

# Phenolic Compounds and Antiradical Efficiency of Georgian (Kakhethian) Wines

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**Abstract:** According to ancient Georgian traditional winemaking technology, the crushed grape is placed in a clay vessel (qvevri) dug in the ground, and alcoholic fermentation is carried out together with solid parts of grape cluster (stem, skin, seeds). Quantitative content of phenolic compounds and antiradical efficiency of Kakhethian wines were studied and findings are compared to the appropriate data of the European wines. Analysis showed Kakhethian wines to considerably surpass the European wines with regard to total phenolics compounds: 1,330-2,430 mg/L (Kakhethian white wines), 210-468 mg/L (European white wines), 2,898-4,416 mg/L (Kakhethian red wines), 1,630-2,340 mg/L (European red wines). Average value of antiradical efficiency of white and red wines of Kakhethian type was found to exceed the average value of antiradical efficiency of white and red wines of European type, by 2.3 and 1.7 times, respectively. Georgian wines in the world market are submitted in an insufficient measure, and the purpose of this work is revealing their positive qualities.

**Key words:** Georgian (Kakhethian) wines, phenolic compounds, antiradical efficiency.

## 1. Introduction

Georgia is the ancient country of viticulture and winemaking. According to some authors “viticulture, or grape-growing, began in Georgia (which lies on the eastern shore of Black Sea, near the Caucasus Mountains) some 9,000 years ago [1]. On the basis of the archeological data, the winemaking in Georgia originated 8,000 years ago [2].

Adverse ecological conditions observable in most part of the modern world, unbalanced nutrition and the various illnesses break the counterbalanced free-radical processes proceeding in living cells. The reasons causing this problem are pollution of an environment, the stressful influences, radiation, chronic intoxications, smoking and other conditions, as a result of which the uncontrollable free-radical reactions develop. Under influence of these reactions the toxic effects of xenobiotics are amplified, and carcinogenesis, mutagenesis, atherosclerosis and autoimmune diseases

are stimulated. In this respect, it is important to identify foodstuff that contain large quantities of compounds having antioxidant activity. In this aspect, the traditional Kakhethian technology of making wine used in Georgia is especially interesting. The wines prepared by this technology are exclusively rich with flavonoids which are characterized by high antioxidant activity and considerably reduce injury of tissues and cells [3].

According to ancient Kakhethian traditional technology of the winemaking, the crushed grape is placed in a clay vessel (qvevri) dug in the ground, and alcoholic fermentation is carried out together with other parts of grape cluster (stem, skin, seeds). During fermentation, from stem, skin and seeds of grape phenolic compounds are extracted in plenty which define the composition and essence of Kakhethian wine. Interaction of these compounds with the oxidizing enzymes contained in the skin, pulp and stem of grapes, define taste and aroma, characteristic of Kakhethian wine. Grape seeds play a main role during

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formation of a wine of the Kakhethian type, as seeds basically increase the content of phenolic compounds in a wine, and give to it characteristic aroma. Stems promote clarification of a wine and enrich it with flavonoids and extractive substances. The grape skin gives to a wine gentle, specific, varietal aroma. Flavonoid compounds define character of a wine. On ageing these compounds are oxidized, therefore the wine becomes soft, velvety and of pleasant taste. Quality of the wine made in a clay vessel (qvevri) is much better than quality of the wine made in a wooden vessel [4]. The wine made in qvevri has specific fruit aroma and well balanced taste. Therefore, qvevri is the best vessel for making of the Kakhethian wine. Besides, its advantage consists still that in the qvevri dug in the ground fermentation occurs in more normal conditions, because of smaller fluctuations of temperature.

The aim of this study was to estimate the total amount of phenols, catechins, proanthocyanidins and anthocyanins in wines of the European and Kakhethian type, and to compare their antiradical efficiency in a system using 2,2-diphenyl-1-picrylhydrazyl (DPPH\*) radical. In this work phenolic compounds of wines of Kakhethian and European types and also antiradical efficiency of these wines for the first time are compared.

## 2. Materials and Methods

White and red wines of the Kakhethian and European type, made from grape varieties (*Vitis vinifera* L.) cultivated in Georgia, Italy and Slovenia, were obtained from wineries and private wine growers. The technology of making of white (W) and red (R) wines, variety of grape used, the country of cultivation, name of wine, factory and year of making are given in Table 1.

