PLANT SCIENCE RESEARCH AND PRACTICES

Vitis Products

Composition, Health Benefits and Economic Valorization

Renato Vasconcelos Botelho
António Manuel Jordão
Editors

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VITIS PRODUCTS

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RENATO VASCONCELOS BOTELHO
AND
ANTÓNIO MANUEL JORDÃO
EDITORS

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The book "Vitis Products: Composition, Health Benefits and Economic Valorization" highlights the nutraceutical value of juice and wine and brings new perspectives to the sustainable use of the byproducts of grape processing. The raw materials generated from the grape processing, including seeds, skins, and leaves have, in addition to many nutrients, bioactive compounds that can be used in the food, cosmetics, and pharmaceutical industries - and thus provide important income sources as well as contribute to the reduction of processing wastes.

Luís António Biasi, Full Professor
Federal University of Paraná
Curitiba, Brazil

This important book presents an overview about the chemical and sensory composition, health beneficial aspects and economic implications of the several Vitis products throughout a considerable number of chapters. Actually, this book is focused on some of the recent scientific and technical advances of a wide group of grape derived products and by-products, all of them performed by important international researchers. For sure that this book will be quite useful for academic staff, but also for different students, as well as for specialized professionals from the grape and wine sector.

Jorge M. Ricardo-da-Silva, Full Professor
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Portugal

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PREFACE

When man appeared, the vine already existed, as fossils of wild grapes of the species *Vitis sezannensis* were found, approximately 35 million years old, from the lower Eocene period, in the southern region of France. The vine is reported in the Bible, and also referred to in the Old Testament. In Genesis 9.10, 11 it is written that after the flood, when Noah left the ark, he planted a vineyard in the region of Mount Ararat, now Armenia. Other biblical quotations always appear to relate the vine to the fertile land as in chapter XIII Numbers. In Egypt, in the ancient empire between 3,000-2,000 BC, racemes of sun-dried grapes were described; and in the new empire between 1,500-1,085 BC, in the necropolises of rulers they exhibited paintings that informed cultivation techniques of the vineyard in the form of tunnels along the oases. Chaldeans and Hebrews were very successful with viticulture. With the increase of the Roman Empire, viticulture spread throughout Europe, dedicating the pleasures of wine to the god Bacchus. With the fall of the empire, wine lost its importance, but in the Middle Ages, supported by the church, viticulture and wine were grown in monasteries, with wine having its dignity elevated as the blood of Christ.

Today, viticulture is spread all over the world, with consumer interest increasing each day. According to OIV data, in 2020 the world area under vines is estimated at 7.3 million hectares and the production of grapes for winemaking was about 77.8 million tonnes, in 2019, resulting in approximately 292 million hectoliters of wine and generating about 13 million tonnes of residue.

Grapevines and their clusters are very rich in chemical components with different and interesting potential health effects, with this situation extending to grape derivatives such as must, wines, vinegars and all other by-products (extracts, oils, flour, leaves, seeds, pomace, etc.). Bioactive constituents present in grapes and vines, mainly polyphenols, are attracting increasing interest from consumers demanding polyphenol-rich foods as a result of epidemiological evidence suggesting the protective effect of polyphenols against chronic diseases directly associated with oxidative damage, such as Alzheimer's, cancer, diabetes and hypertension. In this regard, besides the traditional products from grapes, such as wine and juice, grape *Vitis* by-products are increasingly being re-utilized and transformed into high-value products for the food, cosmetics and pharmaceutical industries. In this context, the book *Vitis Products: Composition, Health Benefits and Economic Valorization* intends to discuss deeply many aspects of the products derived from grapevines, including the diversity and potential of economical possibilities, and also factors involved in their composition, varietal differences, industrial processes and consumer preferences.

This book is comprised of 11 chapters written by a group of international researchers from different countries and institutions, encompassing several areas of research, namely in terms of viticulture and oenology, but also in other areas, such as chemistry and economics, in order to provide up-to-date reviews, overviews and summaries of current research on grape products and their transformation and valorization. In the first chapter, we find a rich description and characterization of wines produced from ancient native grape cultivars of the Crimea region, including research results of the effectiveness of various technological methods and yeast cultures for the production of wines, showing the potential of Crimean native grape cultivars. The second chapter aims to present an interesting description of the use of phenolic compounds quantification as an authenticity marker for red wines produced in Canary Islands. Chapters 3 to 5 explore the potential health benefits of grape-derived products showing an infinite number of possibilities of the use of *Vitis* products worldwide and the composition diversity of these products. Chapter 6 describes the production of grape juice highlighting the various aspects of the production chain, such as the correct choice of grape cultivar according to the provenance region of cultivation, and also the most appropriate preparation technique. Chapter 7 describes the richness and the possibilities for the use of vine leaves, especially for infusion production, relating several aspects, such as the *Vitis* cultivar, the chemical composition and the sensory characteristics of these infusions. Chapter 8 verifies the potential of the use of grape seeds oil and their relevant composition. The authors of this chapter also discuss several aspects of the thermal degradation of seed oils obtained from different grape cultivars. In Chapter 9, other authors present a rich review about the available technologies for polyphenol extraction from grapes and by-products. Finally, in Chapters 10 and 11, we find an interesting view about the future perspectives for wine production and consumption tendencies for the next few years.

It is important to note that this book is not only for technicians actively engaged in the field, but also for students attending technical schools and/or universities and other professionals that might be interested in reading about some fascinating areas of the vitiviniculture industry and discovering the most recent tendencies and knowledge about the valorization of grape and wine products. The elaboration of this rich work was very gratifying and we are immensely grateful for the opportunity granted by Nova Publishers to assemble and edit this book. Finally, we are greatly indebted to the authors that generously share their knowledge and experience with others through their contribution to this book.

Renato Vasconcelos Botelho
António Manuel Jordão

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Chapter 1

CHEMICAL AND TECHNOLOGICAL FEATURES OF NATIVE GRAPE CULTIVARS OF CRIMEA

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ABSTRACT

The Crimean Peninsula, being one of the sub-centers of origin of grapevines, has a wide range of local grape cultivars, but only some of them are used in modern viticulture and winemaking. In the context of global climate change, the systematic study of Crimean local cultivars resistant to unfavorable soil and climatic conditions becomes especially relevant, both from the standpoint of a biological resource for genetic and

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clonal selection, and a raw material base for the development of authentic winemaking. The biochemical features of sugar synthesis during ripening and the associated changes in organic acids, components of the phenolic complex, aromatic compounds and oxidase activity were determined for Crimean native wine grape cultivars. The effectiveness of various technological methods and yeast cultures for the production of red wines from native cultivars, depending on the carbohydrate-acidic and phenolic ripeness of grapes were evaluated. It was shown that the assortment and technological potential of Crimean native grape cultivars allows to develop winemaking in the direction of the production both traditional liqueur wines and authentic dry wines of various styles.

Keywords: cultivars, grapes, wine, phenolic complex, aromatic compounds, technological methods

1. INTRODUCTION

Studies of recent decades have shown (Goryslavets et al., 2015; Volynkin and Polulyahk, 2015; Volynkin et al., 2019) that the modern varieties of Crimean native grape cultivars are formed by natural and artificial (empirical) selection and by hybridization of wild vines that have grown on the peninsula since antiquity, as well as imported from the Balkans, Transcaucasia and Asia Minor. Nowadays, in Crimea there are about 80 native cultivars, out of which 64% are cultivars for wine production. In general, almost all Crimean wine grape cultivars meet the requirements for winemaking, but only 10-12 grape ones are involved in the industrial culture. About 75% of these cultivars are cultivated in the historically established habitat – Solnechnaya Dolina village (the eastern part of the South coastal zone of Crimea); 21% – on the southern coast of Crimea from Yalta to Morskoye, and only 4% – in the western foothill-seaside region of the Piedmont natural zone (Bakhchisarai district and Sevastopol).

The most common cultivars on these area are 'Kokur Belyi' – 658.7 ha, 'Shabash' – 132.4 ha and 'Kefessia' – 74.5 ha; 'Ekim Kara', 'Sary Pandas', 'Kok Pandas', 'Kapselski Belyi', 'Solnechnodolinsky' and others are grown on areas, which don’t exceed 50 ha (Taranenko, 2014; Likhovskoi et al., 2016a). However, recently, there is a widespread expansion of the planting of native cultivars for wine production, including outside the historically developed ampelocenosis, in particular, in the western foothill-coastal region of Crimea.

A growing interest in expanding the use of Crimean native cultivars in the winemaking of the region has a number of reasons. Firstly, the modern concept of quality wines is based on their authenticity, the uniqueness of the organoleptic characteristics due to a certain terroir and cultivar specificity. Secondly, during evolution Crimean native grape cultivars have developed the ability to grow and fruit bear on heavy clay soils characterized by strong chloride-sulfate salinization in the conditions of arid climate of the historical habitat (Polulyakh, 2007). In the context of the global climate change, manifested in a rapid increase in environment temperature and a constant increase in water deficit, the endurance of native cultivars to adverse soil and climatic conditions and their drought tolerance are of particular value in development of authentic winemaking and generative and clone breeding (Levchenko et al., 2017a; Vasylyk, 2019).

The problems of modern Russian and world winemaking require a systematic study of the climatic plasticity of Crimean native cultivars, component composition and biochemical properties of berries, their potential in winemaking under various ampelocenoses.

This chapter presents the previously published and new results of author's of the chemical and technological parameters of grapes of the most common Crimean native cultivars (*Vitis vinifera* L.) growing in the mountain-valley coastal and western foothill-coastal regions of Crimea, and the features of winemaking using them. These are grape cultivars with red berry 'Kefessia', 'Gevat Kara' and 'Ekim Kara', which belong to the ecological and geographical group of wine grape cultivars of the Black Sea basin exclusively of Crimean origin (Goryslavets et al., 2015, Volynkin et al., 2019). Also Crimean native cultivars with white berry 'Kokur Belyi', 'Sary Pandas', 'Kok Pandas' (the ecological and geographical group of grape cultivars of the Black Sea basin, presumably of Greek origin) and 'Shabash', which belong to the eastern ecological and geographical group (Volynkin et al., 2019). 'Cabernet Sauvignon', 'Merlot', 'Shiraz', 'Malbec', 'Chardonnay', 'Riesling', 'Sauvignon blanc', 'Aligote' and 'Rkatsiteli', growing in the same regions, were used as comparison cultivars (classical cultivars). These cultivars present wide distribution in the world and in Crimea; producting high quality wines everywhere.

In the mountain-valley coastal region, vineyards are located in Solnechnaya Dolina village. This zone is almost a semi-desert zone, with an average annual air temperature of 13.2 °C, sum of active air temperatures (above 10 °C) between 3635-3820°C, number of days with a temperature above 10 °C in a range of 186-202 and annual precipitation of 300-400 mm (Likhovskoi et al., 2016b; Rybalko et al., 2019). The western foothill-coastal region of the Crimea (v. Vilino, Bakhchisaray district) characterized by a moderately warm, semi-humid climate: with average annual air temperature of 12.1 °C, sum of active temperatures (above 10 °C) between 3650-3680 °C, number of days with a temperature above 10 °C in a range of 197-209 and annual precipitation between 380-450 mm. The investigated grape samples were taken from ampelographic collection of ARNRIVW "Magarach".

The experimental material was analyzed using the methods of variation statistics (ANOVA) and hierarchical classification. Statistically significant differences in the compounds of differential cultivars or groups of cultivars were identified based on the Mann-Whitney (U-test) criterion. The predetermined probability of an erroneous result (p) was less than 0.05. The text of the article indicates the values of p for which the U-test values are less critical and the differences in the parameters between the samples studied are recognized as significant. In the discussion of the results of the hierarchical cluster analysis of the experimental data Euclidean distances (Ed) are indicated in brackets.

2. Composition of Crimean Native Grape Cultivars

2.1. Content of Sugars and Titratable Acids in Crimean Native and Classical Grapes Cultivars at the Stage of Technical Maturity

Most Crimean wine cultivars belong to mid-late and late ripening cultivars, which are characterized by slow sugar accumulation, but in Solnechnaya Dolina village they can accumulate a large amount of sugars by the time they reach physiological maturity – over 26.0 °Brix. Table 1 shows the carbohydrate-acid complex of native and classical grape cultivars growing in the mountain-valley coastal and western foothill-coastal regions in typical weather conditions during the period of industrial grape harvesting in Crimea (September-October). The limits of the value ranges from 10% to 90% of the used sampling, that exclude critical minimum and maximum values of indicators (emissions) (Ostroukhova et al., 2018a).

Both white and red native grape cultivars demonstrate a wide range of sugar concentrations – from 17.0 to 25.5 °Brix, that discover the possibility of their use for the preparation of wines of various types and styles: dry and sweet, liqueur. The ratio of glucose and fructose concentrations in berries is 0.8-1.0. With the indicated total sugars, the mass concentration of titratable acids in white grapes is from 3.7 to 8.0 g L^{-1} (on average 5.8 ± 1.3 g L^{-1}), while in grapes with red berries – from 3.3 to 5.6 g L^{-1}, which means 1.2 and 1.6 times (at p<0.0001) lower than in classical cultivars growing under similar conditions, respectively (Ostroukhova et al., 2018a; 2018b).

Crimean native grape cultivars, especially these with red berries, are characterized by an intensive decrease in the content of titratable acids during ripening (Figure 1). In some years, in red grapes with sugar accumulation at 17.0 °Brix, the content of titratable acids is less than 4.0 g L^{-1}. In almost 30% of cases, native cultivars, regardless of where they grow, are characterized by the content of titratable acids on 1.0-2.5 g L^{-1} less than the values accepted in the practice of winemaking. The ratio of mass concentrations of tartaric and malic acids in grapes of white native cultivars is 2.8 ± 0.6; while in red cultivars is 3.5±1.3. The low content of titratable acids and correspondingly high pH values are a problem for the native's winemaking of Crimea, as they require additional measures aimed at protecting must and wine from the action of microflora, oxidation, resistance to turbidity of colloidal nature and harmonization of taste.

Table 1. The content of sugars and titratable acids in Crimean native and classical grape cultivars

Grape cultivars	**Total sugars (°Brix)**	**Titratable acids (g L^{-1})**	**pH**
White berry			
'Kok Pandas'	20.5-25.5	3.7-6.3	3.40-3.77
'Sary Pandas'	20.8-25.5	4.2-8.0	3.20-3.81
'Kokur Belyi'	18.5-25.2	4.2-7.0	3.30-3.60
'Shabash'	17.5-21.2	4.3-6.0	3.25-3.73
Native cultivars, mean ± SD	*21.2±2.9*	*5.8±1.3*	*3.47±0.19*
'Rkatsiteli'	17.0-25.0	5.8-7.6	3.00-3.40
'Aligote'	17.3-21.7	5.3-8.4	3.08-3.36
'Chardonnay'	16.3-22.3	5.4-8.8	3.08-3.53
'Riesling'	19.4-20.4	7.7-8.0	2.97-3.18
'Sauvignon Blanc'	17.8-21.0	4.7-7.5	3.37-3.49
Classical cultivars, mean ± SD	*19.6±2.2*	*6.8±1.0*	*3.25±0.16*
Significance level (*p*)	0.007	<0.0001	<0.0001
Red berry			
'Kefessia'	20.2-25.5	3.3-5.6	3.19-4.00
'Gevat Kara'	17.0-21.2	3.9-5.2	3.30-3.99
'Ekim Kara'	19.4-23.4	3.9-5.0	3.29-3.90
Native cultivars, mean ± SD	*20.2±3.3*	*4.5±0.8*	*3.63±0.24*
'Cabernet Sauvignon'	18.8-24.4	5.6-8.6	3.17-3.51
'Shiraz'	20.0-22.0	5.6-8.0	3.01-3.35
'Malbec'	17.0-21.5	6.2-10.2	3.09-3.63
'Merlot'	18.6-24.2	5.6-8.3	3.24-3.44
Classical cultivars, mean ± SD	*21.4±2.2*	*7.1±1.2*	*3.32±0.14*
Significance level *p*	>0.05	<0.0001	<0.0001

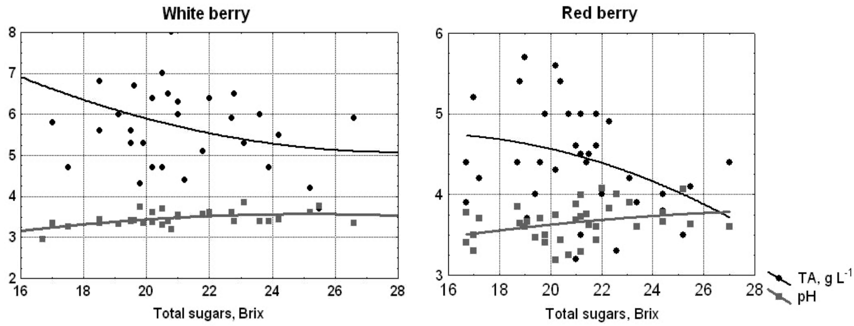


Figure 1. Change in concentration of titratable acids and pH in Crimean native grape cultivars during ripening: TA - titratable acids.

2.2. The Dynamics of the Phenolic Composition of Grapes during Ripening

The important parameters for assessing the effectiveness of using grape cultivars in both winemaking and in selection process is the quantitative content and qualitative composition of the phenolic complex of berries (Levchenko et al., 2009; Ostroukhova et al., 2018c; 2019c; Koyama et al., 2018; Volynkin et al., 2020).

The phenolic compounds, as secondary metabolites of the plant cell, protect the plant from the development of fungal and bacterial infections; neutralize almost all kinds of reactive oxygen and nitrogen species, reducing the oxidative load on the plant; anthocyanins protect the photosynthetic apparatus of the plant, reduce the degree of DNA damage under UV-B radiation etc. (Jaakola et al., 2004; Chang et al., 2011; Falcone-Ferreyra et al., 2012; Cheynier et al., 2013; Gagne et al., 2016; Vicente and Boscaiu, 2018). Under stressful conditions, either stimulation or inhibition of the biosynthesis of specific phenolic compounds occurs: high level of insolation of plants, deficiency of moisture or nitrogen in the soil can lead to an increase in the concentration of flavonoids in berries; the lack of phosphate and low temperatures – to the accumulation of anthocyanins, high temperatures – to the accumulation of flavonols (Donwey et al., 2006; Yamane et al., 2006; Mori et al., 2007; He et al., 2010).

The phenolic composition of grapes play an important role in the quality formation of wines and their adequacy to the physiological human needs (Vivas, 2002; Ostroukhova et al., 2017). On the one hand, the phenolic compounds are considered as initiators and agents of redox processes in the formation and ageing of wine (Vivas, 2002; Danilewicz, 2011). On the other hand, there is a direct participation of phenolic components in the formation of the color and taste of wines and also in their biological value. Hydrolysable tannins of the seeds, quercetin, flavan-3-ols can cause rudeness, bitterness, astringency of wines; on the contrary, berry skins' anthocyanins and tannins of phenolically ripe grapes determine the development of elegant and stable color, soft and velvety taste (Broussaud, 2001; Hufnagel and Hofmann, 2008; Arnous and Meyer, 2010; He et al., 2012; Ren et al., 2017; Vicente and Boscaiu, 2018).

The multivariate biological effect of flavonoids and phenolic acids due to their antioxidant properties has been proved experimentally namely, by the normalization of the cellular metabolism and oxygen transport, regulation of fat metabolism of the liver, strengthening of the walls of blood vessels, cardioprotective properties, anticarcinogenic, antineoplastic, anti-inflammatory and antiallergic activity (Bagchi et al., 2003; Mandal et al., 2009; Dai and Mumper, 2010; Xia et al., 2010; Gengaihi et al., 2014; Bhise et al., 2017). Flavonoids and phenolic acids display the antioxidant properties as antiradical agents binding free radicals and as chelating compounds preventing the formation of radicals. The catechol group (two hydroxyl groups at the 3 'and 4' positions of the B ring) is thought to make the largest contribution to the radical-binding and chelating properties of the flavonoid molecule. At the same time, the 2.3-double bond in the molecule of flavonoids in the C ring which is conjugated to the C_4 oxo-group and C_3, A-5 hydroxyl groups significantly increases the antiradical effect of flavonoids (Pietta, 2000; Amić et al., 2007; Tarakhovsky et al., 2013). The grape phenolic profile, as well as its variability under the influence of natural and anthropogenic factors, is determined by the species and varietal affiliation of grapes (Otero-Pareja et al., 2015; Narduzzi et al., 2015; He et al., 2017; Peskova et al., 2017b; Popov et al., 2017; Ostroukhova et al., 2018c; 2019a; Levchenko et al., 2019, Batukaev et al., 2019).

Table 2. The content (arithmetic mean value, mg kg^{-1}) of phenolic compounds in berries of native grape cultivars with red berries

Phenolic compounds	**Grape cultivars**					
	'Kefessia'		'Gevat Kara'		'Ekim Kara'	
	Total sugars (°Brix)					
	13.1	20.2	12.0	18.0	13.0	22.5
Hydroxybenzoic and hydroxycinnamic acids						
Gallic acid	5.0	1.7	14.7	5.7	6.2	n.d
Caffeic acid	4.6	3.9	16.0	13.0	5.1	6.4
Caftaric acid	115.2	65.1	78.5	17.0	66.1	22.3
p-Coutaric acid	36.1	20.2	20.8	5.9	12.1	3.2
Flavonols						
Quercetin	0.8	0.2	1.3	0.5	0.5	8.7
Quercetin -3-O- β -D-glycosides	13.0	3.1	30.4	11.2	4.5	5.1
Quercetin -3-O- β -D-glucuronide	69.2	51.6	111.1	43.0	26.5	27.4
Kaempferol	0.6	0.3	1.0	0.5	0.6	0.7
Kaempferol-3-O- β -D-glucuronide	5.7	4.2	7.6	3.3	2.7	2.1
Flavan-3-olsand Procyanidins:						
(+)-D-catechin	336.7	114.4	562.6	73.6	471.1	120.2
(-)-Epicatechin	192.9	129.0	284.8	108.8	290.9	113.1
B1: Epicatechine-4→8-catechine	39.8	28.8	47.5	31.9	40.6	34.7
B2: Epicatechine-4→8-epicatechine	139.2	69.2	190.2	76.9	112.1	23.1
B3: Catechine -4→8-catechine	167.9	61.6	230.2	41.6	153.6	43.0
B4: Catechine -4→8-epicatechine	52.1	29.4	58.3	37.3	36.4	18.2
B5: Epicatechine-4→6-catechine	44.7	23.8	6.3	5.9	20.0	11.8
B6: Epicatechine-4→6-epicatechine	110.0	54.1	157.0	19.1	69.8	64.7
B7: Catechine -4→6-catechine	71.8	36.0	81.8	19.3	47.6	12.4
B8: Catechine -4→6-epicatechine	83.8	2.9	118.3	32.5	92.8	42.0
Anthocyanins:						
Cyanidin-3-O-β-D-glucoside	0.6	3.0	8.3	68.1	4.7	7.5
Delphinidin-3-O- β-D-glucoside	2.9	22.4	3.7	190.8	20.9	33.4
Petunidin-3-O-β-D-glucoside	4.2	28.7	7.6	165.8	30.5	53.6
Peonidin-3-O-β-D-glucoside	2.8	18.8	16.1	50.0	18.7	37.5
Malvidin-3-O-β-D-glucoside	31.6	225.4	40.4	304.2	166.1	409.8
Cyanidin-3-O-β-D-glucoside-6ʾ-O-acetate	n.d.	0.3	0.4	10.4	0.2	1.4
Delphinidin-3-O- β-D-glucoside-6ʾ-O-acetate	0.4	0.2	n.d.	37.4	0.7	0.9
Petunidin-3-O-β-D-glucoside-6'-O-acetate	0.6	0.9	0.4	34.3	1.7	2.0
Malvidin-3-O-β-D-glucoside-6'-O-acetate	7.6	37.7	2.5	56.1	14.7	38.2

Table 2. (Continued)

Phenolic compounds	**Grape cultivars**					
	'Kefessia'		'Gevat Kara'		'Ekim Kara'	
	Total sugars (°Brix)					
	13.1	20.2	12.0	18.0	13.0	22.5
Cyanidin-3-O-β-D-glucoside-6'-O-*p*-coumarate	0.9	1.9	2.3	10.4	1.9	23.5
Delphinidin-3-O-β-D-glucoside-6'-O-*p*-coumarate	3.6	12.2	1.6	38.6	10.8	9.4
Petunidin-3-O-β-D-glucoside-6'-O-*p*-coumarate	4.1	12.8	1.7	25.7	14.5	20.1
Peonidin-3-O-β-D-glucoside-6'-O-*p*-coumarate	n.d.	0.3	4.3	n.d.	0.3	8.1
Malvidin-3-O-β-D- glucoside-6'-O-*p*-coumarate	35.7	135.7	10.9	57.0	95.4	191.7
Cyanidin-3,5-O-β-D-diglucoside	0.7	0.2	n.d.	5.1	1.9	0.5
Delphinidin-3,5-O- β-D- diglucoside	n.d.	0	n.d.	1.8	0.2	0.1
Petunidin-3,5-O-β-D-diglucoside	n.d.	0.2	n.d.	3.0	0.6	0.8
Peonidin-3,5-O-β-D-diglucoside	n.d.	n.d.	n.d.	1.1	n.d.	n.d.
Malvidin-3,5-O-β-D-diglucoside	n.d.	0.4	n.d.	1.3	0.3	0.1
Malvidin-3,5-O-β-D-diglucoside-6'-O-acetate	n.d.	n.d.	n.d.	1.3	n.d.	0.2
Malvidin-3,5-O-β-D-diglucoside-6'-O-*p*-coumarate	n.d.	n.d.	n.d.	n.d.	n.d.	7.7
Stilbenes:						
trans-Resveratrol	5.2	14.2	7.3	1.2	8.1	22.6
Piceid	27.0	14.5	16.1	0.5	7.3	2.6

Standard deviation was no more than 8% of the mean values of the content of the components of the phenolic complex and no more than 3% of the mean values of the content of sugars; n.d. not detected.

In this regard, comparative studies of the dynamics of the phenolic complex of berries during ripening of Crimean native and classical grape cultivars from the ampelographical collection of Institute "Magarach" (v. Vilino, Bakhchisaray district) were carried out using the HPLC (Shimadzu LC20 Prominence, Japan). In the berries of the investigated cultivars, 42 monomeric and dimeric phenolic compounds of the flavonoid and non-flavonoid structure were identified (Ostroukhova et al., 2019b; 2020). Tables 2 to 5 shows the content of phenolic components at the beginning of ripening (12.0 - 14.5 °Brix) and at the technological maturation (18.0-22.5

°Brix – for grape cultivars with red berries; 20.0-22.0 °Brix – for grape cultivars with white berries). The total content of identified phenolic compounds in red grapes at the beginning of ripening varied depending on the cultivar from 1352 mg kg^{-1} ('Malbec') to 2142 mg kg^{-1} ('Gevat Kara'); in white grapes – from 669 mg kg^{-1} ('Sauvignon Blanc') to 2411 mg kg^{-1} ('Kokur Belyi').

During ripening of grapes, the content of components in the berries of native cultivars with red berries decreased from the initial values on average by 24%, while the classical cultivars by 10%. In berries of white native cultivars, the content of monomeric and dimeric phenolic compounds decreased on average in 3.5 times (in 'Kokur Belyi' – in 4.1 times), and in classical cultivars it remained at the level of the initial values. At 18.0-22.5 °Brix the lowest concentration of phenolic components was noted in 'Kefessia' (1229 mg kg^{-1}), the largest in 'Gevat Kara' (1611 mg kg^{-1}); in the berries of other red grape cultivars the value of the index was 1415-1481 mg kg^{-1}. In white grapes at 20.0-22.0 ° Brix the lowest concentration of components was noted in 'Shabash' (256 mg kg^{-1}), the largest in 'Riesling' (1006 mg kg^{-1}) and 'Chardonnay' (827 mg kg^{-1}).

An analysis of the qualitative composition of the phenolic complex showed that at the beginning of ripening process in the native grape cultivars with red berries predominated flavan-3-ols, with an average mass fraction of 38%; while in classical ones 31%; procyanidins 39% and 41%, respectively; anthocyanins were 10% and 15%, phenolic acids and flavonols 6-7% and 5%, stilbenes 1% (Figure 2). During technological maturation the content of flavan-3-ols, procyanidins and phenolic acids decreased on average in 2 times (p <0.004), and the dominant components were anthocyanins, whose percentage increased more than 4 times (p<0.004), reaching 55%. The percentage of stilbenes in the grapes during ripening remained at the initial level.

Flavan-3-ols and procyanidins were also the dominant components of the phenolic complex in white grapes of native and classical cultivars: the mass fraction of the components at the beginning of ripening was 35-38% and 50-53%, respectively; at 20.0-22.0 °Brix, 26-35% and 46-48%, respectively. Cultivars with white berries were characterized by an increase in the proportion of flavonols in the phenolic complex during ripening, with an average increase of 5-fold. These data confirm the modern idea (Fournand et al., 2006; Teixeira et al., 2013), that in the berries the biosynthesis of procyanidins and flavan-3-ol completes at the beginning of its maturation and subsequently their oxidative polymerization occurs; on the contrary, the synthesis of anthocyanins carries out from the beginning of ripening of the grapes to the beginning of physiological maturity.

The monomeric ((+)-D-catechin and (-)-epicatechin) and dimeric (procyanidins B_1-B_8) forms of flavanols were identified in the berries of the investigated cultivars. The initial concentration of flavan-3-ol monomers in native red grape cultivars ranged from 529.6 ('Kefessia') to 847.4 ('Gevat Kara') mg kg^{-1} and in white ones from 281.0 ('Sary Pandas') to 632.0 ('Kokur Belyi') mg kg^{-1}. Their content in classic cultivars was on average 1.4 times lower and ranged in red berries from 373.8 ('Malbec') to 656.8 ('Cabernet Sauvignon') mg kg^{-1}, in white berries, from 284.7 ('Sauvignon Blanc') to 334.1 ('Chardonnay') mg kg^{-1}. During ripening the concentration of flavan-3-ol monomers decreased ($p<0.05$) in native red cultivars in 3.2 times from 404.4 to 62.0 mg kg^{-1}, in white ones – in 4.1 times from 186.8 to 60.6 mg kg^{-1}. In classical black grapes, the concentration of components decreased in 2.6 times, in white ones, only by 11%.

The concentration of procyanidins (B_1-B_8) in native and classical red cultivars did not differ significantly at the beginning of ripening, ranging from 510.9 ('Malbec') to 889.6 ('Gevat Kara') mg kg^{-1}. The highest content of procyanidins was distinguished by 'Kokur Belyi' (1647.7 mg kg^{-1}), in the other cultivars the concentration of components ranged from 335.6 to 518.6 mg kg^{-1}. During ripening, the concentration of components decreased ($p<0.05$) in 'Kokur Belyi' in 7.5 times, in other native cultivars – in 2.5-2.6 times: to 249.7-305.8 mg kg^{-1} in red grapes and to 146.4-214.8 in white grapes.

In classical grapes with red berries the concentration of components decreased in 2.0 times, in white ones – only by 7%. It was noted that the proportion of B_2 and B_3 in the procyanidin complex was the largest, and in the sum was 40-46% at the beginning of ripening and 35-48% at the end of the observed period.

Table 3. The content (arithmetic mean value, mg kg^{-1}) of phenolic compounds in berries of classical grape cultivars with red berries

Phenolic compounds	**Grape cultivars**					
	'Cabernet Sauvignon'		'Shiraz'		'Malbec'	
	Total sugars (°Brix)					
	13.5	18.9	13.5	22.0	14.1	21.5
Hydroxybenzoic and hydroxycinnamic acids:						
Gallic acid	n.d.	4.0	8.0	4.1	4.9	3.7
Caffeic acid	4.9	11.6	3.4	4.4	4.8	5.6
Caftaric acid	95.7	23.5	72.5	42.6	21.3	14.5
p-Coutaric acid	19.1	1.9	25.4	13.2	8.0	3.1
Flavonols:						
Quercetin	1.3	0.3	0.8	0.2	1.4	0.1
Quercetin -3-O- β -D-glycosides	15.1	4.1	8.1	8.9	3.5	6.8
Quercetin -3-O- β -D-glucuronid	88.0	26.8	93.3	75.9	16.1	17.4
Kaempferol	0.3	0.4	0.6	0.4	0.3	0.5
Kaempferol-3-O- β -D-glucuronide	5.8	3.3	4.9	26.3	3.1	25.1
Flavan-3-olsand Procyanidins:						
(+)-D-catechin	443.8	150.0	241.5	65.3	204.5	95.3
(-)-Epicatechin	213.0	n.d.	218.8	123.0	290.9	141.4
B1: Epicatechine-4→8-catechine	38.5	36.9	39.6	28.3	31.6	35.0
B2: Epicatechine-4→8-epicatechine	162.4	72.3	137.3	76.8	112.1	52.0
B3: Catechine-4→8-catechine	199.2	73.4	124.3	36.6	96.9	43.6
B4: Catechine-4→8-epicatechine	57.1	18.4	48.3	23.9	42.6	25.7
B5: Epicatechine-4→6-catechine	75.9	59.9	64.1	37.9	85.3	4.9
B6: Epicatechine-4→6-epicatechine	144.2	50.6	107.3	57.7	77.3	46.0
B7: Catechine-4→6-catechine	79.9	31.6	59.4	22.6	41.5	27.1
B8: Catechine-4→6-epicatechine	110.9	76.1	85.5	36.3	67.1	42.1
Anthocyanins:						
Cyanidin-3-O-β-D-glucoside	9.6	28.2	0.4	4.1	2.0	3.3
Delphinidin-3-O- β-D-glucoside	30.3	127.4	1.7	23.9	14.0	30.4
Petunidin-3-O-β-D-glucoside	20.9	79.0	3.3	32.8	22.0	44.3
Peonidin-3-O-β-D-glucoside	18.3	60.6	2.5	41.3	15.9	39.5
Malvidin-3-O-β-D-glucoside	66.4	251.0	27.3	260.8	151.4	329.4
Cyanidin-3-O-β-D-glucoside-6’-O-acetate	1.9	6.4	0.3	1.4	0.8	0.4

Table 3. (Continued)

Phenolic compounds	**Grape cultivars**					
	'Cabernet Sauvignon'		'Shiraz'		'Malbec'	
	Total sugars (°Brix)					
	13.5	18.9	13.5	22.0	14.1	21.5
Delphinidin-3-O-β-D-glucoside-6’-O-acetate	7.7	33.0	0.3	3.9	1.8	3.0
Petunidin-3-O-β-D-glucoside-6’-O-acetate	7.9	25.8	0.8	7.8	3.7	5.2
Malvidin-3-O-β-D-glucoside-6’-O-acetate	27.5	109.5	10.2	100.0	28.4	59.8
Cyanidin-3-O-β-D-glucoside-6ʾ-O-*p*-coumarate	1.5	2.1	0.8	3.9	1.9	11.4
Delphinidin-3-O-β-D-glucoside-6ʾ-O-*p*-coumarate	8.6	23.5	3.3	29.3	15.2	23.4
Petunidin-3-O-β-D-glucoside-6ʾ-O-*p*-coumarate	2.2	5.3	3.9	23.6	16.3	25.1
Peonidin-3-O-β-D-glucoside-6ʾ-O-*p*-coumarate	5.4	8.0	4.2	0.7	0.4	0.7
Malvidin-3-O-β-D- glucoside-6ʾ-O-*p*-coumarate	10.5	27.2	28.0	225.4	111.3	219.9
Cyanidin-3,5-O-β-D-diglucoside	2.3	0.9	0.6	0.6	3.5	0.5
Delphinidin-3,5-O- β-D- diglucoside	0.4	0.3	n.d.	n.d.	0.3	n.d.
Petunidin-3,5-O-β-D-diglucoside	1.0	n.d.	n.d.	2.6	0.9	2.7
Peonidin-3,5-O-β-D-diglucoside	0.3	n.d.	n.d.	n.d.	0.3	n.d.
Malvidin-3,5-O-β-D-diglucoside	0.3	n.d.	n.d.	0.4	0.7	0.4
Malvidin-3,5-O-β-D-diglucoside-6ʾ-O-acetate	0.2	n.d.	n.d.	n.d.	n.d.	n.d.
Malvidin-3,5-O-β-D-diglucoside-6ʾ-O-*p*-coumarate	n.d.	n.d.	n.d.	n.d.	n.d.	1.6
Stilbenes:						
trans-Resveratrol	1.2	1.8	2.0	26.5	9.0	22.6
Piceid	14.9	6.2	17.2	7.2	5.0	1.4

Standard deviation was no more than 8% of the mean values of the content of the components of the phenolic complex and no more than 3% of the mean values of the content of sugars; n.d. not detected.

Table 4. The content (arithmetic mean value, mg kg^{-1}) of phenolic compounds in berries of white native and classical grape cultivars at sugar content 12.0-14.5 °Brix

Phenolic compounds	**Grape cultivars**					
	'Kokur Belyi'	'Shabash'	‘Sary Pandas’	'Chardonnay'	'Riesling'	'Sauvignon Blanc'
Hydroxybenzoic and hydroxycinnamic acids:						
Gallic acid	3.5	3.6	4.4	3.3	n.d.	5.6
Caffeic acid	3.3	1.5	6.1	3.4	15.7	2.3
Caftaric acid	119.8	36.9	55.6	14.2	138.6	7.3
p-Coutaric acid	11.2	9.4	12.4	3.4	15.7	1.5
Flavonols:						
Quercetin	0.4	0.2	0.3	n.d.	0.2	n.d.
Quercetin-3-O-β-D-glycosides	2.0	3.3	8.4	0.2	7.3	3.4
Quercetin-3-O-β-D-glucuronid	13.3	20.2	35.0	19.6	29.3	20.0
Kaempferol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Kaempferol-3-O-β-D-glucuronide	1.4	1.6	2.0	0.6	1.3	n.d.
Flavan-3-ols:						
(+)-D-catechin	288.8	273.1	136.2	163.8	194.7	138.9
(-)-Epicatechin	343.2	92.1	144.8	170.3	108.0	145.8
Procyanidins:						
B1: Epicatechine-4→8-catechine	95.4	17.5	41.3	31.1	27.0	27.3
B2: Epicatechine-4→8-epicatechine	362.0	70.3	52.7	49.7	104.5	67.8
B3: Catechine-4→8-catechine	189.2	126.8	93.8	70.3	143.5	64.7
B4: Catechine-4→8-epicatechine	113.2	14.2	25.8	28.6	22.1	15.6
B5: Epicatechine-4→6-catechine	237.8	23.8	21.8	24.8	52.7	52.6
B6: Epicatechine-4→6-epicatechine	179.6	36.7	35.2	35.9	75.3	32.3
B7: Catechine-4→6-catechine	244.1	43.5	27.6	48.2	48.7	26.6
B8: Catechine-4→6-epicatechine	193.4	59.9	61.2	81.7	44.8	48.7
Stilbenes:						
trans-resveratrol	0.8	0.7	4.1	0.7	0.2	0.3
Piceid	8.5	9.2	13.9	10.1	11.9	8.6

Standard deviation was no more than 8% of the mean values of the content of the components of the phenolic complex and no more than 3% of the mean values of the content of sugars; n.d. not detected.

Table 5. The content (arithmetic mean value, mg kg^{-1}) of phenolic compounds in berries of white native and classical grape cultivars at sugar content 20.0-22.0 °Brix

Phenolic compounds	Grape cultivars					
	'Kokur Belyi'	'Shabash'	'Sary Pandas'	'Chardonnay'	'Riesling'	'Sauvignon Blanc'
Hydroxybenzoic and hydroxycinnamic acids:						
Gallic acid	2.0	4.2	n.d.	n.d.	4.1	n.d.
Caffeic acid	4.6	1.1	4.2	3.2	15.0	1.9
Caftaric acid	48.9	2.3	12.6	42.3	92.4	13.8
p-Coutaric acid	3.7	0.1	0.9	9.1	12.4	2.0
Flavonols:						
Quercetin	0.4	0.9	0.2	0.3	0.5	0.3
Quercetin -3-O- β -D-glycosides	11.2	4.9	12.2	10.1	15.8	6.5
Quercetin -3-O- β -D-glucuronid	72.1	21.0	49.2	60.2	96.2	53.4
Kaempferol	n.d.	n.d.	n.d.	n.d.	n.d.	0.3
Kaempferol-3-O- β -D-glucuronide	24.2	2.1	19.2	12.6	1.3	1.2
Flavan-3-ols:						
(+)-D-catechin	76.0	31.6	48.0	133.6	185.1	107.9
(-)-Epicatechin	110.8	33.1	12.6	162.9	95.8	130.7
Procyanidins:						
B1: Epicatechine-4→8-catechine	31.8	28.2	23.4	35.9	33.6	24.6
B2: Epicatechine-4→8-epicatechine	35.2	23.1	26.1	74.1	100.1	73.2
B3: Catechine -4→8-catechine	53.1	65.4	39.1	79.4	115.2	48.6
B4: Catechine -4→8-epicatechine	21.1	11.7	6.6	22.6	21.3	10.7
B5: Epicatechine-4→6-catechine	3.7	1.0	2.6	6.2	28.7	51.1
B6: Epicatechine-4→6-epicatechine	15.6	0.0	15.0	31.6	42.0	22.5
B7: Catechine -4→6-catechine	22.6	7.0	15.7	41.4	49.2	27.2
B8: Catechine -4→6-epicatechine	31.7	15.4	17.9	59.0	35.2	31.3
Stilbenes:						
trans-Resveratrol	10.7	0.9	0.3	6.3	0.5	2.7
Piceid	7.0	1.8	8.0	13.9	13.6	9.6

Standard deviation was no more than 8% of the mean values of the content of the components of the phenolic complex and no more than 3% of the mean values of the content of sugars; n.d. not detected.

