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Evaluation by a GC Electronic Nose of the Differences in Volatile Profile Induced by Stopping Fermentation with Octanoic and Decanoic Acid to Produce Sweet Wines

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Abstract: Due to their inhibitory effect on the growth and fermentation of yeasts, medium-chain fatty acids can be used for the production of naturally sweet wines. Addition of octanoic acid, decanoic acid or their combinations is able to stop the alcoholic fermentation, reducing at the same time the doses of sulphur dioxide addition needed for the same goal in the classical technologies. Doses in the range of 10–30 mg L^{-1} of these acids were used, and their effect on the aroma profile of the sweet wines obtained was evaluated by using a chromatographic electronic nose with two columns. Based on the chromatographic peaks, which are considered the sensors of this e-nose, differentiation of the wines treated with octanoic or decanoic acids is easily achieved. The acid doses, the type of acid and also the yeast used for fermentations have all detectable influences on the volatile profiles of the wines. Discriminant factor analysis was applied on the e-nose data to separate the wines obtained with different treatments. Several differences in the content of the volatile compounds were identified and discussed in view of their sensory influences and the impact of treatment and yeast, respectively. Special attention was given to the formation of ethyl octanoate and ethyl decanoate which, at acid additions over 10 mg L^{-1}, are formed in quantities which have a detectable influence on the aromatic profile. Ethyl octanoate and decanoate are produced in direct relation to the dose of the corresponding acids, but the yeast named ST leads to higher amounts of ethyl decanoate while the one named ERSA leads to higher amounts of ethyl octanoate. In accordance with the e-nose results, the aromatic profile obtained by stopping the fermentation with decanoic acid and using the ERSA yeast is more complex, the wines thus produced preserving more of the varietal and fermentation aroma. This research will be continued at an industrial scale.

Keywords: electronic nose; sweet wine; medium-chain fatty acids; octanoic acid; decanoic acid; ethyl octanoate; ethyl decanoate; aroma volatile profile

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1. Introduction

The production of naturally sweet wines generally relies on stopping the fermentation, the most common technique for this being the addition of large quantities of sulphur dioxide [1] and lowering the temperature until the yeast is not able to survive. Sulphur dioxide is an additive that is very useful for the antioxidant protection of wines and also for their microbiological stabilisation. However, the usage of high concentrations of sulphur dioxide is not desirable, as some people can be sensitive to this product or its related compounds that are formed in acidic media such as wine [2]. To lower the SO_2 doses necessary to stop the fermentation in order to produce sweet wines, other alternative techniques were sought for some time. Based on the observation that medium-chain fatty acids (MCFAs), such as hexanoic, octanoic, decanoic and dodecanoic acids, naturally produced by the yeast during fermentation [3] to protect themselves against other yeasts, could sometimes even lead to unwanted stuck fermentations [4–6], researchers came up with the idea of adding these acids on purpose in order to arrest fermentation at appropriate times [7]. In this way,

instead of the high doses required to stop fermentation, only low doses of SO_2 are still needed, for the normal antioxidant protection of wines. Taking into account that these acids are natural products, for which—in normal concentrations—no negative effects on human health were found [8,9], the International Organization of Vine and Wine (OIV) also decided to accept this practice of stopping the fermentation by adding medium-chain fatty acids, an OIV resolution being presently under discussion. Several studies were carried out and the results initially showed that doses in the range of 10–20 mg L^{-1} would be sufficient to arrest the fermentation and produce sweet wines [7,10,11].

In this context, looking for an alternative method to produce our traditional wines of Tămâioasă românească at Pietroasa Research Station, we also decided to investigate this procedure and to evaluate the influences that adding medium-chain fatty acids can have on the aromatic profile of this aromatic wine.

In order to evaluate the aroma profile of the resulting wines, an electronic nose with two short chromatographic columns of different polarities was used. The goal was to determine the influences on the aroma of the type of acid used, as well as of the dosage, not neglecting the possible effect of the fermentation yeasts inoculated, which can produce different concentrations of fermentation by-products in such complex media. Differentiation of the groups of wines produced by stopping fermentation with octanoic acid, decanoic acid and their combinations was pursued by using the e-nose.

2. Materials and Methods

2.1. Wine Variants Preparation

The experimental variants were prepared with grapes of the Tămâioasă românească variety cultivated in the Pietroasa Viticulture Centre—Dealu Mare Vineyard, Buzău, at the Didactic Research Station for Viticulture and Pomiculture Pietroasa–Istrita–Branch of University of Agronomic Sciences and Veterinary Medicine Bucharest (USAMV Bucharest). Tămâioasa românească is a representative grape variety for the aromatic sweet wines obtained in this area, its main characteristic being the high accumulation of sugars, which allows for the obtaining of wines with natural residual sugar, suitable for consumption both as young wines or as wines aged for long periods of time.

When they reached about 260 g L^{-1} sugars, the grapes were harvested by hand in 15–20 kg crates and transported to the winemaking line, where they were de-stemmed and crushed. At the same time, 50 mg kg^{-1} potassium metabisulfite was added for antioxidant protection. The resulting mash was left for pre-fermentative maceration for 6 to 8 h at an approximate temperature of 14–15 °C, in the presence of 5 g 100 kg^{-1} of the extraction enzyme Speed Up Aroma (Sodinal, Bucharest, Romania). After maceration, the must was separated and transferred to another vessel for settling in the presence of 1 mL 100 L^{-1} of enzyme complex Enosim Lux (Agrovin, Ciudad Real, Spain), containing PG 4500 U/g, PME 1000 U/g and PL 130 U/g, along with 10 g 100 L^{-1} polyvinylpolypyrrolidone (PVPP) (Laffort, Floirac, France). The settling required about 2 days at a temperature of about 10 °C. At the end, the limpid must was racked, its acidity corrected by adding 1.5 g L^{-1} tartaric acid, and used to obtain the experimental variants.

After that, two strains of *Saccharomyces cerevisiae* yeasts were inoculated in two separated batches. One of the yeast strains, ERSA 1376 (Enologica Vason S.P.A., San Pietro in Cariano, Verona, Italy), abbreviated hereafter as ERSA, is characterized by its capacity to produce intense and persistent fruit aromas, generally typical of Sauvignon Blanc, but also recommended for aromatic white wines from other varieties with a terpenic profile, due to its capacity to preserve and intensify the varietal aromas. The other yeast strain, Zymaflore ST (Laffort, Floirac, France), abbreviated hereafter as ST, is a *Saccharomyces cerevisiae var. cerevisiae* strain recommended especially for the production of sweet white wines, due to its high tolerance for sugar and alcohol, but also low tolerance to SO_2. This yeast too has the ability to highlight some of the varietal flavours of the fermented varieties.

The alcoholic fermentation of the must took place in 220 L vessels. To obtain sweet wines, stopping of the alcoholic fermentation progress was carried out, for each experi-

mental variant and repetition, in glass demijohns of 5 L capacity. Stopping was performed when the alcoholic fermentation was approximately 75–80% completed, that is, at around 12% vol. ethanol. For each experimental variant, the following oenological materials were added in accordance with Table 1, and each variant was prepared in triplicate:

- octanoic acid—in doses of 10, 20 and 30 mg L^{-1};
- decanoic acid—in doses of 10, 20 and 30 mg L^{-1};
- octanoic and decanoic acid combinations—10 mg L^{-1} and 15 mg L^{-1} of each;
- SO_2—60 mg L^{-1} for samples with fatty acids and 120 mg L^{-1} for control samples;
- 0.6 g L^{-1} bentonite was added in each sample, including the control.

Table 1. Experimental variants of Tămâioasă românească wines obtained by stopping fermentation with medium-chain fatty acids.

Wine Samples Fermented with ERSA Yeast	Wine Samples Fermented with ST Yeast	Octanoic Acid mg L^{-1}	Decanoic Acid mg L^{-1}	SO_2 mg L^{-1}
ERSA_0	ST_0	-	-	120
ERSA_oc10	ST_oc10	10	-	60
ERSA_oc20	ST_oc20	20	-	60
ERSA_oc30	ST_oc30	30	-	60
ERSA_de10	ST_de10	-	10	60
ERSA_de20	ST_de20	-	20	60
ERSA_de30	ST_de30	-	30	60
ERSA_ocde10	ST_ocde10	10	10	60
ERSA_ocde15	ST_ocde15	15	15	60

oc—octanoic acid; de—decanoic acid.

At the end, immediately after the treatment with fatty acids, 0.6 g L^{-1} bentonite was added to facilitate clarification. After 3–4 weeks, the wine was passed through sterilising filter pads, using a plate and frame filter and then stored at 13–15 °C.

2.2. Wine Variants Analyses

The main chemical parameters were determined using reference methods recommended by the OIV. Thus, the distillation method OIV-MA-AS312-01A was used to determine the alcohol concentration, the chemical method OIV-MA-AS311-01A and the refractometric method OIV-MA-AS2-02 were used to determine the concentration of sugars, and the potentiometric method OIV-MA-AS313-01 was applied to determine the total titratable acidity and pH.

