CHEMICAL SYSTEMS BEHIND WINE AROMA PERCEPTION: OVERVIEW, GENESIS AND EVOLUTION•

Ana ESCUDERO, Vicente FERREIRA
Laboratory for Flavor Analysis and Enology - University of Zaragoza, E
E-mail: escudero@unizar.es

Key words: flavour, aroma buffer, impact chemicals

1. INTRODUCTION

The aim of this presentation is to show the latest findings in the chemical interpretation of wine aroma. Such findings are mainly related to the understanding of the way in which the aroma chemicals interact to form the different aroma nuances of wine.

To know the wine aroma, initially it is necessary an aroma extraction to GC-olfactometry analysis. By GC-MS we make qualitative and quantitative analysis to obtain quantitative lists. With these, sensory tests are essential to compare with the wine glass aroma. Our work has two parts: the aroma deconstruction and the aroma reconstruction.

The originality of the procedure is the fact that we have been tracking back the key odour molecules finally perceived in the glass of wine. We only analyze the key odorants finally perceived in the glass of wine, not all odorants.

2. AROMA BUFFER

Ethanol and the other major fermentation volatiles form a sort of "aroma buffer" which is not easy to break.

A normal table wine contains several hundreds of volatile compounds, but most of them are at concentrations well below the threshold, which means that they are not really relevant in the perception of the sensory attributes of the wine. The number of odour molecules really active in a normal wine lies between 20 and 40, and the total number of odour molecules that can be really active in the different kinds (without odour problems) of wines is around 70. What we need now is to find a series of rules to put some order into these relatively high numbers.

A first key to such issue consists of realizing that some aroma compounds are present in all wines, independent of their origin and kind. These groups of compounds are of course these volatile aroma compounds produced by fermentation at relatively well-defined proportions. All these 22 compounds are present at concentrations well above threshold in nearly all wines and they form a particular aroma mixture with the aroma we often define as vinous. It is slightly sweet, pungent, alcoholic and a little bit fruity (Escudero *et al.*, 2004). Another compound, β-damascenone, can also be included in this list because although it is not formed by yeast during fermentation, it can also be found in nearly all wines at concentrations above threshold.

• QUAD. VITIC. ENOL. UNIV. TORINO, 31, 2009-2010

3. CLASSIFICATION OF WINE ODORANTS

The buffer can be broken just by certain molecules, and particularly by groups of molecules acting sinergically. The following classification is a new proposal based on observation, but it is based on well-established concepts of flavour chemistry (Belitz, Grosch, 1999).

3.1. Genuine impact compound. This role is played by individual compounds which, in a given wine, are at concentration high enough to transmit to that wine their specific aroma nuances, i.e., the aroma of the compound can be recognized in the wine.

3.2. Major contributor. This role is played by individual compounds or by families of aroma compounds that are present in the wine at a concentration high enough to transmit to the wine a primary generic descriptor (red fruit, citric, minty) of its aroma, but not the specific descriptor of the compound (i.e., the compound cannot be clearly recognized in the wine). The transmitted descriptor in the wine is nearly entirely due to the compound so that, if the compound or family of compounds are removed, then the sensory effect will be very intense qualitatively and quantitatively.

3.3. Net contributors. This role is played by individual compounds or by families of aroma compounds that are present in the wine at a concentration high enough to transmit to the wine a generic descriptor. Such a descriptor is also contributed by other compounds or families of compounds so that if the compound or family of compounds are removed, then a significant decrease in the intensity of the odour nuance will be noted, but a major change in the qualitative aroma profile will not be observed.

3.4. Secondary or subtle contributors. This role is played by those individual compounds or families of aroma compounds that are present in the wine at a concentration below that required to transmit individually to the wine one of its generic descriptors. However, such aromatic descriptor (usually very general, such as sweet or fruity) is noted because of the concerted action of many aroma molecules or families. Accordingly, if the compound or family of compounds is removed from the wine, the sensory effect will be very weak or even null.

