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## **Impact of Grape Varieties on Wine Distillates Flavour**

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#### Summary

Aroma is a phenomenon that occurrs when food and live organism mutually react during the process of consumption.

Many factors influence the making of aroma of wine distillates (e.g. cognac) during the technological process of distillation. It is extremely difficult to bring an objective judgement on the influence of individual factors since aroma is very subjective in its nature. The possibility of objective assessment of the influence of grape varieties on wine distillate was performed in this work using a computer in processing the results of cromatographic analyses of aroma substances. The given results were verified by sensor analyses.

The achieved results have shown that mathematical model for calculating aroma chromatogram similarity can be successfully used for objective assessment of the influence of individual factors on aroma of wine distillates and that grape varieties have significant impact on aroma and the quality of wine distillates.

Key words: cognac, flavour, wine distillate, grape varieties, mathematical model

#### Introduction

The main characteristic of the living world is the sensibility to stimula from the environment, but none of the living beings can register all of them (1,2). Food is one of these significant stimula. It is a complex mixture of organic and inorganic substances forming the so-called physico-chemical consumption phenomenon. Aroma is one of sensory food characteristics provoked by physiological phenomena. According to the *British Standards Institution* definition, aroma is a combination of taste and odour caused by the experience of pain, heat, cold and sense. In other words, aroma is a complete and unique experience generated from not only the taste and odour stimula but from other sensorial receptors too.

This definition states that aroma is a phenomenon occurring when food and live organism mutually react (3). Quality of wine distillates is influenced by many factors during the production process, so we can distinguish the following:

- primary aroma substances generated from the grape varieties
- secondary aroma substances generated during the vinification and fermentation process
- aroma substances generated during the distillation process
- aroma substances generated during the maturation process

Many authors (4–9) have attempted to answer the question whether the phenomenon of aroma is primarily the result of stimula caused by interaction of several hundreds of different aroma substances with human re-

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ceptors recognised inside the brain (1) or if it is influenced by subjective attitude. It is very difficult to bring an objective judgement on the influence of one factor since the aroma has a subjective character too.

In this work the possibility of objective assessment of the influence of grape varieties on wine distillate aroma by using computers has been studied.

#### Materials and Methods

#### Must

Samples of must were taken from the technological process of wine production at »Kutjevački podrumi« plc, from the harvest of the year 2000. The samples were the dominating grape varieties selected from the recommended and allowed varieties of »Kutjevo Vinogorje«. All samples were protected by SO<sub>2</sub> (100 mg/L) and the sample of *Steinschiller* was sweetened with saccharose (28 g/L) according to the permission of the Vinery and Viticulture Institute.

#### Wine

In »Kutjevački podrumi« wines are produced using classical technological procedure: fermentation with indigenous yeast and controlled thermal regime using outer refrigeration of fermentors with running water, with the aim of keeping the average temperature in intervals of 18–20 °C. The average duration of fermentation of all grape varieties and under these conditions was 42 days.

The samples of young wine were taken at the end of fermentation before sedimentation, therefore the wines were insufficiently clear and slightly dull, which is appropriate for the selected procedure for the production of distillate.

#### Distillate

Selected samples of wine were distilled according to the procedure of *Brouillis* and *Bonne chauffé* in copper clip distillation device, as shown in the scheme in Fig. 1.

The samples containing 70 % vol. alcohol were taken from the middle *cognac* fraction, or with recommended alcohol concentration in wine distillates, while the middle *secondes* and the last *tail* fraction were not used (10).

All selected samples of wine were distilled according to the same distillation protocol.

#### Sensory analyses

Sensory assessment of wine samples was performed using the Buxbaum model of positive ranking (2). This model is based on 4 sensorial experiences rated by maximum 20 points.

A sensory analysis of samples of wine distillates was performed according to the method of positive ranking with factor according to the German DLG model (11). This model was based on 4 sensorial experiences, which are marked with grades from 0 to 5, including 0, while the average grade is multiplied by the significance factor.

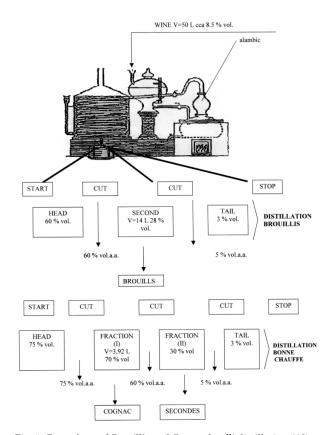


Fig. 1. Procedure of Brouillis and Bonne chauffé distillation (10)

Sensory test of changes during the technological procedure for the production of wine distillates as well as the verification of computerised results of chromatogram similarities was performed only for odour, using the model of Ranking Test (12).

