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ATTEMPTS AT SHORTENING MADEIRIZATION OF FRUIT WINES BY THE METHOD OF SHERRIZATION

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Key words: madeirization of fruit wines, sherrization, apple wine, strawberry wine, currant wine.

Studies were made to check the possibility of shortening the time of madeirization of fruit wines by performing submerged sherrization (at 18° C for 10 days) prior to a 7-14-day process of heating at 45° C. Madeirization at 55° C for six weeks was performed for comparison. Single-fruit wines (apple, strawberry and currant) as well as mixtures of these wines were processed.

INTRODUCTION

One of the methods of improving the taste and flavour properties of wines and of shortening the period of maturation is madeirization i.e. a heat treatment allowing access of oxygen, a process giving wine properties of Madeira-type wines.

The new technologies of grape Madeira production tend to shorten the time of madeirization, both for economic reasons (considerable energy consumption in the extended process) and in an attempt to meet the increasing demand for this kind of wine.

The attempts to shorten madeirization time go in two principal directions. The first involves an increase of the temperature of the process with a simultaneous increase of component reactivity, and is based on the findings of Spricman et al. [25]. The results of studies of the applicability of this method to fruit wines were presented in a previous publication [27]. The second possibility of reducing heating time is the method of sherrization-madeirization used in the production of the "Tavrida" grape Madeira [7]. The wine material is initially subjected to submerged sherrization (i.e. a process of producing sherry characteristics in the wine) to obtain the desired aldehydes content, and then it is mixed and heated for about two weeks. To perform sherrization, well-fermented wines (containing $14-16^{0/0}$ alcohol, less than 2 g sugars per dm³, and not more than 300 mg tannins per dm³) are inoculated with yeast races capable of an oxidative life phase. The most recommended of these are the yeasts Saccharomyces cerevisiae of the Sherry race and the yeasts Saccharomyces oviformis. The process takes place at $16-20^{\circ}C$.

The purpose of the performed research was to determine in laboratory conditions the possibilities of reducing the time of madeirization of fruit wines through the use of submerged sherrization prior to a short heating of the wine.

METHODS

MATERIAL

The experiments were performed with industrial apple, strawberry and currant wines (fortified up to $15^{0}/_{0}$ vol. alcohol content) and with 1:1 and 4:1 mixtures of apple and strawberry wines, and a 1:1 mixture of apple and currant wines. The yeasts *Saccaromyces cerevisiae* of the Sherry race and the yeasts *Saccharomyces oviformis* were used in the sherrization process. Winemaker's tannin was added to some of the samples.

TECHNOLOGY

In the initial stage of the experiment we compared test submerged sherrization of fruit wines with the surface method in order to determine the conditions of sherrization for the sherrization-madeirization method. We applied the yeasts *Saccharomyces cerevisiae* of the Sherry race in the form of yeast sediment. We found on the basis of the chemical composition and organoleptic assessment of the wines subjected to sherrization that madeirization can be shortened by preceding it with submerged sherrization lasting 10-14 days.

In the subsequent part of the studies we performed sherrization-madeirization processing of single-fruit wines. The wines were subjected to submerged sherrization at $18^{\circ}C \pm 0.5^{\circ}C$ for 10 days and then to madeirization at $45^{\circ}C$ for 7 or 14 days. For comparison we also performed madeirization at $55^{\circ}C$ for six weeks. Before sherrization some of the samples were augmented with 0.3 g of winemaker's tannin per dm³ in order to determine the effect on the process of a tannin content exceeding that desirable in grape wines.

Madeirization of fruit wines

In the process of sherrization the wine materials were inoculated with Sherry yeasts of the species *Saccharomyces cerevisiae* and a cell concentration of about 5 milion per cm³ was obtained; the samples were constantly aerated during the process (air flow — $7.5 \text{ dm}^3/\text{h}$).

During madeirization the samples were aerated for five minutes daily. To prevent losses of alcohol and other volatile components of wine, we used a water reflux condenser through which the excess of pumped air could escape. After the end of madeirization, the planned analyses of the wine were performed, the sugars content in the wine was adjusted to 100 g/dm³, the wine was filtered and after two weeks of cellar treatment it was assessed organoleptically.

The next stage of experiments with the sherrization-madeirization method involved wine mixtures. The study of mixtures was prompted by the observation that the majority of white fruit wines are mitures containing apple wine.

The variants of eperiments as well as the parameters of sherrization and madeirization were the same as in the case of single-fruit wines except that instead of Shery-race yeasts we used the yeasts *Saccharomyces oviformis* and that we added the winemaker's tannin only after the end of sherrization. The organoleptic assessment was done after 1.5 months of cellar treatment.