3.5. Aroma enhancer. This role is played by those individual aroma molecules or families of aroma compounds which fail to transmit to the wine their specific or generic descriptors but nonetheless enhance the specific aroma of some other molecule or group of molecules present in the wine. In some case, the enhancement brings about a new aroma quality as a consequence of the mixture of the odours of aroma and enhancer, while in some others the effect of the enhancement is merely the increase of the aroma intensity. In any case, if the enhancer is removed, then a decrease in the intensity of an aroma nuance, not directly related to the aroma of the enhancer, will be noted.

3.6. Aroma depressor. This role is played by those individual aroma molecules or families of aroma compounds whose presence in the wine causes a decrease in the intensity of an odour note. If the depressor is removed from the wine, then an increase in the intensity of the depressed odour nuance is noted.

In summary:

- twenty two compounds form the base of the aromatic perception of wine;

- forty seven compounds (but only 26 aroma types) are mainly responsible for acute sensory differences between wine types and varieties: 16 impact compounds and 31 in families with 10 different odours;
- six particular compounds may act as aroma enhancers;
- more than 30 compounds can spoil or affect negatively wine quality (even if they are not perceived as such).

4. WINE AROMA FORMATION

The most relevant notes of great wines are caused by complex associations of aroma compounds playing different roles (contributors, suppressors or enhancers).

The flowery notes are explained by the base of terpenols (<20 ppb), ethyl cinnamates, β-phenylethyl acetate, vanillins and γ-lactones. The creative, competitive and destructive interactions are important in flowery notes.

The fruity notes in white wine are explained by the base of ethyl esters, acetates and β-damascenone and the freshness by small amounts of cysteinyl-related mercaptans. Spoilers of fruity notes also exist.

Red wines are, by nature, much more complex since, among many other factors, they contain quite large amounts of volatile phenols which exert a suppression effect on fruity notes (Atanasova *et al.*, 2004). This phenomenon is still more intense when the wines have been aged in oak casks, increasing the concentrations of volatile phenols and adding whiskylactones. In this chemical environment, the perception of the different notes, particularly fruity notes, is extremely complex. In addition, great red wines do not have explicit or specific odour nuances, but a large palette of many subtle odours. It is not surprising, therefore, that in red wines, leaving aside whiskylactones, most often we do not find genuine impact compounds, but relatively large groups of compounds which contribute to the different odour nuances.

Up to this date, we have identified several major contributors to the fruity notes of red wines:

1. the concerted action of ethyl esters, including here several recently discovered branched ethyl esters, with norisoprenoids (β-damascenone and β-ionone) and with the enhancing effect of dimethylsulfide, that can impart berry fruit notes to the wine (Escudero *et al.*, 2007);
2. the concerted action of five γ-lactones (γ-octa-, nona-, deca-, undeca- and dodecalactones) that can be responsible for the peach notes of some reds, particularly from certain areas of Spain and Portugal (Jarauta *et al.*, 2006);
3. the concerted action of furaneol, homofuraneol, maltol, sotolon, norisoprenoids and methional that can be responsible for some cherry and chocolate notes of some reds (Ferreira *et al.*, 2005).

It is very interesting to note the hierarchy of the sensory notes and hence of the aroma chemicals in wine. In a recent study relating the odorant composition, measured by gas chromatography-olfactometry, with wine quality, this parameter was found to be related to three major vectors formed by the summation of groups of odorants (Ferreira *et al.*, 2009). The vector with major and more negative influence was formed by the summation of ethyl phenols, TCA and 3, 5-dimethyl-2-methoxypyrazine, while most wines were of course not

corked (no one was classified as such) nor too rich in ethylphenols. Therefore, this result not only means that a wine containing a high concentration of ethylphenols or trichloroanisol is a bad wine, but that the general quality of a commercial red wine is inversely related to the content it has in these compounds, *i.e.*, all these compounds at concentrations far below the recognition threshold are exerting a strong depressing effect on the wine fruitiness as previously suggested (Aznar *et al.*, 2003).