In samples of analyzed wines the total content of phenols was determined with Folin-Ciocalteu reagent [5], catechins and proanthocyanidins-by method of Swain & Hillis [6], anthocyanins-by the methods of Durmishidze & Sophromadze [7]. Standard curves

were constructed: for phenols - on the basis of gallic acid ("Sigma", maximum absorption 765 nm), for catechins - on the basis of (+) catechin ("Theodor Schuchard", maximum absorption 500 nm), for proanthocyanidins - on the basis of cyanidin isolated from grape skin (maximum absorption 548 nm) and for anthocyanins - on the basis of malvidin-3-monoglucoside (maximum absorption 536 nm).

For determination of antiradical efficiency of wine the stable radical of 2,2-diphenyl-1-picrylhydrazyl (DPPH\*) with maximum absorption 520 nm and  $\alpha$ -tocopherol ("Sigma") as the standard were used [8]. Alcohol was removed from samples of analyzed wine (50 mL) by evaporation on the rotary vacuum evaporator at 40 °C, and after that the volume of samples were again made up to initial volume with distilled water. Spectrophotometric measurements were carried out using spectrophotometer SF-26 (Russia). Each experimental variant was repeated five times. Experimental data were processed statistically using MS-Excel-AVERAGEIF function.

## 3. Results and Discussion

According to the data obtained (Table 2), by comparison of the quantitative content of phenolic compounds in the wines made on the Kakhethian and European technologies it is obviously visible that white and red wines of the Kakhethian type (1WK, 2WK, 3WK, 8RK, 9RK, 10RK), under the content of phenolic compounds considerably surpass to the appropriate wines made on the European technology (4WE, 5WE, 6WE, 7WE, 11RE, 12RE, 13RE).

In white wines made on the Kakhethian technology, the total content of phenols varies from 1,296 mg (wine 3WK) up to 2,290 mg (wine 1WK), and in red wines of the Kakhethian type from 2,848 mg (wine 9RK) up to 4,416 mg (wine 8RK) per liter, while in white wines made on the European technology, these parameters varies from 210 mg (wine 7WE) up to 456 mg (wine 6WE), and in red wines of the European type from 1,630 mg (wine 12RE) up to 3,130 mg (wine 11RE)

**Table 1** Wine samples\*.

Wine	Technology of preparation	Grape Variety	Country and Winery	Vintage
1WK	Kakhethian	<i>Rqatsitheli</i>	Georgia, Kakhethi, Oqros Khvanchkara	2005
2WK	Kakhethian	<i>Khikhvi</i>	Georgia, Kakhethi, Private wine grower	2005
3WK	Kakhethian	<i>Ribolla</i>	Italia, Azenda Agricola, Oslavia, Francesko Josko Grauner	2003
4WK	European	<i>Rqatsitheli</i>	Georgia, Kakhethi, Badagoni	2005
5WE	European	<i>Kakhuri Mtsvane</i>	Georgia, Kakhethi, Private wine grower	2004
6WE	European	<i>Tsulukidzis Tetra</i>	Georgia, Racha, Oqros Khvanchkara	2004
7WE	European	<i>Rebula</i>	Slovenia, Vipavska dolina, Vinorodni okolis, deadami Azelen	2006
8RK	Kakhethian	<i>Sapheravi</i>	Georgia, Kakhethi, Vazi + LTD	2005
9RK	Kakhethian	<i>Kabernet Sauvignon</i>	Georgia, Kakhethi, Vazi + LTD	2005
10RK	Kakhethian	<i>Ojaleshi</i>	Georgia, Samegrelo, Vazi + LTD	2005
11RK	European	<i>Sapheravi</i>	Georgia, Kakhethi, Private wine grower	2007
12RE	European	<i>Aleksandreuli</i>	Georgia, Racha, Oqros Khvanchkara	2003
13RE	European	<i>Merlot</i>	Georgia, Kakhethi, Besini	2008

\*WK-White Kakhethian wine; WE-White European wine; RK-Red Kakhethian wine; RE-Red European wine.

**Table 2** The content of total phenolics, catechins, proanthocyanidins, anthocyanins in white and red wines and antiradical efficiency(AE)\*.