Sensory assessment was conducted in two repetition cycles, each group had ten – 10 qualified testers, professional testers, from alcoholic beverages industry, selected by selection procedure (12), with extensive experience in sensory assessment of wine distillates.

#### Analyses of aroma substances

Gas chromatography (GC) analyses were performed on a Hewlett Packard 5890 gas chromatograph with a split /splitless injector and an FID detector. For the headspace analyses of must and wine Hewlett Packard sampler HP 7694 was used. Compounds of interest were resolved on a Stabilwax (Restec, USA) capillary column ( $30 \text{ m} \cdot 0.25 \mu \text{m}$  i.d.  $0.25 \mu \text{m}$ ) with the following parameters: initial oven temperature was 30 °C kept for 4 min, then raised at 10 °C/min to 100 °C, followed by 25 °C/min to 250 °C and kept for 7 min at 250 °C. Injection port temperature was kept 180 °C, pressure was 20 psi, and carrier gas (nitrogen) flow was 3 mL/min. Detector temperature was 250 °C.

A headspace sampler was equipped with a standard 1 mL loop. Carrier gas pressure was 17 psi, vial pressure was 7 psi and injection time was 0.20 min. Samples were heated for 10 min at 100 °C. For analysis of wine distillates a Stabilwax (Restec, USA) capillary column (30 m  $\cdot$  0.25  $\mu$ m i.d. 0.25  $\mu$ m) was used. Initial oven temperature was kept at 35 °C for 7 min, then raised at 10 °C/min to 80 °C followed by 25 °C/min to 200 °C, and kept for 4 min at 200 °C. Qualitative analysis was done by comparison of retention times of standards and the corresponding peaks of samples. The quantification was carried out by comparison of the areas of peaks to those of the internal standard.

# Mathematical model of the processing results of the analyses of aroma substances

The basic assumption in determining the influence of grape varieties on aroma of wine distillate is that volatile substances of the aroma have dominating impact on wine distillate aroma and that other factors can be mathematically neglected.

According to this assumption, for chromatographically determined characteristics of aroma of the grape varieties, it is possible to calculate the chromatographical differences in each stage of the process.

The factor of similarity is calculated using the algorithm of chromatogram similarity (13) where S is factor of chromatogram similarity **a** and **b**, which differs from 0-1 (0 – absolutely no similarity, 1 – absolute similarity).

The choice of peaks was made following these 3 conditions:

- 1. Chosen peak has to be in at least one basic (*must*) chromatogram and in at least one chromatogram in each stage of the process.
- 2. Chosen peak has to be identified by gas-chromatographic method and its quantity has to be defined.
- 3. Chosen peak has to be among the group of substances responsible for the characterisation of grape varieties and quality of wine for distillation as well as for the quality of wine distillate (7,14,15).

#### **Results and Discussion**

For the production of wine distillates according to a selected technological procedure, young and non-cleared wines are used. For that reason all of the selected wines were slightly turbid, which is, according to Buxbaum rated as a negative characteristic. Therefore, all the samples were granted minimal or zero for clearness. Table 1 shows results of the sensory analyses of wines used for distillation. Sensory assessment of wine samples was performed according to the method of positive ranking by Buxbaum model (2) in order to determine the wines with characteristics suitable for distillation (10,15).

Total sensory quality of wines was rated in interval between 13.86 and 15.32, which is a very high score for young wines. The difference in rates of individual wines comes from different characteristics of each wine variety. Statistically significant differences (P=0.05) were determined in the examined sensory wine characteristics (16).

According to the results of sensory ranking, the best rated wine is *Rhine riesling*, which ten examiners rated with very high score (total sensory characteristics 15.32). Among the selected wines, it has the most similar characteristics to those used for production of wine distillates type cognac (10,15).