The analyses of the organic volatile compounds by the electronic nose were performed by using a flash GC gas-chromatograph with two short columns, fabricated by Alpha MOS S.A (Toulouse, France) under the name of Heracles e-nose analyser. The areas of representative chromatographic peaks are selected as the sensors of the electronic nose, as described previously [12,13]. The columns are DB5 (5% diphenyl and 95% dimethylpolysiloxane) and DB1701 (14% cyanopropylphenyl and 86% dimethyl-polysiloxane). Due to the different polarities of the two chromatographic columns (DB5 is non-polar and DB1701 is low-/mid-polar), the volatile compounds which are separated on both columns have different retention times, thus allowing for a higher probability of identification of compounds, in spite of the rapidity of separation (acquisition time for a chromatogram is 46 s). Flame ionization detectors (FID) at the end of each column are used for the detection of volatile compounds. The GC e-nose operation method [13] has the following main parameters: gas injection from the head-space after stirring the vials at 500 rpm in the autosampler oven at 60 °C for 10 min, injector temperature of 250 °C, initial column temperature 40 °C with an increase rate of a 5 °C/s up to 200 °C, temperature and pressure of both detectors of 200 °C

and 35 psi, respectively. To ensure a better separation, the apparatus is also equipped with a Tenax trap placed before the GC columns (sampling temperature at 40 °C, desorption at 250 °C, purge for 50 s and bake-out for 50 s). Hydrogen is used as a carrier gas at pressure of 16 psi. The full description of the apparatus, the methods of analysis for wine, calibration and calculation of Kovats indices were presented in previous papers [12–16].

AlphaSoft v12.42 and the library AroChemBase v. 2010 are the software packages used for data processing, generation of the volatile profiles of wines, statistical analyses for sample discriminations (PCA and DFA) and the identification of chemical compounds based on retention Kovats indices.

Sensory attributes for the identified volatile organic compounds are provided in accordance with the AroChemBase library and other public databases, such as FEMA (Flavor and Extract Manufacturers Association of the United States) or FlavorDB (https://cosylab.iiitd.edu.in/, accessed on 9 November 2022).

Each wine variant was introduced in the chromatograph in triplicate, and results are reported as averages ± standard deviations. To compare the means, ANOVA was performed by using IBM® SPSS® Statistics software v.16 (IBM, New York, NY, USA).

3. Results

3.1. Compounds Identified in Tămâioasă Românească Wines by GC e-Nose

The wine variants produced were analysed to confirm that they are within the range of desired physico-chemical parameters. All wines, irrespective of the methods to stop fermentation and yeast used for fermentation, achieved a concentration of ethanol in the range of 12.1–12.8% vol., total titratable acidity of 6.6–6.9 g L^{-1} tartaric acid, stable pH around 3.1 and a sugar concentration of 65–69 g L^{-1}.

The organic volatile compounds were identified in accordance with their retention time (RT) on at least one of the two columns of the GC electronic nose, but most of them were separated on both columns. The identified compounds were included in Table 2, along with their most usual sensory effect.

Table 2. Compounds identified in Tămâioasă românească wines on both columns of GC e-nose.

Compound	Column DB5 RT (s)	Sensors on DB5 (Peak Area)	Column DB1701 RT (s)	Sensors on DB1701 (Peak Area)	Sensory Attributes
			Aldehydes		
acetaldehyde	3.13	415.49-1-A	3.86	541.82-2-A	pungent, ethereal
2-methyl-butanal	6.23	646.08-1-A	7.10	730.27-2-A	nut, caramel, sweet
2-phenyl-acetaldehyde	19.15	1026.76-1-A	24.19	1176.08-2-A	honey, sweet, rose, herbaceous, floral
(e)-2-undecenal	31.84	1361.38-1-A	36.45	1507.84-2-A	geranium, metallic, pungent, sweet, herbaceous, fruity, fatty
			Alcohols		
2-methyl-1-butanol	7.97	738.67-1-A	11.16	849.51-2-A	malt, wine, ethereal, fusel alcohols, fatty
2,3-butanediol	8.94	768.28-1-A	16.07	971.57-2-A	fruits
2-phenyl-ethanol	21.78	1088.98-1-A	28.09	1279.81-2-A	floral, rose, honey, sweet, spicy
			Ethyl esters		
ethyl butanoate	9.86	796.22-1-A	11.57	860.18-2-A	banana, ethereal, pineapple
ethyl-2-methyl-butanoate	11.84	846.48-1-A	13.51	909.56-2-A	green apple, plum
ethyl hexanoate	17.8	993.12-1-A	19.60	1058.80-2-A	apple, banana, wine, pineapple
ethyl octanoate	25.77	1197.94-1-A	27.50	1264.65-2-A	pear, pineapple, floral, apricot
ethyl decanoate	32.97	1392.28-1-A	34.70	1460.26-2-A	grape, pear, oily, sweet, waxy, fruity, apple, soapy, winey

Table 2. *Cont.*

Compound	Column DB5 RT (s)	Sensors on DB5 (Peak Area)	Column DB1701 RT (s)	Sensors on DB1701 (Peak Area)	Sensory Attributes
Acetate esters					
ethyl acetate	4.76	611.29-1-A	5.71	675.39-2-A	ethereal, aniseed, pineapple
isoamyl acetate	12.94	874.02-1-A	14.81	941.16-2-A	banana, pear
cis-3-hexenyl acetate	18.27	1004.67-1-A	20.29	1076.04-2-A	herbaceous, banana, vegetable
2-phenylethyl acetate	27.80	1253.13-1A	30.28	1339.07-2-A	fruity, sweet
Terpenes					
β-myrcene	17.10	976.36-1-A	17.85	1015.20-2-A	sweet, fruity, spice, woody, metallic
cis-*β*-ocimene	19.76	1042.09-1-A	22.56	1133.75-2-A	citrus, herbal
β-linalool	22.35	1107.22-1-A	24.69	1189.38-2-A	citrus, floral, sweet
nerol oxide	23.88	1147.51-1-A	30.92	1356.24-2-A	sweet, fruity, floral, rose
(*e*)-linalool oxide	24.63	1173.31-1-A	-	-	floral
trans-geraniol	27.47	1242.49-1-A	31.93	1378.40-2-A	sweet, apple, apricot, berries, rose
limonen-1,2-epoxide	23.49	1137.14-1-A	25.92	1221.66-2-A	sweet, fruity, spicy, woody, metallic
α-terpinen-7-al *	-	-	32.78	1407.37-2-A	fat, spice
Heterocyclic compounds					
abhexone **	-	-	33.45	1431.31-2-A	curry
1H-indol	28.94	1283.06-1-A	37.55	1541.25-2-A	sweet, burnt, floral, jasmine, earthy

* *p*-mentha-1,3-dien-7-al; 1,3-p-Menthadien-7-al. ** 5-ethyl-3-hydroxy-4-methyl-2(5H)-furanone.

The identified compounds belong to several chemical classes, which are normally involved in wine aroma. Terpenes are highly correlated with the varietal aroma of grapes, especially in those with muscat-type aroma [17], as is the case of Tămâioasă românească, while the esters, aldehydes and alcohols are modulated by the yeasts used for the grape must fermentation [18]. External factors and conditions can greatly influence the metabolism of yeast and leave a mark on the aroma profile of the fermented media.

3.2. Influence of ERSA Yeast on the Volatile Compounds of Tămâioasă Românească Wines Treated with Octanoic or Decanoic Acid

In Table 3, the main volatile compounds of the wines fermented by ERSA yeasts are quantitatively reported for each experimental wine that resulted after stopping fermentation by using various dosages of medium-chain fatty acids. The concentrations of the volatile compounds identified in each wine are expressed in chromatographic peak areas, which is enough to allow for a comparison of the yeast and medium-chain fatty acid effects.

Similarly, Table 4 contains the results for the wines fermented by ST yeast.

While the aroma profile induced by the Tămâioasă românească grape variety is evident in all the samples, especially as regards the identified terpenic compounds, which do not vary much among samples, the yeasts and the addition of medium-chain fatty acids modulate the aroma produced during fermentation. As observed in both Tables 3 and 4, the varietal muscat-type aroma in all samples is unchanged by the fermentation conditions, the levels of β-linalool, trans-geraniol, nerol oxide, (e)-linalool oxide, limonen-1,2-epoxide, β-myrcene and cis-β-ocimene being not significantly different, irrespective of the yeast used or the addition of the octanoic or decanoic acid to stop fermentation. The influences of yeasts and medium-chain fatty acids are discussed in Section 4.

3.3. Discrimination Analysis Performed by the e-Nose for Samples Treated with Various Doses of Octanoic and Decanoic Acid to Stop Fermentation

For the discrimination of wine samples based on the most significant volatile compounds identified by the gas-chromatograph electronic nose, the areas of their peaks, which play the role of sensors for this type of e-nose, were analysed by Discriminant Factor Analysis (DFA).

Table 3. Compounds identified on both columns of GC e-nose in Tămâioasă românească wines fermented by ERSA yeast, determined after stopping fermentation by using various dosages of medium-chain fatty acids.