Wine	Total phenolics (mg/L)	Catechins (mg/L)	Proanthocyanidins (mg/L)	Anthocyanins (mg/L)	EC <sub>50</sub> (g antioxidant kg <sup>-1</sup> DPPH*)	T <sub>EC50</sub> (min)	AE (× 10 <sup>-3</sup> )
1WK	2,290 ± 38	640 ± 7	690 ± 7.1	--	510 ± 11.7	4.5	0.44
2WK	2,000 ± 13	453 ± 1	1,097 ± 2.4	--	515 ± 16	4.5	0.43
3WK	1,296 ± 46	509 ± 4	392 ± 16	--	847 ± 35	5	0.23
4WK	346 ± 11	39 ± 1	47.8 ± 2	--	1,191 ± 14.1	5	0.16
5WE	278 ± 7	27 ± 2	43.2 ± 1.1	--	1,447 ± 22.4	5	0.12
6WE	456 ± 26	77 ± 2	165 ± 8.7	--	1,219 ± 18.4	4.5	0.18
7WE	210 ± 4	8 ± 2	--	--	893 ± 13.3	5	0.038
8WE	4,416 ± 100	1,010 ± 23	1,203 ± 15	1,270 ± 45	516 ± 16.5	3.2	0.62
9WE	2,848 ± 72	798 ± 2	728 ± 13	317 ± 24	382 ± 14.9	5	0.52
10RK	3,700 ± 85	862 ± 11	872 ± 18	414 ± 20	342 ± 11.5	5	0.58
11RK	3,130 ± 76	582 ± 5	610 ± 55	1,456 ± 36	519 ± 5.1	4.4	0.43
12RE	1,630 ± 50	378 ± 15	980 ± 69	53.2 ± 5	595 ± 14.5	5	0.34
13RE	2,318 ± 73	636 ± 33	826 ± 4	322 ± 18	880 ± 4.3	4.5	0.25
α- Tocopherol					625 ± 22.7	5	0.32

\* Values are the mean of five independent determination ± standard deviation.

per liter. Thus, as a result of making of wine by the Kakhethian technology, the wine is considerably enriched by phenolic compounds.

Special interest represents study of phenolic compounds of the wines made on the Kakhethian and European technologies, from the same variety of a grape. We have compared the wines made by the Kakhethian (1WK, 3WK, 8RK) and European (4WE, 7WE, 11RE) technology, from the autochthonous Georgian varieties of grape (*Rqatsitheli*, *Sapheravi*) and from a variety of a grape cultivated in some

countries of Europe (*Ribolla*) (Table 2).

In the Kakhethian wine (1WK), made of a variety of a grape *Rqatsitheli*, total amount of phenolic compounds, catechins and proanthocyanidins, is higher by 6.6 times, 16 times, and 15 times, respectively, than in wine (4WE), made from the same variety of a grape by the European technology. Approximately the same patterns of relationship is observed and in case of the wines made in Italy by the Kakhethian technology from a grape of variety *Ribolla*, and in Slovenia from the same variety of a grape by the European technology. In

the wine made by the Kakhetian technology (3WK), the total phenols are 1,296 mg/L, and in the wine made by the European technology (7WE) from the same variety of a grape, this parameter is 210 mg/L. Kakhetian wine (3WK) contains catechins and proanthocyanidins in amount of 509 mg/L and 392 mg/L, respectively, and the wine made of the same variety of a grape by the European technology (7WE) contains only insignificant amount of catechins, and practically does not contain proanthocyanidins.

Among the white wines made by Kakhetian technology, the high content of proanthocyanidins characterizes wine (2WK), made of the autochthonous Georgian variety of grape *Khikhvi*, in which the content of these compounds makes 1,097 mg/L, and the content of catechins 453 mg/L (the total of phenols in this wine makes 2,000 mg/L). The wine made by Kakhetian technology from a grape variety *Khikhvi* has straw color, contains high amount of extractive substances, is perfect and harmonious [9].

Among the white wines made from the autochthonous Georgian varieties of a grape by the European technology, the wine (6WE), made of a grape variety *Tsulukidzis Tetra* is distinguished, in which the total content of phenols makes 456 mg/L, catechins 77 mg/L, and proanthocyanidins 165 mg/L. Also it is necessary to note wine (5WE) made of a grape variety *Kakhuri Mtsvane* by the European technology, in which the total content of phenols makes 278 mg/L, catechins 27 mg/L, and proanthocyanidins 43.2 mg/L. This wine tastes very gentle and aromatic.