5. DYNAMICS OF AROMA COMPOSITION

The aroma of wine is not static. The wine aroma is continuously evolving. Aroma decreases by hydrolysis of fruity esters, chemical rearrangements, oxidation or adsorption. Aroma increases by esterification of acids, hydrolysis of precursors, oxidation or extraction. It can be considered as a "living system" in which aroma precursors act as "pumps", delivering a continuous flow of odour chemicals until its exhaustion (the death).
The grape plays an outstanding role in such living system by:
a) conditioning yeast by products (and hence the buffer),
b) direct delivering of odour chemicals (released by yeast),
c) delivering the pool of precursors during aging.

Abstract

This talk presents a revision of our knowledge and understanding of the role played by the different aroma chemicals in the positive aroma attributes of wine. A systematic approach to classifying the different aroma chemicals of wine is presented . One basic idea is that all wines share a common basic aromatic structure formed by ethanol and 27 different aroma compounds, most of them by-products of fermentation. The mixture of those products has the typical vinous aroma and exerts an aroma-buffering effect with the ability to suppress the effect of many odorants added to it, particularly those with fruity characteristics. The ability of the different odour chemicals to break such a buffer, and hence transmit a different aroma nuance to the wine, and the relationship between the transmitted aroma nuance and the aroma of the chemical are used to define the different roles played by aroma compounds on wine aroma. These roles can be as impact compounds, major contributors, net contributors, subtle aroma compounds, aroma enhancers and aroma depressors. The subjects can be individual aroma chemicals or well-defined mixtures of molecules sharing chemical and odour properties (aroma families). Different examples of the aroma chemistry behind some of the most relevant wine aroma nuances from simple or complex wines are also presented and discussed.

Literature cited

Atanasova B., Thomas-Danguin T., Langlois D., Nicklaus S., Etievant P. – 2004 - Perceptual interactions between fruity and woody notes of wine. *Flavour Frag. J.*, 19, 476–482.

Aznar M., Lopez R., Cacho J., Ferreira V. – 2003 - Prediction of aged red wine aroma properties from aroma chemical composition. Partial least squares regression models. *J. Agric. Food Chem.*, 51, 2700–2707.

Belitz H. D., Grosch W. – 1999 - *Food Chemistry*, 2nd ed, Springer-Verlag,Berlin, D, pp. 340.

Escudero A., Gogorza B., Melús M. A., Ortín N., Cacho J., Ferreira V. – 2004 - Characterization of the aroma of a wine from Maccabeo. Key role played by compounds with low odor activity value. *J. Agric. Food Chem.*, 52, 3516–3524.

Escudero A., Campo E., Fariña L., Cacho J., Ferreira V. – 2007 - Analytical characterization of

the aroma of five premium red wines. Insights into the role of odor families and the concept of fruitiness of wines. *J. Agric. Food Chem.*, 55, 4501–4510.

Ferreira V., Torres M., Escudero A., Ortín N., Cacho J. - 2005 - Aroma composition and aromatic structure of red wines made with Merlot. In: Hofman P S T (ed.). *State of the art in flavour chemistry and biology. Proc. 7th Wartburg Symp.*, Deutsche Forsch. Lebensm. Garching, D, 292–9..

Ferreira V., San Juan F., Escudero A., Culleré L., Fernandez-Zurbano P., Saenz-Navajas M. P., Cacho J. – 2009 - Modeling quality of premium Spanish red wines from gas chromatography-olfactometry data. *J. Agric. Food Chem.*, 57, 7490–7498.

Ferreira V. – 2010 - Volatile aroma compounds and wine sensory attributes. In: A. G. Reynolds (ed) *Managing wine quality. Viticulture and wine quality.* CRC Press. Boca Raton, FL, USA, 3-23.

Jarauta I., Ferreira V., Cacho J. – 2006 - Synergic, additive and antagonistic effects between odorants with similar odour properties. In: Bredie W.L.P., Petersen M.A. (eds) *Flavour science: recent advances and trends*. Elsevier, Amsterdam, NL, 205–208.