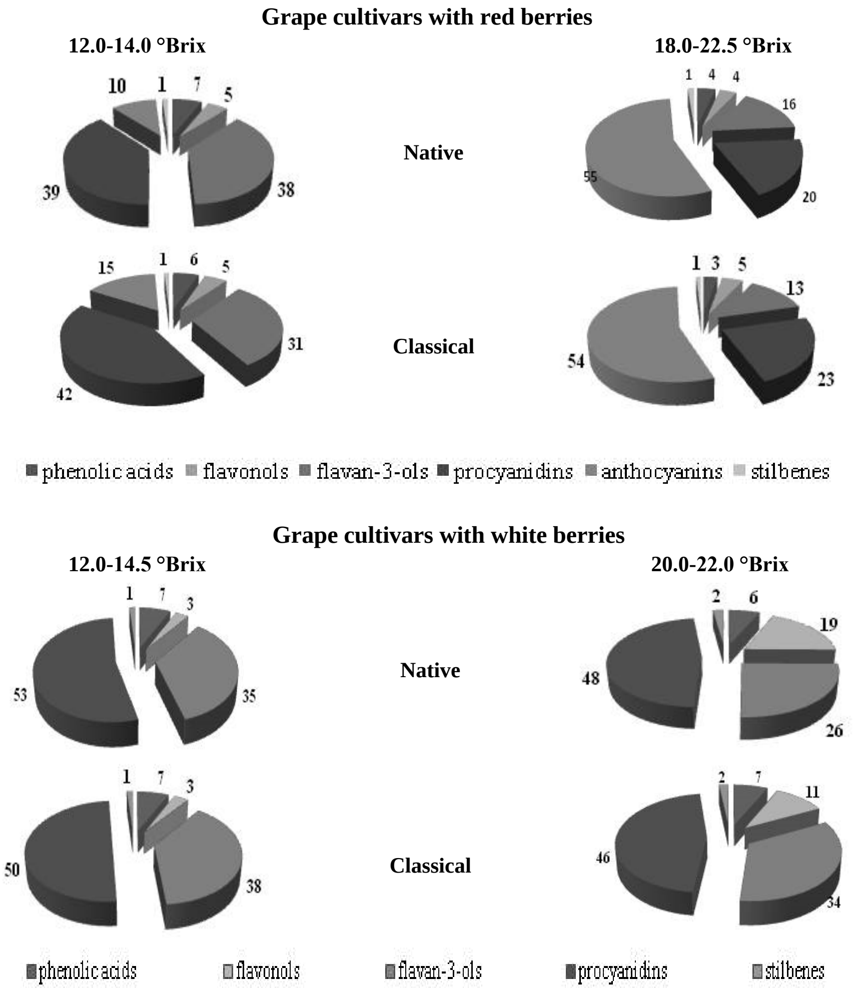
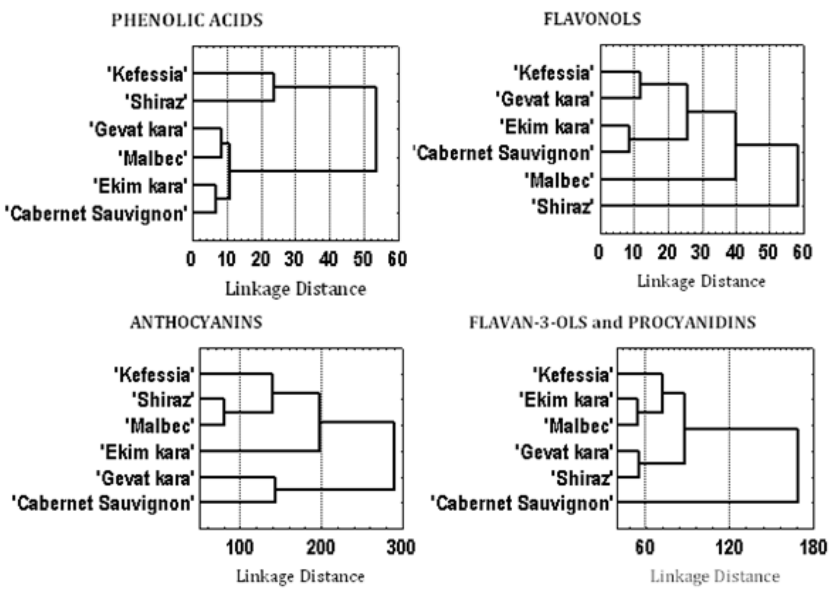


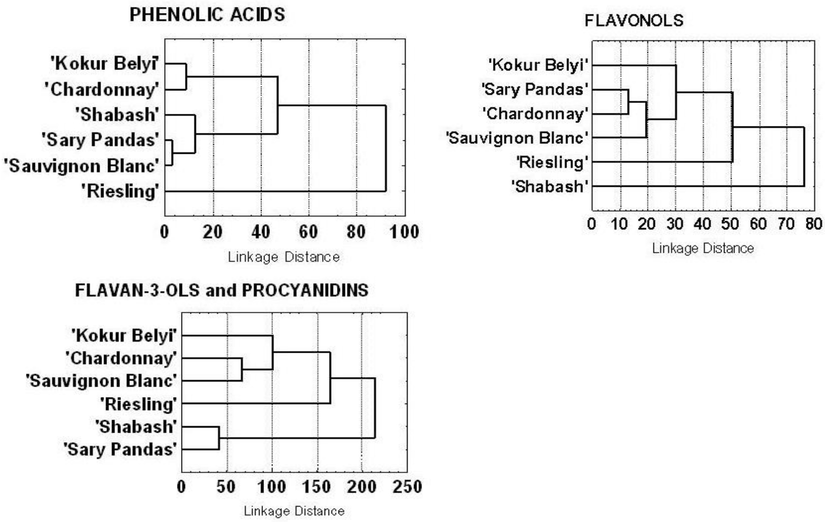
Figure 2. Composition (%, an average values) of a complex of monomeric and dimeric phenolic components of berries with different accumulation of sugars.

It is known that ripening of grapes is accompanied by oxidative polymerization of flavan-3-ol monomers and procyanidins; forming high-molecular tannins, localized in seeds (Fournand et al., 2006; Teixeira et al., 2013). Experimental data indicated a more intensive dynamics of flavanols complex in native cultivars in comparison with classical ones. In general, at 18.0-22.5 °Brix the complexes of monomeric and dimeric flavanols of 'Kefessia', 'Ekim Kara' 'Shiraz', 'Malbec' and 'Gevat Kara' were close to each other, which was reflected by Euclidean distances (Ed) 54-88 (Figure 3). In addition, the flavanols complex of 'Cabernet Sauvignon' differed significantly from that in other cultivars with an Euclidean distances of 145-169. Among the white grape cultivars, ‘Sary Pandas’ and 'Shabash’ form a separate cluster according to the complex of monomeric and dimeric flavanols, resemble to each other (Ed = 42) and significantly differ from classical white grape cultivars (Ed = 148-214). The native cultivar 'Kokur Belyi' according to the complex of these components is the closest to 'Sauvignon Blanc' at 20.0-22.0 °Brix with an Euclidean distances of 73 (Figure 4).



Source: Ostroukhova et al. (2019b).

Figure 3. The results of the cluster analysis of different grape cultivars with red berries based on the phenolic composition at sugar content of 18.0-22.5 °Brix.



Source: Ostroukhova et al. (2020).

Figure 4. The results of the cluster analysis of different white grape cultivars based on the phenolic composition at sugar content of 20.0-22.0 °Brix.

The initial summary content of quercetin, kaempferol and their derivatives in 'Ekim Kara' and 'Malbec' was 34.8 and 24.4 mg kg^{-1}, respectively. In other cultivars with a colored berries the content of components exceeded this level in 3.8 times (p<0.02) and varied from 89.3 ('Kefessia') to 151.4 ('Gevat Kara') mg kg^{-1}. The initial summary content of quercetin, kaempferol and their derivatives in native and classical grape cultivars with white berries varied from 17.1 ('Kokur Belyi') to 45.7 ('Sary Pandas') mg kg^{-1}. The flavonols complex was represented by 66-87% of quercetin-3-O-β-D-glucuronide and 8-20% of quercetin-3-O-β-D-glycoside in black berries and, respectively, by 77-96% and 1-19% in white berries. During ripening, the content of flavonols and their derivatives in 'Ekim Kara' and 'Malbec' increased in 1.7 times. However, in 'Shiraz' the content of flavanols and their derivatives did not change. In other cultivars, the values decreased in 1.5-3.2 times. At the same time, in 'Shiraz' and 'Malbec', the content of kaempferol-3-O-β-D-glucuronide increased significantly (on average in 6.7 times), reaching 26.3 and 25.1 mg kg^{-1}.

In native white grape cultivars the content of flavonols and their derivatives increased in 2.3 times (in 'Kokur Belyi' – in 6.4 times) during ripening, while in classical ones in 3.2 times. In general, at 18.0-22.5 °Brix the composition and concentration of the flavonols complex of 'Ekim Kara' was closer (Figure 3) to 'Cabernet Sauvignon' (Ed = 8.6) and 'Gevat Kara' to 'Kefessia' (Ed = 11.9). 'Shiraz' and 'Malbec' were significantly different from the native and other red cultivars (Ed = 26.5-55.0) and differed from each other (Ed = 58.6). Among white grape cultivars, the flavonols complex of 'Sary Pandas' and 'Chardonnay' (Ed = 13.0) were similar; 'Kokur Belyi' was closed to 'Chardonnay' (Ed = 16.7) and 'Shabash' was significantly different from the rest of the classic and native cultivars with an Euclidean distances of 32.5-76.0 (Figure 4).

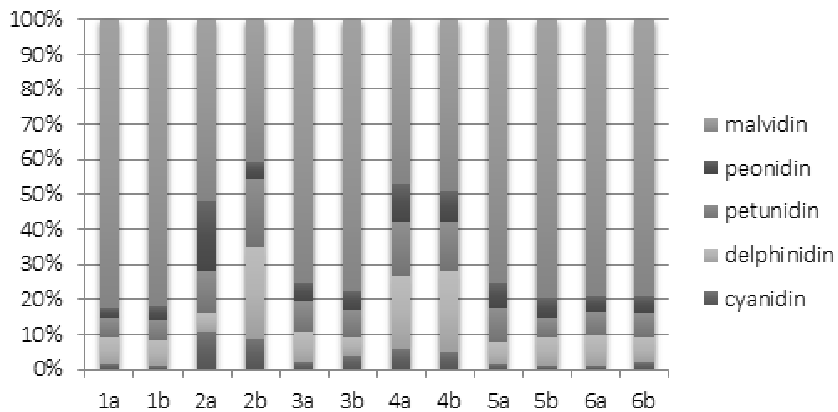
Quercetin, kaempferol and myricetin are the closest precursors of anthocyanins (Jaakola et al., 2004; Tanaka, 2008; Pascual-Teresa and Sanchez-Ballesta, 2008; Teixeira et al., 2013). The 21 components were identified in anthocyanins complex of berries of the investigated cultivars: mono- and diglucosides of malvidin, delphinidin, cyanidin, peonidin, petunidin and their derivatives acylated by acetic acid or by *p*-coumaric acid. At 12.0-14.0 °Brix the concentration of the anthocyanins in 'Shiraz', 'Kefessia' and 'Gevat Kara' was 87.6-100.2 mg kg^{-1}. In other cultivar in average they were 3.5 times (p<0,05) higher and ranging from 223.2 ('Cabernet Sauvignon)' to 389.9 ('Malbec') mg kg^{-1}. Garcia et al. (2017) showed that grape cultivars significantly differ in the initial content of sugars, from which biosynthesis of anthocyanins begins. It can be assumed that in 'Cabernet Sauvignon', 'Ekim Kara' and 'Malbec', this process begins at a lower concentration of sugars than in other investigated cultivars. During ripening, the concentration of the anthocyanins complex in the berries of the classical cultivars increased to 762.5-801.0 mg kg^{-1}; while in 'Kefessia', 'Ekim Kara' and 'Gevat Kara' up to 501.1, 846.1 and 1062.4 mg kg^{-1}, respectively. Thus, the best balance of accumulation of anthocyanins and sugars during maturation of grapes in the observed period was in 'Gevat Kara'. The increase in the content of anthocyanins for this grape variety was an average value of 160.4 mg kg^{-1} per 1 °Brix. For 'Cabernet Sauvignon', this index was 104.7 mg kg^{-1} and for the other cultivars varied from 48.6 ('Ekim Kara') to 79.4 ('Shiraz') mg kg^{-1}.

During the observation period, the total content of monoglucosides malvidin, delphinidin, cyanidin, peonidin, and petunidin in the anthocyanins complex of grapes cultivars varied from 40% ('Shiraz') to 76% ('Gevat Kara'). The content of derivatives of acyl acid varied from 3% to 22% and for derivatives of acylated by *p*-coumaric acid varied from 13% to 46%.

Regardless of the cultivar and monitoring point, malvidin-3-O-β-D-glucoside and their derivatives predominated in the anthocyanins complex (Figure 5), which is a characteristic of the anthocyanin profile of *Vitis vinifera* (Levchenko et al., 2009; 2019; Narduzzi et al., 2015; He et al., 2017; Peskova et al., 2017b). The percentages of components in 'Gevat Kara' and 'Cabernet Sauvignon' were 54% and 39% (53.8 and 104.4 mg kg^{-1}, respectively). In the remaining cultivars, these contents varied between 72 and 80% (65.5-291.1 mg kg^{-1}). During ripening the concentration of these components in berries increased 3.5 times ($p<0.003$). At 18.0-22.5 °Brix, the contents of malvidin-3-O-β-D-glucoside and their derivatives in 'Ekim Kara', 'Shiraz' and 'Malbec' were from 586.2 to 639.6 mg kg^{-1} and exceeded in 1.5 times ($p<0.05$) in the remaining cultivars.

During ripening 'Gevat Kara' was characterized by an increase in the anthocyanin complex of monoglucosides of delphinidin from 5% to 25%, petunidin from 12% to 19% and a decrease in the proportion of monoglucosides of peonidin from 20% to 5% and cyanidin from 11% to 8%. 'Cabernet Sauvignon' during the whole period of observation was characterized by 21-23% of monoglucosides of delphinidin, 14-15% petunidin, 9-11% peonidin and 5-6% cyanidin. In the other cultivars, the proportion of monoglucosides of cyanidin in anthocyanins complex varied in the range of 1-4%, for delphinidin in 5-8% for petunidin in 5-10% and peonidin in 3-9%.

At the end of the observation period, the content of monoglucosides of delphinidin and petunidin were higher in 'Gevat Kara' and 'Cabernet Sauvignon'. The concentration of delphinidin-3-O-β-D-glucoside and their derivatives were 266.8 mg kg^{-1} and 183.9 mg kg^{-1}, respectively, and exceeded in 4.7 times ($p<0.003$) in the remaining cultivars. The concentration of petunidin-3-O-β-D-glucoside and their derivatives were 200.1 mg kg^{-1} and 112.8 mg kg^{-1}, in 3.4 times (p<0.02) higher than other cultivars. The greatest amount of cyanidin-3-O-β-D-glucoside and their derivatives in berries (at 18.0-22.5 °Brix) were also observed in 'Gevat Kara' (88.9 mg kg^{-1}) and the smallest in 'Kefessia' and 'Shiraz' (5.2-9.4 mg kg^{-1}). In the other cultivars the values varied between 15.1 and 36.7 mg kg^{-1}. According to the content of peonidin-3-O-β-D-glucoside and their derivatives in the berries during the observation period, 'Kefessia' was distinguished, in which the concentration of the components was the lowest (19.1 mg kg^{-1}). In the other cultivars, this value did not differ significantly and ranged from 40.2 mg kg^{-1} to 68.6 mg kg^{-1}.



Source: Ostroukhova et al. (2019). 1 – 'Kefessia'; 2 – 'Gevat Kara'; 3 – 'Ekim Kara'; 4 – 'Cabernet Sauvignon'; 5 – 'Shiraz'; 6 – 'Malbec'; a – 12.0-14.0 °Brix, b – 18.0-22.5 °Brix.

Figure 5. Composition (%) of monoglucosides of malvidin, delphinidin, cyanidin, peonidin, petunidin and their derivatives in berries with different contents of sugars.

In both native and classical cultivars, diglucosides of malvidin, delphinidin, cyanidin, peonidin, petunidin and derivatives of malvidin-3.5-O-β-D-diglucoside were acylated by acetic acid or by p-coumaric acid. At 18.0-22.5 °Brix the total concentration of diglycosides of the anthocyanin series in classical cultivars ranged from 1.2 mg kg^{-1} to 5.2 mg kg^{-1}. For

'Kefessia', 'Ekim Kara' and 'Gevat Kara' the values ranged from 0.8 to 13.6 mg kg^{-1}.

The hierarchical cluster analysis revealed the similarity of the anthocyanins complex of 'Malbec' and 'Shiraz', which is characterized by Euclidean distances equal to 81. In addition, 'Ekim Kara' was close to 'Malbec' (Ed = 91) and 'Kefessia' to 'Shiraz' (Ed = 140). The anthocyanin complexes of 'Cabernet Sauvignon' and 'Gevat Kara' differed (Ed = 188-290) from other cultivars, and were characterized among themselves with an Ed = 144 (Figure 3).

The generalization of the data on the dynamics of anthocyanins during ripening makes it possible to comment them as follows. Formation of anthocyanins complex in the berries of the investigated cultivars occurs in the direction of the biosynthesis of components characterized for European grape cultivars, in which the final metabolites of the chains of transformations of anthocyanins is malvidin-3-O-β-D-glucoside and its derivatives (Tanaka, 2006; Pascual-Teresa and Sanchez-Ballesta, 2008; Teixeira et al., 2013; Narduzzi et al., 2015). This is evidenced by a high content of glucosides of malvidin in the anthocyanins complex of 'Kefessia', 'Ekim Kara', 'Shiraz' and 'Malbec'. Dynamics of anthocyanins in 'Gevat Kara' and 'Cabernet Sauvignon', with high concentrations of monoglucosides of delphinidin, petunidin and cyanidin in berries with a relatively low content of monoglucosides of malvidin, at the end of the observed period, indicate the incompleteness of the formation of anthocyanins complex. This can be explained both by the varietal characteristics of these grapes (Fanzona et al., 2012; Zaitsev et al., 2014; Peskova et al., 2017b), and by the fact that at 18.0-18.9 °Brix 'Gevat Kara' and 'Cabernet Sauvignon' did not reach maturity (Ostroukhova et al., 2012; Levchenko et al., 2017a).

At the beginning of ripening (12.0-14.1 °Brix) in native cultivars with colored berries, gallic acid contents were between 5.0-14.7 mg kg^{-1} and for hydroxycinnamic acids were 83.3-155.9 mg kg^{-1}. In white cultivars these values varied from 3.5-4.4 mg kg^{-1} to 47.8-134.3 mg kg^{-1}, respectively (Table 2). In classical cultivars gallic acid content varied from 0.0 to 8.0 mg kg^{-1}, while hydroxycinnamic acids from 11.1 to 170.0 mg kg^{-1} (Table 3). Among hydroxycinnamic acids, 41-87% was caftaric acid at the beginning and at the end of the observations. During ripening, the content of phenolic acids in native cultivars with red berries decreased in 2.6 times, while in classical ones – in 2.0 times (p<0.04) and amounted 25.3-90.9 mg kg^{-1} and 26.9-64.3 mg kg^{-1}, respectively. In white native grapes cultivars, the content of compounds decreased in 3.3 times to 7.7-59.2 mg kg^{-1}, while in classical cultivars the values decreased by 7%. In 'Cabernet Sauvignon' grapes, accumulation of gallic acid was noted. In the plant cell, phenolic acids are the initial materials in the biosynthesis of secondary metabolites and are primarily subjected to enzymatic oxidation (Vivas, 2002; Cheynier et al., 2013). These results indicate a more active participation of hydroxybenzoic and hydroxycinnamic acids in the metabolism of the native cultivars.

The maximum concentration of phenolic acids was noted in 'Kefessia' and 'Riesling' grapes at the beginning and at the end of the observations; the minimum was found in 'Malbec' grapes. At 20.0-22.0 ° Brix, the content of phenolic acids in 'Shabash' was almost 7 times lower than in other white cultivars and amounted 7.7 ± 0.5 mg kg^{-1}. Roussis, et al. (2007) showed that the caffeic and gallic acids, exhibiting antioxidant properties, are able to inhibit the oxidative transformation of the aroma-forming components of the wines. At the end of the observation, the total concentration of these acids in the 'Gevat Kara', 'Cabernet Sauvignon' and 'Riesling' were 18.7, 15.6 and 19.1 mg kg^{-1}, respectively, and exceeded in 2.3 times (p<0.004) other cultivars.

The hierarchical cluster analysis of the experimental data (Figure 3) revealed the similarity of the complex phenolic acids of 'Ekim Kara', 'Cabernet Sauvignon', 'Malbec' and 'Gevat Kara' (Ed = 6.8-10.6). 'Kefessia' differed acids from other native cultivars (Ed = 46.2-51.2) and was closest to 'Shiraz' (Ed = 23.7). Among the white grape cultivars, the phenolic acids of 'Kokur Belyi' was the closest to 'Chardonnay' (Ed = 8.9). 'Sary Pandas' and 'Shabash' were similar to each other with Ed = 11.6 and they were close to 'Sauvignon Blanc' with Ed of 2.8 and 12.4, respectively.

Among the compounds of the stilbenoid series in berries, *trans*-resveratrol and its glycosylated form, piceid, were identified. At the beginning of the ripening process, the total concentration of stilbenes in native cultivars with a colored berry varied significantly and ranged from

15.4 ('Ekim Kara') to 32.2 ('Kefessia') mg kg^{-1}. In classical red cultivars, this value varied within a narrow range of 14.0-19.2 mg kg^{-1}. The contents of stilbenes in berries of white native and classical cultivars were from 8.9 ('Sauvignon Blanc') to 18.0 ('Sary Pandas') mg kg^{-1}. The content of *trans*-resveratrol and piceid was approximately equal in the stilbenes of 'Ekim Kara', *trans*-resveratrol (64%) prevailed in 'Malbec', while piceid prevailed in the remaining cultivars, with proportions from 69% to 93%. In white grape cultivars, the mass fraction of piceid in the stilbenes ranged from 77% to 98%. During ripening, the concentration of stilbenes in 'Cabernet Sauvignon', 'Sary Pandas' and 'Shabash' decreased in 1.9-3.4 times, in 'Gevat Kara' almost in 14 times, reaching the lowest values among all cultivars (1.7-8.3 mg kg^{-1}).On the contrary, in 'Ekim Kara', 'Shiraz', 'Malbec', 'Kokur Belyi' and 'Chardonnay' an increase in 1.7-1.9 times in the content of the components was observed: the values amounted from 24.0 to 33.7 mg kg^{-1} in grapes with colored berries; and from 17.7 to 20.2 mg kg^{-1} in white grape cultivars. The ratio of *trans*-resveratrol and piceid in berries has also changed: at 18.0-22.5 °Brix in 'Kefessia' the content of the components was 50% and in 'Cabernet Sauvignon' piceid dominated (78%). In the other cultivars with colored berries, resveratrol dominated (71-94%). In the stilbenes complex of white grape cultivars, *trans*-resveratrol prevailed only in 'Kokur Belyi' (60.5%). In the remaining cultivars it remained as at the beginning of ripening, the proportion of piceid was 67-96%.

Summarizing the results of the studies of the dynamics of the phenolic complex of berries, we can conclude that native cultivar 'Ekim Kara' and classic ones 'Cabernet Sauvignon' and 'Malbec', at 12.0-14.0 °Brix accumulated in 3.5 times more anthocyanins than other cultivars. The best balances of anthocyanins and sugars during ripening were in 'Gevat Kara' and 'Cabernet Sauvignon' grapes (160.4 and 104.7 mg kg^{-1}per °Brix, respectively). The highest concentration of anthocyanins at 18.0-22.5 °Brix is recorded in 'Ekim Kara' (846.1 mg kg^{-1}) and 'Gevat Kara' (1062.4 mg kg^{-1}). Native cultivars were characterized by more active quantitative and qualitative changes in phenolic acids and flavanols during ripening. At 18.0-22.5 °Brix 'Kefessia' was close to 'Shiraz' by the combination of the components of the phenolic complex; 'Ekim Kara' to 'Malbec'; 'Kokur Belyi', 'Sary Pandas' and 'Shabash' to 'Sauvignon Blanc'.

2.3. Technological Parameters of the Phenolic and Oxidase Complex

Knowledge of the dynamics of the phenolic complex is necessary, but insufficient for the successful use of native cultivars in the production of wines and products of functional action. Phenolic components are unevenly distributed in grape berry: anthocyanins and flavonols are concentrated mainly in the skin of the berries; monomeric flavan-3-ols in the seeds; hydroxycinnamates in the mesocarp; while hydroxybenzoates, benzoic acids and procyanidins (tannins) – both in the skins and seeds of the berries (Spranger et al., 2004; Roediger, 2006). At the beginning of grape ripening, tannins of the seeds are present in a free state, which makes them easily extractable in the processes of winemaking. On the contrary, anthocyanins and tannins concentrated in the skins of the berries are associated with macromolecules of the cell walls which reduces their ability to extract (Cadot et al., 2006; Pastor del Rio et al., 2006). As a result of all these factors, the extraction of seed tannins, the structural features of which determine the excessive roughness and smoothness of the taste of wines is dominated during maceration of the pulp of unripe grapes (Vidal et al., 2002; Vidal et al., 2003; Vivas et al., 2004; Obradovic, 2006; Scollary, 2010). During the grape ripening, permeability of berry skin cell walls gradually increases, thus, increasing extractability of the anthocyanin and others components of grape skin, while extractability galloylated tannins of the seeds that undergo polymerization during this period decreases. It is believed that grapes have reached phenolic ripeness when anthocyanin and tannin extraction from berry skins during grape processing predominates over extraction of seed tannins (Glories et al., 1998; Perez-Magariño et al., 2005; Ribéreau-Gayon et al., 2006; Roediger, 2006).

The term "phenolic ripeness" is mainly used for grapes with red berries. But for the production of white wines, it is also important to know the technological reserve of phenolic components in grapes and the degree of their transition to must and wine during technological processes. However, it is impossible to assess the characteristics of the grape cultivar with respect to the formation of the phenolic complex of wines without considering the activity of grape oxidases. As shown by numerous studies, during processing of grapes phenolic substances are primarily oxidized due to mechanical and hydrolytic disturbances in the compartmentalization of enzymes and their substrates. It is believed that the activation of redox processes in the processing of grapes begins with the oxidation of derivatives of hydroxycinnamic acids to the corresponding quinones catalyzed by monophenomonooxygenase. O-quinones of caffeyl tartaric acid interact with ascorbic acid, sulfur dioxide and flavonols, resulting in regeneration of caffeyl tartaric acid, and then the cycle repeats (Vivas, 2002; Du Toit et al., 2006; Aniszewski, 2008).

We conducted comparative studies of the technological parameters of the phenolic complex and the oxidase activity of the grape must of Crimean native and classical grape cultivars. Among them: concentration of phenolic compounds (Ph) with Folin-Ciocalteu reagent, expressed as gallic acid equivalents; technological reserve of phenolic compounds (TRPh - is the amount of phenolic compounds that can transfer to the must during red winemaking); the degree of phenolic components transition into must in the process of whole berry pressing (Ph_0/TRPh) and 4-hour mash maceration from their technological reserve (Ph_4/TRPh) and polyphenol oxidase activity (PPO – according to the rate of oxidation of pyrocatechol mL must) (Ostroukhova et al., 2009). The phenolic ripeness of the grapes was assessed by colorimetric determination of the potential anthocyanin amount in grapes ($ApH_{1.0}$, mg L^{-1}), the amount of easily extractable anthocyanins ($ApH_{3.2}$, mg L^{-1}) and the fraction of easily extracted anthocyanins of the berry skins was determined from their potential amount (anthocyanin extractability, Ea,%) and the seed tannins in percentage (Mp,%) (Glories, 1985; Roediger, 2006).

Table 6. Technological parameters of the phenolic and oxidase complexes of white native and classical grape cultivars

Grape cultivars	Indicator*			
	TRPh, (mg L^{-1})	Ph_0/TRPh (%)	Ph_4/TRPh (%)	10^2xPPO (item)
'Kok Pandas'	478-691	15-95	17-98	6.7-7.2
'Sary Pandas'	486-1793	16-94	24-94	5.9-10.1
'Kokur Belyi'	478-1984	28-92	34-98	3.2-16.8
'Shabash'	567-1939	20-80	25-41	1.2-11.0
Native cultivars, mean ± SD	1013±728	56±28	58±25	8.3±4.1
'Rkatsiteli'	762-1382	24-50	28-60	4.6-16.3
'Aligote'	440-1117	26-64	28-83	4.5-22.2
'Chardonnay'	341-1305	25-85	23-92	3.7-12.5
'Sauvignon Blanc'	314-1298	23-91	23-97	8.8-19.7
Classical cultivars, mean ± SD	971±311	39±18	46±20	11.7±9.2
Significance level *p*	>0.05	0.010	0.047	>0.05

*the limits of the value ranges from 10% to 90% of the used sampling.

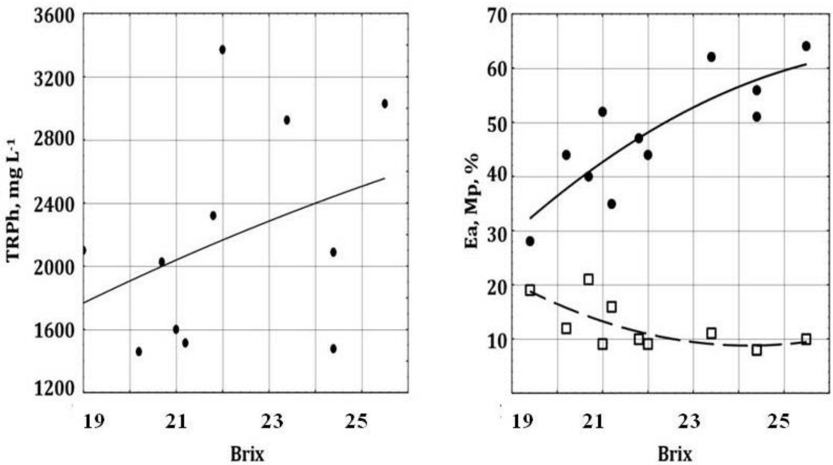
Table 6 and 7 present the results of technological parameters of the phenolic complex of grapes and polyphenol oxidase activity of the must of native grape cultivars from 2013-2018 harvests at sugar content 17.0-25.0 °Brix from the mountain-valley coastal and western foothill-coastal regions. It was revealed that the technological reserve of phenolic components in grapes, both white and red cultivars, varied widely. Statistical analysis of the data revealed that meteorological conditions of the harvest year are the most significant ($p<0.001$) factor in the formation of the technological reserve of phenolic components, including anthocyanins in grapes (Ostroukhova et al., 2018c; 2019c). No statistically significant difference in this indicator was found in grapes native and classical cultivars. However, native grape cultivars are characterized by a significantly ($p<0.05$) higher degree of transition of phenolic components from the solid parts of the berries to the must during processing. The degree of transition of phenolic components in white grape cultivars constitute 56 ± 28% when pressing whole berries; while with a 4-hour infusion of pulp – 58 ± 25%. The degree of transition of phenolic components in native cultivars with colored berries were 33 ± 18 and 36 ± 16, respectively. These features of native grape cultivars can lead to excessive enrichment of white wines with phenolic components, intensify oxidative processes, even though grapes are characterized by an average (0.083 ± 0.041 units) level of polyphenol oxidase activity. On the contrary, in the production of red wines with a rich dark ruby color, intensive extraction of phenolic components during maceration of the pulp of grapes of native cultivars is a positive factor, but only in the case of processing of phenolically ripe grapes.

Table 7. Technological parameters of the phenolic and oxidase complexes of red native and classical grape cultivars

Grape cultivars	**Indicator***						
	TRPh, (mg L^{-1})	Ph_0/TRPh (%)	Ph_4/TRPh (%)	$ApH_{1.0}$ (mg L^{-1})	Ea (%)	Mp (%)	$10^2 \times$PPO (item)
‘Ekim Kara’	1203-3369	9-83	17-81	249-2879	28-64	8-21	6.7-18.5
‘Gevat Kara’	1304-3522	21-53	24-53	317-357	36-51	11-22	3.6-6.4
'Kefessia’	954-3770	14-44	18-58	361-1143	40-64	9-21	2.1-18.1
Native cultivars, mean ± SD	1972±710	33±18	36±17	751±591	46±10	14±5	10.7±8.1
'Cabernet Sauvignon'	1293-2880	13-25	16-46	446-1411	32-59	11-22	5.2-15.2
'Shiraz'	1368-2774	12-77	20-49	1377-1749	36-61	21-30	10.9-25.0
'Merlot'	1208-2621	13-58	18-61	660-1456	42-61	10-28	10.7-28.3
Classical cultivars, mean ± SD	2084±603	21±12	26±13	946±409	45±11	20±7	11.6±6.4
Significance level *p*	>0.05	<0.00001	<0.00001	>0.05	>0.05	>0.05	>0.05

*The limits of the value ranges from 10% to 90% of the used sampling

In the total array of data on phenol maturity indicators, native grapes do not significantly differ (Table 7). It was found that phenolically ripe 'Ekim Kara' and 'Kefessia' grapes were characterized by the technological reserve of phenolic compounds 1.9 - 3.4 g L^{-1}, the fraction of easily extractable anthocyanins at the level of at least 44% and seed tannins − not more than 11%. Wines made from these grape cultivars have harmonious velvety taste and intense ruby color. For comparison, 'Cabernet Sauvignon' grapes that has reached phenolic maturity is characterized by the technological reserve of phenolic compounds 2.4 - 3.5 g L^{-1}, Ea at the level of at least 46% and Mp not more than 15% (Levchenko et al., 2017a). As shown above, the formation of the phenolic complex in 'Kefessia' and 'Ekim Kara' occurs faster than in the comparison cultivar 'Cabernet Sauvignon' (Ostroukhova et al., 2019b). The measurement of the phenolic complex during grape ripening showed (Figure 6), that the relationship between total sugars in the grapes and easily extractable anthocyanin and tannin fraction of the seeds was described by second-degree equations. They reflected an increase in the fraction of easily extractable anthocyanins dependant on sugar concentration increase in grapes at $p < 0.02$ with coefficient of determination $R^2 = 0.68$ and a decrease in tannin fraction of the seeds values at $p < 0.04$ and $R^2 = 0.51$.



TRPh - is the amount of phenolic compounds that can transfer to the must during red winemaking; Ea – is the fraction of easily extracted anthocyanins of the berry skins; Mp – is the seed tannins.

Figure 6. Correlation between phenolic complex parameters of 'Ekim Kara' and 'Kefessia' grapes and sugar concentration.

Figure 6 reflects the tendency of the phenolic compounds' technological reserve in grapes to grow with an increase in sugar concentration in grapes. However, the statistical significance of this relationship has not been revealed in experimental conditions. This suggests a significant impact of unrecorded factors on phenolic compounds accumulation during the ripening of grapes, among which are conditions of the year, peculiarities of micro-plots on vineyards, etc. Figure 6 illustrates that 'Ekim Kara' and

'Kefessia' reach phenolic maturity with sugar content at 21.0 °Brix (for 'Cabernet Sauvignon' – above 21.5 °Brix). This is a positive fact in the regions of Crimea with a hot climate. On the contrary, the periods of formation of the phenolic complex of the 'Gevat Kara' are close with those of 'Cabernet Sauvignon'. At 21.0 °Brix in grapes, wich growing in the southern coastal region of Crimea, phenolic maturity doesn't reach in 45% of cases. Wines from such grapes can be excessively tannic, rough, with unstable color. The processing of such grapes requires the use of special techniques aimed at harmonizing taste and color stabilization. Significant differences in the level of oxidase activity of native and classic cultivars, both with white and black berries, were not detected.

2.4. Volatile Components in Must of Red Native Grape Cultivars

Analysis of the volatile components in the must (after 4-hour mash maceration) 'Ekim Kara', 'Cabernet Sauvignon' and 'Merlot' (total sugars 18.6-22.3 °Brix) from Solnechnaya Dolina village (the eastern part of the South coastal zone of Crimea) was performed by their gas chromatographic separation on Agilent Technology 6890 chromatography (USA) unit with a mass spectrometric detector. Terpene and carbonyl compounds, higher and aromatic alcohols, esters and lactones have been identified (Table 8). In terms of the total concentration of identified components, 'Ekim Kara' is inferior to 'Cabernet Sauvignon', but surpasses (on average in 1.6 times) 'Merlot'.

In terms of proportions, the complex of volatile components of grapes was represented by 64-80% of higher and aromatic alcohols. The alcohol complex of 'Ekim Kara' and 'Merlot' was characterized by a high proportion (60-65%) of aromatic representatives: β-phenylethanol, β-phenoxyethanol and phenylcarbinol. On the contrary, C_6-alcohols prevailed in 'Cabernet Sauvignon', the proportion of which was from 48 to 56%. 'Ekim Kara' was distinguished from other cultivars by the presence of 4-methyl-3-penten-1-ol, 2.6-dimethyl-7-octen-2-ol and 1.5-octadiene-3-ol. These compounds are associated to fruity and floral fruity descriptors (Berger, 2006; Baumes, 2009).

'Ekim Kara' is the most enriched in carbonyl compounds: their share in the complex of volatile compounds is, on average, 28%, and the total concentration is 1896.6 μg L^{-1}. Carbonyl compounds of grapes of different cultivars are represented by 74-96% of aliphatic and aromatic aldehydes, which have a wide range of odors. Moreover, the qualitative composition of the detected aromatic aldehydes is identical in grapes of different cultivars. Compared to other cultivars, 'Ekim Kara' was characterized by a wider spectrum of aliphatic aldehydes and ketones, in particular, the presence of *tran*s-2-hexenal, 4-pentenal, *cis*-2- formation nonenal, octanone-4, tetrahydro-6-methyl-2H- pyran-2-one, as well as 2-amylfuran. The reason for the formation of o-heterocyclic compounds in the must during the fermentation of the pulp may be the oxidative conversion of labile pentoses, fructose, galacturonic acid, the quantitative content of which in the must is increased as a result of enzymatic hydrolysis of polysaccharides and berry glycosides (Lamorte et al., 2008; Lin et al., 2019; Probeigolova and Lutkova, 2019).

The main representative components of esters in the grapes of the studied cultivars were ethyl decanoate and dihydromethyl jasmonate. The share of esters in the complex of aroma-forming components averaged 1%.

The mass fraction of terpene alcohols in the aroma-forming complex of grapes of the considered cultivars did not exceed 4%. It was noted that 50 - 88% of the terpene complex of grapes was made up of geraniol, geranic acid and 3-hydroxy-β-damascone. The highest concentration of 3-hydroxy-β-damascone was found in 'Ekim Kara'. In addition, the distinctive feature of 'Ekim Kara' was the presence of nerol, while 'Merlot' presented a wide range of components of the linalool series: linalool, *trans*- and *cis*-epoxylinalool, linalyl acetate, which have floral shades of smell. Linalyl acetate is common in grapes of all studied cultivars.

The total concentration of identified lactones in grapes ranged from 90.3 ('Merlot') to 125.2 ('Cabernet Sauvignon') μg L^{-1}. The predominant components among lactones (63 - 100% of the total concentration of identified lactones) were γ-butyrolactone and γ-hexalactone associated to a fruity odor descriptor. The compost γ-valerolactone was identified in ‘Ekim Kara’ and ‘Merlot’.

The identified aroma-forming components in grapes are contained in subthreshold concentrations – groups of components with the same odor are involved in the formation of a particular shade of grape aroma. In the complex of volatile compounds of 'Ekim Kara', components with a fruity and berry odor predominated: their share was on average 41%; the proportion of components with floral or plant odors were 27 and 28%, respectively. In 'Cabernet Sauvignon' and 'Merlot', the percentage of volatile compounds with a berry-fruit odor was 38% and 33%, respectively; 'Merlot' was dominated by components with a floral smell (40%), in 'Cabernet Sauvignon' a high proportion of components with a plant smell (32%) was noted. Organoleptic testing revealed that when sugar content exceeds 20.0 °Brix, aroma of 'Ekim Kara' has a well-defined berry-fruit direction: the share of these shades in the total perception of aroma ranges from 60 to 95% (Ostroukhova et al., 2011).

Thus, the presented results of studies of chemical and technological parameters show that the Crimean native grape cultivars have several distinctive features that must be taken into account in winemaking, both when choosing the type and style of wine production, as well as grape processing techniques. Among them: the ability to accumulate a large amount of sugars during ripening, accompanied by a rapid decrease, especially in red grapes, the content of titratable acids and an increase in pH values; a high degree of transition of phenolic components into the must when pressing white grapes, which may cause the intensification of the oxidation of dry wines; for some cultivars ('Gevat Kara') – the delayed formation of the phenolic complex; the prevalence of berry-fruit shades in the aroma of grapes.

Table 8. Concentration (mean values, μg L^{-1}) of volatile components in the grape must

Compounds	Grape cultivars			Compounds	Grape cultivars		
	'Ekim Kara'	'Merlot'	'Cabernet Sauvignon'		'Ekim Kara'	'Merlot'	'Cabernet Sauvignon'
Alcohols (aromatic and aliphatic)				*Carbonyl compounds (aldehydes, ketones)*			
β-Phenylethanol	1207.4	983.0	765.3	6-Methyl-5-hepten-2-one	13.5	n.d.	11.7
β-Phenoxyethanol	105.7	151.2	318.1	2-Octanone	19.1	n.d.	47.2
Phenylcarbinol	1355.9	865.4	1579.8	3-Octanone	0.0	9.4	n.d.
2-Butoxyethanol	14.8	30.0	45.0	4-Octanone	20.7	n.d.	n.d.
1-Penten-3-ol	14.9	18.6	18.3	2-Nonanone	12.3	n.d.	17.3
3- Penten-2-ol	7.7	n.d.	10.3	4-Methoxy-4-methyl-pentanone-2	16.6	n.d.	10.2
2,4-Dimethylpentanol-3	183.4	142.8	165.5	4-Pentenal	4.4	n.d.	n.d.
2-Methylpentanol	12.2	12.0	12.4	*Cis*-2-nonenal	11.7	n.d.	n.d.
Cis-2-pentenol	78.7	44.9	46.1	Nonanal	16.4	9.7	n.d.
4-Methyl-3- penten-1-ol	9.1	n.d.	n.d.	Hexanal	800.7	194.4	467.8
Trans-3-hexen-1-ol	36.0	15.0	31.8	*Trans*-2-hexanal	654.5	n.d.	n.d.
Cis-3-hexen-1-ol	134.0	81.5	58.9	Decanal	27.7	16.9	25.9
Trans-2-hexen-1-ol	1030.8	679.8	1994.4	Phenyl-acetaldehyde	5.9	0.0	48.4
Cis-2-hexen-1-ol	34.5	n.d.	19.7	Benzaldehyde	32.3	38.2	33.0
2-Ethylhexanol	39.7	30.2	21.2	Vanillin	224.0	305.1	259.6
Hexanol -2	n.d.	n.d.	798.2	Furfural	20.1	13.6	16.4
1,5-Octadiene-3-ol	4.2	n.d.	n.d.	2-Amylfuran	7.8	n.d.	n.d.
Heptanol	14.9	n.d.	n.d.				
2,6-Dimethyl-7-octen-2-ol (Dihydromyrcenol)	14.0	n.d.	n.d.	Tetrahydro-6-methyl-2H-pyran-2-one	8.9	n.d.	n.d.
Octanol	21.9	9.1	27.3	*Terpenes*			
1-Nonen-4-ol	18.6	11.4	15.2	Geraniol	29.5	70.7	98.5
2-Nonen-1-ol	n.d.	12.6	9.5	Nerol	19.0	n.d.	n.d.
Trans-2-cis-6-nonadiene-1-ol	n.d.	n.d.	73.5	Geranilacetone	12.8	n.d.	n.d.
Alcohols (aromatic and aliphatic)				*Carbonyl compounds (aldehydes, ketones)*			
Nonanol	n.d.	n.d.	17.6	α-Pinene	0.6	13.6	4.7
4-Pentenal	4.4	n.d.	n.d.	Linalyl acetate	12.5	10.0	13.6
Cis-2-nonenal	11.7	n.d.	n.d.	3-Hydroxy-β-damascone	56.8	27.5	36.1

Compounds	Grape cultivars			Compounds	Grape cultivars		
	'Ekim Kara'	'Merlot'	'Cabernet Sauvignon'		'Ekim Kara'	'Merlot'	'Cabernet Sauvignon'
Nonanal	16.4	9.7	n.d.	Sum*Trans*-, *Cis*-epoxylinalool	n.d.	35.6	n.d.
Lactones				Geranic acid	89.3	41.4	n.d.
γ- Butyrolactone	45.5	21.6	51.6	*Esters*			
γ-Hexalactone	32.0	34.9	45.7	Ethyl hexanoate	n.d.	7.5	n.d.
γ-Heptalactone	n.d.	16.4	n.d.	Ethyl decanoate	84.3	32.3	101.6
γ-Valerolactone	2.8	n.d.	n.d.	Dihydromethyl jasmonate	119.4	30.8	153.6
δ-Hexalactone	n.d.	n.d.	11.6				
Dihydroactinidiolide	16.3	17.4	16.3				

[1]Standard deviation was no more than 8% of the mean values of the content of the components of the phenolic complex and no more than 3% of the mean values of the content of sugars; n.d. not detected.