Peak Area/ Compound *	ERS	ERS_oc10	ERS_oc20	ERS_oc30	ERS_de10	ERS_de20	ERS_de30	ERS_ocde10	ERS_ocde15
Acetaldehyde									
415.49-1	72,627 ± 7300 ^{a}	72,157 ± 3424 ^{a}	70,593 ± 1169 ^{a}	70,331 ± 4569 ^{a}	73,524 ± 2915 ^{a}	72,952 ± 5438 ^{a}	69,304 ± 3392 ^{a}	69,955 ± 2440 ^{a}	71,461 ± 4647 ^{a}
541.82-2-A	61,410 ± 6777 ^{a}	60,160 ± 2272 ^{a}	58,534 ± 1277 ^{a}	58,911 ± 3451 ^{a}	61,650 ± 2444 ^{a}	61,080 ± 4198 ^{a}	58,142 ± 2865 ^{a}	59,126 ± 2031 ^{a}	60,563 ± 3886 ^{a}
Ethyl acetate									
611.29-1	115,742 ± 6491 ^{a}	117,375 ± 6851 ^{a}	120,215 ± 2789 ^{a}	118,769 ± 5080 ^{a}	112,220 ± 11,834 ^{a}	118,661 ± 6686 ^{a}	119,235 ± 4301 ^{a}	121,163 ± 5373 ^{a}	115,826 ± 5595 ^{a}
675.39-2-A	83,543 ± 5404 ^{a}	83,693 ± 5752 ^{a}	86,814 ± 1789 ^{a}	86,370 ± 4473 ^{a}	80,768 ± 9799 ^{a}	85,279 ± 5306 ^{a}	86,397 ± 3045 ^{a}	88,513 ± 3904 ^{a}	83,960 ± 4177 ^{a}
2-Methylbutanal									
646.08-1	572 ± 182 ^{a}	704 ± 114 ^{a}	637 ± 146 ^{a}	574 ± 122 ^{a}	562 ± 192 ^{a}	539 ± 107 ^{a}	529 ± 107 ^{a}	605 ± 160 ^{a}	624 ± 191 ^{a}
730.27-2-A	9672 ± 849 ^{a}	9562 ± 323 ^{a}	9376 ± 263 ^{a}	9409 ± 342 ^{a}	9421 ± 400 ^{a}	9623 ± 267 ^{a}	9354 ± 440 ^{a}	9575 ± 410 ^{a}	9683 ± 356 ^{a}
2-Methyl-1-butanol									
738.67-1	162,167 ± 13,867 ^{a}	163,996 ± 6739 ^{a}	162,758 ± 5876 ^{a}	161,097 ± 10,036 ^{a}	162,962 ± 7171 ^{a}	164,218 ± 8921 ^{a}	159,802 ± 8889 ^{a}	161,917 ± 7062 ^{a}	166,926 ± 6017 ^{a}
849.51-2-A	125,821 ± 10,438 ^{a}	126,833 ± 5224 ^{a}	126,318 ± 4719 ^{a}	124,693 ± 7558 ^{a}	125,635 ± 4788 ^{a}	127,350 ± 6798 ^{a}	124,073 ± 6921 ^{a}	125,375 ± 4629 ^{a}	130,309 ± 5313 ^{a}
2,3-Butanediol									
768.28-1	1841 ± 288 ^{a}	2059 ± 158 ^{a}	1970 ± 165 ^{a}	2001 ± 266 ^{a}	1949 ± 169 ^{a}	1959 ± 275 ^{a}	1936 ± 135 ^{a}	1937 ± 241 ^{a}	2069 ± 250 ^{a}
971.57-2-A	2487 ± 366 ^{a}	2523 ± 409 ^{a}	2252 ± 131 ^{a}	2303 ± 286 ^{a}	2474 ± 485 ^{a}	2397 ± 280 ^{a}	2289 ± 171 ^{a}	2314 ± 176 ^{a}	2546 ± 204 ^{a}
Ethyl butanoate									
796.22-1	5879 ± 639 ^{a}	6030 ± 337 ^{a}	5794 ± 203 ^{a}	5762 ± 451 ^{a}	5865 ± 226 ^{a}	5897 ± 531 ^{a}	5631 ± 182 ^{a}	5674 ± 303 ^{a}	5890 ± 252 ^{a}
860.18-2-A	5373 ± 573 ^{a}	5364 ± 161 ^{a}	5146 ± 140 ^{a}	5162 ± 259 ^{a}	5324 ± 337 ^{a}	5402 ± 225 ^{a}	5066 ± 258 ^{a}	5218 ± 272 ^{a}	5342 ± 341 ^{a}
Ethyl 2-Methylbutanoate									
846.48-1-A	670 ± 247 ^{a}	757 ± 234 ^{a}	643 ± 157 ^{a}	690 ± 203 ^{a}	710 ± 183 ^{a}	685 ± 181 ^{a}	677 ± 102 ^{a}	656 ± 235 ^{a}	715 ± 160 ^{a}
909.56-2-A	705 ± 125 ^{ab}	621 ± 61 ^{ab}	569 ± 36 ^{b}	597 ± 99 ^{b}	577 ± 152 ^{b}	661 ± 49 ^{ab}	630 ± 79 ^{ab}	717 ± 100 ^{ab}	776 ± 94 ^{a}
Isoamyl acetate									
874.02-1-A	72,352 ± 6235 ^{a}	72,544 ± 3861 ^{a}	69,411 ± 2062 ^{a}	68,603 ± 4693 ^{a}	70,707 ± 3031 ^{a}	72,287 ± 5827 ^{a}	68,079 ± 3376 ^{a}	67,802 ± 2575 ^{a}	70,896 ± 3898 ^{a}
941.16-2-A	54,005 ± 4386 ^{a}	53,579 ± 1888 ^{a}	51,668 ± 1421 ^{a}	50,819 ± 3326 ^{a}	52,484 ± 1691 ^{a}	53,943 ± 3714 ^{a}	51,033 ± 3243 ^{a}	50,889 ± 1912 ^{a}	52,947 ± 2999 ^{a}
β-Myrcene									
976.36-1-A	761 ± 0 ^{a}	657 ± 120 ^{a}	608 ± 96 ^{a}	550 ± 62 ^{a}	668 ± 75 ^{a}	549 ± 18 ^{a}	573 ± 82 ^{a}	542 ± 168 ^{a}	655 ± 76 ^{a}

Table 3. *Cont.*

Peak Area/ Compound *	ERS	ERS_oc10	ERS_oc20	ERS_oc30	ERS_de10	ERS_de20	ERS_de30	ERS_ocde10	ERS_ocde15
1015.20-2-A	1128 ± 326 ^{a}	979 ± 213 ^{a}	894 ± 86 ^{a}	941 ± 168 ^{a}	1005 ± 266 ^{a}	1016 ± 120 ^{a}	1012 ± 170 ^{a}	1092 ± 199 ^{a}	1179 ± 207 ^{a}
Ethyl hexanoate									
993.12-1-A	41,346 ± 5969 ^{a}	38,497 ± 3382 ^{a}	36,251 ± 972 ^{a}	36,564 ± 4520 ^{a}	38,987 ± 4042 ^{a}	39,295 ± 5302 ^{a}	35,670 ± 2238 ^{a}	35,523 ± 1519 ^{a}	38,586 ± 3583 ^{a}
1058.80-2-A	30,982 ± 3963 ^{a}	28,826 ± 2273 ^{a}	27,234 ± 656 ^{a}	27,375 ± 3178 ^{a}	29,089 ± 3001 ^{a}	29,164 ± 3698 ^{a}	26,698 ± 1769 ^{a}	26,649 ± 1052 ^{a}	28,876 ± 2681 ^{a}
Cis-3-hexenyl acetate									
1004.67-1-A	8155 ± 1261 ^{a}	8042 ± 768 ^{a}	7476 ± 199 ^{a}	7486 ± 1001 ^{a}	8096 ± 855 ^{a}	8027 ± 1104 ^{a}	7234 ± 504 ^{a}	7209 ± 473 ^{a}	7945 ± 665 ^{a}
1076.04-2-A	7695 ± 1166 ^{a}	7280 ± 593 ^{a}	6801 ± 176 ^{a}	6862 ± 853 ^{a}	7343 ± 842 ^{a}	7324 ± 840 ^{a}	6709 ± 466 ^{a}	6806 ± 376 ^{a}	7386 ± 719 ^{a}
2-Phenylacetaldehyde									
1026.76-1-A	1634 ± 378 ^{a}	1773 ± 229 ^{a}	1599 ± 180 ^{a}	1609 ± 261 ^{a}	1767 ± 131 ^{a}	1713 ± 179 ^{a}	1615 ± 147 ^{a}	1585 ± 272 ^{a}	1724 ± 162 ^{a}
1176.08-2-A	288 ± 104 ^{a}	200 ± 91 ^{a}	166 ± 37 ^{a}	142 ± 72 ^{a}	224 ± 119 ^{a}	183 ± 43 ^{a}	203 ± 68 ^{a}	216 ± 87 ^{a}	236 ± 91 ^{a}
cis-*β*-Ocimene									
1042.09-1-A	644 ± 191 ^{a}	765 ± 173 ^{a}	676 ± 137 ^{a}	692 ± 166 ^{a}	758 ± 87 ^{a}	719 ± 132 ^{a}	707 ± 102 ^{a}	714 ± 170 ^{a}	782 ± 88 ^{a}
1,133.75-2-A	562 ± 113 ^{a}	386 ± 119 ^{ab}	351 ± 38 ^{b}	324 ± 73 ^{b}	368 ± 150 ^{b}	353 ± 84 ^{b}	392 ± 78 ^{ab}	422 ± 95 ^{ab}	450 ± 81 ^{ab}
2-Phenylethanol									
1088.98-1-A	1057 ± 415 ^{a}	1425 ± 197 ^{a}	1266 ± 180 ^{a}	1283 ± 225 ^{a}	1357 ± 115 ^{a}	1237 ± 152 ^{a}	1196 ± 130 ^{a}	1219 ± 225 ^{a}	1303 ± 107 ^{a}
1279.81-2-A	1670 ± 254 ^{a}	1656 ± 198 ^{a}	1639 ± 101 ^{a}	1351 ± 663 ^{a}	1544 ± 265 ^{a}	1416 ± 185 ^{a}	1382 ± 155 ^{a}	1528 ± 137 ^{a}	1791 ± 189 ^{a}
β-Linalool									
1107.22-1-A	1959 ± 995 ^{a}	2255 ± 292 ^{a}	2013 ± 138 ^{a}	1938 ± 64 ^{a}	2187 ± 254 ^{a}	2044 ± 360 ^{a}	1940 ± 227 ^{a}	1961 ± 292 ^{a}	2362 ± 333 ^{a}
1189.38-2-A	1577 ± 295 ^{a}	1393 ± 247 ^{a}	1377 ± 149 ^{a}	1292 ± 125 ^{a}	1279 ± 263 ^{a}	1193 ± 109 ^{a}	1229 ± 154 ^{a}	1357 ± 216 ^{a}	1396 ± 213 ^{a}
Limonene-1,2-epoxide									
1137.14-1-A	226 ± 137 ^{a}	292 ± 58 ^{a}	220 ± 59 ^{a}	166 ± 15 ^{a}	281 ± 53 ^{a}	227 ± 49 ^{a}	227 ± 52 ^{a}	198 ± 115 ^{a}	230 ± 73 ^{a}
1221.66-2-A	0 ± 0 ^{a}	133 ± 52 ^{a}	88 ± 16 ^{a}	106 ± 39 ^{a}	143 ± 53 ^{a}	135 ± 43 ^{a}	52 ± 0 ^{a}	142 ± 36 ^{a}	136 ± 62 ^{a}
Nerol oxide									
1147.51-1-A	455 ± 179 ^{a}	536 ± 131 ^{a}	491 ± 108 ^{a}	486 ± 60 ^{a}	467 ± 99 ^{a}	423 ± 53 ^{a}	480 ± 97 ^{a}	476 ± 198 ^{a}	557 ± 109 ^{a}
1356.24-2-A	196 ± 118 ^{a}	165 ± 65 ^{a}	124 ± 27 ^{a}	170 ± 54 ^{a}	166 ± 58 ^{a}	223 ± 27 ^{a}	181 ± 63 ^{a}	169 ± 79 ^{a}	218 ± 78 ^{a}
(E)-Linalool oxide									
1173.31-1-A	980 ± 309 ^{cd}	804 ± 177 ^{cde}	378 ± 80 ^{ef}	315 ± 75 ^{f}	1529 ± 211 ^{ab}	1147 ± 444 ^{bc}	1884 ± 185 ^{a}	539 ± 337 ^{def}	366 ± 49 ^{ef}

