Prospects for the Application of the Traditional Medoc Method of Red Wines Production in the Southern Regions of Russia*

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Abstract. This paper presents data on the phenolic composition of wine materials Aliberne, Storgozia, Record, and Khersonessky, obtained from promising red technical grape varieties growing in the conditions of the steppe zone of the southern regions of Russia. The mass concentrations of the main groups of phenolic compounds exhibiting biologically active properties were determined: anthocyanins, flavones, flavan-3-oils, oxycoric and oxybenzoic acids, and trans-resveratrol. The obtained data make it possible to recommend the expansion of industrial plantings of red technical grape varieties in the southern latitudes of Russia, varieties: Aliberne, Storgozia, Record, and Khersonessky for the production of qualitatively new wine products with improved properties.

Keywords: Chromatographic System, Phenolic Composition, Active Components of the Phenolic Composition, Liquid Chromatography, Componential Composition, Phenolic Compounds.

1 Introduction

Agriculture has always been one of the most important sectors of the economy of the south of Russia. Viticulture, which provides about 17% of the gross regional product, is one of the most significant branches of agriculture in the southern regions of our country. The Republic of Crimea in 2014 ranked 3rd in Russia in terms of gross grape harvest (13.4% of the gross grape harvest in Russia). Grapes and their processed products are valuable sources of biologically active substances that have preventive and curative properties.

In recent years, it has been established that pink and red wines contain easily digestible bioflavonoids: flavones, flavan-3-ola, anthocyanins, and other phenolic substances that have a P-vitamin effect [1]. Bioflavonoids increase the elasticity of blood vessels, strengthening their walls, and normalize the disturbed capillary permeability [2,3].

Numerous studies confirm the medicinal properties of red wines, so the Black Doctor wine, produced from grapes that make up a valuable gene pool of Crimean native varieties, has a radioprotective, vascular-strengthening, and P-vitamin effect [4]. The study of the phenolic composition of poorly studied grape varieties and their processed products will allow us to expand the range of high-quality wines with preventive and curative properties by identifying the most valuable varieties.

2 Materials and Methods

The qualitative and quantitative composition of phenolic compounds was determined by high-performance liquid chromatography (HPLC) using an Agilent Technologies chromatographic system (model 1100) with a diode matrix and a refractometric detector. For the separation of substances of polyphenolic nature, a chromatographic column Zorbax SB-C18 with a size of 2.1 × 150 mm, filled with silica gel with a grafted octadecylsily phase with a particle size of 3.5 microns of the sorbent, was used. Chromatography was performed in the gradient mode. Chromatograms were recorded at the following wavelengths: 280 nm for gallic acid, (+) - D-catechin, (-)- epicatechin; 313 nm for oxycoric acids; 371 nm for quercetin, and 525 nm for anthocyanins. The components were identified by their retention time. The mass concentrations of anthocyanins were determined in terms of malvidin-3-O-glucoside chloride. All the determinations were carried out in three repetitions. The results of the studies were treated as standard [1-5].

The objects of research were experimental samples of red table dry wine materials from grapes of red technical varieties Aliberne, Record, Storgozia, and Chersonessky, grown in the conditions of the steppe zone of viticulture in the southern regions of Russia. The studied samples of wine materials were obtained by micro-wine making using the traditional Medok method of producing red table dry wines and the technological method- "in red".

3 Results and Discussion

The studied samples of red table dry wine materials according to the main chemical and technological indicators correspond to GOST 32030-2013. The analysis of wine materials obtained by the technological method "in red" (Table 1) showed that the identified component composition of phenolic compounds of red table dry wine materials Storgozia and Chersonessky is represented by the following groups of phenolic compounds: anthocyanins, procyanidins, flavones, flavan-3-ola, oxybenzoic and oxycoric acids

Table 1. Study of the phenolic composition of red table dry wine materials prepared by the technological method " in red»

