at all a new discovery. Nevertheless, some producers have lost sight of its real meaning. Otherwise it is impossible to explain how in particular cases well over 10 tons per acre are still harvested. In many countries, the wine can be marketed as “Quality” wine if it is accepted as fault-free by a tasting authority or if some legally defined minimum Brix has been reached. Sugar content carries with it a mythical importance.

It is out of the question that products from largely overcropped harvests can be convincing as a beverage for pleasure and culture. They cannot be more than anonymous, interchangeable consumer or “processed” wines because they lack essential constituents making up the inner, sensorially transferable quality. Wine is more than an aqueous solution of alcohol, sugar, and acids. Ripeness in the sense of sugar content and extracts alone does not guarantee a pleasurable experience. Yet it is still a wide spread erroneous belief that quality can be determined solely by sugar content. Modern winemakers claim that they don't depend on numbers, but it's a rare one who does not rely on sugar, pH, or acidity reading when it comes to determine whether the grapes are ripe to pick.

Sugar content of the grapes defines exclusively alcoholic ripeness, i. e. the potential alcohol content. Beyond that one can also recognize a physiological ripeness, comprising aromatic and phenolic maturity. It is not directly bound to the alcoholic ripeness. At least not anymore, and even less as global climate change progresses. Therefore one can find completely unimpressive and one-dimensional high Brix wines.

Aromatic ripeness

Ripeness and yield are interdependent. During ripening, more is happening than merely an increase of sugar and a decrease of acidity. These two parameters stand nevertheless in the foreground during the measurement of maturity because they are easy to assess by simple technical means. The concept of “Aromatic Ripeness” is thereby ignored. Long after the increase of sugar content has stopped, the synthesis of aromatic compounds continues. These are the compounds which, at comparable macro-analytical parameters, allow us to differentiate between wines, especially between a cheap table wine and a complex late harvest wine. Otherwise wine description would be reduced to a monotonous repetition of the four basic tastes - sweet, sour, bitter, and salty.

Not only high yield, but also global climate change may explain why aromatic ripeness does not run proportional to alcoholic ripeness. Under dry ripening conditions, aroma synthesis is retarded, as in the case of excessive application of fungicides. Rot caused by fungus can bring the development of ripe aromas to a complete standstill. In extreme cases, that can cause a wine from grapes of 25 Brix or more to remind one of an aroma profile of 17 Brix grapes.

Deficiency of aromatic ripeness might be expressed in three ways:

- The absence of any aroma.

- The appearance of an untypical aging (ATA) flavor in white wines. The olfactory feature of those wines reminds the smell of mothballs, wardrobe, laundry, soap, lemon blossom, etc. Even though ATA is a widespread quality defect frequently occurring in young white wines soon after primary fermentation, it is often badly identified. Its origin is a hormonal stress in the vines as it might be induced by overcropping. Details will be discussed elsewhere.

- Vegy-green aromas, the distinguishing mark of unripe grapes and deriving from a group of compounds called methoxypyrazines.

Green-vegy aroma caused by methoxypyrazines

The green-vegy or herbaceous fraction of wine aroma is reminiscent of the smell of crushed blades of green grass, freshly mown lawn or raw potatoes. Everybody is familiar with this kind of smell from his daily life experience, but optimistic expectancy and the emotional approach many producers have to their own wines prevent them from expecting, searching, or identifying it in them. It can be so intensive that it eventually dominates overall aroma in a way that one cannot recognize any more the desired, pleasurable aroma attributes like ripe fruits, flowers, or minerals. Beside the smell, mouth feel and texture are also adversely affected by sensory synergisms. The acidity seems more than the wine actually has. The tannin of red wines appears harsher and more astringent.

By many wine growers around the world, the aroma pattern of that kind is not identified as what it really is, but confounded with common aroma defects of oenological origin which might be removed by some dubious fining procedure. Nevertheless, it has to be stated that an herbaceous aroma reminiscent of green grass represents a deficient aromatic ripeness which cannot be corrected for by any technical means.

Earliest research upon the occurrence of green-vegy flavor explained its origin in higher aldehydes of the C6-series like hexanal and hexen-2-al which are produced, respectively, by enzymatic oxidation of linoleic and linolenic acid during grape processing. In the meantime, there is evidence that the sensory impact of these molecules is insignificant compared with that of methoxypyrazines. The latter ones are constituents of all green tissues including those of the grapes. They are extracted during vinification and dissolved in the wine where they generally occur in traces of a few 10 ng/L. The most important representatives of this group of compounds are 3-isopropyl-2-methoxypyrazine, 3-butyl-2-methoxypyrazine, and 3-isobutyl-2-methoxypyrazine. The latter one is more abundant in quantity, while the first one reveals highest smell intensity (17).