Table 2 shows results of conducted sensory analyses of wine distillates produced through the procedure of double distillation; first brouillis distillation, followed by bonne chauffé distillation. Sensory assessment of samples was conducted according to the method of positive ranking with weight factors according to German DLG model (11). The ranking was conducted by a group of ten qualified testers with extensive experience in sensory assessment of distillates. Total sensory assessment ranged in the interval between 54.60 and 98.60, which indicates the significant differences among samples. Furthermore, they can be addressed to different characteristics of wine varieties, since other factors in the production of wine distillates were the same for all samples. According to the estimated sensory characteristics, statistically significant differences (P=0.05), among wine distillates were found (16), which confirms this statement. Rhine riesling received the highest score for total sensory characteristics (98.60), which qualifies it as the best sensory distillate produced trough the above mentioned distillation process (15). The wine from which this distillate was produced was also rated as the best among the selected wines.

According to the basic assumption that volatile substances of the aroma have dominant impact on aroma of a wine distillate, gas chromatographic (GC) analysis was

Table 1. Sensory analyses of wine used for distillation – Buxbaum model of positive ranking (2)

Grape varieties		Assessment characteristics							
	Colour (max 2 points)	Clearness (max 2 points)	Odour (max 4 points)	Taste (max 12 points)	(max 20 points)				
Riesling	1.80	0.00	3.46	10.0	15.26				
Pinot blanc	1.45	0.00	3.15	10.0	14.60				
Pinot gris	1.50	0.00	3.14	10.0	14.64				
Chardonnay	1.81	0.00	3.35	10.0	15.10				
Traminer	1.49	0.00	3.46	10.0	14.85				
Rhine riesling	1.80	0.00	3.50	10.0	15.32				
Müller Thurgau	1.79	0.00	3.49	9.80	15.00				
Frankovka	1.69	0.00	3.49	9.80	14.94				
Steinschiller	1.79	0.00	3.10	9.00	13.86				

		TOTAL			
Grape varieties	Colour (max 15 points)	Clearness (max 15 points)	Odour (max 25 points)	Taste (max 45 points)	(max 100 points)
Riesling	15.00	14.70	22.00	37.80	89.50
Pinot blanc	15.00	14.40	16.00	29.70	75.10
Pinot gris	9.30	9.00	12.00	24.30	54.60
Chardonnay	15.00	15.00	14.00	26.10	70.10
Traminer	15.00	14.40	15.00	26.10	70.50
Rhine riesling	15.00	15.00	24.50	44.10	98.60
Müller Thurgau	14.70	14.70	23.50	43.20	96.10
Frankovka	14.70	14.40	14.50	22.50	66.10
Steinschiller	14.40	14.70	15.50	26.10	70.70

Table 2. Sensory analyses of wine distillates - German DLG model (11)

Table 3. Aroma compounds in must samples (mg/L)

$\frac{\gamma \text{ (aroma compounds)}}{\text{mg}/\text{L}}$	Riesling	Pinot blanc	Pinot gris	Chardonnay	Traminer	Müller Thurgau	Frankovka	Steinschiller	Rhine riesling
1-butanol	0.28	0.34	0.29	0.25	0.29	0.30	0.25	0.32	0.27
isoamyl alcohol	0.35	0.37	0.32	0.27	0.37	0.34	1.33	0.99	0.45
ethyl lactate	4.50	5.70	4.43	2.37	n.i.	n.i.	n.i.	6.26	6.54
1-hexanol	0.83	2.04	1.71	0.47	2.30	1.60	2.86	2.17	0.61
linalool	0.16	0.16	0.87	0.31	1.05	1.79	0.37	0.56	0.19
2-phenyl ethanol	n.i.	n.i.	n.i.	0.85	n.i.	n.i.	n.i.	25.20	n.i.

n.i. - not identified

Table 4. Aroma compounds in wine samples (mg/L)

$\gamma$ (aroma compounds)	Riesling	Pinot blanc	Pinot gris	Chardonnay	Traminer	Müller	Frankovka	Steinschiller	Rhine	
mg/L			8			Thurgau			riesling	
acetaldehyde	22.33	10.66	30.77	19.51	24.31	15.69	n.i.	22.25	24.31	
ethyl acetate	41.11	22.02	45.33	32.85	42.73	21.44	12.27	28.47	42.73	
1-propanol	20.56	9.97	28.10	18.94	20.14	9.84	8.64	13.41	20.14	
isobutyl alcohol	43.17	24.63	31.35	26.68	33.52	29.9	30.57	61.64	33.52	
isoamyl acetate	2.74	1.22	2.45	1.82	3.12	1.68	0	1.56	3.12	
1-butanol	0.65	n.i.	0.85	0.55	0.73	0.49	0.72	0.58	0.73	
isoamyl alcohol	190.23	163.29	129.03	115.55	161.37	177.95	n.i.	118.33	161.37	
ethyl hexanoate	0.953	n.i.	0.76	n.i.	0.32	n.i.	n.i.	n.i.	0.32	
ethyl lactate	3.86	2.69	5.98	8.74	n.i.	n.i.	2.33	3.09	n.i.	
1-hexanol	5.22	2.93	2.92	1.71	3.81	2.36	2.65	3.36	3.81	
ethyl octanoate	n.i.	1.50	3.66	0.53	1.93	1.02	n.i.	1.04	1.93	
linalool	1.28	0.70	0.36	0.87	0.63	0.34	0.18	0.13	0.63	
ethyl decanoate	1.33	0.42	0.88	0.23	0.18	0.11	n.i.	0.20	0.18	
2-phenyl ethanol	32.04	17.15	43.37	55.42	15.71	38.82	38.63	53.60	15.71	