Table 3. *Cont.*

Peak Area/ Compound *	ERS	ERS_oc10	ERS_oc20	ERS_oc30	ERS_de10	ERS_de20	ERS_de30	ERS_ocde10	ERS_ocde15
Ethyl octanoate									
1197.94-1-A	71,285 ± 13,666 ^{d}	140,537 ± 18,627 ^{c}	183,934 ± 5719 ^{b}	245,027 ± 43,655 ^{a}	73,573 ± 10,399 ^{d}	71,003 ± 12,528 ^{d}	64,707 ± 5177 ^{d}	121,240 ± 6544 ^{c}	143,604 ± 16,296 ^{c}
1264.65-2-A	53,094 ± 10,103 ^{d}	102,170 ± 12,833 ^{c}	132,385 ± 3664 ^{b}	177,575 ± 33,812 ^{a}	54,366 ± 7752 ^{d}	51,881 ± 8292 ^{d}	48,002 ± 3589 ^{d}	87,525 ± 4553 ^{c}	103,766 ± 12,322 ^{c}
trans-Geraniol									
1242.49-1-A	240 ± 185 ^{b}	461 ± 93 ^{ab}	488 ± 87 ^{a}	431 ± 133 ^{ab}	428 ± 63 ^{ab}	367 ± 66 ^{ab}	407 ± 76 ^{ab}	359 ± 198 ^{ab}	445 ± 90 ^{ab}
1378.40-2-A	639 ± 79 ^{a}	425 ± 150 ^{b}	404 ± 96 ^{b}	336 ± 131 ^{b}	453 ± 135 ^{ab}	345 ± 61 ^{b}	396 ± 77 ^{b}	398 ± 112 ^{b}	432 ± 93 ^{b}
2-Phenylethyl acetate									
1253.13-1-A	1194 ± 708 ^{b}	1889 ± 225 ^{a}	1847 ± 199 ^{ab}	1634 ± 293 ^{ab}	2069 ± 321 ^{a}	1691 ± 188 ^{ab}	1705 ± 154 ^{ab}	1504 ± 540 ^{ab}	1762 ± 150 ^{ab}
1339.07-2-A	1067 ± 220 ^{ab}	885 ± 271 ^{b}	1095 ± 154 ^{ab}	1291 ± 446 ^{ab}	1256 ± 347 ^{ab}	1345 ± 305 ^{ab}	1534 ± 195 ^{a}	1168 ± 178 ^{ab}	1411 ± 213 ^{a}
1H-indole									
1283.06-1-A	380 ± 298 ^{b}	1191 ± 410 ^{a}	1159 ± 277 ^{a}	886 ± 214 ^{ab}	1129 ± 324 ^{a}	1176 ± 241 ^{a}	1129 ± 186 ^{a}	825 ± 495 ^{ab}	1169 ± 257 ^{a}
1541.25-2-A	587 ± 173 ^{cd}	301 ± 278 ^{d}	702 ± 249 ^{bcd}	759 ± 348 ^{abc}	725 ± 162 ^{abcd}	777 ± 163 ^{abc}	1134 ± 154 ^{a}	795 ± 251 ^{abc}	1125 ± 209 ^{ab}
(E)-2-Undecenal									
1361.38-1-A	169 ± 149 ^{d}	296 ± 125 ^{cd}	452 ± 119 ^{bc}	531 ± 225 ^{bc}	373 ± 96 ^{cd}	493 ± 121 ^{bc}	673 ± 91 ^{ab}	552 ± 200 ^{bc}	837 ± 55 ^{a}
1507.84-2-A	614 ± 94 ^{ab}	521 ± 218 ^{ab}	656 ± 148 ^{a}	729 ± 264 ^{a}	518 ± 120 ^{ab}	351 ± 125 ^{b}	457 ± 100 ^{ab}	575 ± 167 ^{ab}	675 ± 143 ^{a}
Ethyl decanoate									
1392.28-1-A	27,190 ± 5754 ^{c}	28,524 ± 7012 ^{c}	26,090 ± 2906 ^{c}	29,330 ± 9233 ^{c}	72,926 ± 10,727 ^{b}	97,502 ± 18,319 ^{a}	104,400 ± 18,163 ^{a}	65,583 ± 6806 ^{b}	72,961 ± 9533 ^{B}
1460.26-2-A	24,616 ± 4933 ^{c}	23,995 ± 4034 ^{c}	22,721 ± 2217 ^{c}	24,617 ± 4572 ^{c}	52,950 ± 8103 ^{b}	70,150 ± 13,245 ^{a}	75,229 ± 12,953 ^{a}	47,774 ± 4823 ^{b}	52,972 ± 7148 ^{b}
α.-Terpinen-7-al									
1407.37-2-A	385 ± 103 ^{a}	225 ± 105 ^{ab}	231 ± 86 ^{ab}	185 ± 129 ^{b}	224 ± 80 ^{ab}	164 ± 64 ^{b}	201 ± 66 ^{b}	202 ± 94 ^{b}	237 ± 76 ^{ab}
Abhexone									
1431.31-2-A	709 ± 124 ^{a}	393 ± 215 ^{b}	386 ± 162 ^{b}	227 ± 185 ^{b}	468 ± 155 ^{ab}	241 ± 91 ^{b}	310 ± 130 ^{b}	342 ± 137 ^{b}	395 ± 131 ^{b}

* Compounds are listed in order of separation on the column DB5. Different letters on each row indicate a statistically significant difference between the averages for the assessed varieties at a probability level of 95% ($\alpha = 0.05$) determined by one-way ANOVA and Tukey test ($p < 0.05$).

Table 4. Compounds identified on both columns of GC e-nose in Tamâioasă românească wines fermented by ST yeast, determined after stopping fermentation by using various dosages of medium-chain fatty acids.