Methoxyparazines are the primary cause of the green-vegy aroma flavor of unripe wines. In some cultivars like Sauvignon Blanc, Cabernet Sauvignon, Cabernet Franc, and probably Dornfelder too, they participate in varietal flavor so far as their concentration does not exceed a certain limit and their contribution to total aroma is in balance with other aromatic compounds (1). If there is not such a balance, methoxypyrazines dominate the flavor by their green-vegy characteristics.

Methoxypyrazines are stored in the grapes before veraison, and their synthesis is accelerated under humid growing conditions. After crossing a concentration peak, they decrease continuously during ripening. This decrease is to be explained by the impact of sunlight and correlates with the breakdown of malic acid. All viticultural factors contributing directly or indirectly to a better exposure of the grapes to sunlight, including leaf removal, accelerate this decrease. Regardless of the photo-degradation induced by sun exposure, high temperatures during ripening act in the same way. High yield and humid climate act inversely. Leaf removal and cluster thinning are more effective means for decreasing methoxypyrazines than a low number of buds during pruning. Fungi attack of unripe grapes yields higher concentrations not only because it compels early harvest, but also by promoting their extraction from the prematurely destroyed skin tissue (3, 13).

Skins, seeds, and stems contain more methoxypyrazines than the respective juice fraction. They are highly soluble and easily carried over from grapes into the wine. During grape processing, they reach their maximum concentration in the liquid phase after one day of skin contact. However, the presence of leaves and stems during skin contact of red grapes can contribute to further enhancement. In white wine vinification, harsh mechanical grape processing like excessive pumping and pressing gives rise to another enhancement, while removal of the last pressings may lower the concentration (13). In juices just pressed, a certain amount of the methoxypyrazines is bound to solids. Thus, a proper juice clarification may contribute to a further decrease (3). However, none of these treatments is able to avoid the appearance of a green-vegy flavor if this is an intrinsic feature of fruit quality.

Chemically, methoxypyrazines are quite stable molecules and resistant against changes of the redox balance of wine. Thus, the common wine treatments related to oxidation or reduction during vinification, stabilization, and aging hardly affect their concentration. However, there seems to be a slow binding to tannins in red wine when these are undergoing polymerization under semi-oxidative conditions like those occurring during micro-oxygenation. The lack of any reactions with absorbing materials is responsible for their stability against fining agents and filtration media. Their most important reaction is their photo-degradation mentioned above, i.e. their breakdown under the influence of light. This reaction may occur in the bottle, too. Wines bottled in white glass are undergoing a slow decrease of their green-vegy character, while those bottled in colored glass preserve it from decay. Current storage conditions in the dark do not allow for any decline of the herbaceous flavor.

Due to the solubility and chemical stability of methoxypyrazines, enological means of reducing their content are more than limited. Therefore, the specific viticultural tools for lowering their amount during grape ripening are of considerable importance (3).

Overcropped vineyard

Short-lived fermentation aromas

Clearly, different factors play a part in the formation of the total aromas perceived in wine. During alcoholic fermentation, the yeast produces a large array of volatile secondary metabolites acting as aroma compounds and used technically to complement the grape-derived aromatics. Having this background in mind, the winery supply industry proposes a large number of active dry yeast strains aiming to drive the sensory profile of the wine in one or another direction. As an alternative, some winemakers utilize spontaneous fermentation in order to impart more complexity and flavor individuality to their wines.

For the synthesis of aroma, the yeast uses suitable precursors available in the juice, essentially assimilable nitrogen (14). However, juices obtained from unripe grapes lack nitrogen. Correspondingly, the sensory result is modest. Unripe wines remain unripe.

All aroma compounds which are produced through and during alcoholic fermentation have a relative short live span. Because of their volatility, they evaporate, if in the course of stressful wine handling the wine is moved too frequently, racked in one form or another, or exposed to a static or turbulent liquid surface (19). Beyond that, they decompose solely through the effects of oxidation and acidic hydrolysis at wine pH. The breakdown is accelerated significantly by heat (8). That is the typical problem of warm cellars and bottle storage areas. If, from an identical juice, wines are produced with different aroma profiles by means of different fermentation procedures and yeast strains, these differences can only be observed while the wine is young, namely when the sensory effects of fermentation measures are most often evaluated (18). During storage, the differences between the lots tend to disappear. After approximately one to two years, and with improper wine handling or storage significantly faster, hardly any differences can be discerned. The aroma at the end of this stage which is still perceptible results overwhelmingly from the grape-derived aroma compounds. In the case of an unripe harvest, green aromas remain if they are not masked by some kind of aging flavor. If grapes from an excessive yield are used, no aroma remains at all with that of ATA as the only possible exception. Without any doubt, aromas derived from yeast metabolism are short-lived and can in young wines simulate a quality which the wine does not retain for long (18). By contrast, primary aromas arising from the grapes are much more stable over time. They vary according to the cultivar. The aroma potential of the grapes takes a decisive importance.