3. Some Features of Winemaking from Native Grape Cultivars of Crimea

Traditionally, crimean red and white native cultivars are used to produce premium class liquor wines, the technology of which involves insisting or fermenting pulp, stopping the fermentation of must/pulp by adding grape or ethyl alcohol, and long-term aging in oak barrels. At the same time, due to the indicated chemical and technological features of the native grape cultivars, their production into dry or semi-dry red and white wines requires additional measures, both in the cultivation of grapes and in its processing.

First of all, this concerns the prevention of a negative effect on the quality of wines by an excessive decrease in the acid content in grapes during ripening. This problem is partially solved (especially successfully in the case of red grape) using scientifically-based varietal agrotechnology (Chervyak et al., 2019; Batukaev et al.,2019; Stranishevskaya et al., 2020), taking into account the soil-climatic and landscape conditions of the grape growing place and variety-specificity; optimization of the grape harvest period;

adjusting the acidity of the must and/or wines using L-tartaric or citric acid. In the case of cultivars with red berries, blends of wine materials from native, classical and/or selection culitvars are used. Most winery of Crimea goes this way. An example is the dry red wine from 'Sun Valley' winery, in which the native cultivar 'Kefessia' is successfully combined with the 'Bastardo magarachskii', breeding of the Institute "Magarach." Partially maintaining the recommended level of titratable acids in wines can be achieved by using a set of measures in the technological process: selection of yeast strains, optimization of methods and processing modes of wine materials. A promising way to improve the technological parameters of grapes of native black cultivars should be considered clonal, classical selection, the use of genetic engineering methods (Likhovskoi et al., 2016b; Levchenko et al., 2020). However, in the last two cases, the question arises of the eligibility of classifying wine products as authentic.

To prevent the oxidation of dry white wines from native cultivars, the same measures are recommended as in the processing of classical ones. Their main task is to limit the extraction of phenolic compounds from the solid parts of grapes and to block oxidases of must. The numerous studies of scientists are dedicated to that topic (Vivas, 2002; Corona, 2010; Patel et al., 2010; Danilewicz, 2011; Antoce et al., 2017; Cojocaru and Antoce, 2019). An effective limitation of the contact of must with the seeds and the skin of berries is achieved by the rapid processing of small batches of grapes, excluding maceration of the pulp and the maximum reduction in the duration of the clarification of the must, for example by flotation, as well as the use of enzyme preparations with pectolytic action and bentonite. Gerzhikova et al. (2007) proposed measures to protect the grape-wine system from oxidation, including low-temperature conditions for clarifying of the must, using gallotannin to block oxidase activity, sulfonating pulp with at least 75 mg L^{-1} sulfur dioxide.

For must fermentation, it is advisable to use yeast cultures with low aldehyde-forming and high glutathione-forming ability. According to the results of the studies of the aldehyde and glutathione-forming ability of *Saccharomyces cerevisiae* crops from the collection of microorganisms for winemaking "Magarach," we recommend the production of dry white wines by fermentation of must on strains I-307, I-525, I-527 (Tanashchuk et al., 2016). A factor of the resistance of wines to oxidative browning is the restriction of air access during fermentation, which contributes to the enrichment of wines with terpene alcohols, C_6-alcohols and the limitation of the accumulation of aliphatic alcohols (propanol, butanol, isobutanol) and acetaldehyde (Peskova et al., 2017a).

For winemaking from red native grape cultivars it was established that pulp sulfitation at 80±5 mg L^{-1}, pulp fermentation to 1/3 residual sugars facilitates transition into wine of up to 75% of phenolic compounds from their technological reserve in grapes. Reducing the sulfur dioxide dose to 60±5 mg L^{-1} contributes to formation of anthocyanin-tannic complexes and stable colour development (Ostroukhova et al., 2015; Levchenko et al., 2017b). We evaluates the efficiency of various technological methods applied in red dry wine production that shape their taste, colour and phenolic complex depending on carbohydrate-acid and phenolic ripeness of the Crimean native grapes (‘Ekim Kara’ and 'Kefessia’) from the South coastal zone of Crimea. For this purpose, we selected several batches of ‘Ekim Kara’ grapes of various phenolic ripeness categories (Table 9). Table 9 provides variation ranges and average values of the indices, showing that the average sugar content in grapes at phenolic ripeness was by 2.8 °Brix higher than this value in phenolically unripe grapes, the technological reserve of phenolic compounds was in 1.2 times higher, the fraction of easily extractable anthocyanins was in 1.5 times higher, while the share of tannins was in 1.9 times less. There was no significant difference in the titratable acidity and pH indices in grapes of different phenolic ripeness. Winemaking schemes involved the following maceration treatments: 1 – fermentation of grape pulp using *Saccharomyces cerevisiae* to 1/3 of residual sugars; 2 - addition of the condensed tannin into the pulp, fermentation of the pulp to 1/3 of residual sugars; 3 – addition of pectolytic enzymes, fermentation of the pulp to 1/3 of residual sugars. At the end of the maceration treatments, the grape pulp was pressed, the must was fermented to complete sugar fermentation. The wines from grapes that reached phenolic ripeness were made with sulfur dioxide dose during pulp maceration at 80 ± 5 mg L^{-1}, from phenolically unripe grapes – at sulfur dioxide dose at 60 ± 5 mg L^{-1}.

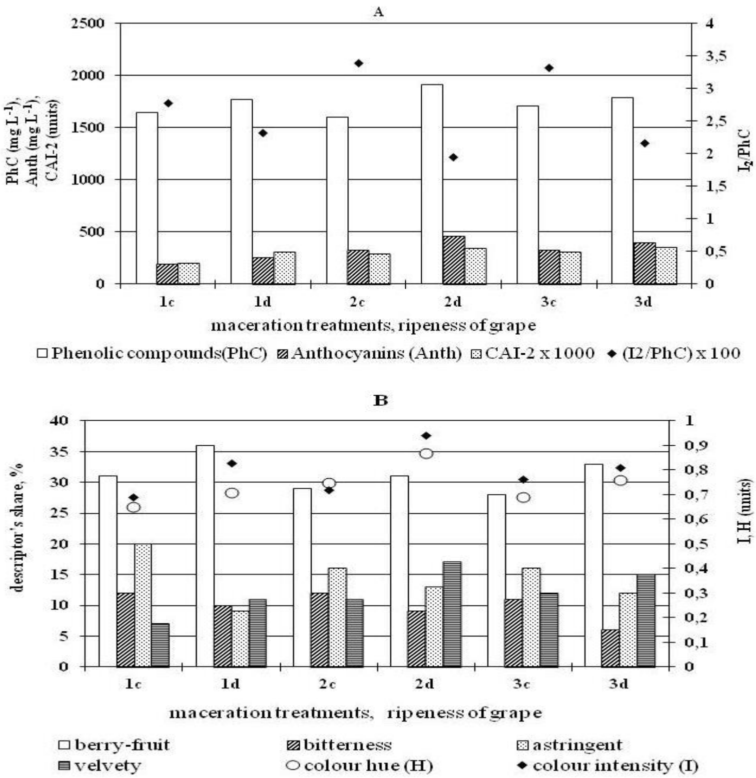
Table 9. Mean values (numerator) and variation ranges (denominator) for 'Ekim Kara' and'Kefessia' grapes used in the research

Indicators	**Grapes**	
	phenolically ripe	phenolically unripe
Total sugars, °Brix	*23.2* 21.0-24.5	*19.5* 18.0-19.8
Concentration of titratable acids (in terms of tartaric acid), g L^{-1}	*4.2* 3.9-5.3	*4.8* 4.0-5.7
pH	*3.63* 3.25-4.08	*3.39* 3.19-3.62
Technological reserve of phenolic compounds (expressed as gallic acid equivalents), mg L^{-1}	*2400* 1920-3490	*1921* 1554-2693
Anthocyanin extractability, Ea, %	*54* 44-63	*37* 26-43
Seed tannins in percentage, Mp, %	*9* 7-11	*17* 13-21

Figure 7 demonstrates that wines from grapes at phenolic ripeness as compared to wines from phenolically unripe grapes obtained by analogous technological schemes, contain significantly ($p \leq 0.01$) more phenolic components, including anthocyanins (on average in 1.1 times more), their oxidized fractions (in 1.5 times more by the value of I_2/PhC – specific reducing ability of the phenolic compounds with respect to iodine according to Schneider, 1997), and anthocyanin-tannic complexes (1.3 times more by CAI-2 – 'chemical age' index by Somers and Evans, 1977).

Tasting these wines demonstrated that they possessed intense dark ruby colour (the colour intensity (Somersand Evans, 1977) – 0.818-0.940, colour hue (H) – 0.71-0.87), harmonious berry-fruit taste with moderate bitterness (descriptor's share – 6-10%), astringency (9-13%) and pronounced velvety taste (11- 17%) and also with a bright aroma of berry direction with shades of flowers, spices and milk cream sensory descriptors.

Wine tasters gave the highest grades to the wines obtained by pulp fermentation to 1/3 residual sugars, while addition of pectinase complex and/or condensed tannin preparations had no significant effect on the tasting assessment, which made 7.76 - 7.86 points (tasting points are not shown in the figure).



Different level of phenolic ripeness of the grapes: 1c, 2c, 3c – unripe; 1d, 2d, 3d – ripe; Maceration treatment: 1c, 1d – fermentation of the pulp to 1/3 of residual sugars; 2c, 2d – addition of the condensed tannin, fermentation of the pulp to 1/3 of residual sugars; 3c, 3d – addition of pectolytic enzymes, fermentation of the pulp to 1/3 of residual sugars. Concentration of sulfur dioxide: 1c, 2c, 3c – 60±5 mg L^{-1}; 1d, 2d, 3d – 80±5 mg L^{-1}. I_2/PhC - specific reducing ability of the phenolic compounds with respect to iodine; CAI-2 – 'chemical age' index: the ratio of the optical density of wine at a wave length of 520 nm after addition of sodium metabisulfite (numerator) and hydrochloric acid (denominator); I – the colour intensity: the sum of the optical density values of wine at 420, 520 and 620 nm wave lengths; H – the colour hue: the ratio of the optical density of wine at 420 and 520 nm wave lengths.

Figure 7. Effect (mean values) of maceration treatment of the mash from 'Ekim Kara' and 'Kefessia'grapes of different categories of phenolic ripeness on the concentration of phenolic compounds and physico-chemical properties (A), colour and taste (B) of wine.

On the contrary, wines from phenolically unripe grapes that were produced by pulp fermentation differed from the wines made of phenolically ripe grapes in lower colour intensity (by 1.1 times); excessive bitterness, astringency (the descriptor's proportion was 20%) and crude taste (the velvety descriptor's proportion was 7%) and the aroma of the wines showed grassy hues. The tasting scores were 7.62-7.69 points. Using pectolytic enzymes and/or condensed tannin preparations during pulp fermentation of phenolically unripe grapes raised concentration of anthocyanins in wines on average by 1.7 times and anthocyanin-tannic complexes by 1.5 times (according to CAI-2). As a result, the wines developed a more intense colour, the developed velvetiness (the share of the descriptor increased on average by 1.6 times), moderate astringency (the share of the descriptor decreased by 1.3 times) and harmony. Wine aroma lost grassy and developed berry hues and shades of milk cream (Probeigolova and Ostroukhova, 2019). Experts evaluated those samples at 7.74-7.85 points.

Thus, pulp sulfitation at 60 ± 5 mg L^{-1}, the use of pectolytic enzymes and condensed tannin preparations during pulp fermentation allowed us to neutralize the negative consequences caused by phenolic unripe by native grapes, and obtain wines with intense colour, harmonious velvety, well-pronounced berry aroma with a spectrum of different shades.

Using various yeast cultures the berry-fruit aroma of wines from the Crimean native red grape cultivars can be enriched with shades of flowers, spices and milk cream sensory descriptors. This is important if you want to produce wines with unique sensory characteristics or a specific style. The influence of *Saccharomyces cerevisiae* I-25, I-250 (which are widely used in industrial winemaking in Russia) and I-651, I-652 (new strains) from the collection of microorganisms for winemaking “Magarach” (Tanashchuk, et al., 2016) on the formation of a aroma-forming compounds complex and the sensory profile of wines from 'Ekim Kara' was studied. New strains I-651 and I-652 were isolated from sediments of spontaneously fermented must of 'Pinot Noir' and 'Odesskii Chernyi' from v. Solnechnaya Dolina (Ostroukhova et al., 2013). It was shown (Figure 8) that strain I-25 enhances varietal berry-fruit tones in the aroma of 'Ekim Kara' wines (mainly due to the formation of acetates, including isoamyl acetate, with a fruity and honey-floral aroma).

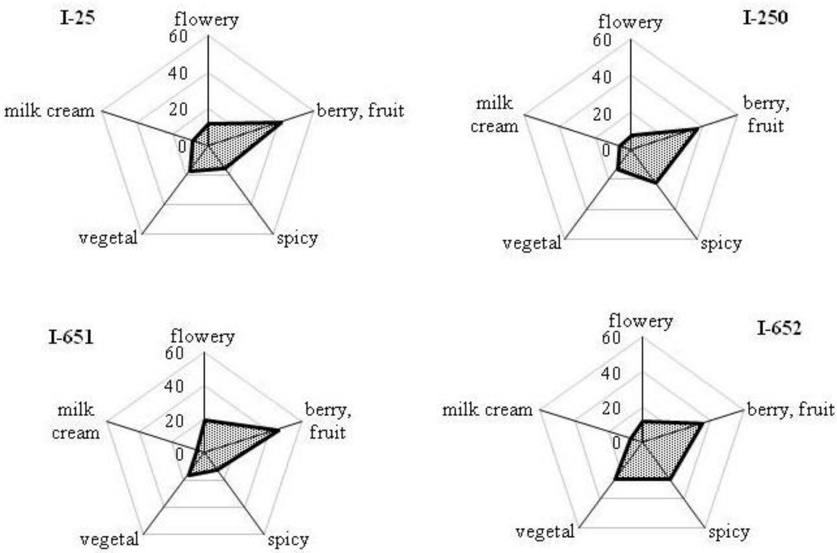


Figure 8. The sensory profile of wines 'Ekim Kara' aroma obtained using different cultures of *Saccharomyces cerevisiae*.

Strain I-250 enhances spicy shades (mainly due to aromatic alcohols – phenylcarbinol, tyrosol). Strain I-651 is characterized by a low ability to form lactones and esters, with the exception of the synthesis of β-phenylethyl acetate and ethyl-9-decenoate, which have a flower scent. In the aroma of the wines obtained using strain I-25, the proportion of floral shades was 20%, which was on average 1.9 times more than in other wines from 'Ekim Kara' grapes (Ostroukhova et al., 2013). On the contrary, strain I-652 significantly surpasses I-25 and I-250 in alcohol, ether and lactone-forming ability and enhances the shades of the spicy direction in wines. The share of spicy descriptor in the aroma of wines fermented on strain I-652 averaged 26% and exceeded that in wines from 'Ekim Kara' grapes obtained using strains I-25 and I-651 by 1.9 times, strain I-250 – by 1.2 times.

Thus, the assortment and technological potential of Crimean native grape cultivars allows developing competitive winemaking in the direction of creating authentic wines of various styles with unique organoleptic characteristics.

CONCLUSION

Modern studies allow us to consider the Crimean Peninsula as an independent subcenter of the origin of the grapevines, while wine grape cultivars domesticated from this gene pool are currently in the industrial culture. Crimean native grape cultivars are distinguished by their ability to grow and and produce good quality crops in the conditions of arid climate on poor rocky soils characterized by strong chloride-sulfate salinization. In the context of the global climate change, the endurance of Crimean native cultivars to adverse soil and climatic conditions makes them especially valuable resource for generative and clonal breeding, as well as for the development of authentic winemaking.

This chapter presents the results of researches that demonstrated chemical and technological features of grapes of the most common Crimean native wine cultivars. Native grape cultivars are characterized by the ability to accumulate a large amount of sugars during ripening, accompanied by a rapid decrease, especially in red grapes, of titratable acids content and pH values increase. Also, native cultivars are distinguished by more active quantitative and qualitative changes in phenolic acids and flavanols during ripening in comparison with classic ones. Crimean native red grape cultivars 'Ekim Kara' and 'Gevat Kara' are capable to accumulate large amounts of anthocyanins. At the same time, 'Ekim Kara' accumulates them already at 12.0-14.0 °Brix. On the contrary, for 'Gevat Kara' delayed formation of the phenolic complex is characteristic. Native white grape cultivars are distinguished by a high degree of transition of phenolic components into the must when pressing berries, which may cause the intensification of the oxidation of wines. A distinctive feature of the aroma-forming complex of native red cultivars ('Ekim Kara') is a high proportion of components with a fruity aroma, including higher and aromatic alcohols, aliphatic aldehydes and ketones, 3-hydroxy-β-damascone and lactones.

Considering the indicated chemical and technological features of Crimean native grape cultivars, the effectiveness of various technological methods for the red wines production, depending on the carbohydrate-acidic and phenolic ripeness of grapes, was evaluated. The possibility to neutralize the negative consequences caused by phenolic unripe of native grapes by regulating the duration of fermentation of the pulp (with subsequent fermentation of the must), doses of sulfitation and the use of pectolytic enzymes and condensed tannin has been demonstrated. We have also shown that the use of different yeast cultures can change the aroma style of wines from native red grape cultivars.

Thus, the assortment and technological potential of Crimean native grape cultivars allows to develop winemaking in the direction of the production both traditional liqueur wines and authentic wines of various styles. A factor in the further expansion of the use of Crimean native grape cultivars in the industrial of Russia is the creation of improved clones of grape cultivars, varietal agricultural technologies and winemaking technologies, taking into account the influence of soil, climatic and landscape conditions of grape growing.

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Chapter 2

Quantification of Phenolics and Usability as Authenticity Markers: The Case Study of Red Wines from the Canary Islands

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Abstract

Phenolic compounds have been tentatively used in some wine regions as potential cultivar identifiers, both exclusively through the anthocyanic profile, as well as by using flavonols or hydroxycinnamic acids. Furthermore research has proved that most phenolic compounds in red

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wine change during ageing process. In the Canary Islands some researchers have even observed significant differences in phenolic content in wines according to their provenance.

The main aspects involved in the phenolic characterization of red wines by HPLC-DAD are shown in this chapter using a relatively accessible, straightforward and non-expensive technique for their quantification. Differences can be observed in the chromatogram depending on ageing, cultivar or even climatic origin of the wine considered. A sample of 250 red wines produced in the Canary Islands labelled with Protected Designation of Origin was used to develop the method and test the convenience of using the phenolic profile in order to differentiate them. These wines were analyzed to characterize their phenolic profile, which was based on 35 different compounds.

Specific polyphenolic profiles could be identified according to the cultivar of vine used to produce the wine. Besides significant differences were found as a function of the Denominations of Origin, vintages, or even warm- and cool-climate areas within the same geographical region. These results evidence the usefulness of phenolic analysis in red wines to relate it with the cultivar profile; to the time elapsed since its elaboration due to its degree of polymerization, or even to the specific climatic conditions of a given vintage or area. It is concluded that the analysis of the phenolic composition of red wine could be easily used as an additional control tool to support wine regions when considering authenticity in the final product.

Keywords: authenticity, Canary Islands, markers, red wine, phenolics.

1. INTRODUCTION

Red wine is one of the most important natural sources of phenolics, containing flavanols, flavonols, anthocyanins, phenolic acids and stilbenes among others. Some of these compounds have been described as bioactive molecules with cardioprotective and healthy properties. Red wine phenols are also remarkably involved in sensory properties such as colour, bitterness, astringency or suitability for bottle ageing (Heras-Roger et al., 2017).

Phenolics are secondary metabolites of the grape whose biosynthesis seems to respond to a series of specific needs of the vineyard, generally related to the plant stress conditions (Winkel-Shirley, 2002). Some studies suggest that their content could depend on factors such as the sun exposure of grapes as they provide protection against UV radiation (Price et al., 1995), insufficient nitrogen fertilizations (Keller y Hradzina, 1998), or even on the water status of the vine (Keller et al., 2008). They have also been described as a defense against fungal attacks or as a possible rejection or claim related mechanism for animals.

The phenolic composition of the red wine depends largely on the raw material used in its elaboration, which is conditioned by factors such as the cultivar, the status of the grape at the harvest, cultivation techniques or climatic conditions (Heras-Roger et al., 2017). In addition, some of these compounds might come from fermentation and evolve during wine ageing. For example, if the wine has been subjected to a barrel ageing process, some phenolic compounds can be directly extracted from the wood used.

The study of phenolic compounds has been carried out in some wine-growing regions hoping to identify any adequate cultivar marker, both through anthocyanin and flavonol profiles, but also through the content of hydroxycinnamic acids. In this sense, wine cultivar differentiation using anthocyanin profiles was previously considered by Jaitz et al. (2010), whereas hydroxycinnamic acids and flavonols presented some cultivar discrimination ability according to Castillo-Muñoz et al. (2007) studies.

The aim of this chapter is to describe the way to determine the detailed phenolic composition from a large collection of red wines in order to use their profiles as potential authenticity markers. Wine phenol differentiation according to cultivar and colorimetric changes occurred during ageing are also thoroughly investigated. Statistical models were obtained where phenolic profiles revealed to be highly influenced by climate conditions. Moreover, our work investigates the detailed phenolic composition of a very diverse population of red wines from the Canary Islands in order to spot and explain the most significant statistical differences between cultivars, vintages and climatic zones.

2. METHODS

2.1. Samples

The phenolic profile of 250 commercial red wines from Canary Islands was determined. 140 samples were analyzed as young wines, 77 were short aged (between 2 and 4 years) and the remanining were aged wines (more than 4 years). Grape cultivar distribution was the following: 94 Listán Negro (LN), 30 Baboso (B), 17 Vijariego (V), 15 Syrah (S), 14 Listán Prieto (LP), 13 Negramoll (N), 12 Merlot (M), 12 Tintilla (T), 12 Ruby Cabernet (R) and 17 Blending of varieties (BL). Some islands and grape cultivars are in minor proportions due to their low production.

2.2. HPLC-DAD Phenolic Quantification

A HPLC Waters 2690 Separation System equipped with a 996 Photodiode Array Detector (DAD) was used to analyse the individual phenolic composition. Ellution was performed on wine previously filtered (0.45 µm) and samples injected (15 µL) on a thermostated (30ºC) Nova-Pak C_{18} reversed-phase column (3.9x150 mm; 4 µm). Chromatographic conditions were adapted from Ibern-Gómez et al. (2002). Milli-Q water was solvent A and acetonitrile gradient grade solvent B (Sigma-Aldrich) both acidified with 0.2% trifluoroacetic acid (99+% Sigma-Aldrich). Flow rate was 1.5 mL/min with a linear gradient for solvent B (0 min, 0%; 2 min, 2%; 8 min, 8%; 15 min, 15%; 20 min, 23%; 25 min, 0%).

Most phenolic compounds were identified directly comparing with external standards while the remaining were identified by their relative retention times and spectral data in the 200-700 nm (Lamuela-Raventós and Waterhouse, 1994; Ginjom et al., 2010; Baiano and Terracone, 2011). Spiking wine samples with available standards was performed for additional confirmation. Detection and quantification limits were calculated according to the three and ten sigma criteria.

The external standards used were (+)-catechin, (-)-epicatechin, quercetin, rutin, malvidin 3-*O*-monoglycoside, gallic, caffeic, coumaric, ferulic, syringic, ellagic, chlorogenic and vainillic acids from Sigma. Linear calibration curves were built as peak area (absorbance) versus concentration (mg/L), presenting a r higher than 0.99 for all the standards within the concentration range studied.

2.3. Statistical Analysis

Every measurement was performed in triplicate and presented as mean value ± standard deviation. Statistics were calculated using SPSS (version 17.0). Correlations were evaluated using Pearson coefficient (r) and one-way analysis of variance (ANOVA) was applied. PCA was used to discriminate cultivar, origin and vintage, considering tests statistically significant when the p value was lower than 0.05.

3. Using Red Wine Phenolics as Authenticity Markers

3.1. Phenolic Composition by HPLC-DAD

Contents of red wine phenolics are summarized on Table 1, being peaks numbered according to the chromatograms detailed on Figure 1. Measurements at 280 nm were used to quantify one noncarbolxylyc phenol, three hydroxybenzoic acids, two flavanols and one flavonol. Three hydroxycinnamic acids and one stilbenoid were identified at 320 nm, whereas 11 different flavonols were quantified using the absorbancies at 365 nm. Finally, five monoglycoside, four acetyl and two coumaroyl individual anthocyanins were quantified at their maximum visible absorbance at 520 nm.

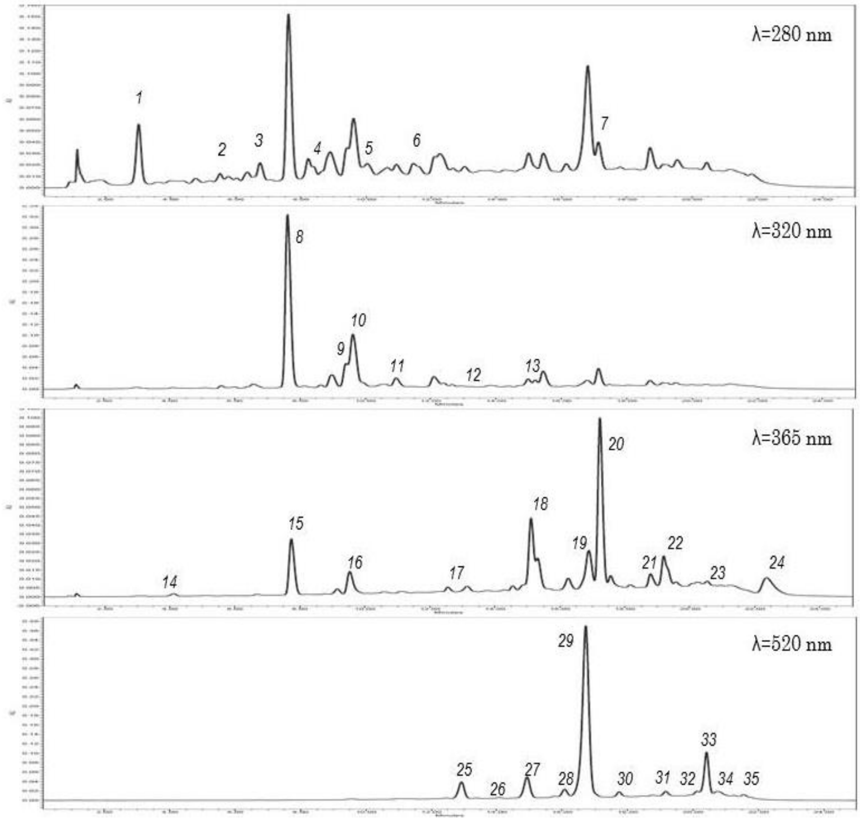

Figure 1. HPLC chromatograms at several wavelengths pointing the peaks of different individual phenolic compounds identified in a red wine sample (Peak number followed in Table 1).

3.2. Phenolic Acids

3.2.1. Benzoic Acids

Gallic acid is the main benzoic acid quantified in red wines. Protocatethuic concentration in our samples is slightly higher than those concentrations previously described by Revilla and González-Sanjosé (2003). The concentration of syringic acid is lower than the rest of benzoic acids and similar to values published by Ginjom et al. (2011).

Table 1. Individual phenolic compounds retention times and concentration ranges identified in red wines

Compound	Peak number	Ret. time$_{(min.)}$	Mean ± S.D.	Minimum - Maximum
Noncarboxylic phenols			mg gallic acid/L	
• Tyrosol	3	5.7 - 6.9	7.19 ± 2.98	2.09 - 25.32
Hydroxybenzoic acids			mg gallic acid/L	
• Gallic	1	2.5 - 3.0	37.66 ± 21.60	3.23 - 113.21
• Protocatechuic	2	3.5 - 4.8	3.39 ± 4.25	0.44 - 43.83
• Syringic	4	7.3 - 8.9	8.30 ± 2.98	2.25 - 21.43
Hydroxycinnamic acids			mg caffeic acid/L	
• Caftaric	8	6.4 - 7.9	53.69 ± 29.80	2.43 - 144.04
• Caffeic	9	8.1 - 9.5	12.12 ± 9.12	0.70 - 55.35
• Cutaric	10	8.2 - 10.0	29.30 ± 12.97	3.74 - 65.85
• Coumaric	11	10.0 - 13.4	7.95 ± 8.04	0.26 - 55.67
• 2-S-Glutathionylcaftaric	12	11.3 - 15.3	0.90 ± 0.52	n.d. - 3.14
Flavan-3-ols			mg/L	
• (+)-Catechin	5	9.4 - 11.7	65.89 ± 29.87	6.59 - 199.72
• (-)-Epicatechin	6	10.0 - 12.3	39.16 ± 16.88	13.28 - 125.17
Stilbenoids			mg caffeic acid/L	
• Resveratrol	13	12.9 - 15.8	5.76 ± 3.41	0.17 - 15.22
Flavonols			mg quercetin/L	
• Myricetin-3-glucuronide	14	3.6 - 4.7	0.56 ± 0.51	n.d. - 1.12
• Myricetin-3-glycoside	15	7.0 - 7.8	1.01 ± 5.55	n.d. - 26.62
• Laricitrin-3-glycoside	16	8.4 - 9.4	2.42 ± 1.19	n.d. - 6.59
• Kaempferol-3-glycoside	17	10.2 - 11.4	0.46 ± 0.35	n.d. - 4.13
• Myricetin	18	14.8 - 15.4	6.99 ± 4.12	0.36 - 18.44
• Quercetin-3-glucuronide	19	15.9 - 16.5	13.06 ± 7.05	1.14 - 40.52
• Quercetin-3-glycoside	20	16.9 - 17.3	8.55 ± 5.57	0.96 - 28.28
• Rutin	7	16.9 - 18.2	7.78 ± 5.44	n.d. - 28.79
• Isorhamnetin-3-glycoside	21	17.6 - 18.5	4.07 ± 2.10	0.23 - 15.40
• Isorhamnetin	22	18.5 - 19.4	3.37 ± 1.94	0.21 - 13.11
• Syringetin-3-glycoside	23	20.0 - 21.3	0.56 ± 0.65	n.d. - 5.37
• Quercetin	24	21.3 - 22.5	2.53 ± 2.49	0.05 - 12.29
Anthocyanins			mg malvin chloride/L	
• Delphinidin-3glycoside	25	13.0 - 15.3	6.27 ± 5.45	n.d. - 31.03
• Cyanidin-3glycoside	26	13.9 - 16.0	1.29 ± 3.20	0.04 - 41.77
• Petunidin-3glycoside	27	15.1 - 16.4	7.42 ± 6.53	0.19 - 34.92
• Peonidin-3glycoside	28	16.2 - 17.0	6.06 ± 6.01	0.10 - 41.89
• Malvidin-3glycoside	29	16.9 - 17.2	59.60 ± 51.02	0.54 - 238.57
• Cyanidin-(6-acetyl)-3glyc.	30	17.3 - 18.4	2.32 ± 1.95	0.14 - 9.07
• Petunidin-(6-acetyl)-3glyc.	31	19.1 - 20.9	2.90 ± 2.57	0.16 - 18.37
• Peonidin-(6-acetyl)-3glyc.	32	20.1 - 21.4	3.67 ± 3.14	0.16 - 20.04
• Malvidin-(6acetyl)-3glyc.	33	20.4 - 21.7	9.83 ± 9.38	0.48 - 60.58
• Peonidin-(6coumaroyl)-3glyc.	34	20.6 - 22.2	6.04 ± 6.01	0.25 - 28.05
• Malvidin-(6coumaroyl)-3glyc.	35	21.1 - 23.5	12.60 ± 10.26	0.13 - 93.04

n.d. - not detected.

3.2.2. Hydroxycinnamic Acids

Main hydroxycinnamic acids from *Vitis vinifera* grapes are tartaric acid esters, outstanding *trans*-caftaric and *trans*-coutaric (Waterhouse, 2002).

These compounds can be partly hydrolyzed, producing caffeic and coumaric acids. In our red wines all these compounds and 2-S-glutathionylcaftaric concentrations were similar to the values obtained by Ibern-Gómez et al. (2002). Commercial standards of ferulic, vainillic, ellagic and chlorogenic acids were added to wines, no peaks attributable to these substances or similar were identified. Hermosín-Gutiérrez et al. (2005) suggested that cutaric acid can be used to discriminate cultivars, but according to our results its content would only separate the analised wine samples in two groups.

3.3. Flavonols

Quercetin flavonols are the most abundant, followed by myricetin and isorhamnetin, which is in agreement with data reported by De Nisco et al. (2013). Some glycosides conjugates from kaempferol, laricitrin and syringetin can be also quantified in low contents as described by Tsanova-Savova and Ribarova (2002). Flavonols show the most significant differences between cultivars in agreement with the description of Castillo-Muñoz et al. (2007). Main flavonols were quercetin and myricetin, which presented significant differences between grape cultivars. Quercetin-3-glycoside is the most prevalent flavonol chemical specie already present in the original grape. The corresponding free flavonol aglycone or the quercetin-3-glucuronide conjugate are released by hydrolysis in the wine. Flavonol contents obtained are slightly higher than those frequently reported in the literature, although similar to those described for the same geographical area (Pérez-Trujillo et al., 2011). These atypical high flavonol concentrations support the assumptions reported by McDonald et al. (1998). These investigators emphasize the important role of the sunlight in flavonol biosynthesis. The higher average solar radiation from Canary Islands might involve a higher flavonol synthesis and accumulation in grapes, and consequently, high values are found in wines. Rutin is another quercetin derivative, whose contents were also higher than those found in Spanish red wines (Hermosín et al., 2005), but within the range described by Kallithraka et al. (2006) for Greek wines, where a high insolation is also observed.

These compounds are present as a mixture of the original flavonol-3-glycosides of the grapes and their corresponding free flavonol aglycones produced by hydrolysis in wine in agreement with Burin et al. (2011). The hydrolysis phenomenon explains the reason why no acceptable flavonol profile according to cultivar can be directly obtained. However, the sum of related flavonoid structures allows to obtain interesting information from those flavonol cultivar profiles lost by hydrolysis (Figure 2). These compounds vary during wine ageing, but the reaction products can be tracked to reconstitute the original cultivar identity.

Pérez-Trujillo et al. (2011) described 'Listán Negro' and 'Negramoll' cultivar wines with flavonol content as double of other single-cutivar wines such as 'Vijariego', 'Tintilla' or 'Baboso'. In our samples, the concentrations from the red wines made with these traditional grape cultivars were significantly lower than those concentrations obtained with the classical cultivars such as 'Shiraz' or 'Merlot'. Tsanova-Savova and Ribarova (2002) characterized flavonol differences as markers of grape cultivar but Blouin and Peynaud (2003) found that the flavonol content depends mostly on sunshine intensity, grape skin thickness and technological processes. Previous studies considered technological processes (Darias-Martín et al., 2002) and climate (Heras-Roger et al., 2014), however they deduced that the differences observed can probably be mostly explained by the grape skin thickness; flavonols accumulate in the skin of grapes and it varies also as a function of grape cultivar.

3.4. Stilbenoids

Resveratrol is the main stilbene in wines and its concentration ranges from 29.2 mg/L of *trans*-resveratrol glycoside to no detectable values (Strevbo et al., 2007). Our values in wines are markedly high, in agreement with previous studies from Canary wines (Pérez-Trujillo et al., 2011). Thus, Canary red wines contain high resveratrol in comparison with those produced elsewhere (Jeandet et al., 1993; Abril et al., 2005). A similar phenomenon was observed in white wines from Canary Islands by Darias-

Martín et al. (2008). This atypical high concentration might be attributed to the high UV natural radiation from Canary Islands, in agreement with that reported by Liu et al. (2010).

3.5. Flavanols

Catechin is considered the main wine flavan-3-ol, but some authors have obtained different proportions with (-)-epicatechin according to grape cultivar. For instance, Hermosín-Gutierrez et al. (2005) obtained (+)-catechin prevalence for ‘Cabernet Sauvignon’ wines, (-)-epicatechin prevalence in ‘Syrah’; and similar quantities in ‘Cencibel’ wines. In our samples, (+)-catechin concentration was predominant in all the red wine, but differences between cultivars were found. Frankel et al. (1995) obtained (+)-catechin (144 mg/L) and (-)-epicatechin (64 mg/L) mean values in agreement with our results.

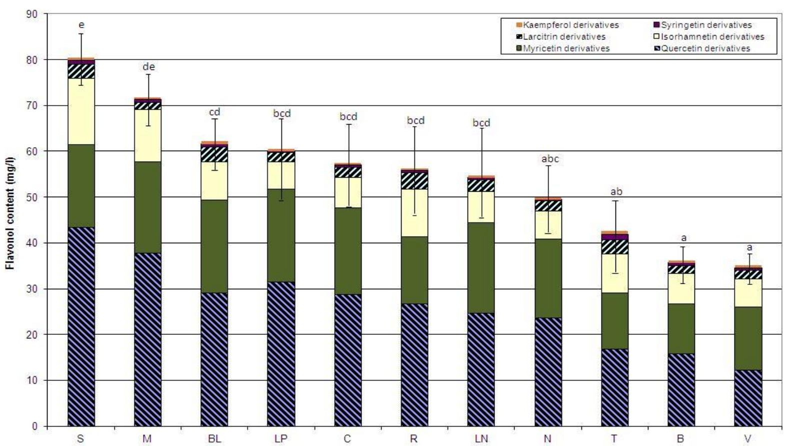

Figure 2. Flavonol distribution obtained in red wines from the Canary Islands elaborated with different grape cultivars. Data expressed as mean values ± SD. Bars with different letters indicate statistical differences (Duncan Test, $p \leq 0.05$). Wine codes: (S) Syrah, (M) Merlot, (BL) blending, (LP) Listán Prieto, (C) Castellana, (R) Ruby Cabernet, (LN) Listán Negro, (N) Negramoll, (T) Tintilla, (B) Baboso, (V) Vijariego.

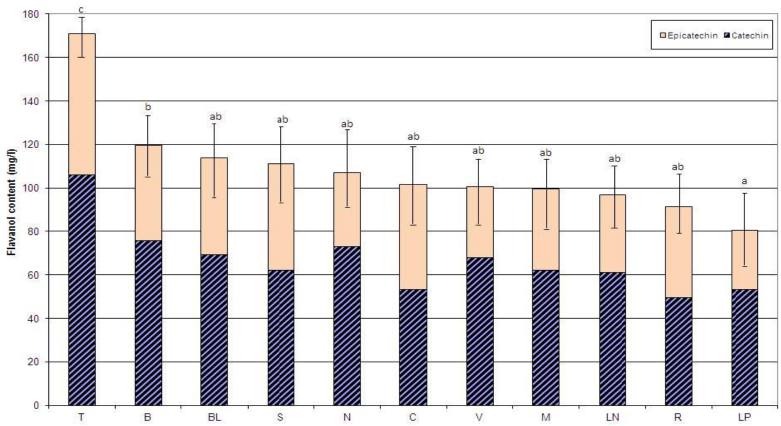

Figure 3. Flavanol distribution obtained in red wines from the Canary Islands elaborated with different grape cultivars Data expressed as mean values ± SD. Bars with different letters indicate statistical differences (Duncan Test, $p \leq 0.05$). Wine codes: (T) Tintilla, (B) Baboso, (BL) blending, (S) Syrah, (N) Negramoll, (C) Castellana, (V) Vijariego, (M) Merlot, (LN) Listán Negro, (R) Ruby Cabernet, (LP) Listán Prieto.

Figure 3 summarizes our results in red wines according to the grape cultivar used. Red wines elaborated from 'Tintilla' cultivar stood out because of its high concentration of flavanols. The profiles agree with previously reported data (Pérez-Trujillo et al., 2011; Porgali and Büyüktuncel, 2012; Van Leeuw et al., 2014); (+)-catechin predominated in all single-cultivar wines and (-)-epicatechin content was in different proportions.

3.6. Anthocyanins

Malvidin-3-glycoside was the most abundant monomeric anthocyanin quantified (Figure 4). Other non-acylated anthocyanins synthesized by grapes were identified in red wines and their concentrations followed the same trend described by Li et al. (2011). Petunidin-3-glucoside was the second most abundant monomeric anthocyanin followed by peonidin and delphinidin 3-glucosides. Cyanidin derivative was the minor anthocyanin quantified. The same pattern was observed for other colored components, like anthocyanin-3-O-(6-acetyl)-glycosides. Only peonidin and malvidin were detected as coumaroyl derived anthocyanins, being the latter the most abundant in the red wines studied.

The acetylation and coumaroyl addition to the glycoside anthocyanins is due to the natural ageing process of red wine. These modifications for ageing are the main reason why no acceptable anthocyanin profile according to cultivar can be directly obtained. However, the sum of these related flavonoid structures allows to obtain information from the original anthocyanin cultivar profiles lost during wine ageing.

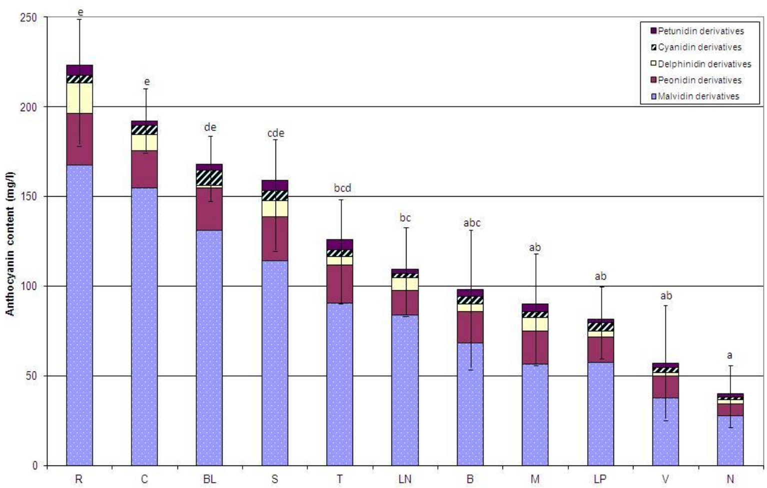

Figure 4. Anthocyanin derivative groups quantified in red wines from the Canary Islands elaborated with different grape cultivars. Data are expressed as mean values ± SD. Bars with different letters indicate statistical differences (Duncan Test, $p \leq 0.05$). Wine codes: (R) Ruby Cabernet, (C) Castellana, (BL) blending, (S) Syrah, (T) Tintilla, (LN) Listán Negro, (B) Baboso, (M) Merlot, (LP) Listán Prieto, (V) Vijariego, (N) Negramoll.

3.7. Cultivar Analysis

Jaitz et al. (2010) achieved an important differentiation of phenol analytical differentiation between 97 red wine samples. Our study counts with 250 red wine samples and showed a great variability due to the 10 grape cultivars and 11 geographical areas considered; however, a considerable differentiation between grape cultivars based on phenolics was achieved.