Peak Area/ Compound *	ST	ST_oc10	ST_oc20	ST_oc30	ST_de10	ST_de20	ST_de30	ST_ocde10	ST_ocde15
Acetaldehyde									
415.49-1	66,323 ± 5163 [a]	69,854 ± 5079 [a]	69,884 ± 6581 [a]	71,488 ± 3658 [a]	71,125 ± 4688 [a]	71,761 ± 4787 [a]	69,472 ± 2697 [a]	71,321 ± 3019 [a]	70,153 ± 1367 [a]
541.82-2-A	56,199 ± 4107 [a]	59,623 ± 4374 [a]	60,106 ± 5730 [a]	61,349 ± 3315 [a]	60,388 ± 3837 [a]	61,488 ± 3592 [a]	59,228 ± 3224 [a]	61,118 ± 3158 [a]	60,523 ± 850 [a]
Ethyl acetate									
611.29-1	111,999 ± 10,461 [a]	110,119 ± 5613 [a]	113,674 ± 5694 [a]	114,301 ± 4325 [a]	105,371 ± 11,220 [a]	113,362 ± 4425 [a]	115,287 ± 3848 [a]	111,644 ± 7355 [a]	110,074 ± 5497 [a]
675.39-2-A	84,110 ± 7345 [a]	82,734 ± 4649 [a]	85,688 ± 4527 [a]	86,356 ± 3276 [a]	77,796 ± 9180 [a]	85,257 ± 3574 [a]	86,628 ± 3142 [a]	83,783 ± 5798 [a]	83,191 ± 4389 [a]
2-Methylbutanal									
646.08-1	426 ± 163 [a]	500 ± 104 [a]	427 ± 81 [a]	528 ± 152 [a]	614 ± 109 [a]	522 ± 144 [a]	670 ± 127 [a]	515 ± 181 [a]	553 ± 187 [a]
730.27-2-A	7644 ± 544 [a]	7941 ± 358 [a]	7936 ± 568 [a]	8091 ± 414 [a]	7974 ± 355 [a]	8165 ± 234 [a]	8025 ± 501 [a]	8046 ± 205 [a]	7950 ± 281 [a]
2-Methyl-1-butanol									
738.67-1	147,793 ± 10,556 [a]	154,833 ± 10,939 [a]	148,307 ± 11,337 [a]	152,818 ± 10,351 [a]	155,016 ± 8510 [a]	156,039 ± 9457 [a]	155,245 ± 7482 [a]	154,468 ± 6279 [a]	152,308 ± 3550 [a]
849.51-2-A	116,655 ± 7801 [a]	121,411 ± 8786 [a]	117,431 ± 9029 [a]	120,754 ± 8438 [a]	121,178 ± 7639 [a]	123,167 ± 7374 [a]	123,206 ± 7051 [a]	122,724 ± 4501 [a]	120,511 ± 2890 [a]
2,3-Butanediol									
768.28-1	1626 ± 231 [a]	1745 ± 161 [a]	1651 ± 148 [a]	1781 ± 136 [a]	1836 ± 71 [a]	1829 ± 217 [a]	1916 ± 121 [a]	1814 ± 185 [a]	1971 ± 252 [a]
971.57-2-A	2181 ± 182 [a]	2320 ± 282 [a]	2190 ± 312 [a]	2208 ± 256 [a]	2362 ± 266 [a]	2285 ± 233 [a]	2201 ± 233 [a]	2296 ± 237 [a]	2270 ± 58 [a]
Ethyl butanoate									
796.22-1	5518 ± 420 [a]	5846 ± 450 [a]	5642 ± 432 [a]	5843 ± 420 [a]	5726 ± 348 [a]	5891 ± 445 [a]	5841 ± 211 [a]	5810 ± 267 [a]	5519 ± 240 [a]
860.18-2-A	5121 ± 348 [a]	5327 ± 327 [a]	5260 ± 446 [a]	5336 ± 343 [a]	5267 ± 423 [a]	5426 ± 237 [a]	5301 ± 339 [a]	5378 ± 291 [a]	5129 ± 241 [a]
Ethyl 2-Methylbutanoate									
846.48-1-A	721 ± 76 [a]	746 ± 38 [a]	737 ± 47 [a]	830 ± 127 [a]	827 ± 142 [a]	799 ± 123 [a]	879 ± 159 [a]	790 ± 125 [a]	831 ± 160 [a]
909.56-2-A	783 ± 96 [a]	762 ± 70 [a]	813 ± 106 [a]	828 ± 96 [a]	835 ± 151 [a]	849 ± 50 [a]	824 ± 134 [a]	859 ± 88 [a]	904 ± 83 [a]
Isoamyl acetate									
874.02-1-A	75,984 ± 4944 [a]	79,100 ± 7034 [a]	75,201 ± 6669 [a]	77,132 ± 7160 [a]	76,972 ± 4478 [a]	78,791 ± 5628 [a]	76,919 ± 3660 [a]	77,859 ± 4546 [a]	70,454 ± 2678 [a]
941.16-2-A	57,751 ± 3825 [a]	59,939 ± 5119 [a]	57,272 ± 4964 [a]	58,625 ± 5438 [a]	58,085 ± 3684 [a]	60,121 ± 4857 [a]	58,360 ± 2772 [a]	58,877 ± 3438 [a]	53,536 ± 2080 [a]
β-Myrcene									
976.36-1-A	658 ± 0 [a]	636 ± 68 [a]	579 ± 78 [a]	637 ± 93 [a]	683 ± 98 [a]	627 ± 78 [a]	640 ± 1 10 [a]	635 ± 81 [a]	585 ± 148 [a]

Table 4. *Cont.*

Peak Area/ Compound *	ST	ST_oc10	ST_oc20	ST_oc30	ST_de10	ST_de20	ST_de30	ST_ocde10	ST_ocde15
1015.20-2-A	1125 ± 233 [a]	1208 ± 125 [a]	1166 ± 245 [a]	1137 ± 140 [a]	1217 ± 211 [a]	1190 ± 111 [a]	1095 ± 241 [a]	1213 ± 138 [a]	1136 ± 170 [a]
Ethyl hexanoate									
1058.80-2-A	24,550 ± 1882 [a]	25,678 ± 3297 [a]	24,034 ± 3239 [a]	24,866 ± 3023 [a]	25,317 ± 2067 [a]	25,298 ± 2618 [a]	24,217 ± 1643 [a]	25,377 ± 2403 [a]	21,972 ± 832 [a]
Cis-3-hexenyl acetate									
1004.67-1-A	7672 ± 709 [a]	8115 ± 1084 [a]	7512 ± 999 [a]	7737 ± 1022 [a]	7975 ± 656 [a]	7832 ± 903 [a]	7453 ± 519 [a]	7772 ± 662 [a]	6608 ± 363 [a]
1076.04-2-A	7185 ± 653 [a]	7568 ± 941 [a]	7037 ± 1004 [a]	7243 ± 868 [a]	7469 ± 700 [a]	7381 ± 751 [a]	7019 ± 652 [a]	7441 ± 722 [a]	6432 ± 315 [a]
2-Phenylacetaldehyde									
1026.76-1-A	1840 ± 249 [ab]	1891 ± 104 [a]	1710 ± 157 [ab]	1767 ± 186 [ab]	1781 ± 148 [ab]	1828 ± 152 [ab]	1757 ± 207 [ab]	1768 ± 127 [ab]	1515 ± 216 [b]
1176.08-2-A	207 ± 84 [a]	232 ± 51 [a]	209 ± 74 [a]	188 ± 74 [a]	251 ± 89 [a]	234 ± 59 [a]	208 ± 105 [a]	245 ± 59 [a]	213 ± 72 [a]
cis-*β*-Ocimene									
1042.09-1-A	739 ± 150 [a]	835 ± 52 [a]	750 ± 114 [a]	796 ± 92 [a]	816 ± 103 [a]	814 ± 82 [a]	804 ± 137 [a]	802 ± 89 [a]	701 ± 114 [a]
1133.75-2-A	400 ± 85 [b]	391 ± 43 [b]	417 ± 66 [ab]	402 ± 93 [b]	448 ± 88 [ab]	445 ± 51 [ab]	444 ± 113 [ab]	486 ± 57 [ab]	560 ± 120 [a]
2-Phenylethanol									
1088.98-1-A	1193 ± 128 [a]	1325 ± 59 [a]	1306 ± 154 [a]	1388 ± 133 [a]	1284 ± 127 [a]	1272 ± 112 [a]	1255 ± 156 [a]	1238 ± 121 [a]	1188 ± 216 [a]
1279.81-2-A	1630 ± 173 [a]	1941 ± 326 [a]	186 9 ± 386 [a]	2030 ± 305 [a]	1718 ± 211 [a]	1648 ± 238 [a]	1577 ± 334 [a]	1934 ± 224 [a]	2025 ± 339 [a]
β-Linalool									
1107.22-1-A	2328 ± 249 [ab]	2432 ± 305 [ab]	2313 ± 366 [ab]	2175 ± 385 [b]	2347 ± 240 [ab]	2274 ± 305 [ab]	2242 ± 361 [ab]	2486 ± 330 [ab]	2857 ± 388 [a]
1189.38-2-A	1120 ± 184 [a]	1315 ± 121 [a]	1324 ± 143 [a]	1285 ± 308 [a]	1284 ± 216 [a]	1258 ± 154 [a]	1153 ± 235 [a]	1366 ± 136 [a]	1403 ± 180 [a]
Limonene-1,2-epoxide									
1137.14-1-A	211 ± 77 [a]	234 ± 18 [a]	188 ± 46 [a]	176 ± 49 [a]	240 ± 54 [a]	210 ± 64 [a]	230 ± 89 [a]	210 ± 58 [a]	182 ± 77 [a]
1221.66-2-A	0 ± 0 [-]	121 ± 49 [-]	102 ± 51 [-]	161 ± 60 [-]	98 ± 35 [-]	117 ± 50 [-]	145 ± 0 [-]	153 ± 51 [-]	149 ± 52 [-]
Nerol oxide									
1147.51-1-A	491 ± 112 [a]	497 ± 36 [a]	538 ± 71 [a]	623 ± 82 [a]	565 ± 67 [a]	551 ± 93 [a]	634 ± 133 [a]	620 ± 92 [a]	713 ± 274 [a]
1356.24-2-A	262 ± 96 [a]	155 ± 42 [a]	141 ± 64 [a]	145 ± 96 [a]	0 ± 0 [a]	187 ± 57 [a]	204 ± 78 [a]	223 ± 36 [a]	250 ± 71 [a]
(E)-Linalool oxide									
1173.31-1-A	1296 ± 230 [a]	723 ± 336 [b]	302 ± 33 [b]	313 ± 65 [b]	1304 ± 186 [a]	1523 ± 288 [a]	1742 ± 199 [a]	599 ± 470 [b]	306 ± 50 [b]