ANALYSES

The chemical analyses included determinations (among others) of aldehydes and acetals by the iodometric method [1], volatile esters by the distillation method [1], tannins by the colorimetric method with FeCl₃ [13], furfurals by the colorimetric method with thiobarbituric acid [16], diacetyl and acetoin by the colorimetric method [4].

The organoleptic analysis was done by a committee using a five-point scale divided into half-point intervals. The final result of the qualification was calculated by summing up the marks for the separate features multiplied by the relevant coefficients of importance: clarity -0.1, colour -0.1, smell -0.2, and taste -0.6. The above coefficients make it possible to compare the results with the 20-point scale; to do this the final qualification has to be multiplied by four.

RESULTS AND DISCUSSION

The chemical composition of the wines used in the study differed significantly from that of grape wines [11]. The processed wines contained $14.7-16.1^{0}/_{0}$ vol. alcohol, 1.3-5.7 g total sugars/dm³, 79-98 total nitrogen/dm³ and 150-630 mg tannins/dm³.

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Determination													
acetals as acetic aldehyde acetal (mg/dm ³)		volatile esters as ethyl acetate (mg/dm ³)		tannins as tannic acid (mg/dm ³)		furfurals as fur- fural (mg/dm ³)		diacetyl (mg/dm ³)		acetoin (mg/dm ³)		organoleptic assessment (final evaluation in points)	
without tannin addition	with tannin addition	without tannin addition	with tannin addition	without tannin addition	with tannin addition	without tannin addition	with tannin addition	without tannin addition	with tannin addition	without tannin addition	with tannin addition	without tannin addition	with tannin addition
55		224		630		7.5		11.0		6.3			
66	79	144	149					14.0 14.1		6.3 8.8			
90	168	254	259	5 63	810	9.8	10.4	18.3	15.5	6.4	8.0	4.3	4.3
121	129	293	270	345	743	12.8	13.0	17.4	18.8	7.4	6.6	4.4	4.3
217	220	305	298	143	533	24.0	25.6	21.2	19.4	3.4	4.2	4.5	4.4
	acetals aldehyd (mg, without tannin addition 66 90 121 217	acetals as acetic aldehyde acetal (mg/dm³)without tannin additionwith tannin addition55667990168121129217220	acetals as acetic aldehyde acetal (mg/dm³)volatile ethyl a (mg/ without tannin additionwithout tannin additionwith tannin additionwithout tannin addition55 6629 14490168 168 254121129 293 305	acetals as acetic aldehyde acetal (mg/dm³)volatile esters as ethyl acetate (mg/dm³)without tannin additionwith tannin additionwithout tannin additionwith tannin addition55224667914414990168254259121129293270217220305298	acetals as acetic aldehyde acetal (mg/dm³)volatile esters as ethyl acetate (mg/dm³)tannins ac (mg/ (mg/ m³)without tannin additionwith tannin additionwith ut tannin additionwith with tannin additionwith with tannin addition55 6622466667914414990168254259121129293270217220305298143	acetals as acetic aldehyde acetal (mg/dm^3) volatile esters as ethyl acetate (mg/dm^3) tannins as tannic acid (mg/dm^3) without tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin addition55 66224630667914414990168254259121129293270217220305298143533	Determacetals as acetic aldehyde acetal (mg/dm³)volatile esters as ethyl acetate (mg/dm³)tannins as tannic acid (mg/dm³)furfural fur (mg/ mg/m³)without tannin additionwith tannin additionwith tannin additionwith tannin additionwith with tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin addition55 66224630 	Determinationacetals as acetic aldehyde acetal (mg/dm³)volatile esters as ethyl acetate (mg/dm³)tannins as tannic acid (mg/dm³)furfurals as fur- fural (mg/dm³)without tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin addition55 6679144149	Determinationacetals as acetic aldehyde acetal (mg/dm³)volatile esters as ethyl acetate (mg/dm³)tannins as tannic acid (mg/dm³)furfurals as fur- fural (mg/dm³)diac (mg/m³)without tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin a	$\begin{array}{ c \hline \hline$	Determinationacetals as acetic aldehyde acetal (mg/dm³)volatile esters as ethyl acetate (mg/dm³)tannins as tannic acid (mg/dm³)furfurals as fur- fural (mg/dm³)diacetyl (mg/dm³)aced (mg/m³)without tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwithout tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin additionwith tannin addition <t< td=""><td>$\begin{array}{$</td><td>$\frac{ }{ } = \frac{ }{ } = \frac{ }{ } = \frac{ }{ } = \frac{ }{ }$</td></t<>	$ \begin{array}{ $	$\frac{ }{ } = \frac{ }{ } = \frac{ }{ } = \frac{ }{ } = \frac{ }{ }$