Name of the indicator Mass concentration, mg / dm3	Mass concentration, mg / dm3 Chersonesos	Storgosia
Oxybenzoic acids		
Lilac acid	9,8	14,2
Gallic acid	30,4	41,5
Oxycoricic acids		
Trans-coutaric acid	*5,5*	*12,0*
Trans-kaftaric acid	*22,1*	*32,7*
Flavan-3-ola		
(+)-D-catechin	49,0	75,2
(-)- epicatechin	32,5	154,7
Flavones		
Quercetin	0,6	0,4
Quercetin-3-o-glucoside	-	23,1
Anthocyanins		
Delphinidin-3-o-glucoside	30,0	6,7
Cyanidin-3-o-glucoside	3,1	-
Petunidine-3-o-glucoside	41,8	22,0
Peonidine-3-o-glucoside	28,0	13,2
Malvidin-3-o-glucoside	259,6	233,8
Delphinidin-3-o - (6' - acetyl-glucoside)	10,3	5,3
Cyanidin-3-o - (6' - acetyl-glucoside)	2,4	1,9
Petunidine-3-o - (6' - acetyl-glucoside)	1,9	4,2
Peonidin-3-o - (6' - acetyl-glucoside)	2,5	2
Malvidin-3-o - (6' - acetyl-glucoside)	13,1	13,9
Delphinidin-3-o - (6' - p-coumaroyl-glucoside)	5,4	3,0
Cyanidin-3-o - (6' - p-coumaroyl-glucoside)	1,1	1,2
Petunidin-3-o - (6' - p-coumaroyl-glucoside)	4,4	3,6
Malvidin-3 - (6' - p-coumaroyl-glucoside)	32,9	24,7
Total of identified anthocyanins	436,5	335,5
Procyanidins		
Oligomeric procyanidins	285	235
Polymer procyanidins	2326	2542

The composition of the main groups of phenolic compounds identified in red table wine materials prepared according to the traditional Medok method, which includes complete fermentation of the pulp, followed by the technological stage of extracting all the extract compounds with endogenous alcohol released during fermentation, within 2-3 weeks from the moment of complete completion of fermentation, is presented in Table 2.

Table 2. Study of the phenolic composition of red table dry wine materials prepared in the traditional Medok

Indicator name	Mass concentration, mg / dm3	
	Aliberne	Record
Oxybenzoic acids		
Lilac acid	8,4	6,7
Gallic acid	17,2	33,6
Oxycoricic acids		
Trans-coutaric acid	*41,2*	*4,3*
Trans-kaftaric acid	*338,1*	*113,3*
Flavan-3-ola		
(+)-D-catechin	46,2	92,0
(-)- epicatechin	58,3	124,2
Flavones		
Quercetin	4,1	10,9
Quercetin-3-o-glucoside	31,3	32,3
Anthocyanins		
Delphinidin-3-o-glucoside	42,2	62,1
Cyanidin-3-o-glucoside	7,3	4,6
Petunidine-3-o-glucoside	55,4	85,5
Peonidine-3-o-glucoside	75,9	76,6
Malvidin-3-o-glucoside	380,5	410,4
Delphinidin-3-o - (6' - acetyl-glucoside)	6,3	4,8
Cyanidin-3-o - (6' - acetyl-glucoside)	11,2	9,2
Petunidine-3-o - (6' - acetyl-glucoside)	3,4	3,5
Peonidin-3-o - (6' - acetyl-glucoside)	6,8	22,2
Malvidin-3-o - (6' - acetyl-glucoside)	91,3	26,3
Delphinidin-3-o - (6' - p-coumaroyl-glucoside)	0,5	1,0
Cyanidin-3-o - (6' - p-coumaroyl-glucoside)	6,8	4,2
Petunidin-3-o - (6' - p-coumaroyl-glucoside)	7,2	8,2
Malvidin-3 - (6' - p-coumaroyl-glucoside)	83,4	72,5
Delphinidin-3,5-di-o-glucoside	-	15,8
Cyanidin-3,5-di-o-glucoside	-	10,7
Petunidine-3,5-di-o-glucoside	-	9,4
Peonidine-3,5-di-o-glucoside	-	45,4
Malvidine-3,5-di-o-glucoside	-	122,0
Total of identified anthocyanins	778,2	994,4
Stilbens		
Trans-resveratrol	2,1	3,6
Procyanidins		
Oligomeric procyanidins	375	356
Polymer procyanidins	7543	7953

Chromatographic analysis of Aliberne and Record wine materials (Table 2) showed that wine materials prepared by the traditional Medok method differ in their component phenolic composition from wine materials prepared by the "red" method, mainly in that in addition to the main groups of phenolic substances (anthocyanins, procyanidins, flavones, flavan-3-ols, oxybenzoic and oxycoric acids), they include a representative of the stilbene group-trans - resveratrol, the content of which in the experimental samples varies in the range from 2.1 to 3.6 mg/dm3. Trans-resveratrol is a substance with high biological and antioxidant activity, it is this compound that is attributed to most of the positive effects caused by the intake of red wines. These actions include strengthening of the cardiovascular system, activation of cellular apoptosis mechanisms, the anti-cancer effect [5-12].