Analytical evaluation of aromatic ripeness

Since Brix as the sole quality criterion has become unsatisfactory and obsolete, there has been no lack of thought to replace the measurement of sugar content by a direct determination of aroma potential (21). In particular Australian research groups have distinguished themselves in this field of research. One analytical approach led to the determination of the so-called glycosyl-glucose content in grapes (20). The starting point of this consideration is that the primary aroma constituents contained in grapes and juice belongs to various groups of chemical compounds. In part they are yet unknown and cannot, because of their diversity, be embraced in one single measurement. Thus, an analytical breakdown followed by simple addition of their individual concentrations is not feasible for determining aromatic maturity.

In addition, the volatile aroma constituents in grapes are present to only a limited extent in the free form which is directly accessible to the sense of smell. The far greater proportion is bound as glycosides to sugars and sensorially neutral. After crushing the grapes and during storage of the wine, the sugar is split and the glycosidically bound aroma compounds are set free, whereby they become sensorially active. The splitting of the glycosides is promoted by the low pH of wine or catalyzed enzymatically. Heat accelerates the reaction as well as enzymes derived from yeast or added in winemaking practice as commercially available aroma enhancing enzymes (2, 6).

The sugars to which the grape-derived aroma compounds are bound can be of various types; nevertheless one molecule of glucose is required per molecule of aroma precursor. In contrast to the heterogeneous mixture of aroma compounds, this glucose is easily measured. The assumption is that it is completely split from the glycosides. Thereby one obtains the glycosyl-glucose. Its amount is proportional to the bound aroma compounds, i.e. the potential primary aroma able to be set free during the winemaking process. The technical procedure for measuring comprises the isolation of the aroma glycosides from a juice sample, its acidic hydrolysis by heat, and the measurement of the freed glucose. This glycosyl-glucose (in mg/L) is the quality index looked for.

Investigations in various countries have shown that the glycosyl-glucose has a tendency to increase with the degree of ripeness and to decline with increasing crop load. In some way and in most cultivars, it is correlated with the aroma intensity of the wine. The disadvantage of this technique is that only the bound and therefore sensorially inactive precursors of grape-derived aromas are measured, while the aromas already present in the free form and capable of being smelled are ignored. Furthermore, the use of this measurement implies that the totality of bound aroma compounds actually become unbound from sugar and sensorially active during the winemaking process. In practice, this reaction commences from the time of crushing the grapes. However, one question remains: How much of the aroma potential measured as glycosyl-glucose actually is converted into sensorially active aroma compounds?

This consideration encouraged the development of another method of determining the aromatic ripeness. Proceeding from the fact that the primary aromas of most grape varieties consist overwhelmingly of terpenes, these are distilled off and quantified in the distillate by means of a colorimetric reaction. One thereby gets the free terpenes which are directly accessible to the smell. After acidification of the sample, the glycosidically bound terpenols are freed and captured through a second distillation. Both fractions – free and bound terpenes – are expressed in mg/L of a reference terpene, for example linalool (7). In some grape varieties like those belonging to the Muscat family, there is a very close correlation between terpene concentration and aroma intensity, while in other ones characterized by non-terpene aromatics like Sauvignon blanc, there is no correlation at all.

Phenolic ripeness

Beyond aromatic ripeness, phenolic maturity enters as a further parameter in the quality of red grapes. Phenols are the building units of all tannins and colored pigments. The grapes must contain them in sufficient quantity and quality if one wants to produce a serious red wine. There are analytical approaches for determining the extractable phenolic potential (4, 5, 10, 12, 16). Unfortunately, their practical use is yet limited because results of the various methods are difficult to compare.

Grapes which are phenolically unripe contain high amounts of extractable, strongly astringent tannin in their seeds. As ripeness progresses, the extraction of less aggressive tannins from the skins increases (11, 15). Small tannin molecules of a low degree of polymerization, like those obtained from unripe grapes or too short a skin contact time, taste nervous and sour, even at low total acidity and high pH. Differences in phenolic ripeness explain why the tannin from unripe grapes can simulate up to 1.5 g/L total acidity while ripe tannin can impart a lightly sweet taste.

