NEGATIVE INFLUENCE OF TEMPERATURE OVER FLAVOR COMPOUNDS FROM WINE

INFLUENŢA NEGATIVĂ A TEMPERATURII ASUPRA COMPUŞILOR DE AROMĂ DIN VIN

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Abstract. *The aromatic profile of wine is offered by the variety of volatile chemical compounds, especially esters, alcohols, carboxylic acids and nitrogen compounds. These substances can determine different aromas depending on concentration. One of the very important factors in forming aromas is the fermentation temperature whose which has an optimal value between 15-17 °C. This study evaluated wines samples which were fermented without temperature control, reaching an average temperature in between 21-24 °C. Following this experiment it was observed how the compounds that give floral and fruity aromas can give unwanted sensations in high concentrations. At the same time, several esters of the fatty acids were observe which give a heavy smell and cause the sensation of fats. The aromatic profile of the sample which was fermented at higher temperature is more affected, even becoming repulsive once the temperature is rising.*
Key words: wine, faults, GC-MS

Rezumat. *Profilul aromatic al unui vin este oferit de varietate de compuşii chimici volatili, în special esteri, alcooli, acizi carboxilici şi compuşi ce conţin azot, care pot imprima diferite arome în funcţie de concentraţia în compuşi. Un factor foarte important în formarea percepţiei aromatice îl reprezintă temperatura de fermentare a cărei valoare optimă trebuie să fie cuprinsă între 15-17 °C. În acest studiu s-au evaluat o serie de probe de vin care au fost fermentate spontan fără control de temperatură, ajungându-se la o medie a fermentaţiei de 21-24 °C. În urma acestui experiment s-a putut observa cum compuşii care dau arome florale, fructate, la concentraţii ridicate conduc la apariţia unor senzaţii generale nedorite. Au fost identificaţi mai mulţi esteri ai unor acizi graşi care imprimă un miros greu, dând astfel o senzaţie de gras. În plus, s-a observat că profilul aromatic al probelor fermentate la temperatură mai ridicată este mai afectat, devenind chiar repulsiv odată cu creşterea temperaturii.*
Cuvinte cheie: vin, defecte, GC-MS

INTRODUCTION

The fact that at the base of the transformation from must to wine it is the alcoholic fermentation is the core of one of the most famous beverage in the wold. The specialists in this area have established certain temperature intervals in which

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the fermentation can bring advantages or disadvantages for the wine quality. A wine's aroma consists of several classes of chemical compounds, each with its own sensation or particularities. For the wine to get as rich as possible in aromas, the ideal fermentation temperature has to be between 15 and 18 °C. A temperature above 20 °C certainly will affect the wine's quality and aromatic profile (Țârdea *et al.*, 2000; Cotea *et al.,* 2009).

A sensorial analyse of wine has a varied vocabulary of descriptors classified into categories and sub-categories which indicate the primary attributes or aromas (which are given by the raw material – generally grapes), middle aromas (or secondary that are given by compounds obtained during alcoholic fermentation) and tertiary dominant aromas (which are given by the wine maturation processes). Among these we note in the primaries: flower, fruit, vegetal, spice, caramel, wood, earth, oxidized or even chemical product, fermentative aromas where the latter are in the category of unwanted aromas that can be flaws. A more clear and detailed classification was offered by Ann Noble in 1984 through what is called the "aromas' wheel" (www.winearomawheel.com). Helping ourselves with the "wine's nose" (www.lenez.com) and with the aromas' wheel still does not make it easy to completely and correctly identify the aromas found in a wine sample. For this, a chromatographic gas analysis is usually needed. This gives us a more complex view due to the chemical compounds that it can identify and whose aroma is approximately known.

A problem in characterizing these volatile chemical compounds is their perception threshold and the fact that most of them can have different sensory perceptions based on the concentration in which they are found in an environment (Yusen *et al*., 2016). The threshold at which a chemical substance is perceived as pleasant or unpleasant is based on each person's olfactory sensitivity and the level of awareness of the smell (Monique *et al.,* 2008). Therefore, an evaluation of the aromatic profile using chromatography was tried taking into account the possibility of the presence of different attributes even for the same compound.