In red wine made from grape variety *Sapheravi* by Kakhetian (8RK) and European (11RE) technologies, the total content of phenols makes 4,416 mg/L and 3,130 mg/L, respectively. The total content of catechins and proanthocyanidins in wine made by Kakhetian technology is 1.7 times and 2 times higher, than in wine made by European technology.

Partially other interrelation is observed in a case of anthocyanins. In red wine made by European technology (11RE) the content of anthocyanins is

1,456 mg/L, but in red wine made by Kakhetian technology (8RK) their content makes 1,270 mg/L. The reason of it, apparently, consists in long process of maceration in a qvevri that causes sedimentation of anthocyanins.

Among autochthonous red varieties of grape of Georgia is distinguished *Ojaleshi*. This wine made by Kakhetian technology is characterized by good color, typical viscosity for red wines, extract content, and harmonicity [10]. In this wine (10RK), the total content of phenols makes 3,700 mg/L, catechins 862 mg/L, proanthocyanidins 872 mg/L, and anthocyanins 414 mg/L.

The characteristic of the wine made by Kakhetian technology from the French variety of grape *Cabernet Sauvignon* cultivated in Georgia is also important. In this wine (9RK), the total content of phenols makes 2,848 mg/L, catechins 798 mg/L, proanthocyanidins 728 mg/L, and anthocyanins 317 mg/L. Comparison of the wine made by European technology from the French variety of grape *Merlot* cultivated in Georgia with the wine made in Argentina from the same variety of a grape and by the same technology is rather interesting. In wine made in Kakheti (13RE) the total content of phenols, catechins, proanthocyanidins and anthocyanins makes 2,318 mg/L, 636 mg/L, 826 mg/L and 322 mg/L, respectively (Table 2), while in red wine made in Argentina the total content of phenols is 1,637 mg/L, the total content of catechins and proanthocyanidins is 13.30 mg/L, and content of anthocyanins is 52.61 mg/L [11]. Thus, according to the given data the Georgian wine considerably surpasses the Argentina wine. It is necessary to note also the wine (12RE) made from the autochthonous Georgian variety of a grape *Aleksandreuli*, which is characterized by pleasant taste and delicate aroma. In this wine the total content of phenols makes 1,630 mg/L, catechins 378 mg/L, proanthocyanidins 980 mg/L, and anthocyanins 53.2 mg/L.

Thus, study of total amount of phenolic compounds, catechins, proanthocyanidins, and anthocyanins of white and red wines prepared by Kakhetian and

European technologies has demonstrated that by content of said compounds Kakhethian wines considerably exceed European wines, that presumably specifies in high medical and prophylactic properties of wines of Kakhethian type. This conclusion has been confirmed by investigation of antiradical efficiency (AE) of wines of Kakhethian and European type (Table 2). According to these findings average value of AE of white and red wines of Kakhethian type 2.3 and 1.7 times exceeds average value of AE of white and red wines of European type, respectively. Among wines, the white (1WK, 2WK) and red (8RK, 9RK, 10RK) wines of Kakhethian type are especially distinguished by their antiradical efficiency.

The data of some authors on the enrichment of white wines of European type by polyphenols should be noted. Williams and Elliot [7] have carried out researches whose goal was the development of a seed-enhanced (polyphenol-enriched) white wine with greater positive health potential. This, seed-enhanced white wine is currently being evaluated in human subjects with regard to its potential effect on the cardiovascular system and inhibition of platelet aggregation. According to the study of Auger et al. [12], white wine prepared from grape variety *Chardonnay*, enriched by polyphenols possesses a protective effect against early forms of atherosclerosis in hamsters, and according to the study of Fuhrman et al. [13], the white wine enriched by polyphenols possesses similar to red wine antiradical properties.

#### 4. Conclusions

As a result of comparison of white and red wines made by Kakhethian and European technologies it is shown that by content of total amount of phenolic compounds, catechines, proanthocyanidins, and anthocyanins, and by antiradical efficiency, the Kakhethian white and red wines considerably exceed European white and red wines, that specifies in high medical and prophylactic properties of wines of Kakhethian type.

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