Phenolic concentrations were set as independent variables and grape cultivars grouping variables, obtaining a discriminant analysis detailed in Figure 5. This statistical procedure was controlled by a leave-one-out test, observing that a 92% of the red wine samples were correctly classified. This statistical tool could be reinforced by adding a greater number of samples from minority cultivars; besides the number of vintages could be reduced for avoiding the variability derived from the wine ageing process. Anyway, despite the great variability due to the 9 vintages and 11 geographical areas considered, the degree of success from the prediction is very high.

Red wines elaborated using traditional grape cultivars were rarely differentiated. Red wines from international grape cultivars well-known because of their phenolic content appeared together forming a group, whereas traditional grape cultivars (‘Listán Negro’ and ‘Negramoll’) commonly used for winemaking stood nearly in the figure. Blending samples are halfway between these two groups, although closer to the bulk of their theoretical varieties of origin (‘Listán Negro’ and ‘Negramoll’). This could be explained due to some of the blendings contain a small percentage of international grape cultivars.

3.8. Wine Ageing Analysis

Wine colour evolution can be attributed to progressive changes in phenolic compounds with the formation of new pigments during wine ageing, such as pyranoanthocyanins. These molecules were detected in HPLC chromatograms with elution times similar to coumaric esters derived from anthocyanins, forming a peculiar “hump”. For the purpose of this chapter no specific pyranoanthocyanin identification can be established due to the lack of mass spectrometric data. The indentification was carried out with UV-VIS spectrum, which was similar to that previously reported by Alcalde-Eon et al. (2006) for pyranoanthocyanins. Nevertheless, these complex coloured compounds could also be quantified using the same technique but a much more sensitive detection device and a longer chromatographic procedure specially designed to maximize their separation during the elution phase.

Figure 6 details these typical pigments "humps" in our chromatographic conditions due to polymeric anthocyanins, being this increase clearly observed in the chromatograms (Figure 7). It can be observed how the area covered by polymeric anthocyanins raises with the ageing of the red wine.

The polymerisation increase evidently entails monomeric anthocyanin losses during wine ageing. Significant differences in flavonols were also observed between vintages (Table 2).

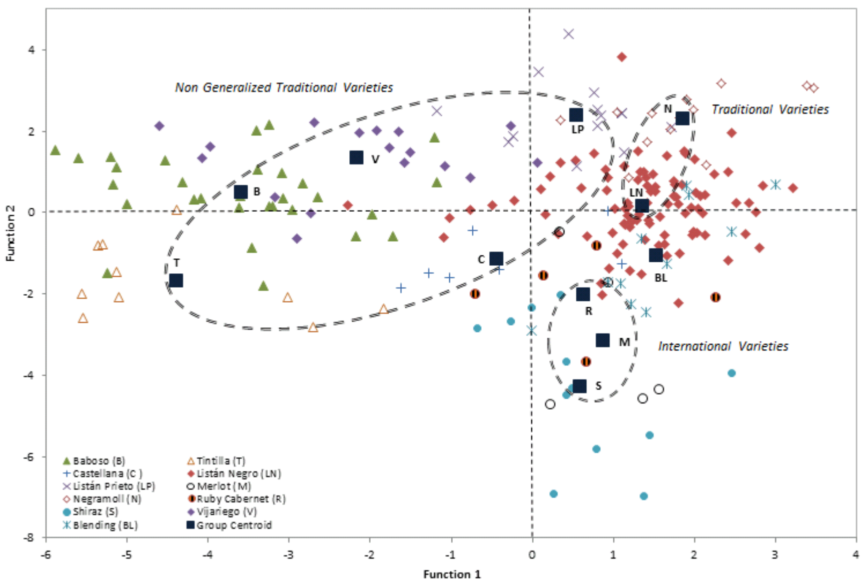

Figure 5. Red wine phenolic discriminant analysis by grape cultivar.

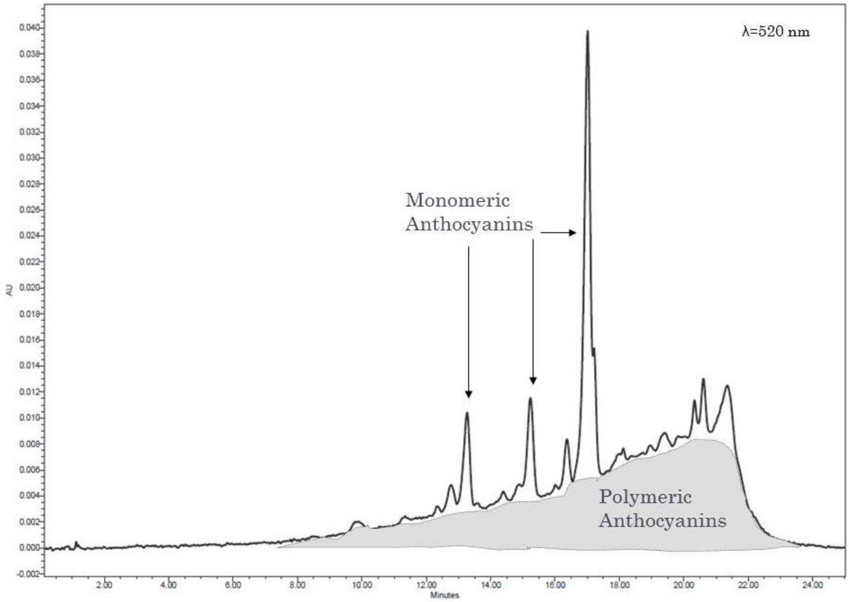

Figure 6. Red wine HPLC chromatogram obtained at 520 nm showing two different anthocyanins group.

Table 2. Influence of ageing of red wines in quercetin concentrations

Ageing (year)	mg of quercetin/L
0.5	57.0
1	53.8
7	27.1
8	20.8

The flavonol decrease during wine ageing is probably due to oxidation processes and polymeric reactions. A slight decrease in glycosilated flavonols together with a modest increase of aglycones was also observed with ageing, possibly due to hydrolysis reactions.

Besides, caftaric and coutaric acids suffered slow hydrolysis processes during wine ageing, generating caffeic and coumaric acid respectively. Caftaric acid decreased significantly between vintages, being minimal for 8 years aged wines (38.3 mg/L) and maximal for young wines (50.5 mg/L). Monagas et al. (2006) found a progressive (+)-catechin and (-)-epicatequin decrease during wine ageing; nevertheless, no significant flavan-3-ols differences between vintages were observed. This probably is because of their initial concentrations in red wines were influenced by other factors, including winemaking practices or grape ripeness.

Anthocyanins and flavonols are the phenolic compounds that have major losses during wine ageing. Both groups are directly involved in wine colour as pigments and copigments. Anthocyanin:flavonol ratio was evaluated finding differences according to ageing, although these differences were not statistically significant. Nevertheless, a higher ratio was observed for young wines than for aged wines (2012 ratio 2.47, 2011 ratio 2.37, 2005 ratio 1.35 and 2004 ratio 1.29).

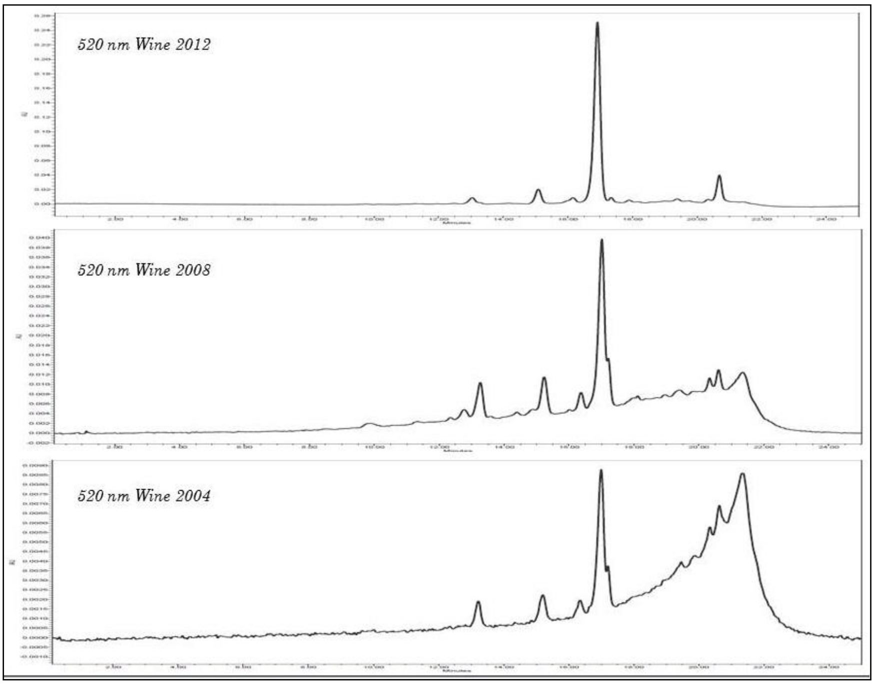

Figure 7. HPLC Chromatograms of red wines with different ageing times.

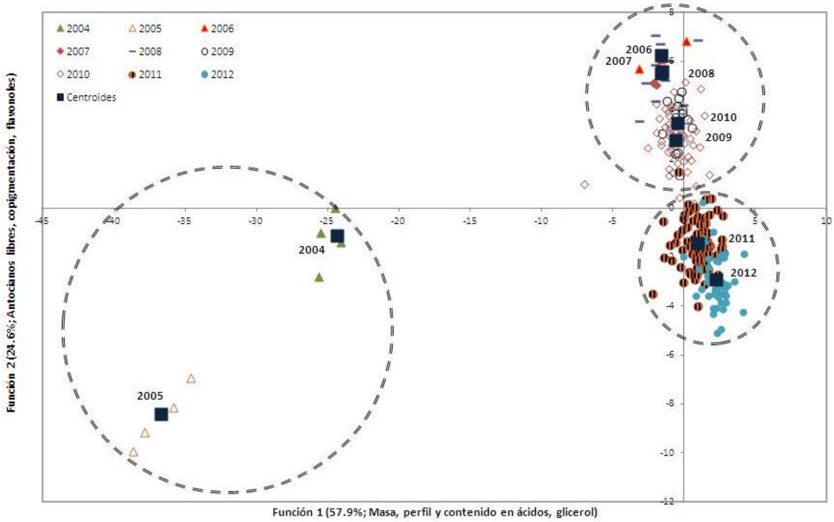

Figure 8. Discriminant analysis according to wine vintage (2004-2012).

Phenolic data were evaluated using a discriminant analysis to investigate the effects of the ageing (Figure 8). The youngest wines (2011 and 2012 vintages) form a cluster, while the older wines are separated into small groups (2004 and 2005 vintages). These groups contain a smaller number of wine samples given that the wine production of the Canary Islands is mostly destined for the young wine market. The statistical treatment applied allows to discriminate the wine samples according to the vintage. So, 92% of the red wines were correctly classified. The content and polymerization of anthocyanins and flavonols, as well as the hydrolysis already described of some phenolic compounds pertmit differentiate between vintages despite the complex process of wine ageing.

Based on these results and given the heterogeneity of the samples, another approach with the phenolic data can be carried out using a discriminant analysis to specifically investigate ageing effects (Figure 9). In this sense, it would be more adequate to group the data according to the time since the wine was made, instead of exclusively from the perspective of the vintage. So, the first group contains data related to the oldest wines; this includes red wines named “Gran Reserva” which were made more than 5 years ago (2004-2007). The second group includes red wines with shorter ageing time in which time has been able to exert a considerable action; they have been elaborated between 3 and 5 years ago (2008-2010) and have evolved since then. Finally, the third group contains those wines considered young in the moment of the analysis (2011-2012).

This analytical assessment was checked by a leave-one out test with a markedly high 99% of red wines correctly classified. Anthocyanins and flavonols were the main compounds involved in these classification groups, which agrees with the individual trends observed when the vintage was exclusively considered. Concentrations were significantly different between the three groups, decreasing with the ageing (i.e., 72.3 > 42.6 > 1.7mg malvidin 3-glycoside/L or 9.2 > 7.8 > 4.3mg quercetin/L for quercetin-3-glycoside). Old wines presented fewer hydroxycinnamic acids, probably due to hydrolysis processes (i.e., caftaric acid 48.3 < 52.1 < 54.5 mg caffeic acid/l). However, ageing seems to increase hydroxybenzoic acids (i.e., gallic acid 62.3 > 46.5 > 31.3 mg/L or syringic acid 13.8 > 12.5 > 9.5 mg /L).

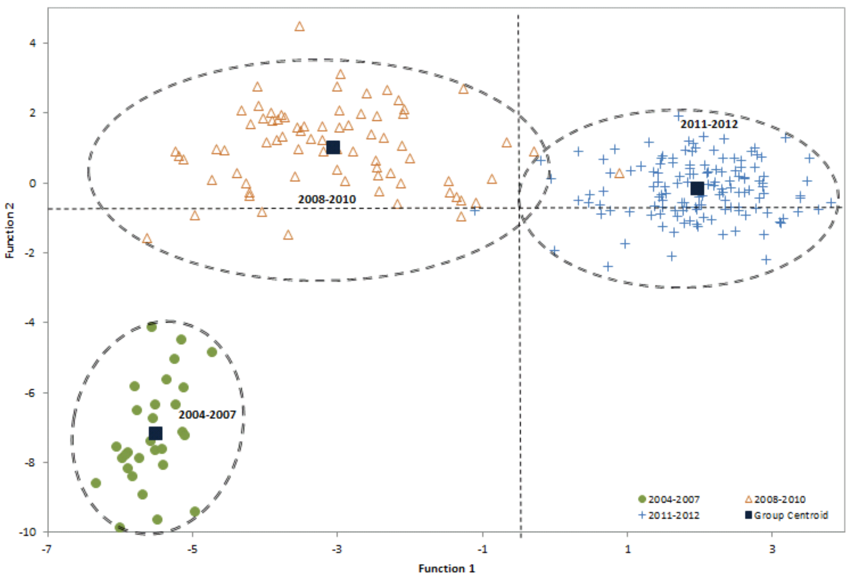

Figure 9. Discriminant analysis according to wine age.

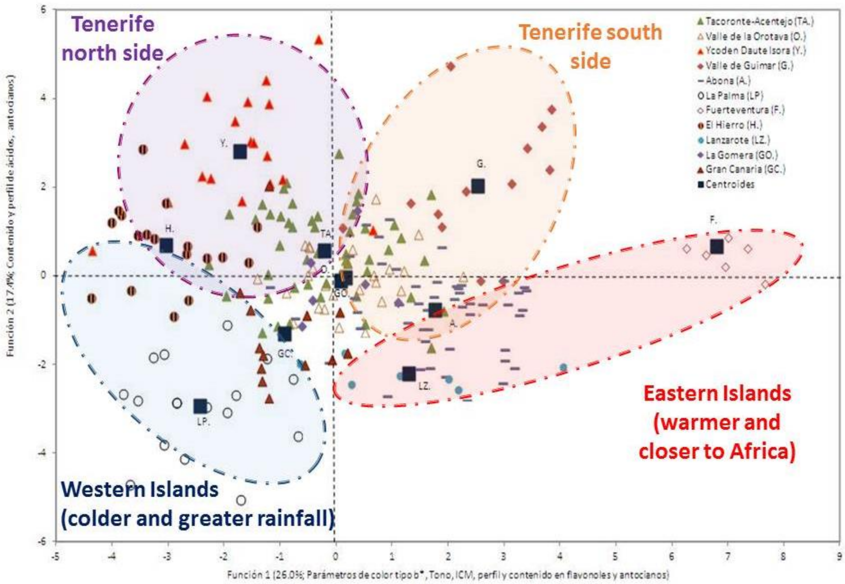

Figure 10. Discriminant analysis according to growing winemaking area in Canary Islands.

3.9. Geographical Analysis

This study contains red wine samples from seven Canary Islands and eleven wine-growing areas, each one of them with its own climatic conditions and singularities in terms of winemaking production and tradition. Discriminant analysis taking the wine-producing area of origin as the grouping variable provides a correct classification of 87.5%, according to the leave-one-out test.

Figure 10 shows how the warmer islands (Fuerteventura and Lanzarote), the closest to the African continent, are located in the lower right zone of the graph. Similarly, the wines produced in the westernmost islands (La Palma, La Gomera or El Hierro), with higher rainfall and lower average temperature, are located in the left quadrant highlighted by a common pattern. Wine production on the highest island (Tenerife) is relatively heterogeneous. Two clear zones can be spotted: 1) Wines from the warmer

South (include two Protected Denomination of Origin (PDO), named Abona and Valle de Güímar, which are located in the right zone of the graph; 2) Wines from the three remaining PDO of Tenerife with a colder climate. These red wines are located in the center-left zone of the graph. This allows to deduce that vine environmental conditions influence the final wine characteristics, which could be due to significant differences in the initial chemical composition of the grapes.

Some authors suggest that the production of flavanols in the grapes increases due to solar radiation, implying differences in the resulting wines (Price et al., 1995). In order to deepen on this phenomenon, the sample data from seven Canary Islands and eleven PDO with diverse climatic conditions were grouped in two different climatic zones. This also permits to homogenize size distributions and establish suitable geographical criteria as has previously reported by Heras-Roger et al. (2014).

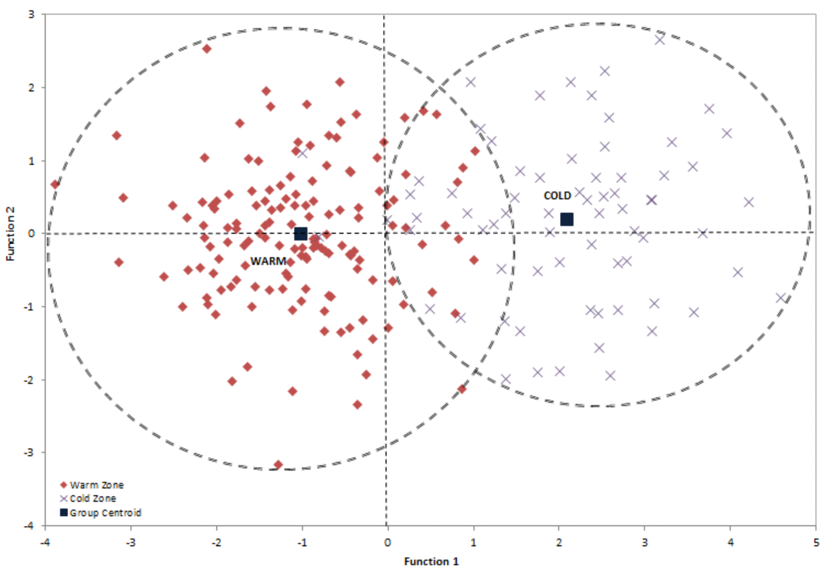

Figure 11. Red wine discriminant analysis according to climatic zone in the Canary Islands.

South Tenerife (Abona, Güímar), Lanzarote and Fuerteventura were selected as warm climatic zones, while the rest were grouped as relatively cold climatic zones due to their lower average temperatures and minor exposure to sunlight. Using the leave-one-out test, a high differentiation was obtained between both areas (Figure 11), with a 94% of red wines correctly classified. This statistical calculation was mainly composed by flavonol and anthocyanin profiles, that are phenolics influencing colour, but also by gallic acid and (-)-epicatechine. Red wines of warm climate presented higher colour intensity and greater phenol content (i.e., for flavonols 61.2 vs 48.3 mg quercetin/L). Similarly, these wines were characterized by high individual flavonol levels (i.e., 16.5 vs 11.4 mg quercetin/L for quercetin-3-glucuronide or 10.7 vs 7.5 mg quercetin/L for quercetin-3-glycoside), in agreement with McDonald et al. (1998), who reported possible relationships between sunshine and wine flavonol content.

CONCLUSION

In this chapter the relation of phenolics and red wines produced in Canary Islands was studied, confirming the following hypothesis:

- The phenolic profile of the wine is largely conditioned by the genotype of the vine, which was associated to the cultivar of grape.
- Environmental factors affect the biosynthesis of phenolics in the grape, and thus, their concentration in the final wine. In the present study these factors were related with the variables geographical area of origin or climate.
- Phenolic compounds in red wine change during wine ageing mainly because of polymerization and hydrolysis reactions. In this chapter ageing was associated with the variables vintage or time since the wine production.

The combination of these considerations with the data found by us, allows to conclude that the detailed analysis of the phenolic composition, with a sufficiently complete database, permits to differentiate with high reliability the red wines according to:

1. Grape cultivar used during the winemaking production. A degree of 92% of correct predictions differentiating 11 categories was achieved. Even with blendings where the presence of minor cultivars is normally not clearly declared in the label of the bottle, it seems likely that they could be efficiently spotted with this method.
2. Area of origin. A 87.5% correct predictions with 11 categories were found. Some areas from the Tenerife island, although present similarities, can be differentiated by their geographical orientation and climate conditions. If geographical areas of all the islands are grouped according to common climate, warm and cold, the correct predictions increased until 94%.
3. Vintage. A valuable degree of correct predictions (92%) with 9 categories were found, these correct predictions increased to 99%, when the ageing time was used. However, if red wines have undergone any atypical ageing, the evolution of its phenolic compounds may not adequately reflect the time since the wine production.

Therefore, this work confirm that the phenolic patterns obtained using a relatively cheap and simple HPLC-DAD technique can help to know the origin, vintage and cultivar of the red wines. Thus, phenol distribution assessed with other techniques could be easily used for routine in food authenticity analysis. Multivariate analysis classified samples mainly as a function of flavonol, anthocyanin and colour parameters, in spite of the high heterogeneity of grape cultivars, areas and vintages.

To summarize, a detailed phenolic analysis permits unambiguous classifications of red wines according to vintage because of the ageing of wines modifies phenolic compounds. It also permits to differentiate according to climatic zone because external factors influence the biosynthesis of phenolics in the initial grapes. Moreover, this analytical tool even permits the classifications of red wines according to cultivar as the natural production of these metabolites by the plant differs depending on the genotype of grapes.

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Chapter 3

POTENTIAL HEALTH BENEFITS OF GRAPE-DERIVED PRODUCTS

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ABSTRACT

Grapes are very rich in components with different and interesting healthy effects, with this situation extending to grape derivatives such as must, wines and all other products (extracts, flour, etc.) obtained from grape and wine by-products. In addition, grapes are rich in bioactive constituents, mainly polyphenols, thus meaning that they and their derivatives are attracting increasing interest from consumers demanding polyphenol-rich foods as a result of epidemiological evidence suggesting the protective potential of polyphenols against chronic diseases directly associated with oxidative damage, such as Alzheimer's, various types of cancers, diabetes, hypertension, amongst others. In this regard, grape and

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wine by-products are increasingly being reutilized and transformed into high-value products for the food, cosmetics and pharmaceutical industries. However, other grape constituents in addition to polyphenols can also have beneficial effects, including fiber, potassium, vitamins, etc. Furthermore, the beneficial effects of grape derivatives are dependent on their bioavailability, which in turn is dependent on the efficiency of their trans-epithelial passage and subsequent metabolism in enteric and hepatic tissue, as well as by gut microbiota. This chapter aims to summarize the scientific evidence concerning the possible beneficial properties of grapes, wine and their derivatives observed in *in vitro* and *in vivo* studies. Furthermore, we will summarise the results obtained after more than fifteen years of working on the evaluation of the potential, benefits of different grape derivatives.

Keywords: antioxidant capacity, bioavailability, oxidative stress diseases, pomace, wine

1. INTRODUCTION

Viticulture is one of the most extended fruit crops worldwide, occupying around 7.4 million hectares. In 2018, 77.8 million tonnes of grapes were harvested, with the resulting wines (41.7 million) and table grapes (32.5 million) being the main grape products consumed, followed by dried grapes (1.3 million), musts and juices (25 million hL) produced using 5.2 million and 3.2 million tonnes of fresh grapes, respectively.

The consumption of grapes and their derivatives has been common in Mediterranean countries for thousands of years (Bartolomé-Monzón, 2019) and is also common in other parts of the world such as China (Norrie, 2003). As such, the nutritional and even medicinal values of grapes and their derivative have been known for almost as long. Greek philosophers and the Egyptians, Romans and Chinese, amongst others, used wine as medicine, either alone or in combination with other medicines ("polypharmacy"), and this use continued throughout the medieval period and for centuries thereafter. The rich history of wine provides an insight into its benefits for human health (Norrie, 2003). However, therapeutic benefits have also been ascribed to other parts of the vine. For example, grape leaves have been cited to alleviate wound bleeding, inflammation, muscle pain, and diarrhea, unripe grapes are recommended for the treatment of sore throats (Ananga et al., 2017), raisins are recommended for anemia in pregnant women and to provide relief against constipation, and sweet grapes have been recommended against smallpox, nausea, and eye infections, and can also provide relief against skin, kidney and liver disorders (Shi et al., 2003).

Nowadays, and especially since the second half of the twentieth century after recognition of the so-called "French paradox", the possible beneficial health effects of wine (Renaud et al., 1992; Pérez et al., 2002; Pignatelli et al., 2006; He et al., 2008) and other vine derivatives (Vinson et al., 2001) have once again come to the fore. As such, numerous research projects have focused on exploring the health benefits of grape components and grape derivatives. As a result, numerous commercial nutritional supplements and nutraceuticals obtained from the grape are now available, with some of these being amongst the most widely consumed supplements in the USA (Ananga et al., 2017).

Grapes are very rich in phenolic compounds, and high levels of polyphenols are also present in grape derivatives such as wines, musts and raisins, as well as in by-products of their manufacture, with the by-products of wineries being of particular interest (Lavelli et al., 2017).

The beneficial health effects of vine derivatives have been linked to the presence of different bioactive components in the plant and its fruits, especially phenolic compounds. The direct and beneficial relationship between the consumption of foods rich in phenolic compounds and their health effects is widely accepted nowadays. Plant polyphenols are some of the most interesting food antioxidant compounds in this regard, and numerous studies have shown their ability to prevent various diseases associated with oxidative stress including cancer, cardiovascular disease, brain dysfunction, weakening of the immune system, cataracts, aging, etc. (Valko et al., 2007; Dai et al., 2010; Tomáss-Barberán et al., 2012; Medina-Remon et al., 2015; Cao et al., 2018).

Phenolic compounds exhibit various mechanisms against oxidative reactions. For example, they can block oxidizing agents by reduction, chelation (mainly of metals such as iron or copper), scavenging various free radicals and inhibiting undesirable enzymatic activities. The scavenger ability to inhibit oxidative enzymes is essential for the homeostasis of biological systems by protecting extracellular and essential cellular components, such as proteins, lipids and DNA (Giao et al., 2008; Cabello-Verrugio et al., 2016). In addition to their antioxidant abilities, plant phenols are also able to cause a significant reduction of pathogenic microorganism, thus contributing to their potential health benefits.

This chapter summarizes the results obtained by our research group over the 30 years that we have been studying the possible health effects of wine derivatives, their components and products obtained from winemaking residues. In line with the above, our results concerning the antioxidant capacity, as evaluated using different methods, potential beneficial health effects and effects on pathogenic microorganisms are presented and compared with those obtained by other research groups.

2. Health Properties of Grape Products: From Antioxidant Properties to a Protective Effect Against Diseases

Grape (*Vitis* spp.) exhibits a rich variety of characteristics directly associated with significant changes in composition between species and varieties and with differences in secondary metabolite, which is probably the most significant. Furthermore, environmental factors, especially climate and soil conditions, and viticulture practices contribute to this variability. In this regard, are numerous parameters that having a strong influence on the biosynthesis of secondary metabolites and their accumulation in fruits and vines (Ali et al., 2010), which is directly correlated with the defensive physiological functions of plant phenols in general, and wine phenols in particular (Sudha et al., 2002).

Our research group has more than 30 years of experience in the study of grapes and their derivatives and therefore has a good understanding of the sources of variability that affect the composition of grapes and, therefore, their derivatives.

The heterogeneity of this composition also induces variability in the potential health effects of all these products, therefore, it becomes very hard to make extrapolations. This barrier can be overcome by appropriate sampling to include a high and representative number of the products being analyzed or considering reference parameters, such as the content of specific phenolic compounds. In accordance with these comments, and whenever possible, studies by our group have involved a large number of samples and at least the total polyphenol content and that of some of the major families, such as anthocyanins, catechins or proanthocyanins, have always been evaluated as reference parameters.

In addition, the main focus of our research has been the effect of the product (wine, raisins, by-products, etc.) rather than the pure, isolated bioactive components. As such, although some of our earlier studies involved pure phenolic compounds, our research has mainly involved working with wines of different types and with products obtained from winery by-products, paying little attention to grapes or other derivatives such as raisins. The reason for this is that we were interested in carrying out applied research involving both the products derived from the majority grape varieties in our region and, as far as possible, the conditions under which these products are consumed, namely the intake of complex matrices containing numerous components that interact with each other, rather than isolated compounds. Moreover, the numerous research studies carried out using isolated products have highlighted the fact that, in general, the combined effects of various antioxidants are more powerful than the sum of the individual actions (synergic effect).

2.1. Antioxidant Activities of Grape Products Evaluated "*In Vitro*"

The beneficial effects of grapes and their derivatives are mainly associated with the antioxidant capacity and the evaluation of this effect is of particular importance.

Since the last few years of the 20th century, numerous authors have studied the advantages and disadvantages of different methodologies for evaluating the total antioxidant capacity (TAC) of foodstuffs or their components (Fogliano et al., 1999; Huang et al., 2005; Prior et al., 2005). In general, these studies have shown that no single assay can provide complete information for evaluating the antioxidant capacity, thus, multiple assays are required to build an antioxidant profile of particular products. In light of this, the studies carried out in our group have, in general, evaluated the TAC of the products studied using more than one method, as will be discussed in the following sections.

2.1.1. Total Antioxidant Capacity of Wines

2.1.1.1. How to Evaluate the Global Antioxidant Profile of Wines

Earlier this century, there was some degree of confusion and contradictory results regarding the antioxidant capacities of wines. As such, and in line with our previous comments about the need to build a global antioxidant profile, in 2007, after observing that studies carried out previously usually used a limited number of methods (frequently one or two, with up to five in the best of cases) and a small group of wines (up to 55 in the best of cases), we considered convenient to carry out a comparative study of different TAC commonly assays used to evaluate the TAC capacities of wines, applying them on a large number of different wines (Rivero-Pérez et al., 2007). Thus, "chemical" TAC assays based on different mechanisms, including SET (single electron transfer) and HAT (hydrogen atom transfer) methods, and "biological" methods, such as biological scavenging activities and the protection of biomolecules via biomarkers of oxidative stress, were chosen to provide a complete TAC profile. From the various "chemical" assays available; DPPH and FRAP (SET), DMPD and ORAC (HAT), and ABTS (both SET and HAT) were chosen. Scavengers with activities against hydroxyl and superoxide radicals were selected, and lipid peroxidation and DNA damage inhibition were selected from the potential oxidation biomarkers.

This choice was based on their frequency of use in published papers, their relevance as biological methods for evaluating scavenger capacity towards reactive oxygen species (ROS), which are generated in the body itself due to aerobic metabolism. Furthermore, biomarkers of oxidative stress are also a biologically relevant indicator of a possible internal imbalance between oxygen species and antioxidants. The latter two groups of methodologies are known as "*in vitro*" biological assays. These methodologies give some idea of the health effects of the diet, in this case, with moderate wine consumption. Furthermore, it has been recognized that a valid *in vitro* assay is an invaluable tool for clinical studies if it can be combined with bioavailability data (Prior et al., 2005; Chedea et al., 2018).

The analytical conditions for each selected method were optimized for application in wines, and the methods were validated (Rivero-Pérez et al., 2007). The results obtained showed high quantitative differences between TAC values for wines, with wide ranges of values being found for all assays tested (Table 1). This fact was correlated with the heterogeneity of the red wines evaluated, which were made from grapes of different varieties and vintages and using different winemaking processes, thus resulting in different compositions and characteristics, for example, the total polyphenol contents (Table 1). Furthermore, quantitative values differed widely between assays due, amongst other factors, to the antioxidant mechanism involved and the sensitivity of each method toward different compounds. For example, DPPH has been reported to be more specific for lipophilic antioxidants, DMPD and FRAP for hydrophilic antioxidants and ABTS and ORAC for both classes (Prior et al., 2005). Low values from ORAC assays of wines had been described previously (Fernández-Pachón et al., 2004) and related to a limitation of this method, which only measures the scavenging activity towards peroxyl radicals (Ou et al., 2002). However, despite the differences observed, linear correlations between methods were noted, thus indicating that "chemical" methods gave similar information.

Table 1. Red wines total antioxidant capacity measured by different assays

Method	Antioxidant capacity	Range
ABTS (mM Trolox)	22 ± 8.3^{c}	4.28-41.0
DPPH (mM Trolox)	14.3 ± 4.6^{b}	1.19-25.5
DMPD (mM TRolox)	13.6 ± 12.5^{b}	0.05-50.1
ORAC (mM Trolox)	0.039 ± 0.019^{a}	0.008-0.091
FRAP (mMFe (II)	35 ± 15.7^{d}	9.41-101
TPP (mg gallic acid/L)	2422 ± 331	1775-3014
Method	*% of Inhibition*	*Range*
HRSA (1:50)*	38± 11.6	5.55-80
SRSA (1:5)*	60 ± *28.3*	0-98.03

Results are the mean ± SD of 321 samples. Values with different letters are significantly different (p<0.05). * Dilution factor of samples.

Wines were found to be better able to scavenge hydroxyl radicals than superoxide radicals, although the results showed significant efficiency against both radicals (Table 1). These findings were associated with the different mechanisms involved in the scavenger activity, with only one mechanism (the donation of one unpaired electron) being involved in the case of superoxide radicals and various (transfer of hydrogen atoms, the stability acquired by the phenoxyl radicals generated and the donation of electrons) in the case of hydroxyl radicals (Jovanovic et al., 1994). Data from ROS scavenger activity assays were not well correlated with those from "chemical" methods, which give complementary antioxidant information that is often required to obtain a complete antioxidant profile of the wines.

As for oxidative stress biomarkers, in general, wines showed a high capacity to inhibit microsomal peroxidation, although a marked variability among wines was detected, ranging from 10–89% inhibition after diluting wines 50 times. They also showed varying abilities to inhibit DNA damage. In general, a total protective effect was not achieved; however, DNA was partially protected, as demonstrated by the presence of DNA fragments with large sizes (mean values of 8076 ± 2351 bp; range: 3594 to 13,302 bp). Moreover, no pro-oxidant effects were detected. The biomarker results indicated that the protective effect of wines against oxidative stress could occur at various levels, with a positive correlation between them.

In agreement with previous comments, a complete antioxidant profile of red wines or other grape products could be established by evaluating at least one TAC methodology, preferably ABTS, both scavenger activities (hydroxyl and superoxide), which give complementary information, and some type of biomarkers, preferably lipid peroxidation inhibition. Furthermore, the evaluation of total polyphenolic (TPP) content is also recommended as a possible reference index for comparative evaluation.

2.1.1.2. Variability Factor

Among the bioactive compounds present in wines, polyphenols, and especially flavonoids (Rice-Evans et al., 1996), have been widely associated with TAC and, therefore, with the positive health properties of wines. Indeed, anthocyanin consumption from moderate wine drinking has been reported to be responsible for the “French Paradox” (Clifford, 2000). Anthocyanins show high antioxidant activity due to their ability to readily donate a hydrogen atom from aromatic hydroxyl groups and to stabilize the unpaired electron by delocalization around the π-electron system (Van Acker et al., 1996). As such, anthocyanins have been reported to be effective scavengers of reactive oxygen radicals (Tsuda et al., 1996), to inhibit lipoprotein oxidation and platelet aggregation (Ghiselli et al., 1998) and to protect against cardiovascular disease (Falchi et al., 2006). In this regard, the contribution of anthocyanins to the antioxidant properties of red wines has been studied by isolating this fraction and comparing the TAC profile with those of the original wines (Rivero-Pérez et al., 2008a). The results showed that the free anthocyanin fraction isolated from wines was responsible for most of the TAC, representing more than 90% of the hydroxyl radical scavenger activity (HRSA). In light of the results obtained, anthocyanins can be considered to be the main phenolic compounds responsible for protection against hydroxyl and superoxide radicals in wines, although they contribute less extensively to the protective action against lipid peroxidation. This latter fact has been associated with the absence of other constituents of wines, such as flavan-3-ol compounds, that are not present in isolated fractions and have anti-lipid peroxidation activity. The implication of anthocyanins in the blocking of hydroxyl and superoxide radicals is well correlated with their health benefits. Furthermore, these results could support the use of grape or wine anthocyanin extracts as dietary supplements.

Aspects of the winemaking process such as aging methods and time contribute to the heterogeneity of the compositions of the resulting wines, markedly affecting phenol levels and modifications, including anthocyanin transformation. As such, the winemaking process can directly affect the TAC profile of wines. In this regard, it has been observed that TAC values are notably different depending on age and time of wood contact (Rivero-Pérez et al., 2008b). In general, young wines present higher ABTS, DPPH and DMPD values, whereas wines aged in wood show higher FRAP and ORAC values and a higher capacity to inhibit lipid peroxidation. Some of these changes have been associated with the compounds extracted from wood, such as ellagitannins, and with the condensation and other transformations of anthocyanins. The aging effect also depends on the grape variety.

Micro-oxygenation does not, in general, result in significant differences in either the antioxidant capacity or scavenger activity of young and one-year-old red wines, although a significant increase in the ability to protect against DNA damage was observed, along with a qualitative decrease in the prevention of lipid peroxidation (Rivero-Pérez et al., 2008c). Overall, the effect of micro-oxygenation on the antioxidant profile of red wine was also variety-dependent.

Thus, Portuguese sparkling red wines showed TAC values (ABTS, FRAP, HRSA and SRSA) in the ranges indicated in Table 1, with sparkling white wines showing significantly lower values (Jordão et al., 2010). This fact was directly correlated with the lower phenol levels and the absence of anthocyanins in white wines. Furthermore, the results appeared to indicate that second fermentation in the bottle affects the antioxidant capacities of red wines slightly.

A study from our group regarding the effect of removing the alcohol on the characteristics of red wines highlighted changes to the antioxidant profile of alcohol-free wines (Del Campo et al., 2011). Briefly, these wines exhibited small quantitative changes in total antioxidant activity, as measured using the ABTS and FRAP methods, but no differences in their lipid peroxidation inhibitory capacity. However, the HRSA capacity decreased by around 20%, with this change mainly being attributed to the removal of ethanol, which is known to stabilize hydroxyl radicals (Bonnefont-Rousselot et al., 2001). This finding was corroborated when similar values to this inhibitory capacity were found in lyophilized (and therefore alcohol-free) extracts from the two wines studied.

2.1.2. Total Antioxidant Capacity of Fresh and Dried Grapes

The health benefits associated with fresh grape consumption are well known and are linked to the content in phenolic compounds (Darra et al., 2012). Grape phenols include a large number of compounds, ranging from simple phenols to polymers, and their contents are influenced by numerous factors, such as edaphoclimatic conditions, grape variety, growing practices, amongst many others (Robredo et al., 1991; Pérez-Magariño and González-San José, 2014). Indeed, a significant amount of information about grape phenols and the antioxidant properties of the most widely cultivated varieties are now available. However, very little information is available concerning indigenous and minority varieties cultivated traditionally in many countries. One study in this regard focused on the TAC of different autochthonous Portuguese red grape varieties (Costa et al., 2015), with the results showing marked differences between varieties and between grapes cultivated in different regions. Thus, the TAC values ranged from 0.7 to 11.6 μmol Trolox/g berry (ABTS), and from 30–68% and 20–76% inhibition for superoxide and hydroxyl radicals, respectively.

Fruit drying is an ancestral method for preserving foods. Indeed, dry grapes, also known as raisins, have been produced and consumed for many hundreds of years, especially in the Mediterranean area. However, the USA is currently the world's leading raisin producer. During the first part of the 21st century, several authors studied the phenolic composition and antioxidant capacity of different varieties of raisins, namely from Tunisia (Ghrairi et al., 2013), China (Meng et al., 2011), the United States (Zhao et al., 2008) and Australia (Bennett et al., 2011). Similarly, a study carried out in collaboration with Portuguese researchers gave some information about samples from the Iberian Peninsula (Sério et al., 2014). Thus, the total polyphenol contents observed for Iberian raisins were similar to those described previously for other raisins, with red raisins being richer than white raisins. Antioxidant capacities were also higher in red raisins, although significant differences were observed, with white seedless raisins exhibiting lower TAC values and scavenger capacities.

2.1.3. Total Antioxidant Capacity of Winery By-Products

The wine industry produces millions of tons of residues. Grape and wine pomace obtained after pressing unfermented or fermented grapes, respectively, represent the main by-product of the wine industry, and their management represents a serious problem for wineries. As such, the productive use of these by-products based on their content of bioactive compounds can help to resolve this problem and offer substantial economic benefits (Yu et al., 2014; García-Lomillo et al., 2017a).

Wine pomace represents about 20-30% of the original grape weight and is rich in bioactive compounds such as polyphenols, although it also has high fiber content, including significant quantities of bound phenolic compounds (Pérez-Jiménez et al., 2009). Wine pomace is usually used to produce extracts rich in antioxidants, which can be used in the cosmetic, pharmaceutical and food industries. These extracts can be obtained from full pomace or from the main constituents, namely seeds and skins, separately.

An alternative to these extracts is to use wine pomace “directly”, with no extraction process. This approach enables a more complete reutilization of this by-product and advantage to be taken of non-extractable compounds, thus allowing the nutritional value and potential health benefits to be improved due to the presence of a greater number of interesting compounds, such as fiber, non-extractable phenols, proteins, etc. Some authors have proposed the use of wine pomace flours obtained after milling whole wine pomace or its main components (seeds and skins) (O’zvural et al., 2011; Mironeasa et al., 2012; Rosales-Soto et al., 2012). An approach developed by our group involves the use of wine pomace as a seasoning with antioxidant and antimicrobial activity (García-Lomillo et al., 2014) that can help to supplement food with minerals, such as potassium, and fiber. Three different types of seasonings have been developed, starting from whole wine pomace and from separated seeds and skins. Significant differences in composition and, therefore, TAC values were detected between these seasonings. Thus, those derived from seed exhibited higher levels of dietary fiber (59%) and total polyphenols (mean values of 43 mg gallic acid/g) but very low levels of potassium (around 4 mg/g), whereas seasonings obtained from skins showed the highest levels of potassium (around 43 mg/g) but the lowest total polyphenol values (mean values of 25 mg gallic acid/g) and lower fiber values (around 49%). Finally, the seasoning obtained from whole wine pomace showed intermediate characteristics (50% dietary fiber, total polyphenol level 33 mg/g gallic acid and 38 mg/g potassium). The extractable fractions for each seasoning showed the highest (142 ± 2 μmol/g, ABTS), lowest (76 ± 2 μmol/g, ABTS) and intermediate TAC values (103 ± 0.2 μmol/g, ABTS), respectively.

TAC measurements for extracts are limited to evaluating the antioxidant capacities of the soluble compounds present in the products evaluated, therefore the extraction procedure is considered to be a critical step (Serrano et al., 2007). This has motivated the development of quick, easy, new, cheap, and reproducible (QUENCHER) assays to measure the antioxidant activity of food materials (Gökmen et al., 2009). The QUENCHER (Q-) protocols bring powdered products and the reagent solutions into direct contact. Thus, the soluble antioxidants in the sample reach the reaction medium by way of normal liquid–liquid partitions and exert their antioxidant capacity after dissolution, whereas the non-extractable antioxidants exert their antioxidant activity by taking advantage of surface reactions occurring at the solid-liquid interface (Gökmen et al., 2009). Our group has developed new protocols to evaluate the scavenger capacity of some of the most biologically relevant radicals (superoxide, hydroxyl, and lipid peroxyl), and has optimized, and validated different QUENCHER assays (Q-FC, Q-FRAP, Q-ABTS, Q-DPPH, Q-ORAC, Q-SRSC, QHRSC and Q-LPSC) for the first time using three different powdered seasonings (Del Pino-Garcia et al., 2015a). The results were very satisfactory and showed some differences between QUENCHER and classical methodologies, which may be very interesting for avoiding supra- or infra- valuation of the actual antioxidant capacities of the products, mainly associated with either a filtered extraction of compounds that will not be extracted in biological media or because they do not consider the effect of non-extractable compounds (Del Pino-Garcia et al., 2015a; Del Pino-Garcia et al., 2017a).