Table 1. Changes of selected components of fruit wines during sherrization-madeirization

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Currant wine											1				
Initial	107		56		368		7.2		5.9		2.0				
10-day sherrization	114	122	61	69			-		20.2	18.4	2.6	2.9			
1-week sherrization-															
madeirization	134	207	126	136	300	645	8.0	10.5	22.6	19.0	3.4	3.4	3.8	3.8	
2-week sherrization-								1				i ·			
madeirization	220	232	162	171	145	495	10.2	14.3	17.2	16.9	3.2	1.1	3.8	3.8	
Traditional 6-week				1											
madeirization	228	295	204	297	65	180	22.1	21.7	19.9	18.5	1.1	0.6	3.8	3.9	
			-]												
Apple wine															
Initial		44	1	31		150		5.3		2.9		1.2		Mastra	
10-day sherrization	44	48	31	31	_	_	-		16.1	18.7	1.2	1.4			
madeirization	88	147	39	39	145	195	8.3	8.9	17.9	18.9	1.2	2.4	33	33	
2-week sherrization-			1									2	5.5	5,5	
madeirization	143	159	70	53	125	165	13.3	12.3	17.9	19.0	2.0	1.1	3.3	3.4	
Traditional 6-week														211	
madeirization	83	101	101	105	48	200	18.7	21.4	4.1	7.6	0.6	1.1	3.9	3.9	

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In all the wine samples, irrespective of the processing method, there was a clear increase of aldehydes, acetals and volatile esters and a drop in tannins content (Tables 1 and 2, Fig.). Such transformations are typical

	Determination										
Wine and sample kind	aldehyd tic alc (mg	es as ace- lehyde :/dm³)	acetals aldehyd (mg	as acetic le acetal (/dm ³)	volatile ethyl : (mg	esters as acetate /dm ³)	organoleptic assessment (final evaluation in points)				
	without tannin addition	with tannin addition	without tannin addition	with tannin addition	without tannin addition	with tannin addition	without tannin addition	with tannin addition			
Apple-strawberry wine in 1:1 proportion											
Initial	98* ⁾	—	38*)	—	175*)	—					
After sherrization**)	308		52		238		4	.2			
1-week sherrization- madeirization 2-week sherrization-	229	202	76	83	264	264	4.5	4.4			
madeirization Traditional 6-week	308	255	97	106	264	273	- 4.3	4.5			
madeirization	55	62	40	40	519	396	4.0	4.4			
Apple-strawberry wine in 4:1 proportion											
Initial	115*)		42*)		185*)			·			
After sherrization**) 1-week sherrization-	273		47		238		3	.9			
madeirization 2-week sherrization-	343	352	142	151	308	334	3.9	3.9			
madeirization Traditional 6-week	370	396	196	210	282	308	3.9	3.9			
madeirization	71	81	73	80	414	308	4.0	4.1			
Apple-currant wine in 1:1 proportion			1								
Initial	90*)		47*)	·	182*)						
After sherrization**) 1-week sherrization-	326		71		246		4	.0			
madeirization - 2-week sherrization-	352	370	210	215	361	396	4.2	3.9			
madeirization Traditional 6-week	396	370	217	217	334	352	4.0	3.0			
madeirization	87	95	106	109	502	396	3.7	3.8			

T a ble 2. Changes of selected components in fruit wine mixtures during sherrization-madeirization

*) calculated content

**) at the start of sherrization the samples conteined 15 · 106 yeast cells per cm³

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for madeirization [3, 10, 11] and they condition the appearance of the characteristic taste and smell properties in the wines.