MATERIAL AND METHOD

The samples used in the experiment were wines obtained spontaneously in fermentation, with no temperature control, in which an average of 21-24 °C was reached. The first spontaneously fermented samples were at a maximum of 28 °C and the second one is a maximum of 32 °C.

The analysis method for determining the volatile compounds is gas chromatography coupled to mass spectrometry detection which was performed in this study using a Shimadzu HS 20trap-GC 2010plus-MS040TQ. Seven millilitres of wine where taken from which sample and analysed. The analysis method used as well as the details about the device's components and its parameters are described in literature (Tarțian *et al.,* 2017).

The results were qualitatively processed by comparing them with tree databases for mass spectrums. In order to obtain quantitative results the samples were processed by benchmark against an internal standard of 4-metil-2-pentanol. The area of the chromatographic peak corresponding to the internal standard was used to

compute the concentrations of the other identified compounds, which were expressed in µval eq. SI (microval equivalent of internal standard).

RESULTS AND DISCUSSIONS

The volatile chemical compounds obtained are in variety of categories: alcohols, esters, carboxylic acids, aldehydes and ketones. Among these, normally found also in wine in different quantities comparative to samples which were fermented at normal temperatures. The fermenting temperature of the wines was different and as expected the concentration of the compounds is different as well or even new compounds to appear. The following table shows the chemical compounds that were identified in the samples analysed using gas chromatography (tab. 1).

Table 1

The concentrations of chemical compounds identified using gas chromatography

Class	Chemical compounds	Concentration (µval eq. SI)		Particularities of flavour
		ferm. 32 °C	ferm. 28 °C	
Alcohols	2-methyl-1-butanol	186.33	20.46	green, malt, onion, fish oil
	3-methyl-1-butanol	1072.6	762.97	floral, cocoa, malt, burnt
	2-nonanol	46.03	ND	cucumber
Alcohols	3-methyl-1-pentanol	66.33	83.00	floral
	1-hexanol	2653.3	ND	characteristic, sweet, pleasant
	2-heptanol	ND	80.45	citrus, earth, fried, mushroom
	3,3,5-trimethylcyclohexanol	81.61	83.87	mint, cool
	2,6-dimethyl-7-octen-2-ol	12.24	10.56	fresh, citrus, lime, floral, clean, weed, woody
	1-octanol	ND	95.39	bitter almonds, floral fat
	2,3-butanediol	203.89	333.01	buttery, rancid butter, plastic, rubber
	1-nonanol	11.08	ND	floral, green. fat, oil
	1-decanol	32.09	16.07	fatty
	benzyl alcohol	9.03	4.76	boiled cherries, musk, rose
	phenethyl alcohol	1503.2	800.80	fruit, honey, lilac, rose
	phenol	6.44	4.44	rubber, plastic, heavy
	1-nonadecanol	87.50	ND	combustible
	phenethyl acetate	42.18	28.65	floral, rose, honey
	isoamyl acetate	10.48	99.02	banana and pear
	ethyl lactate	999.52	404.43	butter, in large quantities: lactic souring
	hexyl formate	ND	98.30	fruity
	amyl formate	ND	14.52	fruity
	ethyl pelargonate (wine ether)	ND	27.12	fruits, banana, apple, rose, tropical, cognac, wax
	ethyl 3-hydroxybutanoate	ND	62.99	red fruit, fresh fruit (marshmallow, roasted nuts)