2.2. Bioactivity of Grape Products Evaluated on Human Cell Lines

The beneficial health effects of grapes and their derivatives mainly arise due to their ability to protect against oxidative metabolic processes that produce, among others, a decrease in the levels of reactive oxygen (ROS) and nitrogen species (RNS) found in the body, thereby protecting biomolecules against oxidative damage (Sanchez-Rodriguez et al., 2019). Numerous studies have linked these effects to the phenolic compounds found in grapes and their derivatives (Del Rio et al., 2013; Medina-Remon et al., 2015). In turn, the protective effect at a cellular level may be associated with the ability of metabolites derived from these phenolic compounds to modulate different intracellular signaling mechanisms that are essential in cell functions such as growth, proliferation and apoptosis (Namal et al., 2013; Del Pino-Garcia et al., 2016a; Del Pino-García et al., 2017b; Gerardi et al., 2019). The studies published in this regard show that, in general, the amount of phenolic compounds required inside cells to exert a protective effect is much lower than that estimated for them to be effective as antioxidants in chemical methods (Chen et al., 2007; Tung et al., 2009; Lakshmi et al., 2014; Yonguc et al., 2015).

Numerous cell models have been used to elucidate metabolic pathways and discover the mechanisms involved in cell signaling, the regulation of gene expression and protein synthesis and cell proliferation, senescence and death cell. In this sense, it is known that polyphenol compounds interfere with biomolecule damage and the redox signaling pathways involved in the prevention of different diseases. The Nrf2-mediated adaptive response to oxidative stress by these polyphenols up-regulates antioxidant gene expression and reduces oxidative stress (Fraga et al., 2018). The cell signaling pathways affected by polyphenols include the MAPK (ERK1/2, p38 and JNK), PI3K/Akt signaling, AMPK/FOXO1/mTOR/SIRT1 signaling, transcription factors Nrf2, NF-κB, AP-1, HIF-1α, p53, Wnt/β-catenin and epigenetic regulation pathways (Dai et al., 2018; Gerardi et al., 2019; Maleki, 2019).

Concerning the beneficial effects of bioactive compounds, one of the principal issues remains their bioavailability, which is dependent on their digestive stability, bioaccessibility (release from the food matrix), the efficiency of their transepithelial passage, and their subsequent metabolism in enteric and hepatic tissue, as well as by gut microbiota (Manach et al., 2004; Tagliazucchi et al., 2010; Alminger et al., 2014; Cueva et al., 2017). Thus, gastrointestinal digestion released bioactive molecules that might be absorbed in the small intestine from food matrices, whereas others remain in the indigestible fraction and reach the large intestine for fermentation by gut microbiota. In light of this, the combination of *in vitro* digestion protocols with cell-based assays has been proposed (Huang et al., 2014), with several of the protocols proposed simulating the different phases of gastrointestinal digestion and colonic fermentation *in vivo* (Saura-Calixto et al., 2010; Minekus et al., 2014).

Studies carried out by our research group with red wine pomace products (Del Pino-García et al., 2016b) indicated that gastrointestinal digestion and colonic fermentation of the wine pomace product enhanced the antioxidant activity of the product, in other words, the antioxidant activity values exhibited by the majority of the fractions digested, isolated after the different phases of *in vitro* digestion, were higher than those obtained upon evaluating the antioxidant activity of the seasoning. Gastrointestinal enzymatic digestion enhanced both TAC values and the free radical scavenging activity, whereas colonic fermentation mainly resulted in a marked increase in the scavenger ability. These effects were associated with both the release of antioxidant compounds during gastrointestinal digestion and colonic fermentation (Table 2) (Del Pino-García et al., 2016a), in agreement with those reported by other groups (Rufián-Henares et al., 2009). In contrast, Lingua et al. (2019) recently evaluated the effect of gastrointestinal digestion on the antioxidant properties of white grapes and their wines, finding that the bioactivity of the digested fractions was not affected by the digestion process, which these authors related to the resistance of phenolic acids and quercetin, the main phenols detected, to gastrointestinal digestion.

Table 2. Characterization of the phenolic composition of the red wine pomace product and of their gastrointestinal digestion and colonic fermentation

Phenolic compounds	Wine pomace product (μg/g)	Gastrointestinal digestión (μg/g)	Colonic fermentation (μg/g)
Phenolic acids			
Hydroxybenzoic acids	263 ± 5.32	224 ± 27.12	653 ± 36.9
Hydroxycinnamic acids	32.3 ± 1.64	14.1 ± 1.15	2.92 ± 0.59
Total Stilbenes	3.15 ± 0.18	0.766 ± 0.108	N.D.
Total Flavan-3-ols	199 ± 9.6	1065 ± 23.87	77 ± 14.2
Total Flavonols	343 ± 46.1	24.5 ± 1.1	N.D.
Anthocyanidins	1729 ± 128	N.D.	N.D.

Concentration of phenolic compounds expressed in μg/g of digested fraction (mean value ± standard deviation, n = 3). ND = not detected.

The polyphenols resulting from colonic fermentation may generate short-chain fatty acids (SCFAs), which may act synergically with fiber, another component of interest in the wine pomace product. The positive physiological effects of fiber (weight control, control of the glycaemic response, prebiotic effect, lower risk of suffering from colonic disease, etc.) are mainly due to the metabolites produced in the colon and fiber itself passes into the intestine unaltered, where the soluble fraction is fermented by the microflora to form compounds of particular interest, such as SCFAs. In general, 95% of the SCFAs produced upon fermentation of fiber are absorbed and metabolized, thus meaning that only 5-10% are excreted in feces. The main SCFAs generated during colonic fermentation are acetic acid, propionic acid and butyric acid. In this regard, our research group has evaluated the SCFA concentration and profile generated during *in vitro* fermentation of skins and seeds from red wine pomace product. Colonic fermentation of skin samples generated 2.5-times more SCFAs than the same process with seeds. Butyric acid was the majority fatty acid obtained from the skin sample.

Although cell culture assays tend to be representative of cells *in vivo* in terms of metabolism, gene expression and enzyme levels, particular care must be taken when extrapolating the results obtained in cell culture to the situation *in vivo*. Indeed, the information obtained from cell culture studies must be validated *in vivo* (Meng et al., 2019). Finally, diseases and tumor cells in which the resistance of cells to damage caused by ROS varies widely because the cell has adapted to oxidative stress. In this sense, a recent review (Focaccetti et al., 2019) highlighted the complexity of this scenario in tumor cells, with polyphenols exerting different and, occasionally, paradoxical effects depending on the dose, cell type and biological status.

2.2.1. Bioactivity of Grape Products on Intestinal Cells

The intestinal epithelium is exposed to the toxicity induced by oxidants in the foods ingested, which may result in oxidative damage to macromolecules and tissues, and therefore intestinal damage. This explains the interest in studying the toxicity induced by oxidative stress and the effect of bioactive compounds from the diet on the intestinal epithelium.

Human colon cancer cell lines, such as Caco-2, SW480 and HT-29, with different degrees of growth rate are usually used in this type of study. Caco-2 is the most widely used in bioavailability studies as they conserve their morphology and the majority of their functions (Rodríguez-Rodríguez et al., 2012). The SW480 cell line is moderately differentiated and invasive and is widely used in metastasis studies (Yoon et al., 2008), and HT-29 cells form a well-differentiated adenocarcinoma.

Studies carried out by our research group with these cell lines have highlighted the absence of cytotoxicity and potential antigenotoxic oxidative stress effects of lyophilized wine extract samples and wine pomace products from grape seed and skin. Regulation of oxidative stress was evaluated by determining reactive oxygen species (ROS) using the DCFH-DA (2′,7′-dichlorofluorescein diacetate) assay, quantifying levels of the endogenous cellular antioxidant glutathione, expressed as GSH/GSSG, analyzing biomarkers for oxidative damage, nitric oxide (NO) production and analyzing the expression of enzymes regulated by the transcription factors Nrf2 and NF-kB.

Studies with lyophilized extracts of normal and alcohol-free red wine in HT-29 cells showed a cytoprotective effect against oxidative stress induced by the oxidizing agent menadione (MND), a compound widely used to induce oxidative stress in cells due to its high toxicity associated with lipid oxidation and protein and DNA damage (Aherne and O'Brien, 2000). Briefly, we found that cells treated with wine lyophilized samples exerted a strong protective effect against lipid peroxidation, carbonyl groups and oxidative damage to DNA (Table 3). The results indicated a saturating protective effect against lipids, with a similar protective effect being obtained despite using larger quantities. This protective effect was mainly associated with anthocyanins and their ability to bind the membrane, thus preventing the propagation of radicals via the oxidation chain of fatty acids.

Table 3. Effect of different concentrations of lyophilized normal (RW) and dealcoholized (D-RW) red wines on biomarkers of oxidative stress on HT-29 cell

	Lipid peroxidation (TBARS % inhibition)	**Protein oxidation Carbonyl group (% inhibition)**	**DNA Damage (% DNA Tail)**
Control	48.2 ± 17.0[a]	69.3 ± 22.6[a]	4.4 ± 2.8[a]
MND	100 ± 0.0[b]	100 ± 0.00[b,c]	100 ± 0.0[d]
RW (1 g/L)	41.2 ± 15.2[a]	82.8 ± 22.8[ab]	25.1 ± 13.0[bc]
RW (0.1 g/L)	48.8 ± 34[a]	100 ± 2.3[c]	31.9 ± 16.5[c]
D-RW (1 g/L)	36.0 ± 7.7[a]	75.6 ± 20.1[ab]	12.7 ± 7.4[ab]
D-RW (0.1 g/L)	35.3 ± 13.2[a]	96.7 ± 20.6[b,c]	20.1 ± 4.2[bc]

Results are expressed as percentage of inhibition (%) comparing with oxidized cell (MND). MND: menadiona; RW: Red wine lyophilized; D-RW: Dealcoholized red wine lyophilized.

Regarding their genoprotective effect (Table 3), the oxidative damage to DNA caused by menadione, evaluated by Comet assay, decreased markedly (Tice et al., 2000). Our findings appeared to indicate some degree of dose-dependent effect, as is also the case for protection against protein oxidation, as quantified using the number of carbonyl groups generated, as a significant effect was only observed at higher doses. These effects were associated with all phenolic compounds in the extract, although the high scavenger capacity of anthocyanins and their higher concentration in the extracts means that they should be considered to be mainly responsible for the effects observed.

Studies carried out in SW480 and Caco-2 cells using red wine pomace products from different wineries characterized by different phenolic compositions, indicating an ability to stabilize intracellular ROS, as evaluated using the DCF method, and no cytotoxicity, as evaluated using the MTT method, with an effect depending on the type of product. Skins with a higher anthocyanin content exhibited a greater antioxidant effect in cells, as demonstrated in a study carried out by Rivero-Pérez et al. (2008a), who found that the free anthocyanidin fraction is chiefly responsible for the total antioxidant capacity and scavenger activity. In addition, the effect of this type of product on gene expression in nitric oxide-generating enzymes has also been evaluated using the SW480 cell line (Del Pino-Garcia et al., 2017b). Nitric oxide (NO) is a molecular and intracellular signaling compound and key biological messenger. It has been found that NO plays a key role in the metabolism in many types of organisms and is synthesized by NO synthases via the reaction of L-arginine with molecular oxygen. Tumor cells exhibit greater survival and proliferative signaling pathways that prevent proapoptotic pathways. The incubation of SW480 cells with a product from grape skin resulted in a decrease in nitric oxide levels due to a reduced expression of the inducible enzyme nitric oxide synthase (NOS), thus showing this product to be a potential NO inhibitor.

Studies in HT-29 cells were also carried out with grape skins and seeds, determining the bioaccessibility and metabolism of polyphenols and dietary fiber throughout the intestine, as well as colonic fermentation (Del Pino-García et al., 2016b). The antiproliferative activity was studied using the MTT colorimetric assay, which was used to evaluate cell viability after treatment with undigested products after gastrointestinal digestion and after colonic digestion. The antigenotoxic effects of the previously digested fractions, in turn, were evaluated using the Comet assay (Del Pino-García et al., 2017b). A non-cytotoxic concentration of 200 μg of fraction/mL culture medium, which showed the potential of the products as anti-cancer agents to block genotoxic compounds, was selected based on these studies. All wine pomace products exhibited an interesting chemopreventive potential, reducing oxidative DNA damage by around 47%. These findings suggest that wine pomace products may act as tumor suppressants because of their anti-proliferative effects, and as tumor blockers as a result of their anti-genotoxic effects against exogenous oxidizing agents. Similarly, the gastrointestinal digestion process did not appear to affect the overall activity exhibited by the bioactive compounds found in skins, which was the most effective before to digestion. However, a gradual improvement in the chemopreventive properties of seeds was observed along the digestive process, such that all products appeared to present a similar chemopreventive potential after colonic fermentation, thereby suggesting their potential chemopreventive effect in colorectal cancer. When HT-29 cells were exposed to *t*BOOH (*tert*-butyl hydroperoxide) as an exogenous pro-oxidant, which significantly increased the oxidative stress and damage within cells, the wine pomace product digestion fraction was able to protect against the oxidation of biomolecules (lipids and proteins) and cell membranes. Thus, MDA levels post-oxidation decreased significantly, leading to increases in lipid peroxidation protection of 65.2 ± 2.6% for the gastrointestinal fraction and 50.6 ± 4.2% for the gastrointestinal and colonic fermentation fraction. Similar modulation of wine pomace products was observed for the Nrf2 transcription factor and for some of its targeted cytoprotective genes, such as HO-1 and SOD2. Furthermore, NOX1 was significantly down-regulated in the oxidized control cells, whereas up-regulation of COX2 and iNOS gene expression was detected.

The effect on glutathione levels in HT-29 cells subjected to oxidative stress with *t*BOOH was highlighted when it was found that treatment with the gastrointestinal fractions from wine pomace product improved the GSH/GSGG ratio (Table 4) when added in the presence of an oxidising agent. We found that this protective effect for GSH levels was due to transcriptional regulation of the genes that code for the enzymes glutathione synthase (GS) and γ-glutamylcysteine ligase (γGCL) involved in its synthesis. Thus, it was found that cells subjected to oxidative stress present overexpression of the γGC gene, whereas this is reduced when cells are incubated with the product during oxidation. Similarly, an increase in transcription of the GSTM2 gene in cells was observed and the antioxidant enzyme GPX2 was overexpressed in the presence of the wine pomace product. Other authors (Goutzourelas et al., 2015) also observed increases in the enzymes of GSH metabolism in endothelial cells treated with grape pomace extract.

Table 4. GSH/GSSG ratio of HT-29 cells oxidized with t-BOOH after treatment with different digested fractions of wine pomace product (WPP)

	GSH/GSSG
Control	22.63 ± 1.5^{a}
Control oxidized (t-BOOH)	2.12 ± 0.3^{d}
WPP- Gastrointestinal fraction	7.18 ± 1.1^{b}
WPP- Gastrointestinal + colonic fermentation fraction	8.85 ± 0.6^{c}

Data are expressed as mean values ± standard error (n = 4). Significant differences ($p < 0.05$) among groups are indicated with Latin letters.

2.2.2. Bioactivity of Grape Products on Endothelial Cells

Endothelial dysfunction plays a key role in the pathogeny and development of vascular diseases involving a close relationship between oxidative stress, the inflammatory process and alterations to vascular endothelium function. This highlights the importance of using endothelial models that allow the role of ROS as key agents in the deterioration of various cell functions. The nuclear transcription factor NF-κB and proinflammatory cytokines, such as tumor necrosis factor α (TNF-α), interleukin-1 (IL-1), interleukin-8 (IL-8) and interferon γ (IFN-γ), participate in the activation of the endothelium, thus accelerating the formation of the atheroma.

The development of a cell model under hyperglycemic conditions is very common for describing conditions of oxidative stress in endothelial cells. One explanation for this could be due to the oxidative stress observed in the vascular system of diabetes patients, which may lead to major vascular complications, and which is well known to be at least partially caused by the hyperglycemic conditions inherent to diseases such as diabetes (Fatehi-Hassanabad et al., 2010).

Studies carried out by our research group (Del Pino-García et al., 2016a) have evaluated the possible protective effects against endothelial dysfunction and oxidative vascular damage of a wine pomace product obtained from red wine pomace. The endothelial cell line HUVECs EA.hy926 was used under conditions of hyperglycemia-induced oxidative stress. The fractions obtained in the different phases of simulated gastrointestinal digestion and colonic fermentation of the seasoning under consideration were studied. The results of that study provided novel and convincing proof of the possible protective effects of compounds released from wine pomace product in the colonic pre- and post-digestion phases.

In addition, evidence has been found that the mechanisms of action via which these compounds restore the redox environment and endothelial function in HUVECs EA.hy926 are related to direct scavenger of ROS, modulation of expression of the NOX4, SOD2 and HO-1 genes, inducing different signaling pathways sensitive to the redox state and their ability to decrease the activity of the enzyme ACE (angiotensin I-converting enzyme). In a more in-depth study of the protective mechanisms of the gastrointestinal and colonic fractions referred to above, using the same EA.hy926 cell mode, Gerardi et al., (2019) demonstrated the molecular mechanisms via which these fractions can act as proinflammatory protein inhibitors by downregulation of the NF-κB pathway or by increasing endogenous antioxidant enzymes and reducing inflammatory activity by regulation of the Aktp38-MAPK/Nrf2 pathway and deacetylation of SIRT-1 (sirtuin-1). Moreover, this study showed an early adaptive response of NF-κB/SOD2 under hyperglycemic conditions. Consequently, this study provided evidence for the molecular mechanisms activated by wine pomace products, thereby providing a solid basis for future clinical studies.

2.3. Bioactivity of Grape Products "*In Vivo*"

Studies and efforts aimed at changing dietary habits towards models considered to prevent diseases related to oxidative stress, such as diabetes, atherosclerosis, myocardial infarction, ischemia/reperfusion processes, inflammatory diseases, cancer, ageing, etc., have increased in number over the past few years.

As noted in previous sections, *in vitro* and *ex vivo* studies provide useful information concerning the possible beneficial effects of consuming a specific product, although such studies are not sufficient to confirm the beneficial effect and must therefore be complemented with *in vivo* studies. In general, beneficial effects are studied in animal models and then in humans in both epidemiological and interventional studies (Estruch et al., 2014; Tressera-Rimbau et al., 2015; Di Renzo et al., 2015; Nova et al., 2019).

The effect of bioactive compounds is dependent on their bioavailability after their intake. As such, it is important to establish the level of polyphenols required to exert a beneficial effect, a topic that remains controversial in the scientific community. Indeed, their positive (antioxidant, anti-inflammatory, etc.) or negative biological effects (prooxidant, proinflammatory) are dependent on concentration and cell type. Moreover, polyphenols undergo modifications, thus meaning that results *in vitro* are often not correlated with effects *in vivo*. To evaluate the effect of ingesting wine and wine pomace products, our research group has carried out studies in experimental animals (Wistar rats) to determine their bioavailability and effect on the antioxidant status of plasma and tissues.

These as-yet unpublished studies into the effect of moderate consumption of different types of wine (young, barrel-aged and alcohol-free) indicate that this consumption regulates the endogenous antioxidant status, although differences were observed between these three types of wine (Table 5).

Table 5. Antioxidant status in plasma, liver and kidney rats (control) and after consumption aged wine, young wine and dealcoholized wine

	Control (C)	Aged Wine	Young Wine	Dealcoholized Wine
Plasma antioxidant capacity				
ABTS (mM TE)	1.95±0.2[a]	2.18±0.18[a]	2.77±0.12[b]	2.54± 0.05[b]
FRAP (mM Fe(II)E)	0.21±0.03[a]	0.29±0.02[b]	0.50±0.07[c]	0.47± 0.04[c]
GSH (μmol/mg protein)				
Liver	14.3 ± 2.63[a]	9.82±1.70[a]	25.9±6.30[b]	24.8 ± 6.13[b]
Kidney	0.23 ± 0.05[a]	0.58±0.14[b]	0.57±0.07[b]	0.79 ± 0.05[c]

Values for total antioxidant capacity of plasma rat's measurement by ABTS and FRAP methods and GSH levels was measurement in liver and kidney. Content expressed as mean values ± standard deviation (n = 5). Significant differences ($p < 0.05$) among groups are indicated with Latin letters.

Thus, consumption of young and alcohol-free wine resulted in a significant increase in total antioxidant capacity (ABTS and FRAP) in plasma, and glutathione (GSH) levels in the liver, for the control group. However, the consumption of barrel-aged did not affect the antioxidant capacity of plasma, thereby agreeing with the findings of other authors (Roginsky et al., 2006). This could be due to the different polyphenol profiles of these wines (Rivero-Pérez et al., 2007). However, consumption of these three types of wine increased glutathione (GSH) levels in the kidney, with the highest levels being found for alcohol-free wine. These findings indicate a potential reinforcement of the endogenous antioxidant defenses, mainly due to the phenolic compounds present in the wines. Similarly, other authors have observed beneficial effects, including a reduction in LDL oxidation, apolipoprotein B levels and blood pressure, arising from the moderate consumption of wine and alcohol-free wine (Chiva-Blanch et al., 2013; Martinez et al., 2013).

More recently, we have evaluated the 25, and antioxidant action of red and white wine pomace products after consumption by Wistar rats (Del Pino-García et al., 2016d; Gerardi et al., 2020a). The intake of single oral doses of 300 mg/kg BW of red wine pomace product resulted in an increase in phenolic acids, as assayed by GC/MS/MS in plasma, associated with a marked reduction in lipid peroxidation and increased nitric oxide bioavailability. Furthermore, we evaluated the effect of different doses and different types of wine pomace products (red and white) on bioavailability by measuring the phenolic acid profile in plasma and urine at different doses (Gerardi et al., 2020a). The bioavailability of red wine pomace product was found to be independent of the concentration consumed. However, the intake of white pomace product resulted in a dose-dependent effect, with the levels of plasma and urine phenolic metabolites increasing with the intake of the wine pomace product. Furthermore, a correlation between the phenolic metabolites from wine pomace product and antioxidant capacity in plasma was observed (Gerardi et al., 2020a).

Other authors have also evaluated the bioavailability of polyphenols from grape pomace in humans, finding a higher inter-individual variability in urine and plasma samples after acute administration of red grape pomace, mainly due to the production of microbial metabolites after colonic fermentation by the microbiota (Castello et al., 2018; Rasines et al., 2018). Similarly, various clinical trials have demonstrated the antioxidant effect of consuming wine polyphenols, finding an increase in the antioxidant capacity of plasma that enhances the antioxidant system in different tissues (Gris et al., 2013; Copetti et al., 2018). In addition, several studies have indicated the effect of consuming wine in preventing lipid peroxidation, finding lower levels of isoprostanes and MDA, both of which are markers for oxidative damage in lipids (Estruch et al., 2014; Marhuenda et al., 2017). A decrease in atherosclerotic complications due to inhibition of LDL oxidation, and an increase in various antioxidant enzymes, has also been reported (Lingua et al., 2016; Kolota et al., 2019).

Another grape constituent, namely dietary fiber, also has a marked influence on the health benefits of grape products. Dietary fiber can improve intestinal motility, promote satiety and reduce the absorption of carbohydrates and triglycerides, thus leading to a reduction in the risk of cardiovascular diseases. Furthermore, dietary fibers from grape products are rich in bonded antioxidants that can reach the colon, where they exert a protective antioxidant action, for example chemoprotection against colon cancer. Studies of our research group, the intake of red wine pomace product by Wistar rats during 30 days results in changes in the fecal contents of SCFAs (Del Pino-García et al., 2017c). To the end of the study, in the rats group supplemented with RWPs the levels of butyric acid increased a 50% compared with control groups. Furthermore, the molar ratio of butyric:propionic:acetic acids in the control group was maintained rather similar from the beginning to the end of the study. However, in the group supplemented with red wine pomace the molar ratio of SCFAs change, ant the faecal content of butyric acids was increased ant that of acetic acid was decreased. The positive effects of the SCFAs are associated with their involvement on regulate carbohydrate metabolism and significantly reduce blood glucose and showing β-cell protection.

2.4. Effect of Winery Products in the Prevention of Oxidative Stress-Related Disease

A large number of studies have shown an inverse association between the risk of several chronic human diseases, many of which are related to oxidative stress and the consumption of grape polyphenols.

2.4.1. Anti-Hypertensive Effects

Hypertension is an important risk factor for cardiovascular disease, and diet has been identified as a factor for preventing and controlling hypertension. This disease is characterized by a chronically elevated systemic arterial blood pressure and are involves complex interactions between genetic, environmental, and demographic factors. Endothelial dysfunction and oxidative stress it is known that are involved in the physiopathology of hypertension. The endothelium is a selectively permeable barrier between the vascular wall and the bloodstream that regulates vascular tone, cell growth, vascular wall permeability and the interaction between leukocytes, thrombocytes and the vessel wall (Yang et al., 2016).

Endothelial dysfunction and oxidative stress are closely related and promote important changes in the vascular system associated with the development of atherosclerosis, hypertension and cardiovascular events (Battino et al., 2018). Thus, hypertension is characterized by increased vascular oxidative stress and impaired endothelial function associated with nitric oxide bioavailability. Elevated levels of angiotensin II are also involved in many forms of hypertension. As such, strategies to improve vascular oxidative stress and endothelial dysfunction by increasing nitric oxide level may allow hypertension to be modulated. A diet enriched with a wine pomace product obtained from red winery by-products has been found to modulate hypertension in spontaneously hypertensive SHR rats (Del Pino-García et al., 2017c). This study showed that consumption of this product had a hypotensive effect, reduced oxidative stress, improved blood pressure and decreased ACE (angiotensin I-converting enzyme) gene expression, with a subsequent decrease in angiotensin II generation, all of which are characteristic symptoms of hypertension (Del Pino-García et al., 2017c). Furthermore, vascular remodeling in diabetic and SHR rats, accompanied by an increase in eNOS activity, was observed (Gerardi et al., 2020b).

2.4.2. Antidiabetic Effects

Diabetes mellitus is one of the most significant public health problems worldwide. Different research studies have suggested the polyphenol-rich foods are beneficial to reducing the risk of diabetes, mainly via their effect on postprandial hyperglycemia (Cao et al., 2018). Furthermore, it has been reported recently that grape pomace polyphenols and other food polyphenols improve insulin response in clinical studies (Costabile et al., 2019; Liu et al., 2019).

Thus, diabetic rats fed with a diet supplemented with a powdered product made from red wine pomace for three months exhibited improvements in several diabetic symptoms, such as polyphagia, polydipsia, weight loss, glucose levels, insulin, atherogenic cholesterol profile, and oxidative damage to plasma biomolecules (Del Pino-García, 2016c). The increase observed in antioxidant gene expression was proposed as a possible mechanism of action for the wine pomace bioactive compounds, including phenolic metabolites and SCFAs (short-chain fatty acids). The dietary fiber, it is known that has a potential antidiabetic mechanism, by their beneficial effect on satiety, decreasing postprandial glycaemia and improvement of insulin sensitivity among others. In our studies, the higher production of butyrate observed after four weeks of wine pomace product supplementation in Wistar rats may have played a substantial role in increasing plasma insulin contents and promoting the recovery of normal fasting blood glucose levels (Del Pino-Garcia et al., 2017). These findings agree with those published previously whereby the inhibition of α-glucosidase suppresses postprandial hyperglycemia in diabetic mice after acute grape pomace extract intake (Hogan et al., 2010). Studies performed by Chiva-Blanch et al. (2013) suggest a beneficial effect for the non-alcoholic fraction of red wine (mainly polyphenols) in insulin resistance, with significant reductions (22-30%) being found in the insulin-resistance index, which is a measure of the sensitivity to this compound. This suggests a positive effect of phenols on glucose metabolism, with alcohol appearing to have little effect in this regard. It is well known that alcohol itself induces oxidative stress but that wine polyphenols appear to counteract this effect (Estruch et al., 2014). In agreement with this, Muggeridge et al. (2019) have also indicated recently that postprandial oxidative stress appears to be counteracted by the ingestion of wine polyphenols (Muggeridge et al., 2019).

2.4.3. Effect on Metabolic Disorders of Obesity

The prevalence of overweight and obesity, and their associated metabolic disorders, is currently considered to be a major threat to public health. Oxidative stress and systemic inflammation are some of the factors that contribute to the pathogenesis of obesity (Karam et al., 2017). As such, antioxidant therapy could be an important strategy for treating obesity-related disorders. In this sense, polyphenols derived from foods have been studied for use as modulators of these disorders. Indeed, there is good evidence for the effect of dietary polyphenols in decreasing inflammation and other obesity-related disorders (Wang et al., 2014; Dallas et al., 2014).

A recent study by our group (Gerardi et al., 2020c) has evaluated the potential beneficial effect of a red wine pomace product against obesity-related disorders in Wistar rats fed with a high-fat diet. The consumption of powdered wine pomace product by these rats reduced the liver levels of biomarkers for oxidative stress (carbonyl groups (CGs) and MDA) (Table 6). Similar results were obtained for plasma biomarkers and inflammation markers.

These findings agree with previous studies in which the supplementation of diet-induced obese mice with grape seed flour was found to ameliorate the immune response, oxidative stress and inflammation (Urquiaga et al., 2018).

Other factors involved in obesity disorders include changes in the gut microbiota, which are considered to be involved in cardiometabolic disorders. Low bacterial levels are associated with increased dyslipidemia, adiposity and inflammatory processes (Canfora et al., 2019). Some authors have suggested that polyphenols may modulate the microbiota to increase the mucin secretion and decrease oxidative stress, thus creating a beneficial environment for the microbiota (Ozdal et al., 2016). Furthermore, it should be remembered that polyphenols are mainly metabolized by the colonic microbiota, which form bioactive metabolites that could induce anti-inflammatory responses, such as inhibiting NF-kB and ROS production.

Table 6. Biomarkers of oxidative stress in obese Wistar rats and obese Wistar rats that intake wine pomace product rats

	CG (µmol/mg protein)	**MDA (µmol/mg protein)**
Control	14.75 ±2.06[a]	1.61±0.27[a]
Obese	24.23±2.57[b]	2.01±0.17[b]
Obese + WPP	16.29±2.09[a]	1.56±0.21[a]

Liver carbonyl groups (CG) and malondialdehyde (MDA). Data are presented as mean ± SD (n = 3). Significant differences ($p < 0.05$) among groups are indicated with Latin letters.

2.4.4 Antimicrobial Activity Against Pathogenic Microorganisms

Different microorganisms may be involved in foodborne outbreaks with different degrees of frequency and severity. Listeriosis is the primary cause of death by foodborne pathogens and presents a very high mortality rate, with a relatively large number of confirmed listeriosis cases being reported in the European Union each year. Listeriosis is mainly caused by the presence of *Listeria monocytogenes*, a Gram-positive bacterium, in smoked fish, cheeses, and ready-to-eat meat products. *Escherichia coli*, a common Gram-negative bacterium in the human gastrointestinal tract, also causes a very large number of confirmed cases in the EU each year. Pathogenic strains of *E. coli* may cause urinary tract infections, diarrhea, respiratory problems, and other illnesses associated with the consumption of food or water contaminated with feces. Staphylococcal intoxication is a less common cause of bacterial food poisoning compared with listeriosis and *E. coli*. However, the presence of heat-stable enterotoxins produced by *Staphylococcus aureus* is responsible for several hundred foodborne outbreaks every year in a wide range of foods, such as cheese, meat, and bakery products (EFSA, & ECDC 2015).

Different phenolic compounds widely found in grape products are known to have antimicrobial activity, therefore grapes, wine, and their derived products may be an interesting source of natural products with antimicrobial activities. Non-flavonoid compounds, mainly phenolic acids, are mainly responsible for the antimicrobial activity of grape products. The antimicrobial activity of grape products has also been suggested to be due to flavonoids (flavan-3-ols and flavonols), with significant contributions from non-flavonoid compounds (phenolic acids and stilbenes) (Friedman et al., 2014). Flavan-3-ols have been reported to be highly effective against *Campylobacter jejuni* and *Campylobacter coli* (Mingo et al., 2016). Using pure compounds, these authors concluded that epicatechin gallate (ECG) was mainly responsible for this antimicrobial action given its low minimum inhibitory concentration (MIC) (10 mg/L) and minimum bactericidal concentration (20 mg/L). However, no galloyl catechins failed to inhibit *Campylobacter* growth, thus indicating the relevance of the galloyl group for antimicrobial activity, as pointed out previously (Scalbert, 1991). ECG and epigallocatechin gallate (EGCG) have also been suggested to be the most effective compounds for inhibiting *Staphylococcus aureus*, *Salmonella*, *Escherichia coli*, *Vibrio* and other Gram-positive bacteria (such as *S. aureus*), whereas they appear to be less efficient (MIC = 800 mg/L) against Gram-negative bacteria due to the presence of an external lipopolysaccharide that prevents or hinders adhesion of active compounds to the membrane (Yoda et al. 2004). Furthermore, flavan-3-ols are also able to inactivate enzymes within the cell, such as those responsible for the synthesis of membrane fatty acids (Zhang et al., 2004).

Other flavonoids, such as flavonols and flavones also show antibacterial activity, although their effectiveness is usually lower than those of flavanols. The relevant role of quercetin and rutin in the anti-listerial effect of wine, and the effectiveness of quercetin, rutin and morin against *S. aureus*, has also been described (Xu et al., 2014; Amin et al., 2015). Contradictory information is available as far as anthocyanins are concerned, with some studies (Cisowska et al., 2011) indicating that anthocyanins are more effective against Gram-positive than against Gram-negative bacteria and that both membrane and intracellular interactions are involved in their underlying antimicrobial activity, whereas other studies (Mingo et al., 2016) suggest little or no antimicrobial activity for wine pomace anthocyanins.

Polymeric compounds can also play a relevant antimicrobial role. For example, Rhodes et al. (2006) reported that the polymeric fraction (molecular weight < 12-14 kDa) of grape extracts showed the strongest antimicrobial activity against *Listeria monocytogens*, *S. aureus* and *E. coli*. The antimicrobial effect of tannins is most likely associated with modifications to the extracellular medium, such as the binding of metals such as iron, desaturation of proteins and inhibition of the extracellular enzymes required for microbial growth (Cowan, 1999). Non-extractable compounds present in solid products, such as grape seasoning, can also carry out these actions. Thus, red wine pomace products have shown bacteriostatic or bactericidal effects against *E. coli*, *S. aureus* and *L. innocua*, with a dose-dependent effect (García-Lomillo et al., 2017b).

In general, higher antimicrobial activities have usually been reported for grape seed extracts than for skin extracts. For example, seeds extracts have been shown to present a more intense bactericidal effect against *S. aureus* than grape skins (Rhodes et al., 2006; Xu et al., 2014). Several authors explained this fact by considering the higher phenolic content of grape seeds and the presence of other families of antimicrobials, such as sterol, which are also present in grape seed products (Lorenzo et al., 2014). However, other authors noted a probiotic effect of some grape seed products due to the presence of fiber and other specific constituents (Alberto et al., 2001), grape variety (Katalinić et al., 2010), the growing practice applied to vines (Corrales et al., 2010), and the procedures used to obtain the grape derivatives. For example, Oliveira et al. (2013) noted that a supercritical CO_2 extract presented a more intense activity against *S. aureus, Bacillus cereus, E. coli* and *Pseudomonas aeruginosa* than those obtained by Soxhlet extraction or ultrasound-assisted leaching. Similarly, these authors observed a significant effect of temperature and pressure. In general, pure compounds have a much lower activity than wine and grape products, thus suggesting a synergic effect for the combination of phenolic compounds (Silvan et al., 2013; Xu et al., 2014).

A beneficial effect of grape products against pathogens has also been observed in their ability to regulate the intestinal microbiota in several different diseases. A high fat diet causes changes in the composition of the microbiota, thus facilitating the growth of harmful microorganisms (Yang et al., 2019). Recently, we have observed that the consumption of wine pomace product by obese rats fed with a high-fat diet modulated their microbiota, reducing pathogenic bacteria such as *Bacteroides* spp and increasing beneficial bacteria such as *Lactobacillus* spp. This modulation is in agreement with that observed by other authors in obese rats, who obtained a reduction in the levels of pathogenic bacteria along with an increase in the beneficial intestinal microbiota, especially *Bifidobacterium* spp and *Lactobacillus* spp (Ozdal et al., 2016; Yang et al., 2019; De Bruyne et al., 2019). This increase in beneficial bacteria is known to regulate the presence of pathogens in the intestinal microbiota. *Bifidobacterium spp*. is known to inhibit the growth of pathogenic bacteria (Saulnier et al., 2009), and *Lactobacillus* spp. reduces intestinal permeability, thus hindering the entry of pathogens, and improves the immunological functions of the intestine, thereby mitigating the intestinal inflammatory response (Hervert-Hernandez et al., 2011).

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Chapter 4

OVERVIEW OF THE RECENT INNOVATIONS IN *VITIS* PRODUCTS

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ABSTRACT

There are currently about 68 different species of the genus *Vitis*, with a wide variety of morphological and physiological characteristics,

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however, all plants of this genus are lianas, woody, or climbing vines. Grapevines are one of the most economically important crops in the world. Indeed, the growing consumer demand for sustainably produced with numerous nutritional benefits healthy food has grown the market for products obtained from the grapevine, such as table grapes, raisins, and infusions, besides, the leaves in gastronomy. This chapter aims to review the biology and anatomy of the most important *Vitis* species, overview the recent innovations in *Vitis* products worldwide. It will also be taken into account the development of products using grapes and grape products and how scientific knowledge increased the ability to respond to the challenges that have emerged with the new consumer trends.

Keywords: anatomy, gastronomy, grapes, histology, infusions, physiology, spirits, vinegar, *Vitis vinifera,* wine

1. Introduction

The genus *Vitis*, one of the 16 genera in the Vitaceae family, has about 68 different species (The Plant List, 2013), predominantly in the temperate and subtropical climate zones of the Northern Hemisphere, mainly distributed in Norte America (~ 20 species) and Asia (~ 40 species) (Mullins et al., 2003; Wan et al., 2008a; 2008b; Keller, 2020). Since they are the result of specific adaptations to different geographic areas, with their ecological climatic conditions, each species of *Vitis* can be considered ecospecies defined as a population that differs from each other through their own morphological and phenological characters.

Within this genus, two large groups of vines are distinguished by their agronomic characteristics: the American group and the Eurasian group.

American Group: Comprise several species that became economically important to the production of wine and grape juice. For their resistance to pests and diseases, some species of this group are used as rootstocks or in breeding programs. Some of the more important species from this group are the *Vitis lambrusca* L., *Vitis aestivalis* Michaux, *Vitis riparia* Michaux, *Vitis rupestris* Scheele, *Vitis berlandieri*, *Vitis candicans* Engelmann and *Vitis cineria* Engelmann (Keller, 2020).

Eurasian Group: About 40 species have already been described in this group, although some are little known. A large part of these species is found in eastern Asia. The Eurasian species *Vitis vinifera* L., native to Asia near the Caspian Sea, has been imported to Europe and gave rise to the overwhelming majority of grape varieties cultivated today and dominates the grape and wine trade worldwide. *Vitis silvestris* (Gmelin) Hegi, *Vitis amurensis* Ruprecht, *Vitis coignetiae* Pulliat, and *Vitis romanetii,* are other species that are included in this group (Keller, 2020).

2. *VITIS* MORPHOLOGY AND ANATOMY

2.1. *Vitis* Morphology

Nowadays, a large part of the cultivated grape varieties was originated from the Eurasian species *Vitis vinifera* L. The *Vitis* genus species are liana with a large elongation capacity, polycarpic and deciduous. However, some species, such as *Vitis rupestris* and *Vitis monticola*, whose character is more shrub, of erect size, and with many shoots and branches, do-not have the characteristics of a climbing plant so marked (Magalhães, 2008).

There are several vine training systems. The most traditional is the "latada" or trellised vine, also known as a pergola. In this system, the vines are training horizontally along wires with inert tutors for support (Magalhães, 2008). Being a liana, the trunk of this species is sufficiently flexible during the first years, which allows it to correct its position according to the training systems. However, as age advances, the trunk increases in volume, losing flexibility, although this is not the rule, dispensing tutors to support the stems and their production (Keller, 2020).

As a whole, the constitution of the grapevine is quite simple (Figure 1). It consists of a belowground part, the root system and, in the aboveground part, the trunk, shoots, leaves, tendrils, clusters with flowers or berries, being the roots, trunk, and the horizontal arms, called cordons, the permanent structures of vine (Zabadal, 2002; Keller, 2020).

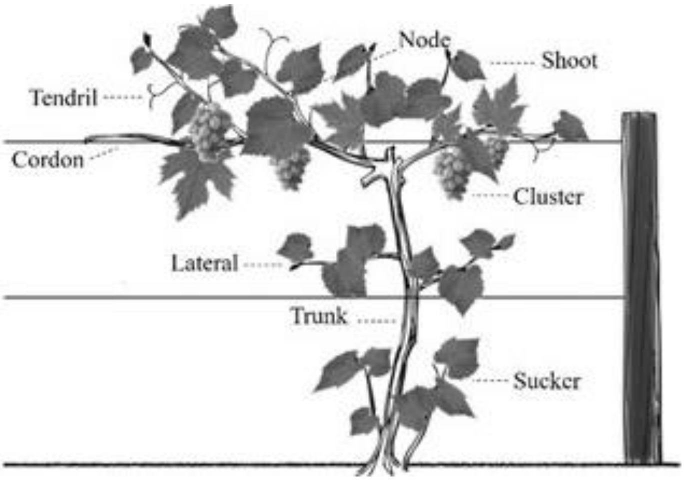


Figure 1. Grapevine structures.

2.2. *Vitis* Anatomy

2.2.1. Roots

The grapevine root system performs several functions as a result of the different tissues that comprise, such as physical support to the vine to the soil; water and nutrients uptake; synthesis and storage of phytohormones, mainly cytokinins and gibberellins (Magalhães, 2008; Keller, 2020).

The form of the root system developed from seeds tends to form a primary root or taproot with a major axis, from which several secondary roots are formed. In grapevines obtained by clonal propagation, the main roots developed directly from a cutting, from these, secondary roots are formed (Mullins et al., 2003; Osmont et al., 2007).

Structurally, the root has a more or less cylindrical shape. The root tip consists of (i) a root apical meristem that allows the root to grow, protected by a root cap; (ii) a zone of elongation growth; and (iii) a maturation zone where root hairs are formed, increasing greatly absorption of water and minerals (Figure 2A). The young roots are protected by the epidermis, but as the root develops, the epidermis dies and is replaced by the exodermis giving the brown color to the root.