n.i. - not identified

performed. Chosen aroma substances belong to the group of substances responsible for characterisation of different varieties and quality of wine for distillation as well as for the quality of wine distillates. Tables 3, 4 and 5 show the participation of determined aroma substances in samples of must, wine and wine distillates, and all results are in accordance with results published in (7,14,15). In several samples some of the volatile substances were not identified. For the calculation of the

chromatographic similarity factor they were taken into the calculation as 0 value.

Table 6 shows similarity factors calculated from the aroma compounds determined by chromatography between *Rhine riesling*, the sort with the best sensory characteristic of distillate, and other varieties in each step of the process (must, wine and distillate). From Table 6 it can be seen that similarity factors increase from must to distillate.

$\frac{\gamma \text{ (aroma compounds)}}{\text{mg}/\text{L}}$	Riesling	Pinot blanc	Pinot gris	Chardonnay	Traminer	Müller Thurgau	Frankovka	Steinschiller	Rhine riesling
acetaldehyde	57.15	13.76	14.11	38.58	41.60	27.50	13.29	39.74	68.20
ethyl acetate	86.57	14.20	44.31	57.49	75.58	49.18	32.16	59.48	43.03
methanol	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	15.85	n.i.	28.22
1-propanol	24.75	4.70	18.20	21.00	5.28	13.62	23.79	17.40	10.07
isobutyl alcohol	53.62	9.39	15.37	30.42	34.94	33.76	68.78	72.70	40.25
1-butanol	n.i.	n.i.	n.i.	n.i.	0.89	n.i.	1.80	n.i.	1.45
ethyl hexanoate	2.47	1.57	n.i.	2.34	2.36	2.16	n.i.	2.38	n.i.
isoamyl alcohol	148.79	189.9	88.80	165.39	193.05	233.46	507.23	166.57	234.85
ethyl lactate	3.07	1.41	n.i.	n.i.	2.54	2.05	3.63	2.57	3.06
ethyl octanoate	5.92	2.69	2.92	4.18	4.55	4.80	n.i.	6.22	4.04
ethyl decanoate	1.74	0.91	1.18	n.i.	0.94	1.28	n.i.	2.65	1.27
2-phenyl ethanol	2.97	4.52	3.45	4.75	2.73	8.36	8.76	7.34	28.78

Table 5. Aroma compounds in wine distillate samples (mg/L)

n.i. - not identified

Comparing must sample of *Rhine riesling* grape variety to other must samples, similarity factors rise from 0.089 to very high 0.996, which confirms the significant difference among the different varieties of wine.

The similarity factors in wine samples compared to *Rhine riesling* have a somewhat narrower range, from 0.274 to 0.997, which confirms the decrease of differences among samples due to the influence of vinification process. The obtained results are in accordance with the published data (17-20). According to those results, fermentation changes are the most significant for the definition of secondary aroma profiles, which primarily depend on the kind of substances developed in the metabolic processes during fermentation. The kind of aroma substances depends on the type and sort of the yeast, structure of fermented substances, presence of carbohydrates, long-chained fatty acids, organic nitrogen and substances containing sulphur as well as temperature, dynamics of fermentation and the activity of enzymes.

Similarity factors among distillate samples compared to distillate produced from *Rhine riesling* grape variety were in range between 0.930 and 0.978, which confirms the assumption that through technological phase of the production of distillates the differences in characteristics of each variety are diminished, but still enough to indicate the difference among grape varieties.