	ethyl benzoate	53.47	43.96	flower, fruit, chamomile, celery, fat
	diethyl succinate	359.01	ND	floral, fruity, cotton, fabric, wine
	ethyl dodecanoate	ND	27.32	floral, fruit, leaves
	ethyl octanoate	340.78	4.85	apricot, pineapple, floral, brandy, fat
	ethyl decanoate	607.30	755.90	sweet, fruit, pear, apple, cognac, wax
	isopropyl myristate	54.83	23.68	dairy
	ethyl pentadecanoate	14.30	23.33	wax
	methyl isopalmitate	7.76	5.81	fruity
	ethyl palmitate	142.82	134.40	wax
	ethyl stearate	5.60	8.89	wax
Carboxylic acids	benzoic acid	40.77	49.73	fat, convulsive
	octanoic acid	286.56	777.13	cheese, fat, grass, oil
	acid acetic	2438.3	2521.6	irritating, pungent
	isobutyric acid	ND	128.24	burned, butter, cheese, sweat
	butanoic acid	347.38	246.88	butter, cheese, sour
	hexanoic acid	138.26	581.69	cheese, oil, viscous, sour
Aldehydes and ketones	acetophenone	ND	46.86	almonds, flower, meat, must
	benzophenone	6.17	68.47	geranium, sweet, rose
	benzaldehyde	62.88	16.72	bitter almond, burnt sugar, cherry, malt, burnt pepper

ND-not detected

As the table shows, a large part of the chemical compounds that are part of a wine's aroma give it floral and fruity notes. These are specific to wines, although it depends on the concentration in which they are present. An example is ethyl octanoate which in low concentration can give a fruity aroma (pineapple, apricot), floral, but it can also give a fatty note if it is present in larger concentrations. This difference was also observed in the analysed samples. Another fruity ester which in large concentrations gives unwanted waxes notes is ethyl decanoate. Diethyl succinate has an aroma specific to a floral wine, fruity but there can also be notes of cotton, fabric. Among these floral-fruity compounds that can be repelling at the same time there are other compounds which keep their pleasant aromas. Some examples of these are the esters hexyl format, amyl format, ethyl pelargonat, ethyl 3-hydroxybutanoate and isoamyl acetate. Sweet, fruity and pleasant aromas are also given by the 3-methyl-1-pentanol and 1-hexanol, these being the middle alcohols (with the number of carbon atoms between 4 and 6) known in literature for having a pleasant smell. An important alcohol is the phenethyl alcohol – a compound that is found in different quantities in the two samples. Its concentration in the sample fermented at 32 °C is 0.183 g/L which is above the 0.1 g/L threshold that signals a stingy, herby aroma, while the concentration in the sample that was fermented at 28 °C is 0.097 g/L and is within the threshold that gives it a pleasant aroma such as honey, fruity, floral like lilac or rose (Cotea *et al.,* 2009).

Others prevailing aromas that were observed in both samples and in rather high concentrations are the fatty aromas of oil, or wax, buttery and cheesy. A clear example is the ethyl lactate which determined the lactic souring that was present in high concentrations. Other compounds are butanoic, hexanoic and octanoic acids whose smell is cheesy, sour or even oily. The wax smell can be sense because of the ethylic esters of the hexadecanoic and pentadecanoic acids respectively. The fatty sensation is also given by 1-decanol which is found in both samples, although in a higher concentration in the sample where the fermentation reached 32 °C.

A clear observation is the presence in high concentrations of the acetic acid which indicates that the wine vinegary process. It is known the fact that this happens during the alcoholic fermentation of the must when the temperature reaches 28-30 °C and instead of the continuation of the alcoholic fermentation, an acetic fermentation starts. Due to the fact that in our experiment the fermentation reached the temperatures of 28-30 °C it was expected that the prevailing smell of the wine to have such a sensorial shift, being more unpleasant in the sample fermented until 32°C. Aside from acetic acid which is prevailing in the wine vinegary process there is also hexanoic acid which is found in the analysed wines. We observed that in the case of the sample fermented at 28 °C the quantity of hexanoic acid is greater than in the case of the sample fermented at 32 °C. Ethyl lactate is a compounds that in large quantities determines lactic souring, behaviour observed especially at the sample fermented at 32 °C (Cotea *et al.,* 2009).