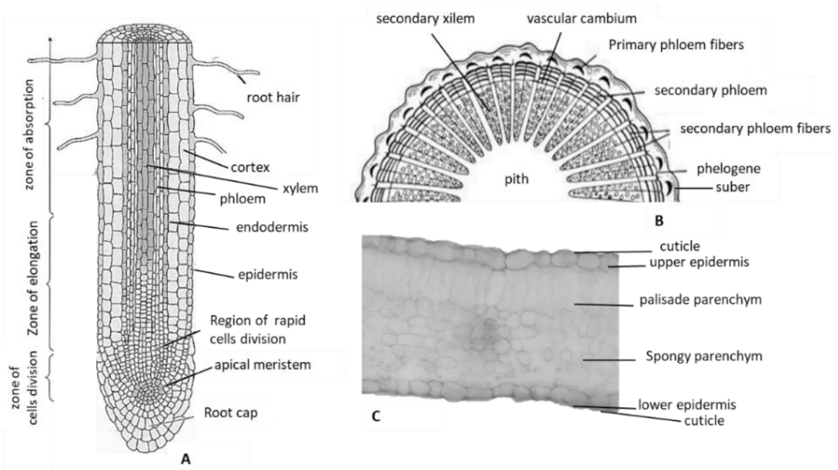


Figure 2. Schematic representation of the apical region of the root (A) (adapted from Taiz and Zeiger, 2010), stem (B) (adapted from Esau, 1948), and a cross-section of a mesophyll leaf (C).

Concentrically from the outside, a root is formed by the epidermis, followed by the cortex formed by parenchyma cells, and the endodermis which contains the Casparian strip, a layer of cells with thickened cell walls that regulate solute transport. The cortex is responsible for nutrient uptake from the soil and the storage of starch and other nutrients. In the vascular cylinder are groups of specialized cells organized into a vascular system, constituted by the xylem, responsible for the movement of water and mineral salts, and phloem that transports the products of photosynthesis (Mauseth, 2017).

The secondary structure of the root appears as a result of the formation of two secondary meristematic tissues, the vascular cambium, and the phellogen. So, as the roots grow, procambial cells develop into the vascular cambium, which forms new, secondary phloem cells toward the outside and secondary xylem cells toward the inside.

In the late spring of the first year, the periderm is formed replacing the dead epidermis (Magalhães, 2008). The periderm consists largely of protective cork and also includes phellogen, and a phelloderm, a living parenchyma tissue (Raven et al., 1992; Mullins et al., 2003).

2.2.2. Stem

The stem comprises the trunk, arms, and shoots (Figure 1). In fact, in the aerial part of the grapevine, a trunk branch into several arms whose disposition depending on the training system established by the winegrower. In the turn of their arms, some lignified grows are formed, normally of small dimensions, until the formations of the last year, called shoots or canes (Magalhães, 2008). These shoots arise from the development of the primary buds that are normally the fruit-producing shoots on the vine (Hellman, 2003), and consists of a succession of internodes and small more prominent areas, nodes with the buds, where the leaves, clusters, and tendrils were inserted during the active phase of the vegetative cycle (Magalhães, 2008). The nodes are protuberance in the shoot that separates the internodes and where lateral organs of the shoots, such as the buds, leaves, clusters, and tendrils, are attached (Keller, 2020). The internode is the smooth area of a cane between the different nodes (Zabadal, 2002). The length of the internodes along a cane is not constant, it depends, among others, on the edaphoclimatic conditions and water availability of the season (Hellman, 2003), the vine training system, and varietal genetic trait (Magalhães, 2008).

In the herbaceous phase, the shoot has a primary structure, formed by the protective tissue, the epidermis that develops a waxy cuticle on its outer cell walls as a protective layer of all aboveground organs. Underlying the epidermis, a cortical zone develops filled mostly with cortical parenchyma whose cells contain in their vacuoles calcium oxalate crystals (Magalhães, 2008), and phenolic compounds (Keller, 2020). The outermost cells of the cortical parenchyma contain chlorophyll, showing some photosynthetic activity. The vascular system of the young shoot is located in the central cylinder, consisting of the primary xylem and primary phloem (Magalhães, 2008).

In the second-year shoot, it is possible to identify a secondary structure, which results from the activity of the vascular cambium, which is formed in the first place, and from the phellogen, which is formed later in that outer zone (Figure 2 B). At the beginning of the grape ripening phase, the green color of the shoot gives place to the brown color by the formation of the suber that comes to replace the epidermis (Magalhães, 2008).

2.2.3. Leaves

The leaves of the various species and cultivars of the genus *Vitis* differ considerably from each other in terms of shape and morphology (Magalhães, 2008; Keller, 2020). However, most of them present a hand-like shape with three loops (Koundouras et al., 2008; Boso et al., 2011; Monteiro et al., 2013). Leaves are arranged in spiral phyllotaxy in juvenile vines and alternate phyllotaxy in mature vines. The petiole is a stem-like structure that connects the leaf to the shoot, depending on the species and cultivar, its length is variable (Magalhães, 2008). The leaf margins are toothed, each tooth ends in a hydathode, a water-excreting gland (Mullins et al., 2003). The teeth number and their sharpness, in the likeness of the petiole, differ greatly among *Vitis* species and cultivars (Keller, 2020).

Anatomically, the vine leaf is a typical mesomorphic leaf (Karabourniotis et al., 2000). The mesophyll is heterogeneous and asymmetric due to the presence of palisade parenchyma in the upper surface, where the majority of chloroplasts are found, and spongy parenchyma in the lower surface, with a large volume of intercellular space and a small quantity of the chloroplasts (Pinto et al., 2011) (Figure 2C). In the mesophyll, minor veins constituted by xylem and phloem are present and surround by fibers. The major veins of the vascular system are in the midrib of a leaf (Cosme et al., 2018). A dermal tissue, the epidermis, surrounds the entire leaf. Mostly in the abaxial surface of the leaf, epidermal cells transformed into stomata are observed (Vilela and Pinto, 2019), through which the vine makes fundamental gas exchanges in the photosynthetic process. The presence of a cuticle is also observed on the outer walls of leaf epidermal cells (Cosme et al., 2018).

2.2.4. Fruits

The grapevine fruit is classified as a berry because the seeds are protected by a thick pericarp (Keller, 2020).

The berry growth and ripeness are characterized by an evolution of weight and volume and occurs mainly in two distinct phases: herbaceous growth and grape ripeness (Kennedy, 2002). The herbaceous period growth occurs between 45 to 65 days and is characterized by intense metabolic activity, starting with the formation of the berry until the skin color change. The maturation phase begins with the grape color change until harvest (Coombe, 1992).

The berries size differs greatly between grape varieties, even within the same variety or the cluster itself. The berry size can also be influenced by the grapevine nutrition status, soil fertility, and water availability, particularly in the herbaceous growth phase. The berry shape (Figure 3) is characteristic of the grape variety and can be spherical, ovoid, elliptical, or oblate (Magalhães, 2008).

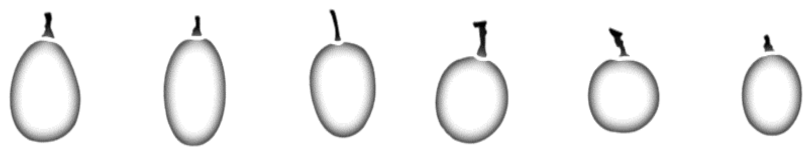


Figure 3. Different berry shapes.

The berries' color depends on the type and amount of phenolic compounds present. Thus, in red grape varieties, these can show more or less intense pink, purple or bluish tones. In white grape varieties, the most common colors are yellowish, greenish, or golden tones (Ribéreau-Gayon et al., 2000; Magalhães, 2008).

From outside to inside, the berry is constituted by the outer exocarp also called skin (heterogeneous region constituted by cuticle, epidermis, and hypodermis), the median mesocarp (thin-walled parenchyma cells with large vacuoles), and the inner endocarp (crystal-containing cells and an inner epidermis). In the middle of the berry appear the seeds involved by the endocarp (Hardie et al., 1996; Magalhães, 2008; Fontes et al., 2011).

3. Grape Valorization

One of the most produced fruit in the world are grapes. In the year 2018, approximately 77.8 million tons were produced (OIV, 2019). They are consumed as both fresh and processed products, such as table grapes (fresh grapes), dried grapes (raisins), grape juice, wine, wine spirits, vinegar, jam, jelly, grape seed extract, and grape seed oil.

In the year 2018, 44.4 million tons of grapes (57%) are used in wine production, 28.0 million tons (36%) are consumed as table grapes, and 5.4 million tons (7%) as dried grapes (raisins) (OIV, 2019).

3.1. Table Grapes

Table grapes are grown in vast areas that include Mediterranean, tropical and subtropical regions. In 2018, the major grape-producing countries were China (9.5 million tons, 35%), Turkey (1.9 million tons, 7%), and India (1.9 million tons, 7%). These three countries account for approximately 50% of the total world table grape production. From 2000 to 2014, an increase of 71% in the table grape production was observed, mainly related to the increase in the production in China, which increased in this period by 80% (OIV, 2019).

The increasing interest in grapes is also associated with the health research literature that refers that they have numerous health benefits. As they are one of the richest fruits in carbohydrates (15 to 18 g/100 g on average) and with relatively high caloric content, their Glycaemic Index (GI8) is quite low (from 43 to 59). They are also considered an excellent source of manganese and vitamins B6, thiamine (vitamin B1), vitamin C, and potassium (FAO-OIV Focus 2016). Furthermore, they are a rich sources of phenolic antioxidants (between 115 and 361 mg/kg total phenolic compounds), contributing to their potential health benefits (Teissedre et al., 1996; Cantos et al., 2002; Pastrana-Bonilla et al., 2003).

There are more than 50 table grape varieties-that are grouped by color and by the presence or absence of seeds. The main table grape cultivars worldwide are ‘Thompson Seedless,’ ‘Red Globe’ and ‘Flame Seedless.’ However, ‘Muscat’ is a major table grapes cultivar in Italy and ‘Chasselas,’ ‘Muscat de Hambourg’ and ‘Alphonse Lavallée’ in France (Vidaud et al., 1993). ‘Thompson Seedless’ (‘Sultanina’) and ‘Flame Seedless’ are the major cultivars in California, which produce 90% of the table grapes in the United States. 'Perlette,' 'Sugraone' ('Superior Seedless'), 'Midnight Beauty,' 'Flame Seedless,' 'Princess,' 'Ruby Seedless,' 'Crimson Seedless' and 'Autumn Royal' are produced in Coachella Valley also in the United States. The phenolic compounds present in red table grape varieties ('Red Globe,' 'Flame Seedless,' 'Crimson Seedless,' and 'Napoleon'), and in the white varieties ('Superior Seedless,' 'Dominga,' and 'Moscatel Italica') were analyzed by HPLC-DAD-MS, by Cantos et al. (2002). These authors detected anthocyanins such as peonidin 3-glucoside, cyanidin 3-glucoside (and their corresponding *p*-coumaroyl derivatives), malvidin 3-glucoside, petunidin 3-glucoside, and delphinidin 3-glucoside, as well as caffeoyl tartaric acid, *p*-coumaroyltartaric acid, and the flavonols quercetin 3-glucuronide, quercetin 3-rutinoside, quercetin 3-glucoside, kaempferol 3-galactoside, kaempferol 3-glucoside, and isorhamnetin 3-glucoside. Flavan-3-ols were detected and identified as gallocatechin, procyanidin B1, procyanidin B2, procyanidin B4, procyanidin C1, (+)-catechin, and (-)-epigallocatechin. Anthocyanins were the main phenolic compounds in red grapes ranging from 69 ('Crimson Seedless') to 151 ('Flame Seedless') mg/kg fresh weight of grapes, whereas flavan-3-ols were the most abundant phenolic compounds in the white grape varieties ranging from 52 ('Dominga') to 81 ('Moscatel Italica') mg/kg fresh weight of grapes (Canto et al., 2002).

The main maturity index for table grapes is the sugar concentration, °Brix. Table grapes are harvested when the grapes reach the optimum acceptability for consumers usually with 15 to 17 °Brix and/or °Brix: titratable acidity ratio greater than 20 (Zoffoli and Latorre, 2011). It has been assumed by several countries a minimum maturity standard to guarantee pleasant grapes for the consumer. However, the value differs among countries. An °Brix of 16 has been accepted for most table grape cultivars. Nevertheless, a 15 °Brix concentration is tolerable in low acid grape varieties such as 'Red Globe' (Nelson, 1985). Another important factor for consumer acceptance is berry firmness. Also, table grapes presented larger berries and firmer pulp in comparison to wine grapes, favoring shipping. Other quality criteria for table grapes are good appearance, free of decay, thin skin, large size, good texture, and flavor (Nelson, 1985).

With the improvement of living standards and enhancement of the public's quality consciousness, the table grape is becoming one of the most worldwide consumed fruit. Indeed, consumption has steadily increased for its pleasant taste and rich nutrition. The fresh table grapes are highly perishable with their, high–moisture content, and nutrients and–are very susceptible to fungi attack causing rots (Tripathi and Dubey, 2004), especially during the hot harvest season. Therefore, quality maintenance during postharvest is a challenge in table grapes. Postharvest technologies and supplier chain management strategies are developed and applied to table grape quality control to avoid potential losses (Costa et al., 2011; Ciccarese et al., 2013). Among those technologies, the cold chain emerged as the vital and broadly adopted technology to preserve the grape's safety and quality. Grapes must be cooled as soon as possible within 12 hours of harvest. After cooling they are moved to a storage room to await transport. A logistics environment (covering storage, handling, and transport) maintained within specified temperature ranges is defined as a cold chain, currently, this concept should be also extended to a consumer's home (Jevšnik et al., 2008; Ovca and Jevšnik 2009, Joshi et al., 2010).

3.2. Dried Grapes

Dried grapes, usually named raisins, are prepared from clean selected fresh grapes of some vine varieties (FAO-OIV Focus 2016), Figure 4.

Raisins are an important grape product. Today, the United States (US) is one of the largest raisin producers and the fifth largest grape producer. According to the OIV report from 2019, Turkey (381 thousand tons, 29%) and the US (263 thousand tons, 20%) are the main dried grape producers followed by China (190 thousand tons, 15%), Iran (150 thousand tons, 12%) and South Africa (71 thousand tons, 6%). Raisin production increased by 10% in the period between 2000 and 2014 (OIV, 2019). The main grape types used for commercial drying are all *V. vinifera* cultivars (Jackson and

Looney, 1999). Dried grape varieties usually presented small, seedless, and early ripening berries that remain soft and not sticky. ‘Thompson’ seedless grapes, first introduced in 1876, account for 95% of the California crop used for raisin production; they are the source of both sun-dried and golden raisins, followed by ‘Fiesta’ (3%) and ‘Zante Currant’ (1.5%). The remainder is produced from ‘DO Vine,’ ‘Muscat of Alexandria,’ ‘Sultana,’ ‘Monukka,’ ‘Ruby Seedless,’ ‘Flame Seedless,’ and ‘Perlette’ varieties (Arthey and Ashurst, 2001).

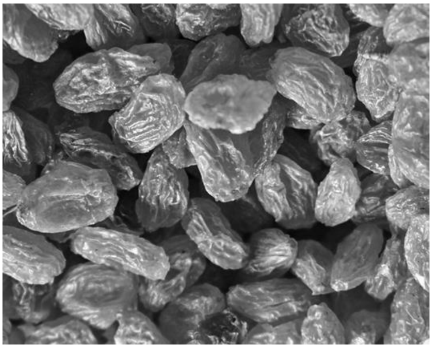


Figure 4. Dried grapes.

The dried grapes quality depends on the grape properties that are influenced by several factors, and some of them cannot be manipulated by grape growers such as the grape variety, the age of vine, soil, and climate conditions, while some others, such as soil management, irrigation management, nitrogen and potassium nutrition, canopy management, insect-pests, and disease management, can be improved by the grape grower. Besides the fresh grapes parameters at harvest, post-harvest factors such as proper handling of harvested bunches, adoption of an appropriate method for grape drying also influenced raisin quality. To get good quality raisins, both physical (berry size, berry color, and the nature of waxy cuticles) and chemical parameters (moisture content, sugar content, and acidity) are important at harvest (Uhlig and Clingeleffer, 1998). For efficient drying, grapes should have a high sugar content of 20–24° Brix. Among technological quality parameters for producing a healthy safe product, microbiological quality is also of essential importance.

One of the most used methods in food preservation is drying that can eliminate moisture content to a low level and reduce microbial and enzymatic degradation or any moisture-mediated deteriorative reactions. Also, drying can take some benefits such as a considerable reduction in weight and volume, minimizing packing, storage, and transportation costs (Xiao et al., 2015). Drying is one of the most frequently used methods for grape processing. Grapes drying is an option to increase the fresh grape's self-life, as they presented high moisture and sugar contents, respire and transpire actively after harvest, and are very sensitive to microbial spoilage during storage, even at refrigerated conditions (Xiao et al., 2010).

The grape drying process could be performed in a different way to respond to the market and the consumer's demands. Differences in the thickness and toughness of the skin between varieties influence the rate of water loss in the raisin drying process (Winkler et al., 1974). The drying methods are the "drying-on-vine," where grapes are dried on the vine directly. Drying in the open sun (traditional method), where grape bunches are spread over either the ground or on a platform in a thin layer directly exposed to the sun (this method can be done also in shade). This natural sun drying and shade drying are still the most common drying methods performed in many countries for grape drying (Pangavhane et al., 2002). Although the investments and operation of natural sun drying are small and simple, it has several disadvantages, such as long drying time (generally taking more than two or three weeks), contamination by dust and insects, laborious to obtain uniform products, and nutrients deterioration caused by long exposure to solar radiation, Figure 5.

Figure 5. Grape drying process.

Many raisins drying and processing modifications are being practiced improving the quality. Consequently, the use of suitable drying technology and the selection of appropriate drying conditions are therefore essential in the production of raisins products. Such as drying under controlled conditions in drying chambers or by using freeze-drying. Grapes that are processed in such a manner, moisture is removed from the product using a very low temperature and vacuum (De Torres et al., 2010). Also, drying in the shed is performed, whose method consists of pre-treated grape bunches that are spread on meshes inside the drying shed and protected from direct sunlight are performed (Ramos et al., 2004).

In grapes drying, the low moisture diffusion rate has become the basic problem during the dehydration process. This problem is due to the thin wax layer that surrounds the grape (Jairaj et al., 2009; Bai et al., 2013). Indeed, the existence of waxes in the skin cuticle becomes drying a difficult task, because the wax layer impedes water loss. So, it is necessary to eliminate the wax layer before drying (Esmaiili et al., 2007).

For raisin processing, pre-treatments including chemical pre-treatment (contain two or three solutions such as NaOH, K_2CO_3, $NaHCO_3$, olive oil, and ethyl oleate solution) (Doymaz, 2006), physical pre-treatment (Kostaropoulos and Saravacos, 1995; Di Matteo et al., 2000; Salengke and Sastry, 2005; Adiletta et al., 2015), and blanching have been investigated and applied to remove the waxy cuticle on the grape skin surface that controls the moisture diffusion rate through the berries and enhance drying rate by increase grape skin permeability to water (Gabas et al., 1999; Pangavhane et al., 1999; Bai et al., 2013).

Drying has a great consequence on the quality of the grape raisins product, such as its color, texture, and nutrients (Yang et al., 2009). In dried grape products a light color is desirable. The extent of browning in the dried product is determined amongst other factors by the activity of the polyphenol oxidase (PPO), particularly in the berry skin. Grape varieties that present a naturally low level of PPO dry to a lighter color (Rathien and Robinson, 1992). The browning in the dried grapes could also be increased by low (<21°Brix) or very high sugar levels (>23°Brix) (Uhlig and Clingeleffer, 1998).

3.3. Grape Juice

The simplest processed product made from grapes is juice. The International Organization of Vine and Wine (OIV) defines grape juice as a grape must that is ready to be used or consumed unfermented with the exclusion of all enological usage. Grape juice concentrate could be obtained by processing grape through partial juice dehydration. The main objective to produce concentrated grape juice is to increase juice stability and at the same time handling and store it easier (FAO-OIV Focus 2016).

The methods for grape juice preparation are very different, from the grape varieties used and local traditions. For white grapes, the juice is extracted from the crushed grapes using a press. The juice is filtered and bottled. It may be preserved either by adding SO_2 or by pasteurization. It is also possible to extract the juice from the grapes after heat treatments, to obtain the solubilization of some compounds. Although the flavor of the juice is better-than cold-pressed grapes, hot pressing can increase yields by as much as 20%. Red grape berries are heated up at 60-63 °C for 10-15 min in stainless steel vats or tubular heat exchangers, to extract anthocyanins (Patil et al., 1995). During this treatment is requested to control the warming to prevent excessive tannins and pectins solubilization from the cluster and the grape skins. For juice extraction, continuous press is recommended. Applying this kind of press, after the heating, treatment with a clarifying enzyme (pectinase) is requested, and then the product pass through the press. Then the extracted juice is pasteurized at 88-90°C, cooled, and stored at low temperature (-2°C to 5°C) to have good sedimentation of the colloids (Dillon et al., 1994). In white grapes juice, browning is one of the most important quality changes (Yokotsuka et al., 1988). The intensity of juice browning depends on the polyphenol oxidase activity (*o*-diphenol oxidase) and the type and concentration of certain phenolic compounds present in the grape juice, namely caftaric acid, (+)-catechin, (-)-epicatechin, and (-)-epicatechin gallate (Sapis et al., 1983). Protein haze could also appear mainly in the grape juice produced from white grape varieties with some unstable soluble proteins (Pocock et al., 1998). Sometimes juice can be clarified with fining agents such as egg albumin (use to remove polymerized tannins related to astringency), casein (used for removing phenolic compounds with low molecular weight) and/or bentonite (used for protein stabilization), or using enzyme treatment (Patil et al., 1995). The clarification process occurs in two steps: enzymatic treatment (depectinization) and fining (to remove haze-causing compounds). Pectolytic enzyme degrades the pectin that would result in pectin-protein complexes flocculating. Afterward, fining agents are added to further flocculation and sedimentation depends upon the ionic charges on protein, polyphenols, and fining agents. Bentonite and gelatin are mainly used in the fining process to remove proteins and polyphenols, respectively (Kulcan et al., 2015).

3.4. Distilled Spirits and Liqueurs

Spirit drinks are beverage products that represent a major channel for the wine industry all over the world. This channel is largely the result of the flavor quality and reputation that these products have acquired on the world market over the years (Christoph and Bauer-Christoph, 2007).

Distillation is a very old technique, discovered by the first alchemists (Plouvier, 2008). In 2000 b. C. the Egyptians already knew the art of distilling well, which only later reached the Mediterranean countries, to the Greeks and Romans. This liquid was mainly produced and used for medicinal purposes and the preparation of perfumes (Léauté, 1990; Plouvier, 2008). According to Plouvier (2008), the distillation process was later developed by the Arabs and it was from the Arabic language that the words “alcohol” and “alembic” were derived.

Distilled spirits have alcoholic strengths between 30 and 50%, v/v and are produced by distillation from fermented grapes and/or also from “wine”; their flavor is not only characterized by aroma compounds originating from original grapes and the alcoholic fermentation, but also distillation, storage, and aging. Liqueurs are spirits with an ethanol content of 15%, v/v, and sugar content of 100 g/L. They can be produced by flavoring ethanol of grape origin, with natural plant materials such as fruits, fruit juice, herbs, cream, chocolate, steam-distilled essential oils, distilled spirit drinks, or natural/ artificial flavoring extracts (Christoph and Bauer-Christoph, 2007).

A very known spirit is Armagnac (the oldest *eau-de-vie* of France). Cognac is more popular outside France and is mainly appreciated by the absence of defects (Cantagrel et al., 1993). These two grape-based Eaux-de-vie are similar in many respects but, each has its own identity. The first difference between Cognac and Armagnac is terroir. The base ingredients of a spirit produce the flavor, but where that raw material grew dictates terroir. It's about the composition of the local soil, climate, and even cultural practices. Armagnac and Cognac terroirs, both in the Nouvelle-Aquitaine region, are located some 300 km from each other, which means differences in the soil and climate. Under Armagnac, there are fine quartz sands, continental and riverbed sediments, and siliceous clay. This terroir is divided into 3 crus: Bas-Armagnac or Black Armagnac characterized by siliceous clay land which is poor in limestone, occasionally acid; Haut-Armagnac or White Armagnac, characterized by soils which are predominantly limestone except along its southern part where soils are siliceous clay and the Ténarèze, a land of transition where the vine is grown on clay and limestone soils (Burnez, 2016).

Cognac soils are mainly limestone and Cognac is divided into 6 crus: Grande Champagne, where is produced the finest Cognac Eaux-de-vie; Petite Champagne, sits astride the Charente and Charente-Maritime departments; Borderies, a small production area around the village of Burie; Fins Bois, located on the periphery of the three aforementioned areas and where the majority of the wines are produced (42%); Bons Bois and Bois Ordinaires (Burnez, 2016).

In Cognac, 97% of the grape variety used is Ugni-Blanc. In the Armagnac region, a blend containing Ugni-Blanc (55%), Folle Blanche (2%), Colombard, and Baco (a hybrid of Folle Blanche and the American Noah), is used, which produces well-rounded *Eaux-de-vie* with a ripe fruit aroma (35%). The differences in the use of the grape varieties in these two regions come from the fact that in the Armagnac region, wine is produced intended for consumption without being distilled. This is not the case in

Cognac, where the highly-acid wine is not pleasant if left unaltered (Burnez, 2016).

Another difference between these two spirits is the distillation method. Most Armagnac is obtained using the Armagnac continuous still (Figure 6), while Cognac is obtained by distilling with the Charentais still (Figure 7). The *eau-de-vie* obtained at the end of the distilling process has an alcohol content between 52% and 72% (Burnez, 2016).

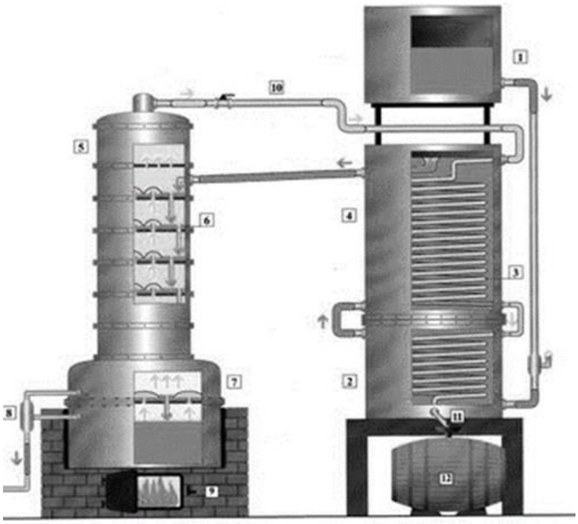


Figure 6. Constitution of the Armagnac continuous still. 1-wine vat, 2-cooler, 3-serpentine, 4-wine heater, 5-column, 6-distillation plate, 7-boiler, 8-wine residue drainage, 9-furnace, 10-swan´s neck, 11-spirit flow, 12-Armagnac barrel. Adapted from Burnez (2016).

On the other hand, distilling with the Charentais still comprises two distillations cycles (Figure 7). The first heating cycle results in alcohol between 20-30 degrees called "brouillis," which will be redistilled during the second cycle known as "bonne chauffe" at 70-71 degrees. This last distillation will become Cognac. Cognac and Armagnac are high-quality spirits that are aged in permanent contact with Limousin oak (*Quercus robur*) barrels over the years, acquiring the color and bouquet that make them unique. A similarity is that labels on Cognac and Armagnac bear the same references attesting to the number of years of aging: VS Very Special:

young; VSOP Very Superior Old Pale or ***; Napoléon or XO (Extra Old): aged for 6 years at least; Hors d'Age: aged for 10 years at least; Millésime: from a single harvest and XO Premium: aged for over 20 years (Burnez, 2016).

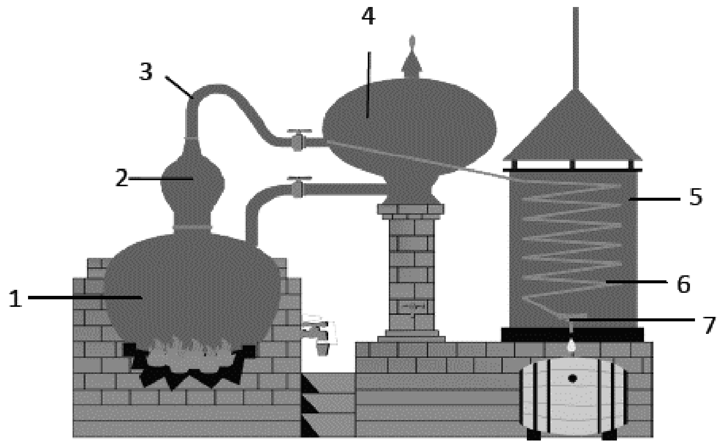


Figure 7. Constitution of the Alembic Charentais. 1-boiler, 2-hat or capital, 3-swan neck, 4-wine heater or preheating, 5-condenser, 6-coil, 7-door-alcoholometer. Adapted from Alves de Mira (2009).

In Portugal, the French distillation processes are also used (Figure 7) and aging is normally carried out in oak wood barrels (Alves de Mira, 2009).

In Portugal, five regions produced aged wine spirits entitled to Denomination of Origin (O.D.): Lourinhã, Vinhos Verdes, Ribatejo, Douro, and Bairrada, and the grape varieties allowed for the production of wine in each of the regions are mentioned (Belchior, 1987a; 1987b).

The influence of the wood characteristics and the phenomena involved in aging are important steps to obtaining a wine spirit with superior chemical and sensory qualities. The wood characteristics are strongly conditioned by several factors: the wood botanical species and its geographical origin and the level of toasting of the barrel. Together and accounting with the aging time, hydroalcoholic environment, technological operations carried out, the size and state of use of the wood barrels, and the conditions of the wine-cellar, are important parameters that determine strongly the chemical and sensory characteristics of the spirits (Belchior et al., 2001; Canas et al., 2002; Canas, 2003; Caldeira et al., 2006; Canas et al., 2008).

Besides wood, the wine characteristics to produce wine spirits are relevant for their chemical and sensory quality. They are different from the wine characteristics for consumption. Wines intended for the manufacture of wine spirits must have a flawless flavor and a fine-developed aroma (Léauté, 1990; Cantagrel, 2008). The production of good spirits requires wines from healthy grapes which will allow its conservation for some months without the need to apply sulfur dioxide (Belchior, 1987a; 1987b). According to several authors (Belchior, 1987a; 1987b; Léauté, 1990; Jurado et al., 2008), the distillates of best quality wines are those that do not contain sulfur dioxide. During the distillation, their presence in wines causes~~,~~ the formation of mercaptans, which impart unpleasant aromas to the Spirit (onion, garlic, among others).

Moreover, the titratable acidity of the wine must be greater than 4g/L (expressed as g/L tartaric acid) to ensure microbiological stability and, thus, protecting and conserving wine until the moment of distillation (Belchior, 1987a; 1987b; Garreau, 2008). However, according to Garreau (2008), it is not uncommon to find musts intended to produce Armagnac with a pH below 3. The high acidity during distillation seems also favor the hydrolysis of some wine constituents, which give rise to the releasing of aromatic compounds from the terpene group, giving the spirits specific floral aromas and it seems to promote, also, the formation, in small amount, of ethyl acetate (Ferrari et al., 2004; Ledauphin et al., 2006).

The alcoholic strength of wines for distillation should not be high since musts with high sugar content usually give rise to wines with a higher volatile acidity, which can pass to the distillate a vinegar aroma. Besides, wines with a low alcoholic strength also originate spirits with an alcoholic strength slightly lower. Thus, constituting a quality factor, because to produce the same amount of distillate, a greater volume of low alcohol wine is required, causing a greater concentration of aromatic substances (Léauté, 1990; Garreau, 2000; Cantagrel, 2008).

The tannin content of the wine to be distilled should be low, as high concentrations of these compounds are responsible for the astringency, roughness, and bitterness of the distillate. Early distillation of wines is also recommended to avoid changes caused by bacteria and/or yeast, or by oxidation during conservation. According to Belchior (1987a; 1987b), to obtain quality spirits, oxidation reactions in wines should not occur, therefore it is advisable to distill wine as soon as finish the fermentation. In both Portugal and France, wines must be distilled until the 31st of March, since from this time, due to the heat, it is already quite difficult to preserve them (Garreau, 2008).

In Portugal, a wine spirit made from the distillation of wines, also known as “aguardente”, is used in Port wines fortification. Although ” aguardente” constitutes around one-fifth of the volume of Port, it was found by Pissarra et al. (2005) and later, by Rogerson and Freitas (2006) to be the major contributor of aromatic compounds including α-terpineol (76 to 91%); linalool (58 to 91%); benzaldehyde (87 to 94%) and esters such as ethyl hexanoate (81 to 90%), ethyl octanoate (94 to 98%); ethyl decanoate (98 to 99%) and ethyl hydrocinnamate (100%). “Aguardente” volatiles makes an essential contribution to young Port wine aroma, adding flower, fruity, balsamic, and spicy aroma complexity.

Another interesting spirit is Grappa. It is of Italian origin (northern Italy, rooted in Piedmont, Trentino, Veneto, Lombardy, Friuli, and Sardinia) and it is the only distillate from the residue originated after pressing of the grape wine, named marc. Grappa probably owes its name to the grape stalk, used as raw material for its production, with the skins. The term Grappa appears officially until the end of 1800, and, in the same century are codified procedures for its production (Distilleria Castelli, 2020).

Mainly two types of marc are sent to the distillery: fermented and non-fermented (virgin). The former has an alcoholic content because it has fermented with grape must, whereas the latter is nearly always white and, save for rare exceptions, not fermented with the grape must. Therefore, it is up to the distiller to ferment it most suitably before distilling it.

There can be used several processes of distillation that have evolved through time (Poli Grappa Museum, 2020), Figure 8.

3.4.1. The Artisan Still

The still used in the artisan distillation is the discontinuous type since at the end of every boiling of the marc, the cycle must be interrupted, and the pot emptied and then refilled with other new marc. As well as being a traditional choice for Grappa making, the use of the discontinuous still enables a higher quality product to be obtained compared to the continuous still used in industrial production.

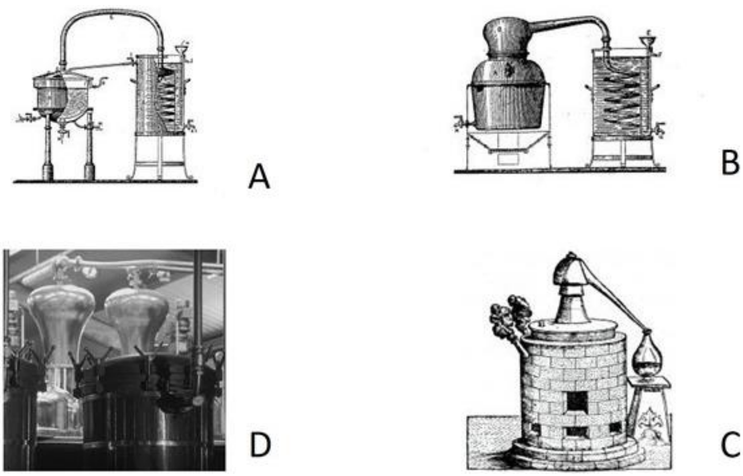


Figure 8. Figure representations of the stills used in the Grappa process.
A - The Artisan Still; B - The direct-fire still; C - The bain-Marie or double boiler still and D - The Steam still. Adapted from Poli Grappa Museum (2020).

3.4.2. The Direct Fire Still

This traditional still consists of a copper pot of medium or small capacity with a mouth for adding the marc and a capital at the top. This, in turn, is connected to a tube, called gooseneck, to make the vapors flow into a coil immersed in cold water and be condensed. The copper pot used to contain the marc is placed in a masonry furnace at a suitable height so that the fire or naked flame can be lit under it. This still is hard to manage because it is difficult to control the temperature of the fire and therefore it is easy to "toast" the marc with too much flame thus obtaining Grappa with unpleasant fragrances.

3.4.3. The Bain-Marie or Double Boiler Still

As the name implies, this still uses the very old bain-Marie or double boiler method. In this case, the boiler has a double wall; in the interspace, there is steam or very hot water that heats the marc placed inside the boiler. The ethyl alcohol and the substances contained in the marc evaporate, pass through the distillation column, and are then condensed into a coil. Cutting off the heads and tails also occurs here. This still is very widely used, especially in the Trentino and Upper Adige regions, and ensures a very gentle extraction of the marc aromas. It is commonly used to distill fruit and grapes.

The Steam Still

This still dates to around the mid-19th century and is certainly the most widely used today for making Grappa in an artisan way. It consists of a series of copper pots inside which the marc is put on perforated copper baskets, thus preventing it from being squashed due to the weight.

The adjustable flow of steam is gently blown at the bottom of each pot and passes through the marc, thus extracting the alcohol and aromatic substances. These alcoholic vapors are made to pass through the distillation column, which enables the concentration of the alcohol and the aromas.

The alcoholic vapors flow into a coil immersed in cold water and are condensed. Also, in this case, cutting off the heads and tails is done by the distiller, according to the temperature and alcoholic content of the liquid coming out.

The optimum graduation of Grappa is about 75 degrees but the lowest alcoholic gradation allows to better preserve the primary aromas of the grape. Also, the use of marc from a single grape has its importance once the use of marc of single grape varieties, suitably aged, gives great quality.

Aging can be a minimum of six months while the maximum age can reach 20 years or more, at the discretion of the manufacturer who decides on the quality of the distillate (Distilleria Castelli, 2020).

Pisco, another spirit, is a South American high alcoholic drink. Both Peru and Chile export Pisco, and both countries claim to be the original producers of this spirit. Pisco is made only from certain grapes varieties, brought to South America from Spanish conquistadores, which are fermented and distilled into a potent “aguardiente.” It is the essential ingredient in the famous pisco sour and is even celebrated with a national Pisco Sour Day (Dia del Pisco Sour) in Peru. The resulting liqueur or “aguardiente” is briefly aged and then bottled. In Peru, pisco is never diluted, according to the very strict, specified rules governing its production. In Chile, pisco is sometimes mixed with distilled water to reach the desired alcohol content (The Spruce, 2020).

Distilling pisco from freshly fermented grape juice is done in a small batch traditional pot still – either an alembic or falca still.

The traditional copper alembic pot still is more commonly used by Pisqueros in Peru. Each alembic is made by hand by a specialist craftsman who will make the copper pot still to meet the specific instructions of the master distiller. The alembic has a pot, where the grape ‘mosto’ (juice) is heated, a swan neck where the vapors rise and reflux, a line arm that transfers the vapor to the condenser, and a condenser that cools the vapor to yield the pisco distillate of between 38 – 48% alcohol by volume (ABV) from a single distillation.

In contrast to the alembic, the ancient falca (flat top) still contains a percentage of gold in the copper to create better quality pisco. These falca stills are housed in concrete and brick at ground level, leading below ground to the body of the stills and the heat source. Falcas do not have a swan’s neck – instead, they have a near-horizontal ‘canon’ that captures the distillate *en route* to the condenser (Figure 9).

According to The Pisco People (2020), the type still used in the distillation process can affect the aroma as well as the flavor of the pisco. Pisco produced in a copper alembic still tends to have a cleaner aroma and taste because the swan neck does a better work of removing impurities from the distillate, including agricultural chemicals that have been used in the grape-growing process. In contrast, the falca stills tend to concentrate the aromas and flavors producing pisco with more body as well as conserving more of the subtle aroma of the grape variety.

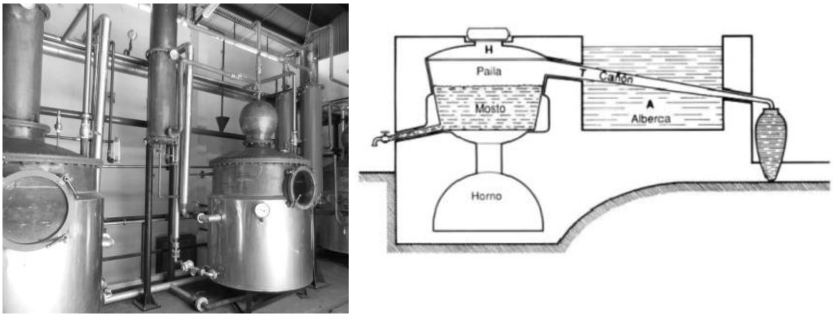


Figure 9. Representation of the flat top still housed in concrete and brick at ground level, leading below ground to the body of the stills and the heat source. Falcas have a near-horizontal ‘canon’ that captures the distillate *en route* to the condenser. Adapted from The Pisco People (2020).

3.5. Grape Infusions

Grape infusions made from dried leaves or dried grapes can be a profitable valorization of vineyards’ by-products. Winemaking leads to the production of by-products considered organic wastes like pulp and skins, grape pomace, seeds, grape stems, and grape leaves (Oliveira et al., 2013). One application, in the beverage sector, is the use of dried non-fermented/semi-fermented, and even fermented grapes, skins, seeds (Vilela and Pinto, 2019), and leaves (Fernandes et al., 2015) to be used in the preparation of infusions or tisanes.

The fermented/semi-fermented or fermented grapes, skins, and seeds can be dried using an oven, or lyophilized, and afterword’s minced. The dried/lyophilized and minced material can be used to prepare the infusions (Vilela and Pinto, 2019).

The application of grapes to the preparation of infusions or tisanes is particularly interesting when the grape used is a Muscat family grape, with a pleasant aromatic fragrance, mainly due to their high content in terpenes alcohols (Ribéreau-Gayon et al., 1975). On the other hand, red grapes, like Touriga Nacional, can provide a beautiful pink-red color infusion, with some red-fruit flavor characteristics (Rodrigues, 2019).

One characteristic of grape and grape leaves infusions is their important nutraceutical property due to their composition. Grapes and vine leaves contain a wide range of polyphenols including flavon(ol)-glycosides and glucuronides, quercetin-3-*O*-beta-D-glucuronide (most abundant flavonoids), isoquercitrin, anthocyanins, oligomeric proanthocyanidins, (+)-catechin, (-)-epicatechin monomers, and dimmers, and gallic acid. The phytoalexin *trans*-resveratrol, another polyphenolic substance belonging to the stilbene group, can also be found in the grapevine leaves (Xia et al. 2010; Fernandes et al. 2013; Rizzuti et al. 2013).

The potential use of vine leaves for the preparation of herbal infusions or tisanes is dependent on their aroma profile (Fernandes et al., 2015). A vine leaf infusion is soothing and skin conditioning. To make vine leaf infusion, grapevine leaves are added to boiling water and this mixture is strained.

In vine leaves, also appear organic acids mainly, malic, tartaric, and oxalic acid. The latter is an organic acid found in many plants including leafy greens, vegetables, fruits, nuts, and seeds (Noonan and Savage, 1999). In plants, it's usually bound to minerals, forming oxalate. The terms "oxalic acid" and "oxalate" are used interchangeably in nutrition science. The Human body can produce oxalate on its own or obtain it from food. Vitamin C can also be converted into oxalate when it's metabolized (Traxer et al., 2003). Once consumed, oxalate can bind to minerals to form compounds, including calcium oxalate and iron oxalate. This mostly occurs in the colon but can also take place in the kidneys and other parts of the urinary tract. For most people, these compounds are then eliminated in the stool or urine. However, for sensitive individuals, high-oxalate diets have been linked to an increased risk of kidney stones and other health problems (Worcester and Coe, 2010). So, some caution must be taken when drinking infusions prepared with grape leaves extracts.

3.6. Pharmaceutical and Cosmetic Industries

The phenolic compounds present in the infusions or the grape extracts can act as free radical scavengers, helping the human endogenous antioxidant system (Katalinic et al., 2006; Valko et al., 2007).