The decrease of differences characteristic for each variety of grapes from wine to distillate is the consequence of the distillation process. The obtained results confirm the findings of many authors (10,15,21). They state that the participation of volatile components from wine decreases significantly during the process of distillation but also at the same time a completely new aroma substances occur. During the distillation, in *alambic*, the

Table 6. Similarity factors (S) calculated from the aroma compounds determined by chromatograph, between *Rhine riesling* and other varieties in each step of the process (must, wine and distillate)

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Grape varieties	S <sub>must</sub>	Swine	S <sub>distillate</sub>
Frankovka	0.089	0.274	0.954
Steinschiller	0.249	0.939	0.953
Müller Thurgau	0.096	0.996	0.978
Pinot gris	0.949	0.961	0.937
Pinot blanc	0.969	0.984	0.956
Traminer	0.109	0.987	0.969
Chardonnay	0.933	0.953	0.974
Riesling	0.996	0.995	0.930

whole range of energetically and structurally very complex chemical reactions take place, such as hydrolyses, esterification, oxidation, dehydration, acetylation, catalytic copper reactions *etc.* Such reactions generate a large amount of substances from *Maillard reactions*, with concentration above 2 mg/L for each individual substance, and an even greater number of volatile components in a relatively small (below 1 mg/L), almost negligible concentrations, which still significantly influence the aroma profile and the quality of young distillates. (*15,21*).

The aim of sensory analyses was to verify the results of the analyses of aroma substance as well as the calculation of similarity factor and they were performed using the model of Ranking Test (12) for odour only. As the reference, odour profile of *Rhine riesling* grape variety was taken. Results are presented as sums for the ranking of the must, wine and distillate samples. According to the findings of the panel of ten testers on 5 %

Table 7. Ranking test

Reference (R. riesling)	Riesling	Pinot blanc	Pinot gris	Chardonnay	Traminer	Müller Thurgau	Frankovka	Steinschiller
Must	10	21	29	43	58	69	80	50
Wine	18	31	51	59	39	12	80	70
Distillate	18	51	68	32	38	12	80	61

level, the range of Ranking Test (for the 8 samples) was between 27 and 63, and all the values outside these limits are statistically significantly different from other samples. (16)

From the results shown in Table 7 it is visible that the distillates produced from wines *Müller Thurgau* and *riesling* are significantly better than the others, while the weakest distillate comes from wine *frankovka*. The results of Ranking Test are in accordance with the results of the analyses of aroma substances determined by cromatography and by similarity factors. This proves that grape variety has the main influence on the characteristics of a distillate.

#### Conclusions

The obtained results have shown that grape variety has significant influence on aroma and quality of wine distillates. In fermentation conditions at temperatures that do not excede 20 °C and in conditions of double distillation in *alambic*, with the exemption of distillate's middle fraction, the variety has a dominating influence.

The aroma of wine distillates is significantly influenced by its volatile substances, therefore other factors can be mathematically neglected. On the contrary, mathematical model for chromatogram similarity calculation can be successfully used for objective assessment of the influence of individual factors on the aroma of wine distillates as well as for monitoring the changes in aroma substances trough the phases of technological procedure for the production of wine distillate. The continental region of the Republic of Croatia is well known for the production of high quality wines. In this paper it is demonstrated that by using specific grape varieties (*Rhine riesling, riesling, Müller Thurgau*) and the procedures of *Brouillis* and *Bonne chauffé* distillation, the distillates of highest quality can be produced.

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### Utjecaj vinskih sorta na aromu destilata

#### Sažetak

Aroma je fenomen koji se pojavljuje tijekom konzumiranja hrane u organizmu. Pri stvaranju ukupne kakvoće (*tip cognac*) vinskih destilata upravo taj fenomen ima dominirajuću, a vrlo često i odlučujuću ulogu. Na aromu vinskih destilata utječe mnogo činitelja tijekom njezina stvaranja u tehnološkom procesu proizvodnje. Medjutim, objektivnu je prosudbu o utjecaju pojedinog činitelja iznimno teško donijeti jer aroma ima i subjektivni karakter.

U ovom je radu ispitana mogućnost objektivne procjene utjecaja sorte na aromu vinskih destilata primjenom računala u obradbi kromatografskih rezultata analize tvari arome, a navedeni su rezultati provjereni senzorskim analizama.

Dobiveni su rezultati pokazali da se matematički model za kompjutorsko izračunavanje sličnosti kromatograma arome može uspješno koristiti pri objektivnoj procjeni utjecaja pojedinih činitelja na aromu vinskih destilata, te da sorta grožđa bitno utječe na aromu i kakvoću vinskih destilata.