Table 4. *Cont.*

Peak Area/ Compound *	ST	ST_oc10	ST_oc20	ST_oc30	ST_de10	ST_de20	ST_de30	ST_ocde10	ST_ocde15
Ethyl octanoate									
1197.94-1-A	53,385 ± 5333 ^{d}	129,918 ± 2183 ^{c}	175,314 ± 33,106 ^{b}	243,330 ± 30,130 ^{a}	60,200 ± 6905 ^{d}	57,131 ± 8451 ^{d}	53,848 ± 5173 ^{d}	123,993 ± 15,280 ^{c}	137,807 ± 3202 ^{c}
1264.65-2-A	40,095 ± 4020 ^{d}	94,435 ± 15,863 ^{c}	128,602 ± 24,295 ^{b}	178,860 ± 22,634 ^{a}	44,669 ± 5099 ^{d}	42,868 ± 6192 ^{d}	40,595 ± 3980 ^{d}	91,417 ± 11,194 ^{c}	102,126 ± 3520 ^{c}
trans-Geraniol									
1242.49-1-A	293 ± 176 ^{a}	352 ± 19 ^{a}	347 ± 56 ^{a}	388 ± 106 ^{a}	371 ± 147 ^{a}	304 ± 61 ^{a}	357 ± 96 ^{a}	380 ± 53 ^{a}	373 ± 152 ^{a}
1378.40-2-A	447 ± 108 ^{a}	509 ± 83 ^{a}	444 ± 102 ^{a}	447 ± 126 ^{a}	446 ± 75 ^{a}	395 ± 101 ^{a}	364 ± 130 ^{a}	476 ± 52 ^{a}	465 ± 68 ^{a}
2-Phenylethyl acetate									
1253.13-1-A	1263 ± 210 ^{b}	1616 ± 96 ^{ab}	1506 ± 141 ^{ab}	1572 ± 237 ^{ab}	1593 ± 204 ^{ab}	1555 ± 123 ^{ab}	1630 ± 208 ^{a}	1626 ± 124 ^{a}	1482 ± 270 ^{ab}
1339.07-2-A	1248 ± 210 ^{a}	947 ± 159 ^{a}	1022 ± 262 ^{a}	1315 ± 440 ^{a}	1094 ± 116 ^{a}	1260 ± 270 ^{a}	1408 ± 311 ^{a}	1288 ± 183 ^{a}	1294 ± 205 ^{a}
1H-indole									
1283.06-1-A	510 ± 195 ^{b}	973 ± 196 ^{ab}	839 ± 273 ^{ab}	1048 ± 357 ^{ab}	971 ± 253 ^{ab}	1146 ± 466 ^{a}	1479 ± 525 ^{a}	1375 ± 308 ^{a}	1273 ± 453 ^{a}
1541.25-2-A	684 ± 107 ^{c}	619 ± 196 ^{c}	577 ± 191 ^{c}	748 ± 137 ^{abc}	682 ± 140 ^{c}	726 ± 190 ^{bc}	802 ± 269 ^{abc}	1027 ± 117 ^{ab}	1069 ± 156 ^{a}
(E)-2-Undecenal									
1361.38-1-A	572 ± 156 ^{ab}	437 ± 44 ^{b}	373 ± 127 ^{b}	524 ± 159 ^{b}	416 ± 131 ^{b}	446 ± 93 ^{b}	617 ± 187 ^{ab}	737 ± 155 ^{a}	735 ± 139 ^{a}
1507.84-2-A	395 ± 126 ^{cd}	580 ± 134 ^{bcd}	658 ± 145 ^{ab}	859 ± 143 ^{a}	360 ± 144 ^{d}	393 ± 156 ^{cd}	359 ± 179 ^{d}	638 ± 39 ^{abc}	768 ± 72 ^{ab}
Ethyl decanoate									
1392.28-1-A	22,344 ± 3694 ^{c}	24,711 ± 4347 ^{c}	23,607 ± 4337 ^{c}	25,987 ± 1720 ^{c}	75,717 ± 9326 ^{b}	109,065 ± 20,283 ^{a}	127,502 ± 22,464 ^{a}	74,607 ± 9252 ^{b}	83,732 ± 4696 ^{b}
1460.26-2-A	22,424 ± 3758 ^{c}	24,842 ± 4229 ^{c}	23,574 ± 4248 ^{c}	25,518 ± 1808 ^{c}	55,160 ± 6529 ^{b}	79,389 ± 14,933 ^{a}	92,663 ± 16,640 ^{a}	54,676 ± 6636 ^{b}	61,401 ± 3125 ^{b}
α-Terpinen-7-al									
1407.37-2-A	178 ± 130 ^{a}	163 ± 46 ^{a}	195 ± 24 ^{a}	189 ± 91 ^{a}	150 ± 23 ^{a}	163 ± 34 ^{a}	190 ± 46 ^{a}	199 ± 47 ^{a}	213 ± 55 ^{a}
Abhexone									
1431.31-2-A	472 ± 218 ^{a}	464 ± 133 ^{a}	345 ± 125 ^{a}	368 ± 158 ^{a}	402 ± 158 ^{a}	306 ± 161 ^{a}	229 ± 173 ^{a}	434 ± 61 ^{a}	405 ± 77 ^{a}

* Compounds are listed in order of separation on the column DB5. Different letters on each row indicate a statistically significant difference between the averages for the assessed varieties at a probability level of 95% ($\alpha = 0.05$) determined by one-way ANOVA and Tukey test ($p < 0.05$).

3.3.1. Discrimination of Samples Considered Altogether, Irrespective of the Yeast Used for Fermentation

In order to determine if the e-nose is able to discriminate among samples prepared in the presence of various dosages of octanoic acid, decanoic acid or their combinations, all the samples were taken into account, irrespective of the yeast used for fermentation (Figure 1). Even with a low validation score for the DF analysis, discrimination was possible in this way for groups of wines with different medium-chain fatty acid treatments, but also based on the different yeasts used.

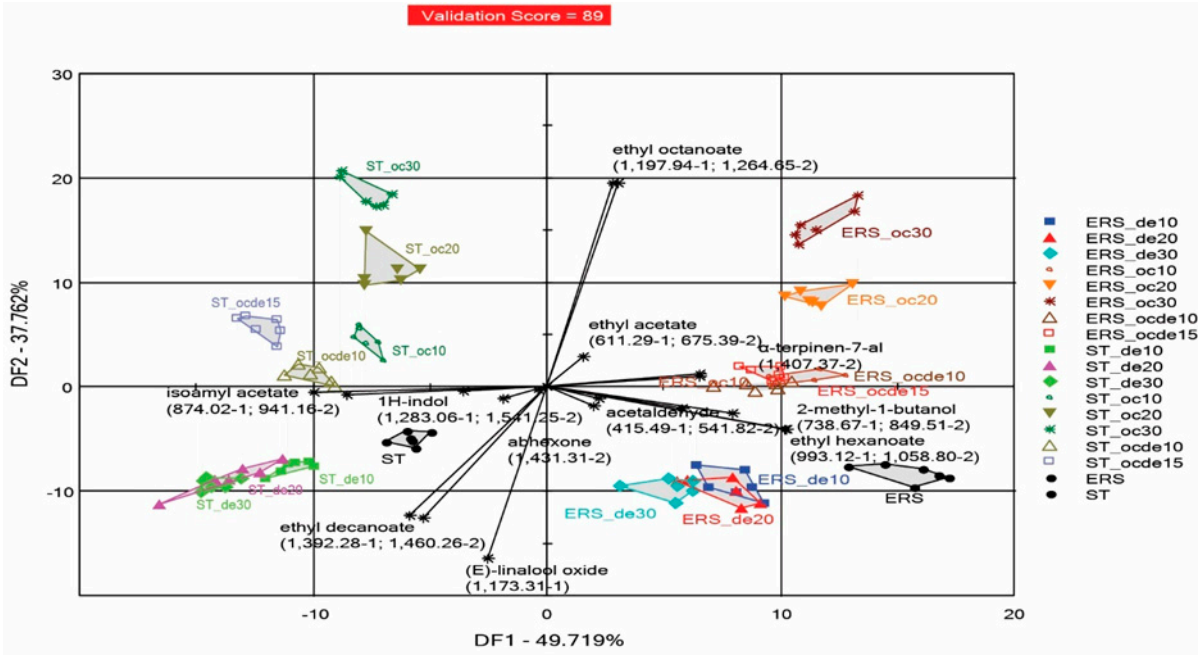

Figure 1. Discriminant Factor Analysis for the classification of all wine samples prepared by fermentation with two different yeasts (ERSA and ST) and by stopping fermentation with various dosages (10, 15, 20, 30 mg L^{-1}) of two medium-chain fatty acids (octanoic and decanoic acids).

Based on the volatile compounds determined by the GC-nose, the samples are mainly separated in accordance with the yeast inoculated to perform the must fermentation (Figure 1). The axis DF1, representing 49.72% of the total variance of the experimental data, essentially includes the effects of fermentation aroma compounds produced by the yeasts. Thus, it is clear that the ST yeast produces more isoamyl acetate aroma (banana) while ERSA induces more 2-methyl butanol, acetaldehyde and ethyl acetate. Some primary aroma-related compounds are also part of DF1, such as indole (more for the ST fermented wines) and ethyl hexanoate and α-terpinen-7-al (more for the ERSA fermented wines). Thus, the groups of samples fermented with ST are separated to the left of the diagram, while the groups of samples fermented with ERSA are present in the right side of the diagram.

DF2, representing 37.76% of the sample group variance, is clearly differentiating the samples based on the treatment with either octanoic or decanoic acid. The medium-chain fatty acids are not determined with the type of columns the GC-nose is endowed with; however, their esters, produced by the yeasts in the presence of these acids, are clearly revealed. Thus, the DF2 axis includes the effects of ethyl octanoate and ethyl decanoate, along with some linalool oxide, which is correlated with the presence of decanoic acid and especially the ST yeast. Accordingly, the samples treated with octanoic acid are all grouped in the upper quadrants of the diagram, where the influence of ethyl octanoate in the wine aromatic profile is clear, while the samples treated with decanoic acid are all grouped in the lower quadrants of the diagram, where the main factor influencing the aromatic profiles of wines is the ethyl decanoate. As expected, wines for which the fermentation was stopped

by a combination of octanoic and decanoic acid are placed in between the wine groups of octanoic and decanoic, respectively, being closer to the DF1 axis.