Besides the antioxidant activity (Yoo et al., 2014; Alov et al., 2015), grape polyphenols also possess anti-inflammatory properties (Działo et al., 2016) and antiviral, antibacterial, and antifungal, activity (Czemplik et al., 2011; Anani et al., 2015).

Moreover, in the semi-fermented grape-skins and seeds (from the fermentation of white wines) or fermented grape-skins and seeds (from the end of the fermentation of the red wines) we can also find nutraceutical compounds provided by the wine yeast metabolism (Guerrini et al., 2018, Vilela, 2019).

Grape extracts can also present insulinotropic and anti-lipogenic effects (Doshi et al. 2015; Nabavi et al. 2015); anticancer effects (Del Pino-García et al., 2016); neuroprotective effects (Mas et al., 2014a) and anti-aging effects (Wittenauer et al., 2015).

So, Viti's by-products can also be used in the pharmaceutical and cosmetic industries (Figure 10). Grape extracts prepared from grape by-products, due to their natural substances compared to chemicals ones, are closer and more recognizable for use in our skin, so they have a very low risk of being recognized as "foreign" and thus cause irritation and allergies. They help to maintain long beauty thanks to the active ingredients mentioned above. On the other hand, they are more biodegradable and thus less polluting than synthetic substances. So, after years of work, many cosmetic companies (Wine Cosmetics, Caudalie, Marks and Spencer, among others) have developed lines of natural cosmetics products based on active ingredients coming from the vine, grapes, and wine.

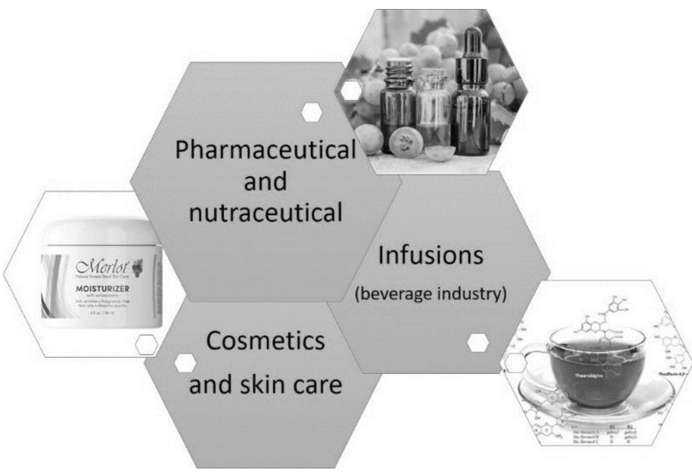


Figure 10. Schematic representation of the main industries that use grape or grape by-products constituents to create health-promoting products.

3.7. Vinegar

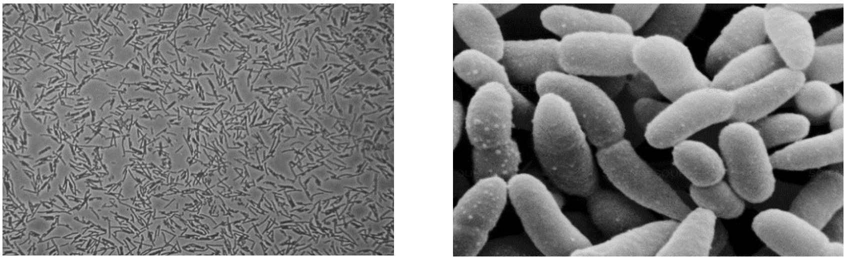
Only a product obtained by bacterial and chemical oxidation of ethanol resulting from the fermentation of grape sugars can be denominated “wine vinegar.” Made with fermented red or white grape juice or wine, wine vinegar has wine-like characters reminiscent of buttery aroma compounds (diacetyl and butyric acid) (Gibson and Newsham, 2018). Better quality and more expensive wine vinegar are matured in a wood barrel for up to 15 years, revealing complex and mellow flavors. Furthermore, wine vinegar can be made using individual types of wine such as champagne, sherry, or balsamic. The most highly prized vinegar comes from Italy (balsamic) and France (sherry), and recently also from Portugal, in that case, a Port Wine vinegar was launched for the first time in the market by a Portuguese company.

Vinegar production dates back at least 200 BC, and it is an explanatory example of microbial biotransformation. Nevertheless, vinegar has been seen as a “waste” in the family of fermented products (Solieri and Giudici, 2009). Since remote antiquity, vinegar has been used as a diet condiment and food preservative, as well as a remedy for people and animals. In those days, its production was considered a chemical process. In 1732, the Dutchman Boerhaave stated that the “mother of vinegar” was a living organism (Solieri and Giudici, 2009) but, it was only in 1864 that Pasteur argued that the transformation of wine into vinegar was due to the development of the veil of *Mycoderma aceti*c on its surface (Solieri and Giudici, 2009).

Wine vinegar can be differentiated by its production systems. In traditional vinegar (Orléans or French method), the oxidation of ethanol into acetic acid is performed by a static culture of acetic acid bacteria (Figure 11) at the interface between the liquid and air. Acetic acid bacteria are a widespread group of gram-negative, obligate aerobic rods which oxidize ethanol (alcohol) into ethanoic (acetic) acid. Occur mainly in sugary, acidic, and/or alcoholic habitats and they play a positive, neutral, or detrimental role in foods and beverages.

They are benign, non-pathogenic microorganisms ubiquitous in the environment, particularly in alcoholic ecological niches such as flowers, fruits, fruit flies, honeybees, and in water and soil. They are generally found as spoilage organisms in alcoholic beverages. *A. aceti* has a long history of safe use in the fermentation industry to produce acetic acid (vinegar) from alcohol. Acetic acid bacteria are classified into the genera *Acetobacte*r, *Gluconacetobacter*, *Gluconobacter*, *Acidomonas*, and the recently described genus *Asaia* (Gomes et al., 2018).

The wood barrels are filled to 2/3 capacity, have side holes for air circulation, and adds a funnel with an extension to the base of the barrel to allow the wine to be added at the bottom of the barrel, preventing the alteration of the "mother of vinegar," that is, the biofilm formed by acetic acid bacteria on the surface. The vinegar produced by this traditional system is generally considered of high quality because of its organoleptic complexity (Figure 12). The vinegar chemical and sensory quality results from the quality of the initial wine; the metabolism of the acetic acid bacteria, which produce oxidation reactions, and ester formations (besides the basic transformation of ethanol to acetic acid); the interactions between the vinegar and the wood and; the aging process, which integrates all of the previously mentioned characteristics (Mas et al., 2014b).



A B

Figure 11. Optic Microscope photography of acetic acid bacteria (A), and *Acetobacter aceti* bacteria. (B) (60x. Photograph by David M. Phillips/Science Source). Enhanced SEM Image. Image from Scimat/Science Source (https://www.sciencesource.com/archive/Acetic-acid-bacteria-SS2388368.html).

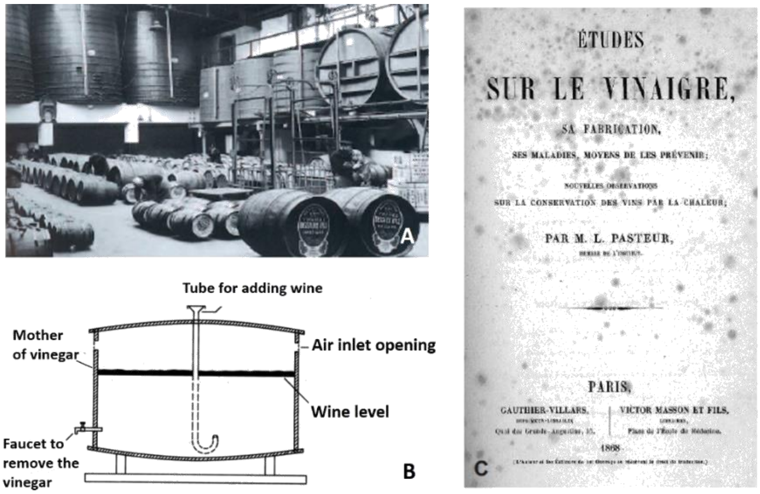


Figure 12. Vinegar brewery in 1950 (A), Orléans barrel details (B) and Studies about vinegar, from Pasteur (1868) (C). Adapted from Mas et al. (2014b).

Pasteur also showed that the oxidation of ethanol to acetic acid by *Mycoderma aceti* involved an uptake of atmospheric oxygen (Pasteur's flat vat). Pasteur foresaw the continuous fermentation process and also the high strength system, both made possible nowadays with the submerged system and computerization (Bourgeois and Barja, 2009).

German rapid acetification system contrast with the Orléans system. This process of acetification was industrialized by Schüzenbach (1793-1869) and was named German or "Rundpump" (round pump) because the wood shavings were continuously sprinkled with the mash by a circulation pump and a rotating sprinkler (Figure 13). The wood shavings served as a support for the bacteria. Wood shavings are still in use. Alternative materials like bines, maize cobs, or rushes are cheaper than beechwood, but not as efficient (Bourgeois and Barja, 2009).

Advances in technology allowed the development of the submerged fermentation process (Figure 14), used firstly to produce antibiotics, and then subsequently to the production of vinegar, thanks to computerization. The Frings Acetator is an example of this advance. Annual production is half a million liters of vinegar at 10% acidity (Bourgeois and Barja, 2009).

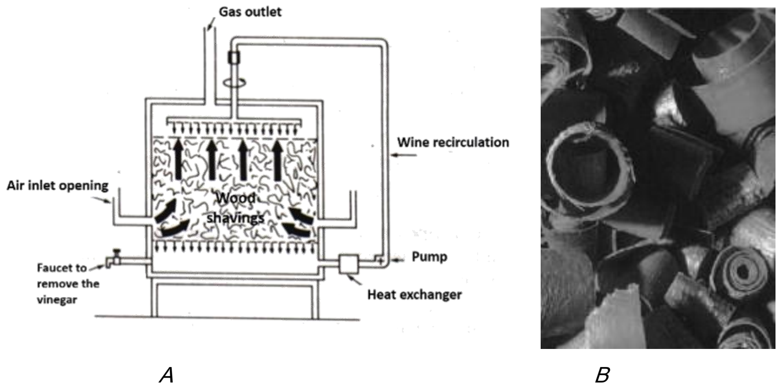


Figure 13. Schematic representation of a German rapid acetification system (continuous system) (A) and a filled with wood shavings (B).

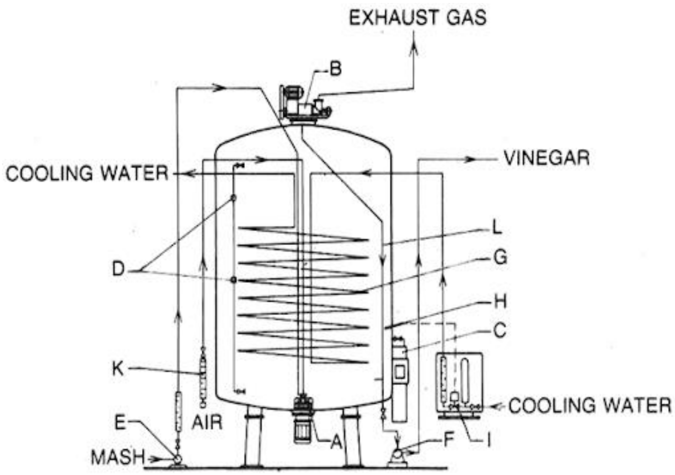


Figure 14. Schematic representation of the Frings Acetator. A – Aerator; B – Defoamer; C – Alkoograph; D – Level switch; E – Charging pump; F – Discharging pump; G – Cooler; H – Temperature gage; I – Cooling water valve; K - Air meter; L – Recycling pipe.

One vinegar nowadays "in-faction" not only for the traditional use but also for use in molecular gastronomy dishes is Balsamic vinegar. It is the slowest acetification system. A minimum of 12 years of aging in wood before use is required. The acetification begins with 70 L of grape juice, which is reduced to concentrate on 30 L by cooking (Lambert, 2010). This concentrate is then poured into a container and left to decant over the winter.

In spring the fermentation begins, and the grape-juice concentrate is poured into the first wood barrel (500 L), where yeasts, mainly from the *Zigossacharomyces* genera start the alcoholic fermentation (Solieri et al., 2013). In the summer, the acetic acid bacteria (mother of vinegar, *Acetobacter aceti*) start the vinegar fermentation. 20 L is then decanted from this large barrel into the first of a diminishing series of 5 barrels, of a different wood type. During the next 12 years, the liquid will evaporate at an average of 10% year. The level of each barrel will be maintained at two-thirds of its capacity by a process of topping up from the preceding barrel (Figure 15). In the 13th year of this, 3 L of mature, aromatic, agri-sweet vinegar is drained off a maximum of 20% of the liquid contained in the last small barrel (Mas et al., 2014b).

The consumer's perception of the vinegar is the most important factor for its consumption. Vinegar is a difficult product to taste, due to the pungency of the high acetic acid content that may mask other flavors, and a vinegar sensory tasting panel requires well-trained tasters, and specific attributes must be chosen for differentiating among samples (Tesfaye et al., 2002). Nevertheless, aromatic compounds have a decisive effect on the quality and consumer acceptance of vinegar. Mas et al. (2014b) reported that more than 100 different chemical compounds in the aroma/flavor of wine vinegar have been identified, including acetals, acids, alcohols, carbonyl compounds, ethers, lactones, phenols, and volatile esters (Callejón et al., 2009). Also, during the aging process, contact with wood generates an increase in aromatic complexity (Callejón et al., 2010). However, the aroma depends not only on the production system but also on the type of wine used. For example, Callejón et al. (2008) verified that Sherry vinegar presents several volatile compounds, such as diacetyl (buttery aroma), isoamyl acetate (banana-like aroma), isovaleric acid (cheese aroma), ethyl acetate (glue), and sotolon, with the characteristic aroma of Tawny Port wines (Ferreira et al., 2019).

Vinegar made or aged in wood has a distinct profile of polyphenolic compounds, which in addition to their antioxidant activity, are responsible for the vinegar color and astringency (Mas et al., 2014b). Acetification is an aerobic process, and oxygen is critical to the growth of the bacteria. The rate of acetification is related to the oxygen solubility in the medium, it is also a decisive factor in the phenolic composition that can be used to choose the acetification method. Submerged systems, like the Frings Acetator, uses excess oxygen to safeguard and accelerate the process, while oxygen is limited in superficial cultures (Orléans method) because it is continuously taken up by acetic acid bacteria. Moreover, oxygen affects the classes of polyphenolic compounds; the flavonol content is largely influenced by oxygen availability during submerged fermentation, while surface acetification systems do not affect phenolic aldehydes, which are released from wood barrels into the vinegar (García-Parrilla et al., 1998).

Figure 15. A bottle of Balsamic vinegar and a series of successively smaller wooden barrels, each made from a different type of wood. Retrieved from https://www.simplyrecipes.com/a_guide_to_balsamic_vinegar/, accessed 24th February 2020.

3.8. *Vitis* Uses in Gastronomy

For as long as there has been food, there has been gastronomy. But it wasn't until the 1800s that gastronomy started to develop as an actual field of study and science (The Reluctant Gourmet, 2011). Instead of simply learning how to make food and prepare a meal, people began to focus on how dining could be a sensory experience.

All gastronomies evolve and are a blend of products and traditions. Cooking with wine or vine products exemplify many of the similarities and contrasting characteristics in components, texture, flavors, and color that we can find in a pleasant meal (Istrati et al., 2015) and is also a blend of products (grapes, wine, and vine leaves) and country traditions.

Grapes, when fully ripped, are sweet. Sweet taste indicates a source of energy, and Humans enjoy sweet and avoid bitter and sour tastes, primarily related to toxic compounds and danger (Plotnik and Kouyoumdjian, 2011). A healthy cuisine, or a healthy way of preparing food, is sometimes difficult to achieve. Alija and Talens (2012) developed a new concept for creating healthy desserts without the addition of fat or sugar by taking advantage of the natural sweetness of fruits and never forgetting the surprise of provocation. Grapes can be used as fresh fruit (table grape) and processed fruit such as jam, grape juice, wine, jelly, molasses, and raisins. Grapes have tremendous potential for use in the development of healthy desserts, or even main courses, promoting amazing sensory experiences with innovative culinary dishes (Cosme et al., 2017). But, not only grapes can be used in culinary, grape leaves (or vine leaves) have been used in Greece and Turkey to produce dishes such as "abelofylla yemista" (dolmades, stuffed grape leaves) and "sarma" (which means – wrapped), respectively (Sat et al., 2002; Dogan et al., 2015). These dishes are similar in the way they are prepared. Vine leaves, briefly blanched or brined with salt, are rolled around a filling made of rice, meat, or another product, Figure 16 (Yerasimos, 2002; Cosme et al., 2017).

Wines can also be used for cooking. For instance, red wines provide new colors to the dishes. Red wines with a deeper red color may be used to tinge the food with their natural red pigments (anthocyanins). Of course, it is a challenge, once in an aqueous solution, the color of anthocyanins is dependent on their structure and affected by the pH. At very acidic pH (pH~1), anthocyanins are present in their flavylium cation form which presents a red color. At pH 3-4, the flavylium cation is involved in two parallel reactions in equilibrium: deprotonation to form the violet quinoidal base and hydration at the C-2 position yielding the non-colored hemiketal form (De Freitas et al., 2017). So, drastic changes in wine pH may influence the final color of the culinary dish that is being prepared.

A B

Figure 16. ‘Sarma’ (SAR’-mah) and ‘Dolma’ (dole-MAH’) in Turkish cooking. cooked spicy rice wrapped in grape leaves; grape leaves roll stuffed with meat (B). (Cosme et al., 2017).

Wine can be used in a wide range of dishes (soups, sauces, and stews; sweet desserts and sorbets) to add flavor, some acidity, sweetness (in the case of Port wines), and savoriness, from glutamate (Vilela et al., 2016), and the aromatic dimension offered by alcohol and other volatile constituents (Jordão et al., 2015). Still, astringency and bitterness, characteristics of wines, can be a challenge in the kitchen. Tannins may precipitate with proteins, making a sauce lose its velvety. The alcohol content of wines also influences the liquid content of the culinary dish promoting the extraction and dissolution of aromatic molecules, boosting their volatility, and intensifying the final aroma (McGee et al., 2004; Cosme et al., 2017).

CONCLUSION

The genus *Vitis* is composed of more than 68 species. Plants that belong to this genus are deciduous woody climbers with a solid root system, and, in the aboveground part, the trunk, shoots, leaves, tendrils, and clusters with flowers or berries.

Vitis uses comprise, besides wine and table grapes, a myriad of products such as grape juices, raisins, spirits and liqueurs, vinegar, infusions, and, more recently, due to the scientific advances in chemistry and phytochemistry, healthy compounds have been found, making *Vitis* products also useful candidates for the cosmetic and pharmaceutical industry.

Nowadays it cannot be forgotten the gastronomy and emergent field of use of grapes and grape products.

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Chapter 5

VALORIZATION OF GRAPE AND WINE BY-PRODUCTS

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ABSTRACT

The grape processing, either for the production of wine or juice, originates a great amount of waste and by-products, consisting mainly in seeds and skins, which must be properly handled and discarded or reutilized before the final disposal. In addition, the costs with drying and the storage of this material are economic limiting factors, making its exploration even more difficult. On the other hand, this biomass contains high concentrations of nutrients such as dietary fibers and phytochemicals, especially polyphenols, that are secondary metabolites with great bioactive properties. Therefore, the recovering of these substances represents a great

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potential for its application as nutraceuticals and functional ingredients in the food industry, or in cosmetic formulations and pharmaceutical industry. Thus, the valorization of grape processing by-products aiming the prospection of compounds with great added value constitutes a promising alternative, not just from the environmental point of view, but also for the development of functional food products with high nutritional quality and health benefits. Studies *in vitro* and *in vivo* indicate that phenolic compounds might exert benefic effects to the human health, acting on the prevention of several degenerative diseases. Having this in mind, the goal of this chapter is to highlight the current trends on the valorization of the by-products originated during grape processing as natural raw materials for the recovering of bioactive compounds, as well the reduction of environmental impact and the sustainable use of natural resources, considering the concept of biorefinery in the industries of this sector.

Keywords: bioactive compounds, biological activities, biorefinery, by-products, functional foods, grape processing

1. INTRODUCTION

The grape is one of the most worldwide-cultivated fruit crops and its production is mainly directed to processing of derived products such as wine and grape juice, originating a large amount of solid wastes or residues. In 2018, the world production of grapes was 77 million tons, whereas 57% (w/w) of this total were employed in the wine production, contributing to the economic expansion of the viticulture activity (OIV, 2019). Besides the vinification process, grapes are also employed in grape juice production, a non-fermented beverage with excellent nutritional value especially due to its bioactive compounds composition (Toaldo et al. 2015). During wine and grape juice processing, three forms of waste are originated: grape stem (non-pomace), grape pomace and grape juice sediment. Non-pomace residue (grape stem) represents the lower amount of waste originated during grape processing, corresponding to 3-5% (w/w) of the total processed grape (Dwyer et al. 2014). Grape pomace (grape seeds and skins) is the major waste resulting from wine and juice processing, corresponding to 20% of the total processed grape (w/w), being an excellent source of dietary fibers and phenolic compounds with great biologic value (Dwyer et al. 2014). Grape juice sediment is a waste collected exclusively during the grape juice elaboration in the centrifugation or clarification step, in which the suspended solids are removed, representing approximately 4 to 8% (w/w) of the total volume of processed juice. The clarification step during grape juice processing is optional, however it contributes to minimize the turbidity problems, enhancing the final product quality (Haas et al. 2019).

The by-products resulting from wine and grape juice processing contain high concentrations of nutrients, such as dietary fibers and phytochemical compounds, especially polyphenols, which are secondary metabolites with bioactive properties. However, these materials present high water content (humidity), making their utilization harder (González-Centeno et al. 2010; Haas et al. 2016). Therefore, the application of drying techniques is mandatory for the valorization of these by-products, aiming to reduce the water activity and consequently minimize the undesirable chemical and biochemical reactions, such as phenolic compounds degradation. Polyphenols are associated to important biological activities, and *in vitro* and *in vivo* studies reveal benefic effects of these substances in the human health promotion, such as prevention of chronic pathologies, including diabetes, cardiovascular and neurodegenerative diseases (Apostolou et al. 2013; Sahpazidoua et al. 2014).

In this context, the consumers demand for food products that exert benefits to the human health has led to the pursuit of new ingredients and products rich in bioactive compounds. The utilization of bioactive substances from grape by-products represents a great advance in the nutraceuticals and functional ingredients field, especially for food products enrichment and fortification, such as cereals, dairy, meat and fruit products. Besides the food products enrichment, due to their biological and nutraceuticals properties, these by-products are also rich in antioxidant and antimicrobial compounds. These properties represent an interesting alternative for their application in the food industry to inhibit chemical and microbiological reactions in different products, allowing the reduction in the utilization of synthetic preservatives and antioxidants. Furthermore, these by-products can be also employed as raw materials for bioconversions, especially for the production of methane, bioethanol and biodiesel. A number of technological solutions for the complete utilization of grape processing by-products are available, enabling their transformation into several target products in different industrial segments, such as food, cosmetic and pharmaceutical industries.

Given the above, the aim of this chapter is to highlight new trends on the valorization of by-products originated during grape processing as raw material for the prospection of bioactive compounds (flavonoids, phenolic acids and stilbenes) and dietary fibers, as well for bioconversions, in order to minimize the environmental impact with the sustainable use of natural resources.

2. General Aspects Related to Grape and Wine by-Products

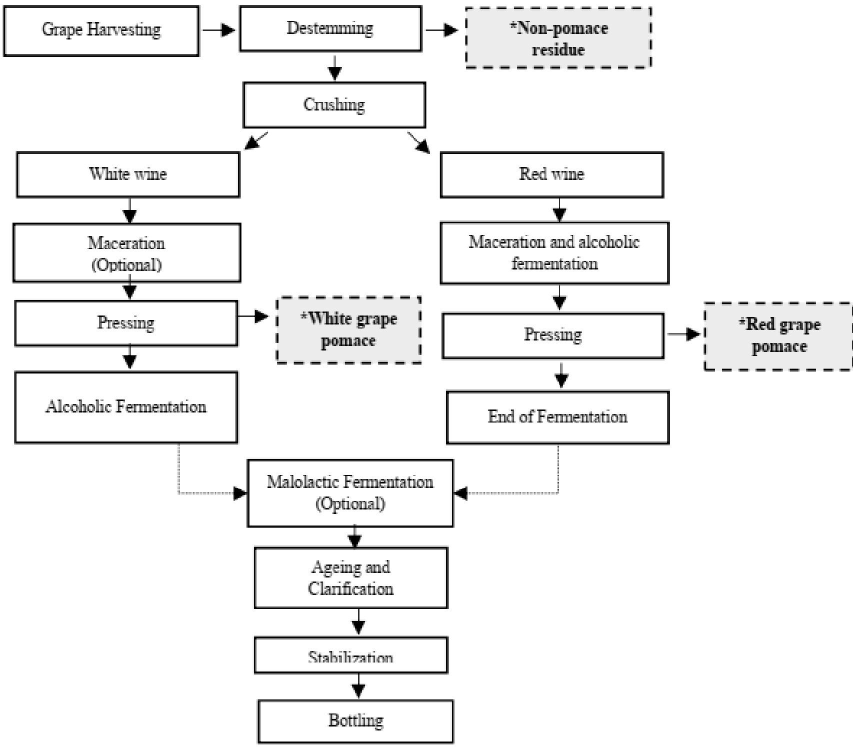
2.1. By-Products of Grape and Wine Processing

Grape (*Vitis* spp.) is one of the most cultivated crops in the world and its production is mainly destined to the elaboration of wines and juices (García-Lomillo and González-SanJosé, 2017), wherein the *Vitis vinifera* and *Vitis labrusca* species are the most employed. The characteristics of each grape variety directly influence on the bioactive properties of juices and wines, and consequently on the by-products obtained during the raw material processing (Devesa-Rey et al. 2011; Haas et al. 2019). The world production of grape juice and wines has been constantly growing, leading to an increase in the production of solid wastes or residues, corresponding especially to grape pomace (skins and seeds), non-pomace residue (grape stem) and grape juice sediment. The last one is exclusively obtained in the grape juice processing.

The wine and grape processing residues are commonly discarded into the environment or destined to the animal feed, however, their utilization for this goal is restricted due to the anti-nutritional factors especially associated to the presence of tannins. These compounds, present in the fruit skins, seeds and stalks, are oligomers and polymers of catechin and epicatechin, and are also related to the characteristic astringency of certain fruits and beverages.

Moreover, grape residues might be also harmful to the environment when discarded without previous treatment, which is attributed to their high organic matter and acidity. Viticultural waste presents, in general, high concentrations of organic matter (20-30 kg m^{-3}) in terms of chemical oxygen demand (COD) (Eleutheria et al. 2016). Additionally, the utilization of these residues as natural fertilizers pose as the main challenge the increase in the soil acidity, which constitutes one of the biggest problems faced by the agricultural practices, since it reduces the availability of plant nutrients. An estimative points that approximately 30% (w/w) of the grape remains without utilization after processing. It is noteworthy that the utilization of by-products in the food enrichment is a world trend, especially for the development of new products with nutraceuticals and functional properties (Mildner-Szkudlarz et al. 2013; Zhou et al. 2019).

The main solid wastes originated during winemaking process are presented in Figure 1. The wine elaboration initiates with the grape harvesting. Then, the grapes are directly destined to the destemming step. In this step, the grape stem is separated from the other solid parts, constituting the first solid residue resulting from the grape processing for wine elaboration (non-pomace residue). This residue corresponds to approximately 3 to 5% (w/w, wet-base) of the total raw material utilized (Sahpazidou et al. 2014). After destemming, the grapes are crushed for the juice extraction. The following step is the maceration in the presence of grape solids (red wine vinification) aiming at the extraction of phenolic compounds and pigments present in this matrix, especially in the grape skins. After the maceration, the primary fermentation process starts with the yeast inoculation in the grape must (alcoholic fermentation) (Bautista-Ortín et al. 2005; Amienyo et al. 2014). The alcoholic fermentation corresponds to the stage with the key biochemical transformations during the vinification process, including the transformation of glucose and fructose into ethanol and carbon dioxide, and the formation of a high number of secondary products, such as glycerol, succinic acid and others (Ribéreau-Gayon et al. 2006).



*Solid residues originated in each step of winemaking process.

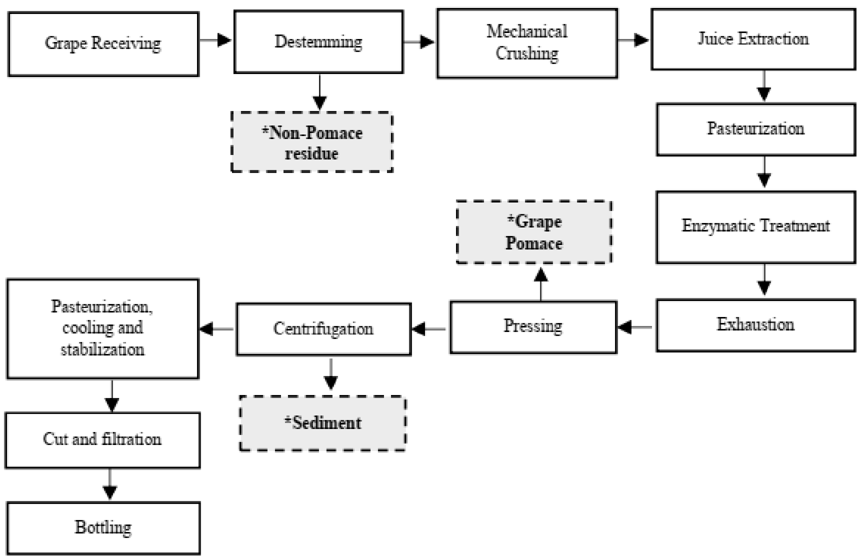
Figure 1. General fluxogram of the vinification process of red and white grapes, with the main solid residues originated. *Source:* Adaptaded from Beres et al. (2017).

After the primary fermentation (red wine), grape skins and seeds are separated from the juice at pressing, originating the main solid residue resulting from the vinification process – the grape pomace. This residue is constituted by grape skins and seeds, corresponding to approximately 20 to 30% (w/w, wet-base) of the total processed grapes (Dwyer et al. 2014). The seeds represent 5% (w/w) of the grape and correspond to approximately 38 to 52% (w/w) (dry matter) of the solid waste produced by the wineries, whereas the skins represent 5 to 10% (w/w) (dry matter) of the solid waste produced (Brenes et al. 2016). During winemaking, part of the phenolic compounds present in the red grapes are transferred to the wine. However, 70% of the phenolic composition remains in the grape pomace after the fruit is processed (Ratnasooriya and Rupasinghe, 2012). Distinct to the red wine vinification process, the grape pomace is not usually implicated in the fermentation step during the white wines elaboration, which influences significantly the phenolic composition of this residue (Dwyer et al. 2014). In addition, the white grape pomace presents higher contents of pulp and reducing sugars than the red grape pomace (Mendes et al. 2013).

After the alcoholic fermentation, a secondary fermentation process (malolactic fermentation) might take place, especially for the elaboration of red wines. In this secondary fermentation process, lactic acid bacteria transform malic acid (dicarboxylic) into lactic acid (monocarboxylic), contributing to the complexity of wine aroma and flavor, besides providing microbiological stability to the final product. Ultimately, the wine is aged, clarified, stabilized and bottled for the commercial market (Laufenberg et al. 2003, Peixoto et al. 2018).

Regarding the grape juice processing, the main solid residues originated are indicated in Figure 2. The grape juice elaboration begins with the grape harvesting. After harvest, the grapes are destined to the destemming step, in which the stem is separated from the grape solids, as previously described in the vinification process. After destemming, the grapes are crushed in the mechanical crusher for berries disruption. Following crushing, the grapes are heated under controlled temperatures and pectinolytic enzymes are added to promote the extraction of skin pigments. Subsequently, the hot or cold maceration and juice extraction are carried out. The hot maceration and juice extraction are frequently applied to enhance the extraction and the diffusion of compounds naturally present in grapes, such as phenolic compounds, which are mainly located in the grape skins, seeds and pulp, and directly related to the nutritional and sensory characteristics of the juice. After the grape juice extraction, the residual solid material is then separated from the liquid juice through a dynamic exhaustion system (optional step). This operation aims to increase the separation of the juice from the grape solid material (seeds and skins), forwarding them directly to the pressing step. This operation is performed in a mechanical press, achieving the separation of the main solid residue originated during the grape juice processing, the grape pomace.

In the course of the vinification and grape juice processes, different technologies might be employed, contributing to the diverse nutritional characteristics observed in the solid wastes originated in each process. Among these differences, the alcoholic fermentation process with subsequent alcohol production during the vinification process represents a significant impact on the bioactive composition of the residues produced (Haas et al. 2018; Meini et al. 2019).



*Solid residues originated in each step of grape juice processing.

Figure 2. The main solid residues originated during the grape juice processing. *Source:* Adapted from Toaldo et al. (2015) and Haas et al. (2018).

The juice resulting from the pressing step presents a turbid appearance due to the suspended solids. Therefore, the juice centrifugation is recommended as an additional step of the traditional process of grape juice elaboration (Toaldo et al. 2015; Haas et al. 2018). The sediment separation is a particular step of the grape juice processing. This residue is collected in the centrifugation step, in which the suspended solids are removed, avoiding precipitation and the deposit of solid material in the final product. The suspended solids in the juice correspond to 4 – 8% of the total volume of processed juice. The centrifugation step is optional during grape juice processing, however this step contributes to the sensory quality of the product and also greatly minimizes the turbidity problems. After the solid residues separation, the grape juice is cooled (0 to 2°C), filtered, pasteurized and bottled prior to be introduced on the market.

The solid wastes originated during the vinification and grape juice processing are mainly redirected to composting or directly discarded into the environment. The incorrect disposal of these materials might result in several environmental problems associated to the soil and water contamination. Different applications have been assessed to encourage the utilization of wineries wastes in special grape pomace, which is the main residue originated during the wine and grape juice processing. Among these applications, it can be highlighted the flavonoid compounds extraction, which can be applied as food supplement; the isolation and purification of anthocyanins for the utilization as natural pigments in substitution of synthetic dyes; and the prospection of antimicrobial agents and stabilizers for utilization in the food, cosmetic and pharmaceutical industries (Garcia-Lomillo et al. 2017). The valorization of grape processing by-products is supported by their phytochemical composition with biological properties, promoting numerous health-related benefits.

Besides the application of grape processing by-products in the food industry, the concern with costs reduction of the treatment of wineries wastes has led to the development of new techniques to recycle, reutilize and recover these by-products rich in nutrients and bioactive compounds. This material might be employed in several food industry segments, as well as substrate for bioconversions aiming at the production of bioenergy and bioproducts.

2.2. Bioactive Composition of Grape and Wine Processing By-Products

The by-products originated during grape processing are valuable sources of polyphenols and dietary fibers, which when ingested in the dietary intake promote several health-related benefits. Phenolic compounds are secondary metabolites present in vegetal and plant materials, which exhibit important antioxidant activity. Their chemical structure corresponds to at least one aromatic ring, with one or more hydroxyl groups directly attached to the structure. They might vary between simple molecules to highly polymerized compounds, being divided into different classes: flavonoids, phenolic acids and stilbenes, according to structural characteristics (Ribéreau-Gayon et al. 2006). On the other hand, the dietary fibers are polymeric compounds constituted especially by cellulose, xyloglucans, arabinans, pectin, lignin and structural proteins (Meini et al. 2019). These fibers accumulate particularly in grape skin and seeds and remain into the pomace after the raw material processing for the elaboration of grape juice and wine, making this pomace an excellent source for the reutilization of dietary fibers (Zhu et al. 2015).

The flavonoids group presents two aromatic rings joined by a central pyran ring, and the different substituents of the ring originate the different classes of flavonoids such as flavonols, flavan-3-ols, flavones, flavanones, isoflavones and anthocyanidins (Zhu et al. 2012). Phenolic acids are distinguished by presenting a benzene ring, a carboxylic group and one or more hydroxyl or metoxyl group attached in the molecule, conferring the ability to scavenge reactive species such as the hydroxyl radical and singlet oxygen (Marinova and Yanishlieva, 2003). The derivatives of benzoic and hydroxycinnamic acids constitute the phenolic acids group. Stilbene compounds can be synthesized by vines as a defense response to the environmental stress factors, such as infections and UV irradiation, being the resveratrol (3-4’-5-trihydroxystilbene) the main compound of this group. Resveratrol is one of the most relevant stilbenes in the nature, present in two isomeric forms, *cis* and *trans*, and the synthesis of this compound in grapes occurs especially in the skins (Moreno-Arribas and Polo, 2009).

The phytochemical compounds present in the grape by-products are influenced by the variety, maturation degree and sanitary conditions of the grape, as well by the climatic conditions and viticultural practices. The *V. labrusca* grape varieties, for instance, may present higher concentration of polyphenols such as hydroxycinnamic acids derivatives (Nixdorf and

Hermosín-Gutiérrez, 2010), catechins (Burin et al. 2014) and anthocyanins (Lago-Vanzela et al. 2011), in comparison to the *V. vinifera* grape varieties.

Regarding the main phenolic compounds present in the by-products from grape juice and wine processing, it is well known that the non-pomace residue (grape stem) is rich in flavonoids, being the (+)-catechin the major compound in red (721-1691 mg kg^{-1}) and white (385-1858 mg kg^{-1}) grape varieties (Anastasiadi et al., 2012). Other compounds, such as caftaric acid, isorhamentin-3-*O*-(6-*O*-feruloyl)-glucoside, quercetin-3-*O*-rutinoside, quercetin-3-*O*-glucuronide, kaempferol-3-*O*-rutinoside and kaempferol-3-*O*-glucoside, are also frequently found in this kind of by-product (Gouvinhas et al. 2018). The quercetin-3-*O*-glucuronide corresponds to 61-83% of the total flavonols present in the non-pomace grape residue (Dias et al. 2015). In addition to these phenolic compounds, the non-pomace grape residue is also an excellent source of stilbenes. The *trans*-resveratrol concentration (265-542 mg kg^{-1}) can be approximately eight times higher in this by-product than in grape skins, and sixty three times higher than the concentration found in grape seeds (Pugajeva et al. 2018).

Relating to the phenolic composition of the red grape pomace, this matrix is rich in anthocyanins, being malvidin-3-*O*-glucoside, peonidin-*O*-glucoside, petunidin-*O*-glucoside and delphinidin-*O*-glucoside, the major compounds found in the grape pomace of *V. vinifera* varieties (Ribeiro et al. 2015). On the other hand, in the grape pomace of *V. labrusca* varieties (*V. labrusca* L.), the diglucoside forms, such as malvidin-3,5-diglucoside and cyanidin-3,5-diglucoside, are primarily found (Ribeiro et al. 2015). The anthocyanins exhibit important biological activities, in addition to their utilization as natural pigments in food products. The grape pomace is also rich in hydroxybenzoic and hydroxycinnamic acids, flavan-3-ols compounds, flavonols and stilbenes (Beres et al. 2017). The grape skins are rich in hydroxycinnamic acids, especially caftaric acid, while the grape seeds present higher concentrations of gallic and protocatechuic acids (Teixeira et al. 2014). The phenolic content is higher in seeds (60-70%), followed by skins (28-35%) and pulp (10%) (Ribeiro et al. 2015). The major phenolic compounds in grape skins are (+)-catechin and (-)-epicatechin (Andrade et al. 2019). The seeds present 60 to 70% of the total extractible polyphenols, attracting the interest of food and pharmaceutical industries for the recovery of natural antioxidant compounds from this matrix (Souza et al. 2014; Bucić-Kojić et al. 2013).

Another promising source of polyphenols is the grape juice sediment obtained during the centrifugation step in the grape juice elaboration. This residue presents as major compounds (+)-catechin, (-)-epicatechin, *trans*-resveratrol and anthocyanins glucosides, especially malvidin-3,5-diglucoside. The average concentration of (+)-catechin and (-)-epicatechin is 680 mg kg^{-1} and 298 mg kg^{-1}, respectively (Haas et al. 2019). The grape juice sediment is a potential source of *trans*-resveratrol, which draws the attention for its utilization as an alternative source of this phytochemical compound. In addition, this residue shows an intense color, associated to the high content in anthocyanins such as, cyanidin-3,5-diglucoside, delphinidin-3-*O*-glucoside, malvidin-3,5-diglucoside, cyanidin-3-*O*-glucoside, peonidin-3-*O*-glucoside and malvidin-3-*O*-glucoside, whereas the major anthocyanins are malvidin-3,5-diglucoside (1226 mg kg^{-1}) and cyanidin-3,5-diglucoside (165 mg kg^{-1}) (Haas et al. 2019).

As stated before, besides the phenolic composition, the grape by-products are important sources of dietary fibers, which are the main compounds in grape pomace (43 to 75%) (Gül et al. 2013). The pectic substances are the main polymers present in grape cell wall and, consequently, in the grape pomace, corresponding to 37-54% (w/w) of the polysaccharides in the cell wall. The cellulose is the second major polysaccharide in the grape cell wall (27 to 37% w/w). The dietary fibers content in the non-pomace grape residue represent 90% of the total dry matter, wherein cellulose is the major polymer (40 to 49%) (González-Centeno et al. 2010). The dietary fibers intake represents health benefits, contributing to the passage of food through the gastrointestinal tract, avoiding constipation, besides the regulation of glucose absorption and reduction of cholesterol levels, and cardiovascular diseases incidence (Macagnan et al. 2016; León-González et al. 2017).

Besides polyphenols and dietary fibers, the grape pomace is also considered a source of lipids from the grape seeds (14-17%). This by-product presents an interesting fatty acids profile, such as poly- and monounsaturated fatty acids, showing lower content of saturated fatty acids. The major fatty acids present in the oil extracted from grape seeds (*V. vinifera*) correspond to linoleic C18:2n-6, essential (40-78%), oleic C18:1n-9 (12-28%) and palmitic C18:0 (2-6.8%) acids (Fernandes et al. 2013; Firestone, 2013; Gül et al. 2013).

2.3. Biological Activities and Potential Health Benefits of Grape and Wine by-Products

The pursuit for alternative sources of bioactive compounds encourages the food industry to reutilize the by-products originated during the grape processing for the enrichment of food products. Several *in vivo* and *in vitro* studies show that the viticultural residues might exert numerous biological activities, which is directly related to their phenolic composition (Tomé-Carneiro et al. 2012; León-González et al. 2017). As a result, there is an intensifying search for sustainable alternatives to supplement the daily diet with these by-products. In this sense, the use of grape processing by-products has been promising for the development of functional and nutraceuticals products, due to the unique combination of phytochemical compounds such as flavonoids, phenolic acids, stilbenes and dietary fibers found in these residues. Considering the increasing risk factors for the development of numerous chronicle diseases in humans, the inverse relationship between the intake of food containing great amounts of antioxidant compounds and the occurrence of these diseases, there is a great trend towards the reutilization of natural substances present in by-products from food processing (Teixeira et al. 2014).

Clinical and pre-clinical studies have shown that vegetable food products might act as potential therapeutic agents for the prevention of several pathologies such as diabetes, cardiovascular and neurodegenerative diseases and cancer (Ramana et al. 2018). It is well known that the polyphenols present in the vegetable sources exhibit beneficial biological activities to the human body when regularly ingested. The recommended dietary intake of phenolic compounds for a healthy individual is approximately 1700 mg per day, in which phenolic acids and flavonoids represent 46% and 52% of the total polyphenols ingested in the daily diet respectively (Grosso et al. 2014).