It was found that the applied processing brought about an increase of aldehydes content in the wines, and in many samples sherrization caused a considerable accumulation of these compounds already before madeirization (Fig. 1, Table 2). The brief madeirization (1-2 weeks) following sherrization led to a further increase of aldehydes content in the wines. In strawberry wine treated with the sherrization-madeirization method there was a six-fold increase of aldehydes content (compared with the initial sample) although the largest amount of these compounds was found after traditional madeirization. On the other hand, in currant wine the brief madeirization (two weeks at 45° C) gave better results than traditional madeirization; however, the differences in the amounts of formed



Fig. Changes of aldehydes content in fruit wines after madeirization; 1 - strawberry wine, 2 - sample without tannin addition, 3 - sample with tannin addition, 4 - currant wine, 5 - apple wine, 6 - initial sample, 7 - sherrization (10 days), 8 - time of heating, 9 - 1 week, 10 - 2 weeks, 11 - shortened method, 12 - 3 weeks, 13 - 6 weeks, 14 - traditional method

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aldehydes were not great. In turn, apple wine and the mixtures subjected to traditional madeirization showed a minimum increase of aldehydes, and after heating in the shortened method this increase was 3-9-times. Since heating after sherrization caused only a slight increment of aldehydes, sherrization turned out to be a particularly useful process in this case. The addition of winemaker's tannin had no significant effect on aldehvdes content, both during sherrization and during the subsequent two-week madeirization. Bezzubov et al. [2] report that wines after madeirization contain 100-300 mg aldehydes/dm³. Values of this order were attained with the sherrization-madeirization method (from 140 to about 400 mg/dm³) which means that a two-week processing at 45°C after sherrization suffices to obtain the desired level of aldehydes. Martakov et al. [7] found that submerged sherrization ensures a five-six times more rapid formation of features typical for madeirized wines during the heat treatment stage. Madeirization time is reduced to 15-20 days and the process takes place in a mild temperature range $(45-50^{\circ}C)$.

During heat treatment there occur secondary processes alongside the oxidation reaction. The course of these processes is illustrated among others by changes in the content of acetals, esters and furfurals [11].

The acetals content increases during wine maturation. The yeast cells do not play any direct role in their formation [14] and hence no significant increase of acetals was observed after the sherrization process (Tables 1 and 2). In currant and strawberry wines treated with the sherrizationmadeirization method the accumulation of acetals was lower than in the traditional process. In apple wine and its mixtures on the other hand the shortened processing method led to highter amounts of acetals. It was in these wines, however, that the aldehydes content was similar. This observation indicates the need for more extended cellar treatment of Madeira wines during which higher alcohols and esters are formed and the acetals content increases leading to a mellowing and greater harmony of the Madeira bouquet [12].

During madeirization there occurred an increase in the content of volatile esters (Table 1 and 2). In the studies of fruit wines performed to date an increase of these compounds to the level of 190-600 mg/dm³ was obtained [6]. The esters content in most of the samples from these experiments was in this range but the initial levels were fairly high. It was also found that during sherrization the increase of the esters content was relatively small. During the two-week heating at 45° C the increase of the content of these compounds was also lower than in the traditional method but the time of heating was three times shorter and the temperature was 10° C lower. During madeirization not only the quantity but also the qualitative composition of esters undergoes changes. This observation is confirmed by Bezzubov et al. [2] who found in wines subjected to heat treatment esters which were absent in the initial material.

The degree of changes occurring during heat treatment is also characterized by the altered contents of tannins, furfurals, acetoin and diacetyl.

The drop in tannins content during madeirization is due to oxidation, polimerization and sedimentation [11]. The oxidation of tannins is the preliminary stage of oxidative deamination which is the principal source of aldehydes formed in the course of madeirization [8].

In most of the samples subjected to traditional madeirization the observed reduction of tannins content was more intense than in the shortened method. At the same time the rate of these changes was greater in the first stage of the process, following which it decreased substantially (Table 1). For example, in strawberry wine after madeirization with the traditional method the amount of tannins dropped from 630 to 143 mg/ /dm³, whereas the sherrization-madeirization method reduced this content to 345 mg/dm³. It seems that may be due to the applied temperature and to the duration of the process.

A higher furfurals content was found in wines subjected to traditional madeirization. The increase of these compounds in the studied samples was slight, and their highest content, 25.6 mg/dm³, was in strawberry wine madeirized for six weeks at 55°C. Sherrization at 18°C did not favour furfurals accumulation and the subsequent heating at 45°C for 7 and 14 days brought about only a slight increase of these compounds. Kiskovskij and Skurichin [5] report that the formation of furfurals does not require the presence of oxygen and that their ultimate content depends mainly on the temperature of the process and on the amount of sugars.

The contents of acetoin and diacetyl in the various single-fruit wines are given in Table 1. Sherrization itself did not cause a large increase of acetoin content, bringing about a much greater accumulation of diacetyl. For example in apple wine with the tannin addition the content of the latter compound rose from 2.9 to 18.7 mg/dm³. The subsequent heating caused an increase of acetoin content (in strawberry and apple wine) which indicates the further chemical and biochemical formation of this compound. In turn the prolonged heating in wine undergoing traditional madeirization resulted in a drop of acetoin content below the initial value and this decrease progressed with the duration of heating. In the same samples there was observed a parallel increase of diacetyl content which may be evidence of the transformation of acetoin into diacetyl with the participation of Fe ions present in the wine [9].