3.3.2. Discrimination of Samples Fermented with One Type of Yeast (ERSA or ST)

In order to determine more clearly the influence of the medium-chain fatty acids, DF analysis was also performed separately for the wines fermented with ERSA yeast (Figure 2) or ST yeast (Figure 3).

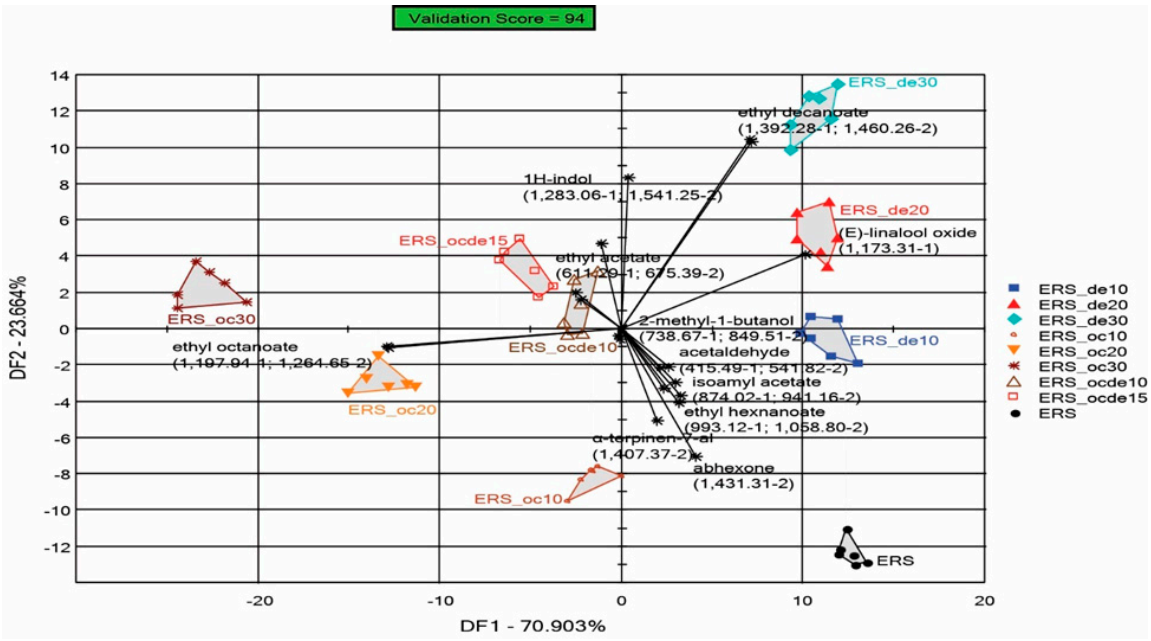

Figure 2. Discriminant Factor Analysis for the classification of all wine samples prepared by fermentation with ERSA yeasts and by stopping fermentation with various dosages of octanoic and decanoic acids.

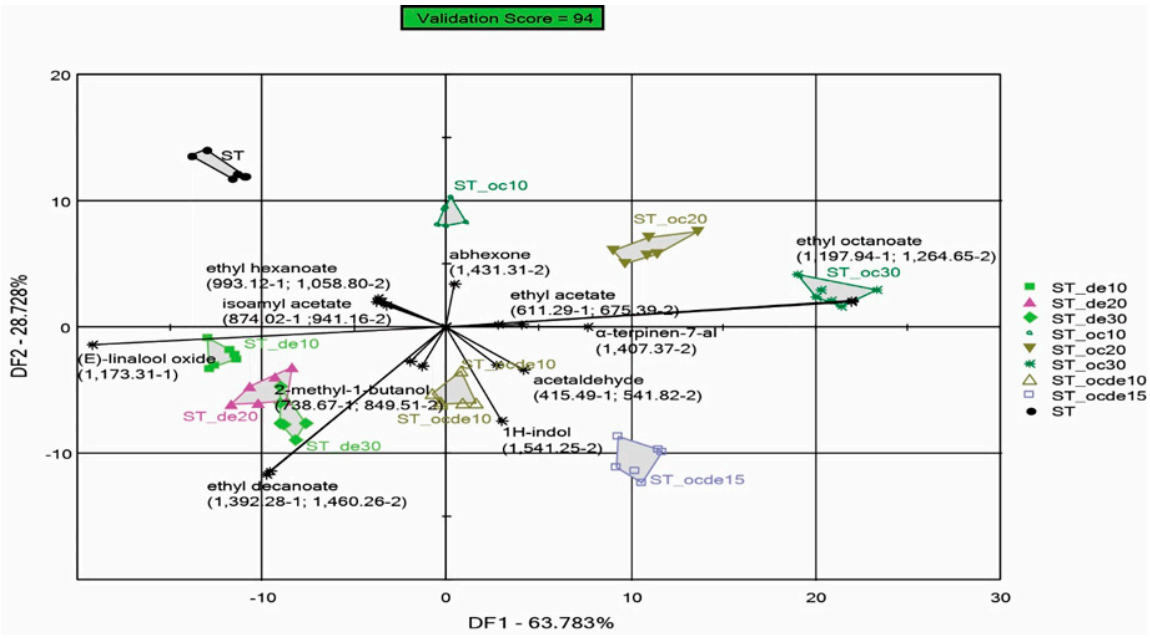

Figure 3. Discriminant Factor Analysis for the classification of all wine samples prepared by fermentation with ST yeasts and by stopping fermentation with various dosages of octanoic and decanoic acids.

For the wines fermented with ERSA yeast, the use of octanoic acid to stop fermentation leads to simpler aromatic profiles, with lower concentrations of other volatile compounds; the resulting ethyl octanoate has a major influence, especially at dosages higher than 10 mg L^{-1}. On the contrary, as a result of using decanoic acid to stop fermentation, the presence of ethyl decanoate in the wine fermented with ERSA leads to a very complex aromatic profile, especially for the doses lower than 20 mg L^{-1}.

Similarly, for the wines fermented by ST yeast, stopping the fermentation with octanoic acid leads to a simpler aromatic profile, in which, aside from ethyl octanoate, acetaldehyde, ethyl acetates and α-terpinen-7-al also have their influences. For this yeast too, the wines treated with decanoic acid at no more than 20 mg L^{-1} maintain a complex aroma profile.

It is already obvious from both diagrams that doses of 30 mg L^{-1} of either acid influence the wine aroma too greatly. Doses of 10 mg L^{-1} of either octanoic or decanoic acids have the smallest influence on the wines, their wine aromatic profiles placing relatively close to the ones of control wines (red circles in Figures 2 and 3).

4. Discussion

The influences of the yeast on the volatile aroma profile depended on their metabolism. Some volatile organic compounds, aside from those directly coming from the grapes (terpenes) were significantly influenced by the yeast during fermentation. For instance, exotic fruits aroma of isoamyl acetate and 2-phenylethyl acetate are enhanced by the ERSA yeasts, which is known to be an ester-producing yeast. Further, the pineapple/banana note is enhanced by the higher concentrations of ethyl ester of butanoic and hexanoic acid, as well as ethyl octanoate and ethyl decanoate naturally produced by this yeast even in the absence of octanoic or decanoic acids addition. Moreover, slightly higher concentrations of fermentation alcohols (2,3-butanediol, 2-methyl-1-butanol, 2-phenyl-ethanol), along with other specific wine spicy aroma compounds (abhexone) are produced by ERSA yeast. The other yeast (ST) has higher sugar concentration and produces higher alcohol amounts, but intervenes less in the aroma profile of the varietal wine, by producing slightly lower concentrations of the same fermentation compounds. Other volatile compounds contributing to overall wine aroma were found to be produced in similar quantities by both yeasts. Among these compounds we find several more acetic acid esters (*cis*-3-hexenyl acetate, ethyl acetate) and aldehydes (acetaldehyde, 2-phenyl-acetaldehyde, 2-methyl-butanal, 2-undecenal), which, being in low concentrations, show that the quality of the wine was not affected by oxidation. The fact that the wines were not much affected by oxidation is proven also by the low production of linalool oxide from the grape-derived β-linalool.

The influences of medium-chain fatty acids are especially observable in the increased levels of ethyl octanoate and ethyl decanoate, which, as discussed further, are correlated with the octanoic and decanoic acids used for the arresting of the fermentation. Other volatile compounds are also increased, as compared to the control wines, in the presence of the added medium-chain fatty acids. Thus, the values recorded on column DB5 for the fruity-sweet2-phenylethyl acetate increase in case of treatment with either octanoic or decanoic acid, irrespective of their dose or the yeast employed. 1H-indol, a floral-earthy aroma compound, even though present in small amounts, shows higher levels in the wine treated with octanoic or decanoic acids. The (e)-2-undecenal, with its specific herbaceous-orange peel aroma, also increases for ST yeast especially in the presence of octanoic acid and for ERSA yeast for both octanoic and decanoic acids, the effect being dose-dependent. This (e)-2-undecenal tends to be associated with oxidation of wines, and so does the (*e*)-linalool oxide. For this last compound, which results from the oxidation of *β*-linalool, it was observed that its concentrations are also increasing as compared to control in wines obtained after treatment with medium-chain fatty acids. The *β*-linalool/(*e*)-linalool oxide ratio is higher when the linalool is less oxidized, and for our wines we observed that the presence of octanoic acid tends to suppress oxidation of this compound in a dose-dependent manner, resulting in an increasingly more fruity-terpenic aroma. Thus, the *β*-linalool/(*e*)-linalool oxide ratio on chromatographic column DB5 was determined to be 2 for control, 2.8 for

10 mg L^{-1} octanoic, 3.6 for 10 mg L^{-1} octanoic + 10 mg L^{-1} decanoic, 5.3 for 20 mg L^{-1} octanoic, 6.2 for 30 mg L^{-1} octanoic and 6.5 for 15 mg L^{-1} octanoic + 15 mg L^{-1} decanoic, while for decanoic acid alone the ratio showed no protection from oxidation, its value being 1.4, 1.8 and 1.0 for doses of 10, 20 and 30 mg L^{-1} decanoic acid, respectively. On the chromatographic column DB1701 a similar behaviour was observed, the ratio for control and doses of 10, 20 and 30 mg L^{-1} decanoic acid being 1.8, 1.8, 1.5 and 1.3, respectively, while for treatments with 10, 20, 30 mg L^{-1} octanoic acid, 10 mg L^{-1} octanoic + 10 mg L^{-1} decanoic and 15 mg L^{-1} octanoic + 15 mg L^{-1} decanoic the values were 3.4, 7.7, 6.9, 4.2 and 9.3, respectively. Some of the volatile compounds are, however, decreased by the medium-chain fatty acids. This is the case of α-terpinen-7-al, a spicy aromatic compound, and abhexone, which may impart a curry-like nuance. Compared to the control wine, these compounds are found in lower concentrations in all samples treated with octanoic or decanoic acid and fermented with ERSA yeast.