Anthocyanins. The main substances responsible for the color of grapes are anthocyanins, which are part of the phenolic complex [13]. Anthocyanins have a wide range of biological activity for the human body, among which the ability to increase the elasticity of blood vessels, increase the permeability of capillaries, improve the supply of the brain and have a beneficial effect on the hematopoietic function of bone marrow cells, high bactericidal activity against gram-negative bacteria, P-vitamin and antioxidant activity are particularly distinguished [14-16]. The HPLC method established that the total amount of anthocyanins in the wine materials prepared "in red" was: in the Storgozia wine material-335.5 mg/dm3 (9.7% of the total phenolic substances (SFV)), in the Chersonesos wine material - 436.5 mg/dm3 (13.7% SVF); in the wine materials produced according to the traditional Medok method: in the Aliberne wine material – 778.2 mg/dm3 (8.4% SFV), in the wine material, the record is 994.4 mg/dm3 (10.2% SFV)

. Procyanidins and flavan-3-ols.

Flavan-3-ols, which are structural elements of procyanidins, together with procyanidins exhibit higher antioxidant activity than vitamins C and E and are also able to inhibit the biosynthesis of prostaglandins, which in due time leads to the suppression of inflammatory processes in the human body [17, 18]. According to the literature data, the amount of flavan-3-ols and procyanidins is more than 90 % of the total amount of polyphenols contained in grapes and wine [19]. In the course of the study of the phenolic composition of red table dry wine materials produced by the "po-red" method and the traditional Medok method (Table 1,2), it was found that the total mass concentration of flavan-3-ols and procyanidins in the "po-red" wine materials was: in Storgozia wine material-3006.9 mg/dm3 (86.7 % SFV); in Chersonesos wine material-2692.5 mg/dm3 (84.2 % SFV); in wine materials prepared according to the traditional Medok method: in Aliberne wine material-8022.5 mg/dm3 (86.8).

Flavones.

The flavone group is represented in red wines by quercetin and its derivative-quercetin-3-O-glucoside. Flavones have high antioxidant properties, inhibit cell aging, increase the elasticity and permeability of capillary blood vessels, and improve coronary circulation. According to the literature data, the content of quercetin and quercetin-3-O-glucoside in wines does not exceed 5 mg/dm3 [2]. Studies have found that the mass concentration of flavones in the wine materials "in red" varied from 0.6 mg/dm3 in the wine material Chersonessky to 24.5 mg/dm3 in the wine material Storgozia, which did

not exceed 0.7% of the SFV; in the wine materials prepared according to the traditional Medok method: in the wine material Aliberne-35.4 mg/dm3 (1.1% SFV), in the wine material Record – 43.2 mg/dm3 (0.4% SFV).

Phenolic acids. In red wine materials prepared both according to the traditional Medok method and "red", non-flavonoid forms of polyphenols are represented by phenolic acids, which are divided into oxycoric (trans-caftaric, trans-coutaric) and oxybenzoic (lilac, gallic) acids. These phenolic acids reduce the level of cholesterol in the blood and affect the inhibition of HIV infection in the human body. Phenolic acids, which have high antioxidant activity, are localized mainly in the seeds and partially in the skin of grapes. Leifert W. R. found that the total phenolic substances of grapes to be extracted during fermentation are distributed in the following sequence: 60-70% - in the seeds, 28-35% - in the skin, and 10% - in the pulp of grapes. The content of phenolic compounds in seeds varies from 5 to 8% and about 63 % of them go into the wine. Identified values of mass concentrations of phenolic acids (oxycoric, oxybenzoic) in.

4 Conclusions

Analysis of the mass concentration of phenolic substances in experimental samples of red table dry wine materials by HPLC showed that the technological method "in red" and traditionally Medok, can significantly ensure the transition of flavonoid and non-flavonoid groups of phenolic substances from the solid parts of grapes, which for wine materials produced "in red", range from 3197.4 mg/dm3 (wine material Chersonesos) to 3466.3 mg/dm3 (wine material Storgozia); for wine materials of the Medok production, method-the range from 9243.1 mg/dm3 (Aliberne wine material) to 9724.3 mg/dm3 (Record wine material).

Chromatographic detection showed that the use of the Medok method of preparing red table wines provides extraction of trans-resveratrol from grapes to wine material in an amount of 2.1 to 3.6 mg/dm3, which was not observed in wine materials prepared by the "red" method.

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