The changes of colour went in two directions: the wines became either darker or lighter. The apple wine with the tannin addition grew slightly darker and acquired a grey shade. The strawberry wine became also darker but its colour remained orange-red. In turn, the currant wine grew markedly lighter and its colour changed from orange-red to orange.

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The organoleptic assessment revealed that the properties formed in wines as a result of heat treatment were correct and typical of fruit Madeiras. Some of the samples had a less harmonious bouquet and slightly perceptible sherry features which are probably due to an insufficient duration of cellar treatment.

The sensory evaluation, similarly as chemical analysis, demonstrated the dependence of wine quality on the applied method of heat treatment. The mixed wine materials assessed after sherrization were rated similarly as wines subjected to sherrization and madeirization but they displayed separate features typical for sherry and no features of madeirized wines. The mixtures and all single-fruit wines with the exception of apple wine, processed with the sherrization-madeirization method, were of a quality similar to that of traditionally madeirized wines. The addition of winemaker's tannin did not cause a noteworthy improvement of wine quality and hence it appears to be redundant.

The sherrization-madeirization method requires a more precise control of the process parameters than does the brief method (5-7 days at 70°C). Moreover the former involves a twice longer period of heating than the latter but at a much lower temperature (45° C). A similar effect in the traditional method is attained after heating at 55°C for six weeks.

CONCLUSIONS

1. The application of submerged sherrization (10 days) in the process of madeirization allows for a considerable shortening of heating (to two weeks) and a reduction of the temperature of the process to 45° C. The quality of wines obtained with the sherrization-madeirization method is similar or superiour (mixed wines) to the quality of traditionally madeirized wines. The smell of some samples contained slight sherry tones.

2. Sherrization greatly increases the content of aldehydes in fruit wines and this conditions the production of good-quality wines with the shortened madeirization process.

3. It is advisable to season the wines after the termination of the process in order to improve harmony and ensure the accumulation of acetals, esters and other compounds.

4. The addition of 0.3 g of winemaker's tannin per dm^3 turned out to be unproductive since it usually failed to improve the organoleptic properties of the wines.

5. The sherrization-madeirization processing variously affected the separate wine materials and mixtures, thereby confirming their different chemical composition in comparison to grape wine.

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PRÓBY WYKORZYSTANIA METODY SZERYZACJI DO SKRÓCENIA CZASU MADERYZACJI WIN OWOCOWYCH

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Streszczenie

Do doświadczeń użyto win owocowych: jabłkowych, truskawkowych, porzeczkowych oraz kupaży tych win. Część próbek wzbogacono w garbniki przez dodatek taniny winiarskiej w ilości 0,3 g/³. Wina po alkoholizacji do 14,7-16,1% obj. alkoholu poddawano szeryzacji wgłębnej w temp. 18°C w ciągu 10 dni, a następnie maderyzacji w 45°C w ciągu 7 i 14 dni. W celach porównawczych przeprowadzono również maderyzację w temp. 55°C w ciągu 6 tygodni (metoda "tradycyjna"). W procesie szeryzacji win jednoowocowycsh stosowano drożdże rasy Sherry z gat. Saccharomyces cerevisiae, a w przypadku kupaży — drożdże Saccharomyces oviformis (stężenie kom. ok. 5 mln/cm³). Podczas procesu prowadzono ciągłe napowietrzanie win (przepływ powietrza — 7,5 dm³/h). W czasie ogrzewania prowadzono codziennie 5 min napowietrzanie próbek. Analizę organoleptyczną przeprowadzono po dosłodzeniu próbek do 100 g/dm³ cukrów i 2-tygodniowym leżakowaniu. Stwierdzono możliwość zastosowania szeryzacji wgłębnej (10-dniowej) do znacznego skrócenia czasu ogrzewania win (do 2 tygodni) i obniżenia temperatury procesu maderyzacji do 45°C.

Zmiany składu chemicznego w metodzie szeryzacyjno-maderyzacyjnej przebiegały podobnie jak w przypadku maderyzacji w temp. 55° C w ciągu 6 tygodni (tab. 1 i 2, rys.), a oceny organoleptyczne otrzymanych win były zbliżone lub wyższe niż win maderyzowanych metodą tradycyjną.