Consequently, with all the modulation of aroma in the presence of certain yeasts and medium-chain fatty acids, the aroma profile of the final wine can be significantly influenced and difficult to differentiate based only on sensory analysis.

The electronic nose proved to be a very useful and rapid tool able to discriminate among the types of treatments applied for stopping the fermentation, as well as the dosage of fatty acids used. This discrimination was mainly due to the partial transformation by the yeasts of the medium-chain fatty acid used for interrupting the course of fermentation into their corresponding ethyl esters as a mechanism of detoxification [19]. The concentration of the ethyl esters produced was proportional to the dose of acid used (in the range of 10–30 mg L^{-1}), as proven by the peak areas determined on both chromatographic columns of the e-nose (Figures 4 and 5). The yeast had also an influence, the ST strain producing more ethyl decanoate than ERSA when decanoic acid is added to the medium, while ERSA naturally produces more ethyl octanoate than ST, a fact observed in control wines to which no medium-chain fatty acid was added.

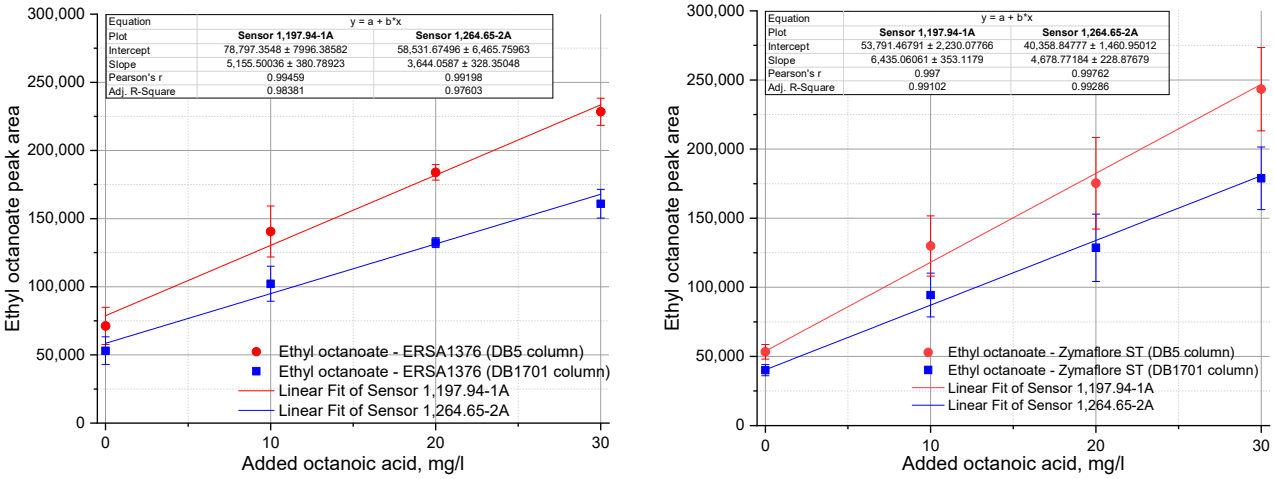

Figure 4. The increase of ethyl octanoate generated by the ERSA yeast (**left**) and ST yeast (**right**) with the dose of octanoic acid added in the range of 0–30 mg L^{-1}.

In both yeast strains, the concentrations of octanoic and decanoic acids of 10 mg L^{-1} were sufficient to inhibit fermentation, an effect observed also by Viegas et al. [6] on strains of *S. cerevisiae* and *Kluyveromyces marxianus*.

As it was demonstrated that the inhibitory effect of octanoic and decanoic acids is due to their undissociated form [6,20,21], the decrease of pH is prone to increase the inhibitory effect, especially in acid media such as wine, where the pH generally ranges from 2.9–3.8 [22].

The results also demonstrate that decanoic acid is more efficient than octanoic acid in inhibiting yeast growth and fermentation, the outcome being correlated with the molecular

chain length [20], and higher liposolubility [23] and its ability to induce leakage from the yeast cells [24].

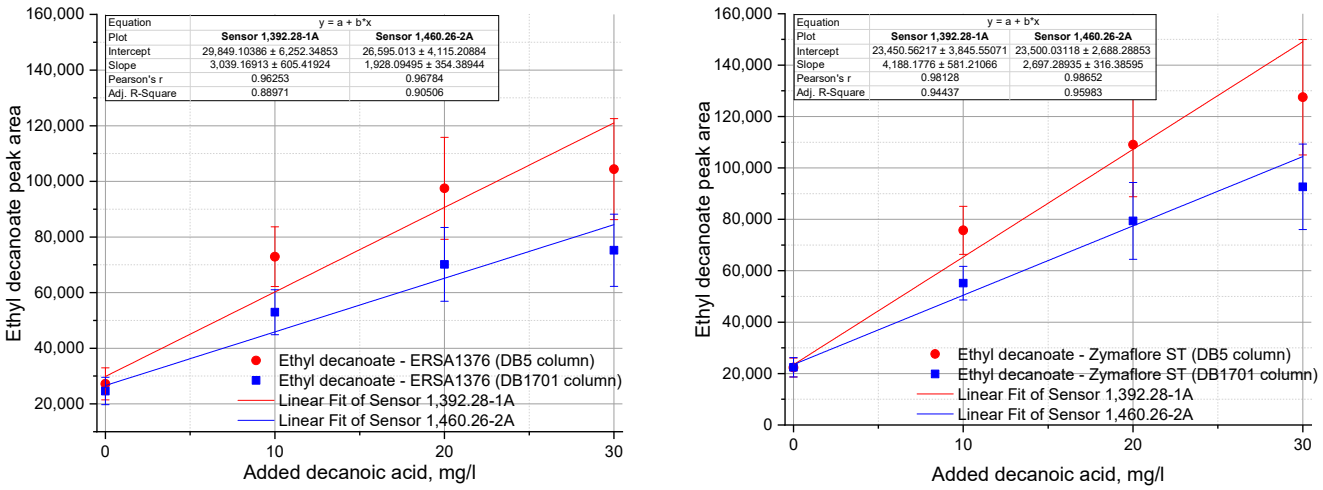

Figure 5. The increase of ethyl decanoate generated by the ERSA yeast (**left**) and ST yeast (**right**) with the dose of decanoic acid added in the range of 0–30 mg L^{-1}.

Ethanol, by contributing to the permeabilization of the yeast membranes [20] or activation of plasma membrane ATPase [25], can have a synergistic effect [20,26] on the inhibition induced by the octanoic and decanoic acid; however, some antagonistic effect was also documented [20,23] as the ethyl-esters produced are less inhibitory than the acids [23].

5. Conclusions

This research work showed that the wine fermentation can be stopped by any of the medium-chain fatty acids used—octanoic and decanoic acids—alone or in combinations. All the dosages employed were able to stop the fermentation of either of the two yeasts studied, allowing at the same time for a reduction of the added SO_2, from 120 mg L^{-1} to only 60 mg L^{-1}. However, the aroma profile of the wine, even though based on the same main compounds, is influenced by the choice of the acid, by its dose and by the yeast strain, which all together determine the final concentrations and ratios of volatile compounds produced.

Being sufficient to stop the fermentation with less influence on the aroma profile of the wine, the dose of 10 mg L^{-1} of either acid can be recommended.

The DFA analyses and the e-nose discrimination of wine samples based on their volatile profile indicates that decanoic acid leads to a more complex aroma in wines, some of the volatile compounds being preserved in overall higher concentrations.

If the goal is not to change much the volatile profile of wines obtained from the Tămâioasă romanească grape variety, in the case of decanoic acid being used to stop the fermentation, the yeast ERSA, producing less ethyl decanoate from the added acid, is recommended. However, in the case of octanoic acid being used to stop the fermentation, the yeast ST was observed to produce lower levels of the corresponding esters and is therefore recommended in association with the use of this fatty acid.

It should also be taken into account that, as the ethyl esters are less inhibitory than the acids, a yeast strain which produces higher amounts of ethyl esters also lowers the efficacy of the corresponding acids in stopping the fermentation.

This research will be continued at an industrial scale, and a sensory analysis with a panel of experts will also be performed to decide on the technological interventions most suitable for obtaining sweet wines from grape varieties with muscat aroma.

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