From the category of the compounds that give strange, unpleasant aromas, are the 2,3-butanediol which has a smell of plastic, rubber and was found in relatively large quantities in both samples. (www.odour.org.uk). Hydroxybenzene gives the same heavy rubber smell and 1-nonadecanol which can give a sensation of fuel. In the same category is the 3-methyl-1-butanol alcohols which give a cocoa (which in wine is not a sensorial advantage), malt or burnt aromas and its isomer, the 2-methyl-1-butanol whose common aroma descriptor is the malt to which onion or fish oil are added (www.thegoodscentscompany.com). Aside from these, another compound which attracts attention through its various aromas is the 2-heptanol. This is usually found in wine and it gives citric aroma when it is found in trace quantities (www.pubchem.ncbi.nlm.nih.gov). If the concentration is, however, greater than usual for a wine sample, then the 2-heptanol gives earthy, mushroom or fried notes which can be sometimes disturbing (www.phenol-explorer.eu; www.leffingwell.com).

Analysing each compound class we can see that the alcohols are largely responsible for the unpleasant and repelling aromas in the samples, especially the methylic isomers of butanol. Aside from these, but also giving unwanted aromas, are the carboxylic acids which significantly contribute to the sensations of sour, cheese, butter or oil. Their proportions are relatively close to each other with the exception of the octanoic acid which was found in higher quantities in the sample fermented near 28 °C. Generally known for their wide palette of pleasant aromas, the esters give in our case fruity-floral notes, especially through the isoamyl acetate and ethyl octanoate. Contributing in a positive manner is the class of

aldehydes and ketones through the sweet, pleasant aromas of the benzophenone and benzaldehyde. Aside from the volatile compounds presented in the table there were also others identified that belonged to these classed, but for which the literature does not give information regarding their aroma or smell.

CONCLUSIONS

By carefully consideration the concentrations of the compounds that give fruity-floral pleasant aromas, but also at the same time give unwanted aromas, we see that the sample fermented at a maximum of 28 °C shows stronger pleasant aromas in contrast to the one fermented at a maximum of 32 °C which has more repelling sensations. In this study, the pleasant and positive notes are generally given by esters, aldehydes and ketones and the repelling notes which prevail are contributing to the unpleasant aroma by the carboxylic alcohols and acids that are resulted mostly from the fermentation process. Furthermore, in this study the fact that a fermentation at high temperatures, that are above 20 °C causes the appearance of unwanted aromas in the wine which greatly decrease its sensorial quality by processes of acetic fermentations, lactic and tartaring souring, and also cheesy, fatty, waxy sensations.

REFERENCES

1. **Cotea D.V., Zănoagă C., Cotea V.V., 2009 -** *Tratat de oenochimie* Vol. I and Vol. II, Editura Academiei Române.
2. **Monique A.M. Smeets Hendrik N.J. Schifferstein S. R. Boelema G. L.-M., 2008 -** *The Odor Awareness Scale: A New Scale for Measuring Positive and Negative Odor Awareness*, Chemical Senses, vol. 33, 8, p. 725–734.
3. **Tarțian A.C., Cotea V. V., Niculaua M., Zamfir C.I., Colibaba C. L., Moroşanu A. M., 2017** - *The influence of the different techniques of maceration on the aromatic and phenolic profile of the Busuioacă de Bohotin wine*, BIO Web of Conferences, 9, 02032.
4. **Țârdea C., Sârbu Gh., Țârdea Angela, 2000** - *Tratat de vinificație*, Editura "Ion Ionescu de la Brad", Iaşi, p 329-337.
5. **Yusen W., Shuyan D., Liping Z., Zhen G., Meng L., Shiren S., Wenping X., Caixi Z., Chao M., Shiping W., 2016** - *Aroma characterization based on aromatic series analysis in table grapes*, Scientific RepoRts, 6, 31116.
6. ******* http://www.winearomawheel.com
7. ******* https://www.lenez.com/en/kits/wine
8. ******* https://pubchem.ncbi.nlm.nih.gov
9. ******* http://www.thegoodscentscompany.com
10. ******* http://phenol-explorer.eu
11. ******* http://www.leffingwell.com/odorthre.htm