Tannins form complexes with colloids of a non-phenolic nature, in particular polysaccharides and proteins. Depending on the kind and concentration of the proteins and polysaccharides, the same tannin molecules can be sensorially perceived as "good" or "bad" tannin. Complexation with acidic polysaccharides increases their astringency. Neutral polysaccharides like mannoproteins diminish their astringency (9).

A part of the tannins complexes with colloids is extracted from the grape skins. Such tannins associated to proteins or polysaccharides taste softer as the phenolic ripeness of the grapes advances. They impart to the red wine mouthfeel and weight. In contrast, the tannins from the seeds show a lower degree of polymerization without colloidal complexation. They are highly astringent, explaining thus why some red wine maceration processes use seed removal. Unripe tannins can only partially be improved during aging with the oenological tools of tannin management.

Sensory evaluation of physiological ripeness

For the evaluation of ripeness, Brix is losing its significance, while the practical application of analytical assessments of aromatic and phenolic maturity is narrowly limited. Most often, the size too small of grape lots precludes the routine use of these expensive procedures. Therefore, the sensory evaluation (16) of physiological ripeness is of increasing importance. Such an evaluation uses the human senses of touch, taste, and sight. It includes:

- The visual assessment of the grape quality: Lightly transparent, yellowish-green colored skins with golden shades indicate ripeness of white grapes; green skins reveal a lack of maturity. Red grapes should release color from the skin when rubbed between the fingers. When perfect ripeness is reached, the berries can be easily removed from the stalks. A brown, wooden stem tissue of red grapes points out a perfect phenolic ripeness.

Unripe grapes

Ripe grapes

- Squeezing the berries: Ripe berries remain deformed after mild squeezing with the fingers, but unripe berries are elastic and turn back to their initial form. When the berries are crushed completely, brown and hard seeds are easy to detach from the juice pulp if the grapes are ripe. In premature fruit, the seeds are green, soft, or mealy; they have a bitter flavor and adhere to a gelatinous pulp.

- Smelling and chewing the berries: It is easy to distinguish unripe berries from ripe ones only by smell. To be ripe, the pulp should be free of herbaceous notes and viscosity. Gelatinous adherence of the pulp to the skin or seeds goes along with a lack of maturity. The skins should be crumbling after chewing and not tough.

Representative fruit sampling is crucial to overcome the variability of ripeness within a vineyard block. It requires selecting berries from many different clusters and from a different part of the cluster each time as one walks through one or two rows. Generally, more than one evaluation will need to be performed in each vineyard. The proceeding seems tedious at the first glance, but it is efficient when it comes to avoid picking unripe grapes.

Concentration cannot replace ripeness

Since the implementation of must concentration devices, hope has been nourished in some segments of the wine industry that by means of this technology, unripe and thin wines obtained from overcropping can be converted to ripe and mouthfilling products. This hope has not been fulfilled. Wines disadvantaged by lack of ripeness and overcropping offer not only a shortage of sensorially positive flavor compounds, but also components of unripeness. Through concentration all components are concentrated in the proportion they are provided at by the grapes. Therefore, ripe musts can be improved with concentration while in the unripe ones; the green-vegy flavor is concentrated.

These quite obvious results prove that any quality deficiency of the grapes cannot be overcome by enological means in the cellar. Basically, quality can only be produced in the vineyard. In the cellar it can at best be preserved. What the wine does not have cannot be brought to it by fining, filtration, or any other treatment. In some circles, however, the mistaken belief still rules that bad wine can be made better through excessive cellar equipment or the treatment with diverse fining agents or additives in various packages and brands. Most of them are unnecessary or even counterproductive, even though they are strongly supported by diverse commercial interests. In extreme cases, the wine is processed to death and fined to emptiness. Wines obtained from unripe grapes do not require enology, nor do they offer any scope for its application. In the best case a limiting of the damage is possible.

Summary

Sugar content of grapes is an unreliable parameter to predict grape and wine quality. Under conditions of progressing global climate change, extreme climates, overcropping, and harvest of premature fruit, the correlation between Brix and overall quality lacks any practical significance. Alternatively, the concept of physiological maturity, including aromatic and phenolic ripeness, is presented. Analytical and sensory means of their assessment in grape samples are discussed. Deficiencies in physiological ripeness cannot be corrected for by enological tools.

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