In addition to the dietary intake of polyphenols, it is necessary to consider the digestion, absorption and the metabolism of these compounds in the human body (Attri et al. 2017). Despite of the consistent evidence of the bioactive properties of these substances, there is still conflicting information about the mechanisms implicated in the absorption and metabolism of polyphenols, especially when considering the complexity of their chemical composition and the *in vivo* gastrointestinal digestion process. In general, plant-based foods are complex matrices, wherein numerous factors might interfere in the process of digestion, and thus in the absorption of nutrients and specific substances such as polyphenols. Therefore, the better comprehension of the absorption pathways of nutrients and phenolic compounds in a specific food matrix and the possible effects in the human body are exceptionally relevant to establish the bioactive potential (Cilla et al. 2018). The phenolic compounds only exert their health-related properties when they reach the target tissue in the human body in biological active concentrations. In other words, the bioactive compounds must be initially released from the food matrix and be bioavailable to be absorbed by the body. The bioavailability might be described as the fraction of certain compound that becomes available for the intestinal absorption (Cardoso et al. 2015).

The phenolic compounds present in the grape processing by-products are prone to several structural modifications along the gastrointestinal digestion. Among polyphenols, phenolic acids seem to be the more resistant compounds in this process, and thus more relevant to explain the biological activity of these substances in food (Corrêa et al. 2017; Lingua et al. 2019). Similarly, to the phenolic acids, stilbenes also exhibit health-related benefits in the human body, and the main compounds of this group in grapes are the *trans*-resveratrol (3,5,4′-tri-hydroxystilbene), resveratrol-3-*O*-β-D-glucopiranoside, piceatannol (3,4,3′,5′-tetra-hydroxy-*trans*-stilbene) and resveratrol dimers (Garrido and Borges, 2013; Ruiz-Moreno et al. 2015). Evidences show that the *trans*-resveratrol decreases the incidence of cardiovascular and carcinogenic diseases (Singh et al. 2015; Yang et al. 2020). In the same way, the flavonoids compounds also exert important biological properties, since they are able to absorb the UV irradiation, which is the main cause of inflammation, oxidative stress and DNA-damaging, resulting in numerous skin diseases such as photoaging, hyperpigmentation, melanoma and skin cancer (Chea et al. 2017). Among the flavonoids compounds, (+)-catechin shows effect against free radicals and metal-chelating activity (Modun et al. 2008), whereas (-)-epicatechin shows vasodilatory properties (Padilla et al. 2005). Phenolic compounds are widely employed in the cosmetic elaboration of sunscreens for photoprotection. This is an interesting alternative, since these substances present a lower risk of triggering allergic reactions or photosensitivity when compared to the synthetic chemical photoprotectors commonly employed in sunscreen formulations.

Several studies indicate that the grape by-products exhibit anticarcinogenic action (Hudson et al., 2017; Sahpazidoua et al. 2014). The non-pomace residue, which is a source of phenolic acids (gallic, caffeic, coumaric, ferulic and syringic acids), flavanols (catechin and epicatechin), flavonols (quercetin, rutin and kaempferol) and stilbenes (*trans*-resveratrol), may prevent breast, kidney, thyroid and colon cancer. The capability of this by-product to inhibit the growth of kidney and thyroid cancer cells is enhanced, in addition to the reduction of low density lipoproteins, intracellular reactive species of oxygen and the oxidative stress (Anastasiadi et al. 2012; Sahpazidoua et al. 2014; Goutzourelas et al. 2015). Additionally, to the anticarcinogenic activity, the treatment with the non-pomace grape residue decreases the expression of the inflammatory-COX-2 enzyme after the induction by the UV irradiation (Che et al. 2017).

Similarly, to the non-pomace grape residue, the grape pomace also exerts important biological effects in *in vivo* systems. The supplementation of the diet of mice with grape pomace, for instance, promoted anti-inflammatory activity. The same behavior was also observed with grape seeds-rich diet (Terra et al. 2009; Hogan et al. 2010). The pharmacokinetic profile and the phenolic metabolites excretion after the acute administration of a beverage elaborated with red grape pomace were also investigated in the literature. A total of 35 and 28 phenolic metabolites were quantified in the urine and plasma of mice respectively, wherein the main metabolites identified corresponded to phenil-γ-valerolactones, hydroxybenzoic acids, simple phenols, hydroxyphenil-propionic acids and hydroxycinnamates (Castello et al. 2018). Phenolic compounds act on the prevention of oxidative damaging due to their capacity to decrease the lipid peroxidation and raise the total antioxidant capacity of the plasma (Toaldo et al. 2015).

On the other hand, grape seeds definitely contribute to the bioactive potential of the grape pomace due to their anti-inflammatory action, inhibiting the expression and production of different inflammatory markers. Different mechanisms are suggested for this anti-inflammatory activity, being mainly attributed to the synergism of phenolic compounds, especially the flavonoids, which represent the major phenolics in grape seeds (Harbeoui et al. 2019). Flavonoids are considered fundamentals for the nutraceutical, pharmaceutical, medicinal and cosmetic applications. This aspect is attributed to their antioxidative, anti-inflammatory, antimutagenic and anticarcinogenic properties, along with their capacity in the modulation of the main enzymatic cells functions (Panche et al. 2016).

Concerning the grape juice sediment, *in vitro* and *in vivo* investigations about its biological properties are still lacking in the literature. However, considering the phenolic composition of this material (Haas et al. 2018), it might be suggested that its dietary intake might promote health-related benefits. Nevertheless, investigations relating to its biological relevance are necessary to establish the possible benefits associated to the consumption of this by-product.

Besides the phenolic compounds, the grape by-products are rich in dietary fibers, reason why the non-pomace and the pomace grape residues are employed in food enrichment intending the increase of these nutrients in the daily diet (Zhao et al. 2015). The dietary fibers correspond to the part of the vegetal that is resistant to the enzymatic digestion, being divided into water-soluble and insoluble dietary fibers.

Pectin, gums and mucilage correspond to the soluble fibers, whereas cellulose, hemicellulose and lignin represent the insoluble fibers (Dhingra et al. 2012). The major fiber content in grapes is accumulated in seeds and skins, which after the elaboration of the wine and grape juice remain in the pomace. The insoluble fiber is present in larger concentration in the grape pomace, corresponding approximately to 61.20 g $100g^{-1}$, whereas the soluble fiber is present in an average concentration of 4.06 g $100g^{-1}$ (Bender et al. 2020). The average intake of dietary fibers recommended for a healthy adult is approximately 20 to 35 g per day (Schakel et al. 2001). The fibers composition of grape pomace contributes to its chemopreventive property and antitumor activity (Sánchez-Tena et al. 2013). Studies indicate that the consumption of grape fibers-rich supplement prevents the cardiovascular diseases and reduces the LDL levels (Tomé-Carneiro et al. 2012). The consumption of dietary fibers leads to reduction on the glycemic responses, plasma cholesterol levels, carbohydrates absorption, as well as on the insulin response and the triacylglycerol levels, which are contributing factors to the development of coronary diseases (Rodríguez et al. 2006). The consumption of dietary fibers contributes to the fecal bulk, reducing the time of intestinal transit, the cholesterol levels and the glycemic index, as well as stimulating the proliferation of the intestinal microbiota (Dhingra et al. 2012; Slavin, 2013).

The postulated role of the dietary fibers consumption in human health led to the development of food products and ingredients rich in these nutrients. A trend towards to the search of new sources of dietary fibers has been observed, which might be employed for food enrichment in the different segments of food industry (Dhingra et al. 2012). In this sense, the by-products originated during wine and grape juice elaboration represent an important low-cost source of phenolic compounds and dietary fibers with functional and nutraceutical goals. The identification of new sources environmentally available of bioactive compounds has become very interesting for the food sector. Thus, the grape processing by-products are valuable sources of phytochemicals, which can be recovered as functional compounds by the food, pharmaceutical and cosmetic industries.

2.4. By-Products of Grape and Wine Processing Used as Novel Ingredients in Foods

The grape processing by-products are potential sources of phenolic compounds and dietary fibers and their utilization for the development of new products with functional properties is a crescent trend in the food sector, which is constantly searching for innovation. There are numerous promising applications for bioactive compounds extracted from the grape processing by-products (Dias et al. 2015; Ahmad et al. 2015; Garcia-Lomillo et al. 2017), besides, the dietary fibers are also interesting for food enrichment. The grape processing by-products are employed in foodstuffs with various goals and purposes, adding a great value to these products. These by-products can be applied in the different segments of food industry such as meat products, cereals, dairy and fruit-based products (Table 1) (Gil-Sánchez et al. 2018).

There is a great interest of the food industry for the replacement of synthetic pigments and antioxidants by natural substances, encouraging the application of the grape by-products as additives and adjuvant agents in the manufacturing technology. The concern about potential risks of chemical additives employed in food products led to an increase in the natural additives demand. In this sense, the grape processing by-products have been described as an excellent alternative to the synthetic antioxidants, especially due to their high content of phenolic compounds (Garcia-Lomillo et al. 2017). Nevertheless, the application of these by-products in the formulation of new products is limited to some extent by their high water content, becoming a very perishable media, susceptible to microbial growth and chemical degradation (González-Centeno et al. 2010). The fresh grape presents a water content of 73-85%, whereas the grape processing by-products such as non-pomace residue, grape pomace and grape juice sediment present a water content of 55-80%, 50-72% and 73-74% respectively (González-Centeno et al. 2010; Haas et al. 2016).

The application of drying techniques decreases the water activity and, as consequence, reduces the undesirable biochemical and microbiological reactions, such as the phenolic compounds degradation (Choe and Oh, 2013; Gan et al. 2017). Therefore, the utilization of drying techniques, which enables the application of grape by-products in the industry, is mandatory to promote the reduction in the water content, extending the shelf life of this material, besides reducing the volume and costs with packaging, storage and transport (Chikwanha et al. 2018).

Although the application of drying techniques in grape by-products is indispensable for enabling their utilization in the different food formulations, the chosen technique may result in certain alterations in their phytochemical composition, affecting their bioactive properties. It is well known that polyphenols are susceptible to high temperatures and the presence of oxygen, being the main reasons for the carefully selection of the more suitable drying technique to minimize the undesirable chemical changes and preserve the bioactive characteristics of the material. Due to the low thermal stability of bioactive compounds, the freeze-drying is considered the most efficient drying method to retain the biological properties of phenolic compounds. However, this technique presents an operational cost from 4 to 8 times higher than the traditional air-circulation drying method. This economic factor makes the freeze drying unsuitable for processing large amounts of by-products (Ratti, 2001). Therefore, the air-circulation drying has been indicated for industrial applications, wherein the bioactive compounds are slightly affected when the temperatures are set between 55 and 65°C, allowing the retention of the grape by-products bioactive characteristics, being a drying technique much less expensive than the freeze drying (Haas et al. 2017).

Table 1. Transformation and valorization of grape processing by-products for application in food products

Grape and wine by-products	Grape species and varieties	By-products processing descriptions	Food products applications	Nutritional and technological properties	References
Grape pomace	Pinot Noir, Freisa, Croatina and Barbera (*Vitis vinifera* L.)	The grape pomace was dried (65°C) and ground (0.7 mm particle size). The extraction was carried out applying water as solvent; the solid/liquid ratio was 1:10 (w/w). Different volumes of the aqueous extract were added to the skimmed milk for the fermented milk elaboration.	Fermented milk	The incorporation of grape pomace to the fermented milk formulation promoted the lactic acid bacteria growth (*Streptococcus thermophilus* and *Lactobacillus acidophilus*).	Azevedo et al. (2018)
Grape pomace	Pinot Noir (*Vitis vinifera* L.)	The grape pomace was freeze-dried and ground (0.18 mm particle size). The grape pomace was incorporated into the yogurt formulation in concentrations of 1, 2 and 3%; for the salad dressing formulation, the concentrations of 0.5 and 1% were chosen.	Yogurt and Salad dressing	The incorporation of grape pomace into the formulations of yogurt and salad dressing promoted the increase in the dietary fibers and polyphenols contents, besides the reduction of the lipid oxidation during storage.	Tseng et al. (2013)
Grape pomace	Siahe sardasht (*Vitis vinifera* L.)	The grape pomace was dried (50–55°C), and ground (250 μm particle size). The grape pomace was then incorporated into the sausages formulation in a concentration of 1%.	Sausages	The incorporation of grape pomace in the sausages formulation led to a reduction in the thiobarbituric acids reactive substances (TBARS) and the oxidation levels of the final product.	Riazi et al. (2016)
Grape pomace	White grapes (*Vitis vinifera* L.)	The white grape pomace was freeze-dried, the skins were separated from the seeds and then ground (150 μm particle size). The wheat flour mixes were prepared adding 10, 20 and 30% (w/w) of white grape pomace (skins and seeds).	Cookies	The addition of grape pomace decreased the hardness and brightness of the enriched samples. The grape pomace added promoted an increasing in the dietary fibers content, phenolic compounds content and antioxidant activity in samples.	Mildner-Szkudlarz and Bajerska (2013)

Grape and wine by-products	Grape species and varieties	By-products processing descriptions	Food products applications	Nutritional and technological properties	References
Grape pomace	Isabel (*Vitis labrusca* L.)	The grape pomace was dried applying two techniques: freeze-drying and air-circulation drying. The dried samples were ground (0.5 mm particle size) and incorporated into the yogurt formulation in concentrations of 0, 1, 3 and 5% (w/w).	Yogurt	The grape pomace incorporation into the yogurt formulation did not affect the viable cells of lactic acid bacteria (*Lactobacillus* and *Streptococcus)*. The yogurt added with freeze-dried grape pomace presented lower content of polyphenols and antioxidant activity than the yogurt added with the air-circulation dried grape pomace.	Demirkol and Tarakci (2018)
Grape pomace	Chardonnay and Barbera (*Vitis vinifera* L.)	The grape pomace was dried (54°C), ground (250 µm particle size) and stored at 4°C. The grape pomace was incorporated to the cheese formulations in concentrations of 0.8 and 1.6%.	Cheese	The differences in the proteolysis and microbial counting were not statistically significant for the enriched and control samples. An increase in the phenolic content and antioxidant activity was observed for the enriched cheese samples (1.6% of grape pomace).	Marchiani et al. (2016)
Grape pomace	Isabel and Niágara (*Vitis labrusca* L.)	The grape pomace was dried in air-circulation oven (40°C) and ground (0.5 mm particle size). The grape pomace (20 g) was macerated with 100 mL of ethanol 80% (v/v), being filtered, concentrated and re-suspended with water up to 50 mL. A concentration of total polyphenols of 60 mg per kg of meat was employed to prevent the lipid oxidation in raw and processed chicken meat.	Raw and cooked Meat products	The grape pomace added to the meat products effectively reduced the thiobarbituric acid reactive substances (TBARS) and the free radicals, besides delayed the lipid oxidation.	Selani et al. (2011)

Table 1. (Continued)

Grape and wine by-products	Grape species and varieties	By-products processing descriptions	Food products applications	Nutritional and technological properties	References
Grape seeds and skins	Cencibel (*Vitis vinifera* L.)	Grape skins and seeds were dried at 80°C and ground (0.5 mm particle size). The grape skins and seeds were incorporated into chicken hamburgers formulation in a concentration of 2%.	Chicken hamburgers	The grape skins and seeds addition to the chicken hamburgers enhanced the oxidative stability of the final product.	Nardoia et al. (2017)
Grape skins	Red grapes (*Vitis vinifera* L.)	Anthocyanins were isolated from the red grapes skins as "enocyanins" and applied in the formulation of different products.	Dairy desserts, ice cream, juices and beverages	Anthocyanins were employed as natural food colorants.	Garcia-Lomillo and González-SanJosé (2017)
Grape skins	Barbera (*Vitis vinifera* L.)	The grape skins were dried (50°C), ground with different particle sizes (125, 250 and 500 μm) and stored at 4°C. The grape skins were incorporated into the candy formulations in concentrations of 63 g kg^{-1}.	Candy	The candy enrichment with grape skins increased the concentrations of anthocyanins, flavonols and procyanidins resulting in an increase of the antioxidant activity. The candy added with grape skins exhibited good textural properties.	Cappa et al. (2014)
Grape seeds		The grape seeds were ground (particle size < 0.5 mm) and then were added in different concentrations (0%, 2.5%, 5.0% and 7.5% w/w) in substitution of the wheat flour in the bread formulation.	Breads	The addition of grape seeds to the bread formulations did not change the water absorption. The stability and extensibility of the dough formulated with grape seeds were higher than the control samples. The grape seeds addition did not modify the specific volume of the dough. It was observed an increase of the antioxidant activity of breads formulated with grape seeds.	Meral and Dogan (2013)

Grape and wine by-products	Grape species and varieties	By-products processing descriptions	Food products applications	Nutritional and technological properties	References
Grape seeds	Merlot (*Vitis vinifera* L.)	The grape seeds were dried and ground (particle size < 100 mesh). The grape seeds were then added to cereal bars formulations in concentrations of 5% (w/w).	Cereal Bars	The cereal bars enriched with grape seeds presented higher antioxidant activity than the control samples (without grape seeds addition).	Rosales Soto et al. (2012)
Grape seeds	Concord, Isabel and Bordô (*Vitis labrusca* L.)	The *in natura* grape seeds were added during grape juice elaboration in concentrations of 50, 100 and 200 g kg^{-1} of grape.	Grape Juice	The grape juice enriched with grape seeds presented higher total polyphenols concentration and antioxidant activity.	Toaldo et al. (2013)

The drying of grape by-products enables their utilization in several foodstuffs, allowing the development of new products that attend the high standard of quality required by the market, including safety, nutritional and sensory attributes, which is still a great challenge for the food industry. Researches associated to the composition and the bioactive properties of these matrices support the utilization of technological processes to allow the achievement of safe ingredients and products, minimizing the losses of bioactivity and functionality of these ingredients (Ratti, 2001; Tseng et al. 2012).

However, it is well known that phenolic compounds are susceptible to light, temperature, pH, enzymatic activity, presence of metals and oxygen. These factors might promote their degradation, oxidation, epimerization and polymerization (Bakowska-Barczak and Kolodziejczyk, 2011, Galmarini et al. 2013). Therefore, the utilization of methods that preserve the functional and nutritional characteristics of these compounds becomes crucial. Among the most promising alternatives is the microencapsulation, applied to enhance the stability and bioavailability of phenolic compounds. In this technique, the target compound is enclosed by an encapsulating material, providing a physical barrier between the compound and the medium (Aizpurua-Olaizola et al. 2016; Tolun et al. 2020). In this technique, the selection of the encapsulating agent is essential for an efficient spray drying process. Among the encapsulating agents, the maltodextrins are the most suitable polymers, especially due to their absence of toxicity, high solubility and low viscosity (Ferrari et al. 2013; Tolun et al. 2020).

The spray drying technique is employed especially to encapsulate food compounds, which are susceptible to high temperatures. In this process, the rapid evaporation of water maintains the particles at low temperatures without significantly affecting the nutritional value of these products. There are several microencapsulation methods, however, the atomization employing a spray drying equipment is the most applied one, since it allows the continuous production through an economic process that can be easily scaled. In a typical atomization drying process (Figure 3), the feed solution and the encapsulating agent (polymer) are pulverized in a vertical chamber, applying a suitable atomizer configuration. The heat is transferred to the liquid solution through a counter-current or co-current flow of heated gas. The contact between the solution droplets and the heated gas instantly evaporates the aqueous solvent, resulting in solid particles with an outer polymer layer protecting the target compound from the external medium. In the end of the process, the microencapsulated material is separated through a cyclone placed outside the dryer and recovered into the bag filter, which retains the finest powder particles (Shabde and Hoo, 2008). The spray drying technique promotes the stability of phenolic compounds; as a result, the encapsulated polyphenols can be applied for food enrichment in a more satisfactory manner in the food industry (Tolun et al. 2020).

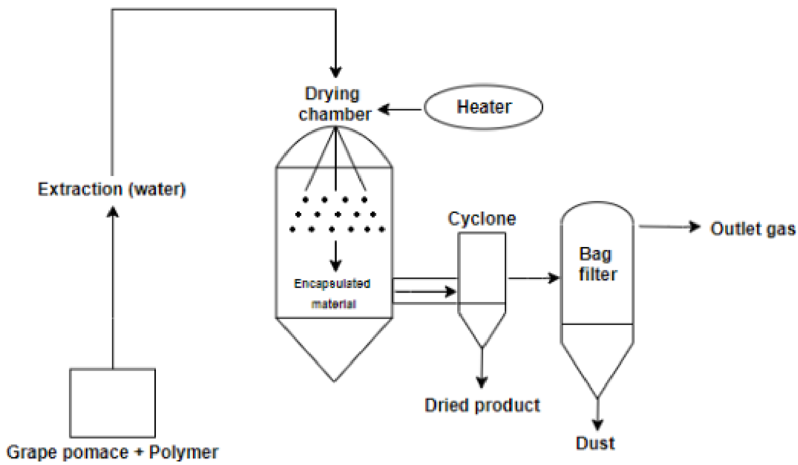


Figure 3.

The bioactive compounds of grape processing by-products can be also utilized as natural colorants, adjuvants in the manufacturing technology and in food preservation as antioxidants agents. The anthocyanins isolated from the red grapes skins are widely used in the food industry as a natural pigment. Its excellent coloration properties and stability allow the application in different food matrices such as dairy desserts, ice cream, beverages and others (Garcia-Lomillo and González-Sanjosé, 2017). The grape processing by-products can be also utilized as technological adjuvants in dairy products. The incorporation of a polyphenol-rich extract in dairy products can delay the coagulation and reduce the syneresis, due to the effect of hydrophobic interactions between casein and phenolic compounds (Silva et al. 2015).

The utilization of phenolic compounds from the grape pomace represents a biotechnological innovation, which aims to expand the market of functional dairy products. The grape pomace is utilized in fermented dairy products aiming at the bioactive enrichment of these products. This by-product might be added before the fermentation process, as part of the ingredients in the yogurt elaboration or after this step. The addition of phenolic compounds to the dairy products has been proposed as a promising strategy to promote health-related benefits. The grape pomace might be successfully incorporated to the skimmed milk to enhance the lactic acid bacteria growth (*Streptococcus thermophilus* and *Lactobacillus acidophilus*) during fermentation process (Azevedo et al. 2018). This by-product can be also added to the yogurt to enhance the nutritional value and extend its shelf life, promoting dietary fibers enrichment, besides delaying the lipid oxidation during the cold storage (Tseng et al. 2012).

Additionally to the application of grape by-products for the nutritional enrichment of dairy products, their use as preservative in meat products due to their great antioxidant capacity has been very effective (Nardoia et al. 2017; Demirkol and Tarakci, 2018). The utilization of synthetic antioxidants is very restrictive in some countries due to their toxic effects or carcinogenic potential, which encourages the use of natural antioxidant agents (Ahmad et al. 2015). Nutritional and technological strategies have been developed to assist the preservation of sensory characteristics of meat and extend the shelf life of meat products. Thus, the phenolic compounds extracted from grape processing by-products have been employed as natural antioxidants in substitution of synthetic compounds (Riazi et al. 2016; Nardoia et al. 2017). The grape processing by-products such as grape pomace and seeds, when incorporated to meat products, contribute to the reduction of lipid oxidation, besides contributing to the sensory characteristics and exerting antimicrobial effect in food products (Nardoia et al. 2017). The antioxidants extracted from the grape by-products might be added to the fresh or processed meat to limit the oxidative rancidity, delay the development of undesirable flavors and enhance color stability. The grape pomace, for instance, was employed to raw and cooked meat products to prevent lipid oxidation (Ahmad et al. 2015). The addition of grape pomace (1%, w/w) to sausages decreased the lipid oxidation levels, suggesting its application is an excellent alternative to enhance the sensory aspects and technological quality of these meat formulations (Riazi et al. 2016). The grape pomace can be also employed as preservative in the meat industry, since it can inhibit the bacterial growth such as *Bacillus cereus, Bacillus coagulans, Bacillus subtilis, Staphylococcus aureus, Escherichia coli* and *Pseudomonas aeruginosa* (Jayaprakasha et al. 2003). The utilization of antimicrobial compounds from natural sources is stimulated due to the adverse effects provoked by the synthetic antimicrobial agents. The non-pomace grape residue also presents proved antimicrobial activity against Gram-positive (*Listeria monocytogenes, Staphylococcus aureus* and *Enterococcus faecalis*) and Gram-negative (*Pseudomonas aeruginosa, Escherichia coli and Klebsiella pneumoniae*) bacteria (Dias et al. 2015). This antimicrobial activity is especially related to the presence of phenolic compounds such as kaempferol-3-*O*-rutinoside, kaempferol-3-*O*-glucoside and caftaric acid.

The grape processing by-products can be also added to cereal products for their nutritional enrichment, especially breads, cookies, cereal bars and others. Breads enriched with freeze-dried skins from grape pomace decreased the cholesterol levels, low density lipoproteins and the lipid peroxidation, besides increased the antioxidant activity in mice with hypercholesterolemia induced by diet (Mildner-Szkudlarz et al. 2013). The flour elaborated from grape skin presents high potential of application in the bakery, and its use is indicated in breakfast cereals, breads, cookies, cakes and cereal bars. It also presents potential application in vitamin supplements and juices. The grape seeds incorporated to the white bread showed an effect in the glycemic response or satiation of healthy adults (Coe and Ryan, 2016). The application of grape seeds flour in bakery products and cereal bars represents an excellent alternative for dietary fibers enrichment (Rosales Soto et al. 2012). The grape pomace can be also applied as additive to the wheat flour, as in cookies enriched with white grape pomace, which presented dietary fibers content and antioxidant activity higher than the cookies without the addition of this by-product (Mildner-Szkudlarz et al. 2013). Moreover, the addition of antioxidants obtained from grapes might considerably enhance the oxidative stability and free radicals scavenge in raw or cooked chicken hamburgers (Sáyago-Ayerdi et al. 2009). The antioxidant dietary fiber is described as a portion of the dietary fiber, which contains significant amounts of natural antioxidants associated to non-digestible compounds. This antioxidant activity is attributed to the secondary metabolites such as the grape polyphenols (Tseng e Zhao, 2013). The antioxidant fibers (extracted from grape skins or seeds) might be applied in numerous foodstuffs as a source of fibers and natural antioxidants, especially to dairy products such as yogurts and bakery products, inserting important health-related benefits. As mentioned above, the grape pomace is a valuable by-product for food enrichment, however, it can be also processed for extraction of oil (8-15% w/w) from the seeds present in this residue. The grape seeds oil attracts a great attention of the consumers due to its unique fatty acids profile. This oil presents especially triacylglycerols rich in unsaturated fatty acids such as linoleic (C18:2), essential; and oleic (C18:1), representing approximately 68% of its total fatty acid composition (Beres et al. 2017). However, due to the high cost related to its extraction (Dwyer et al. 2014), this oil is mainly employed in the pharmaceutical and cosmetic industries, being an excellent source of antioxidant compounds and sterols, which assist tissue regeneration and restructuration.

The antioxidants obtained from natural sources can be utilized to inhibit the oxidation in edible oils. The grape pomace is a low-cost source of natural antioxidants, which present a great potential to prevent oxidation in oils. Phenolic compounds are recognized as free radicals scavengers, whereas anthocyanins and phenolic acids effectively prevent the lipid oxidation. The red grape pomace presents higher oil oxidation inhibition than the white grape pomace, what is related to the higher content of phenolic compounds, especially anthocyanins, in the red grape varieties (Bakota et al. 2015).

2.5. Bioconversion of Grape and Wine By-Products to High Value Products and Energy

The valorization of viticultural wastes is possible when considering the biorefinery concept, in other words, the utilization of the viticultural by-products as raw material for bioconversions aiming at the production of chemical products, materials, biofuel, heat and energy. In this sense, the bioconversion of grape processing by-products, pursuing the recovery of high added value products and energy, is a crescent tendency (Sette et al. 2020).

Biorefineries are facilities which convert the biomass into numerous products for different industrial segments in a sustainable form. The products obtained through the biorefineries might be biofuels (hydrogen gas, methane, bioethanol and biodiesel), chemical products (sugars, carboxylic acids, bioethanol and biobutanol), bioelectricity, biomass, biomaterial (biopolymers), biofertilizers and animal feed (Jin et al. 2018; Gallego et al. 2019). The biorefineries are classified according to the raw material (biomass) and the technology utilized for obtaining the target products. The first-generation biorefineries obtain their chemical products from sugars available in plant constituents, which have starch or saccharides. However, this kind of production directly compete with the food production. The second-generation biorefineries utilize the lignocellulose biomass derived from plant residues, such as the grape processing residues obtained during wine and grape juice elaboration, which are rich in lignocellulose materials constituted mostly by cellulose, lignin, hemicellulose, and present lower concentrations of proteins, minerals and secondary metabolites (Kamm and Kamm, 2004).

The application of food processing by-products in biorefineries to obtain multiple products with high added value presents numerous advantages, such as the total utilization of raw materials which would be discarded. As a result, the biorefinery concept enables the minimization of residues generation during processing and encourages the whole utilization of renewable sources, reducing the environmental impacts. In addition, the energetic self-efficiency of the food production chain can be achieved, for instance, through the production of biogas. The bioconversions aim to separate the biomass components to attribute a utilization that allows to obtain the highest yield in terms of biovalue. Therefore, the biorefinery approach applied to the vinification process predicts the ideal exploration of by-products in different industrial segments (Myrto-Panagiota et al. 2017).

In this regard, the viticulture sector produces a great amount of solid residues and by-products, especially biomass, which requires a reutilization. This is possible with the implementation of systems and processes that enable the promotion of their valorization, through bioconversions, for example, which reduce the environmental impact that would be related to their accumulation into the nature (Jin et al. 2018; Gallego et al. 2019).

The winemaking process residues (pomace and non-pomace), for instance, are rich in lignocellulose biomass and might be utilized as sources of high added value products applying green technologies in the biorefineries facilities. On this subject, the conversion of lignocellulose biomass contained in these plant waste-material might be performed aiming at the production of bioenergy and bioproducts, valuing these materials and reducing their disposal into the environment (Sette et al. 2020).

Different technologies are applied to the plant-based material to separate the biomass constituents and convert them into high added value products, such as chemical products, energy and biofuels (Cherubini, 2010). Mechanical treatments are commonly used in the biorefinery processes to reduce the biomass volume. These technologies include pressing, milling and pelletizing, which do not alter the biomass composition, only the size and form of the particles, promoting an improved mass transfer, enzymatic hydrolysis and biodegradability of the biomass (Menon and Rao, 2012). Some chemical processes might be applied to modify the biomass chemical structure, such as acid or basic hydrolysis, transesterification, hydrogenation and oxidation. The biochemical processes such as enzymatic conversion, anaerobic digestion and fermentation can be applied for the production of biofuels. When the anaerobic digestion of grape pomace is performed, a methane-rich biogas is produced (Martinez et al. 2016). The cellulose and hemicellulose present in the biomass can be enzymatically hydrolyzed in glucose and xylose, monosaccharides which in turn can be utilized to produce ethanol, hydrogen and butanol (Hafid et al. 2015).

The non-pomace grape residue presents high concentrations of lignin, cellulose and hemicellulose (Amendola et al. 2012), which can be used for the production of energy, fuels, materials and chemical products. The grape pomace is traditionally used in fermentation processes to obtain ethanol-rich extracts, which, according to their purity and alcohol content, are then used to produce solvents and fuels. The hemicellulose (pectin and glucomannan) found especially in the non-pomace and pomace grape residues is widely utilized for the ethanol production, to be employed as biofuel. Several products might be obtained through chemical and biotechnological processes of grape by-products, such as ethanol, organic acids, oils and pigments. The volatile fatty acids extracted from these plant residues can be employed for the production of bioplastic, biodiesel, bioelectricity generation and biofertilizers (Venkata Mohan et al. 2016).

The wine and grape juice processing by-products can be successfully used as raw material following the biorefinery concept. The utilization of these residues meets the necessity of minimizing their disposal, reducing the energy consumption and increasing the sustainability of the food industry. This approach has positive economic and environmental impacts, contributing to a greener and sustainable production of high added value products for numerous purposes.

CONCLUSION

The recovery of phytochemical compounds from the grape and wine processing by-products represents a sustainable and economic source of high value bioactive compounds, which can be recycled and return to the food chain as functional and nutraceutical ingredients, under the concept of the circular economy.

The grape by-products are important sources of bioactive compounds and dietary fibers, which could be employed for food enrichment, such as in meat products, cereals, dairy and fruit-based products. The utilization of grape by-products as a source of functional ingredients is a promising field. In this context, the recovering of bioactive compounds and dietary fibers might be an interesting alternative, especially intending the reduction of environmental impact and prioritizing the sustainable use of the natural resources. Besides, following the crescent trend towards the utilization of healthier food products and ingredients, the by-products originated during wine and grape juice processing might be successfully employed in the food industry to delay chemical and microbiological reactions, enabling the reduction in the utilization of synthetic preservatives and antioxidants, without compromising the stability, quality and safety of the final product. The grape processing by-products can be also employed as raw materials in bioconversions, aiming at the production of bioproducts and bioenergy, especially biogas.

Several technological solutions for the total reutilization of grape processing residues are available, enabling the transformation of numerous target products for different industrial segments, especially food, pharmaceutical and cosmetic industries. Therefore, the search for technologies that value the viticultural wastes grounded on the generation of high added value products must be encouraged, since it promotes economic and environmental benefits for the viticulture sector, contributing to the enhancement of local and global economy.

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Chapter 6

PRODUCTION OF GRAPE JUICE - A BRIEF REVIEW

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ABSTRACT

The consumption of grapes and several fruits is often associated with a low risk of developing chronic diseases, such as cancer, cardiovascular diseases, cataracts, hypertension, among others. This fact can be attributed to the high content of compounds with bioactive properties, known as phytochemicals, such as phenolic compounds, carotenoids, vitamins and endogenous metabolites, which are present in plants. In the processed

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grapes segment, the growth in consumption and juice production occurs mainly due to the change in the consumption habit for healthy foods, since this product also has bioactive properties, such as phenolic compounds. For the production of quality juices, attention should be paid to various aspects of the production chain, such as the correct choice of grape cultivar according to the provenance region of cultivation, and also the appropriate preparation technique of the most. It is noteworthy that an important factor of grape juice quality is the coloring matter content, provided that this factor is directly linked with the acceptability of the juice by the consumer, considering that juices with low color intensity are not attractive. Thus, this chapter describes the most important topics related with grape juice production.

Keywords: grape juice, grape processing, grape composition

1. INTRODUCTION

Grape juice can be defined as the product of extracting the liquid from the pulps and skins of ripe grape berries. It must not be fermented, and has the characteristic color, aroma and flavor of the grape that gave rise to the juice. In addition, it may or may not be subjected to a treatment that ensures its presentation and conservation. For the color, juice can be classified as red, pink or white. Regarding processing and constitution, the most important types are: whole juice, which refers to juices with no added sugar and in its natural concentration; and concentrated juice, which is the partially dehydrated juice with the minimum concentration equivalent to 65º Brix in natural fruit solids; dehydrated juice, which is the product in solid form, obtained by dehydrating grape juice, whose moisture content does not exceed 3%, and reprocessed or reconstituted juice, which is has gone through the process of diluting the concentrate and/or dehydrated juice (Rizzon and Meneguzzo, 2007). Still, there is the sweetened juice which is the one that receives added sucrose and the nectar, which is the drink that contains other constituents besides the liquid of the fruit itself (at least 50% of juice from the same fruit) (Brasil, 2009).

World grape production is approximately 73 million tons, with 37% on the European continent, 34% on Asia, and 19% on the American continent

(OIV, 2018). Around 55% of the harvested grapes are destined for wine making, 35% for consumption of table grapes, and the rest is divided between juices and raisins (OIV, 2016). Thus, there are 4 million tons of grapes specifically for juice production, generating around 10 million hectoliters of juice, with the world's largest producer of this type of grape being Italy, followed by China and the USA (OIV, 2018). In Brazil, the production of grapes destined for processing to make wines, juices and other derivatives is around 800 thousand tons per year (Mello, 2019).

The world revenue in the grape juice segment amounts to US$4,804 m in 2020. The market is expected to grow annually by 2.0% (2020-2023). In global comparison, most revenue is generated in the United States (US$1,037 m in 2020), followed by Canada (US$512 m), Germany (US$459 m), India (US$343 m) and Brazil (US$281 m). In relation to total population, per person revenues of US$0.6 are generated in 2020. The average per capita consumption in the world stands at 0.2 L in 2020 (Statista, 2020).

2. Methods of Grape Juice Extraction

The extraction of the juice from the fruits occurs basically by two processes: sulphiting or heating. The sulphiting method, also known as Flanzy process, is a procedure aimed mainly at the production of large volumes of juice. The process involves destemming and crushing the grapes, followed by smothering with sulfur dioxide. This substance, when applied to the grape, promotes the extraction of the skin color and guarantees the microbiological and enzymatic stability of the juice. The Flanzy process foresees that the crushed grape is added with sulfur dioxide, at the rate of 0.8 to 1 g/L. The maceration in the presence of SO_2 enriches the juice in coloring matter, aromatic compounds, enzymes and vitamins. The contact time is 2 to 4 days, after which the juice is separated by pressing and stored in tanks. For the commercialization of the juice, it must go through the desulfitation process, which consists of reducing the sulfur content of the final product. The juice is vaporized by means of a nebulizer inside an autoclave, where it is kept under constant vacuum and a temperature between 60 and 65ºC. The juice can be bottled hot or cooled using heat exchangers (Marzarotto, 2010).

Source: Authors.

Figure 1. Stainless steel pot (pan) for grape juice extracting by steam entrainment.

Another method that can be used is the Welch process, which consists of heating the grape until the berries soften, releasing the juice contained in them. The heating can be carried out with the whole grape or crushed at temperatures between 70 and 90°C for color extraction, afterwards the juice is separated and bottled. This methodology was used for the first time by Thomas Welch, in 1869, using the theory developed by Louis Pasteur (pasteurization) in the conservation of fresh grape juice (Marzarotto, 2010). Currently, a derivation of the Welch method has been used with the use of an extraction pan by steam dragging (Figure 1). It is a system composed of a heat source (boiler, furnace, heating vessel or gas or diesel oil burner), which heats a container with water. A second pan is attached to the upper part, with small holes in its lower part, in which the grape is inserted intact and without the stems. The water vapor formed by the boiling water rises and passes through the grape berries, softening them. In this way, the juice from the softened berries is released and collected directly into a container.

The juice thus obtained can be immediately bottled, still hot, or cooled for the lees to decant for later pasteurization (Guerra, 2016). This procedure has the potential to produce products with better organoleptic quality and without sulfite residues, being widely used in the preparation of small volumes, quite common in small agricultural properties.

3. Grape Juice Composition

The chemical composition of grape juice depends, especially, on the original vine cultivar, the stage of ripening of the grapes, the climatic conditions of the growing region and the treatments to which the product is subjected. Moreover, the juice composition must be similar to original grape, if it is not subjected to any treatment that could change its concentration or composition (Rizzon et al., 1998; Bates et al., 2001; Marzarotto, 2010).

Thus, nutritionally, the juice is similar to the grape itself, because its composition has the main constituents such as sugars, minerals, acids and vitamins. In addition, it presents sources of bioactive compounds, such as phenolic compounds that are directly related to sensory characteristics such as color and flavor. The rich constitution of grape juice makes it considered a differentiated drink, since it has an energetic, nutritional and therapeutic effect (Rizzon and Meneguzzo, 2007; Dávalos and Lasunción, 2009; Marzarotto, 2010). On the other hand, the technology adopted, especially with regard to temperature and extraction time, allows different levels of extraction of substances present in grapes, giving rise to important variations in the chemical and organoleptic composition of the grape juice (Rizzon et al., 1998; Marzarotto, 2010). Grape juice has a high content of sugar, glucose and fructose, considered, therefore, an energetic food, being easily assimilated by the human body, as they are simple glycids (Rizzon et al., 1998; Bates et al., 2001). The sugars present in the grape vary from 15 to 30%, depending on the cultivar and the level of ripeness of the grape (Santana et al., 2008).

The main organic acids present in grape juice are tartaric, malic and citric acids, which confer a low pH, ensuring a balance between sweet and acidic tastes (Rizzon et al., 1998; Bates et al., 2001; Rizzon and Meneguzzo, 2007; Marzarotto, 2010).

The mineral elements that are absorbed by the vine's root in the form of salts that accumulate in the fruits, are also present in the juice, such as potassium, calcium, magnesium, manganese, sodium, iron, phosphates, sulfates and chlorides (Rizzon et al., 1998; Rizzon and Meneguzzo, 2007; Marzarotto, 2010). The nitrogenous substances are also present in the juice, in the form of polypeptides, proteins, ammoniacal nitrogen and amino acids. Thus, grape juice is an important source of amino acids, since the amino acids considered essential for the human organism are present, and can contribute to supply the human daily needs of these nutrients (Rizzon et al., 1998; Rizzon and Meneguzzo, 2007; Marzarotto, 2010).

The B complex vitamins (thiamine, riboflavin and niacin), ascorbic acid and inositol, as well as pectin, which contributes to increasing its viscosity, and consists of molecules of galacturonic acid, are also present in grape juice (Rizzon and Meneguzzo, 2007).

Phenolic compounds are aromatic hydroxylated substances, with great structural diversity, ranging from one molecule to polymers, found naturally in cereals, vegetables, fruits, tea, herbs, chocolate, coffee and wine. Approximately 8 thousand types of phenolic compounds are known, being generically classified as simple phenols and polyphenols, based on the number of subunits of phenols present (Araújo, 2011). These compounds are secondary products produced by plants, which have different functions in plants, and can act as defense compounds against herbivores and pathogens agents. Others have a role in mechanical support, as an attractor for pollinators or fruit dispersers, in protecting against ultraviolet radiation or reducing the growth of adjacent competing plants. In addition, in food phenolic compounds are responsible for color, astringency, aroma and oxidative stability of the foods (Belitz et al., 2009; Taiz and Zeiger, 2009; Pinto et al., 2011).

Phenolic compounds are the elements responsible for the color and astringency of red grape (Rizzon and Meneguzzo, 2007). The color of the juice significantly influences the acceptability of the product and is used as a strong indicator of quality, which highlights the importance of developing products with an attractive appearance for the food industry (Coultate, 2004; Araújo, 2011; Roberto et al., 2013).

In vegetables, anthocyanins are the phenolic compounds responsible for most of the red, pink, purple and blue colors (Lopes et al., 2007; Taiz and Zeiger, 2009). In addition, the types and amounts of anthocyanin pigments are different between grape species. Differences in anthocyanin types help to explain why some grapes have better color stability and are more suitable for juice processing than others (Bates et al., 2001).

The concern for a healthy diet motivates the search for products that besides being nutritious, have properties to protect the organism from illnesses. In this scenario, research has demonstrated the important role of resveratrol, a molecule present in wines and grape juices in the prevention of diseases, especially those linked to the cardiovascular system (Freitas et al., 2010). Epidemiological, clinical and *in vitro* studies have demonstrated the biological effects associated with the diet with phenolic compounds, such as antioxidant, anti-inflammatory, antimicrobial and anticancer activity, in addition to helping to fight chronic and vascular diseases (Dávalos and Lasunción, 2009).

Grape juice and wine are a good source of phenolic compounds, however, juice consumption has advantages over wine, due to the absence of alcohol, which allows the juice to be consumed by most people, including children, pregnant women and those who have some restriction due to health or religious conditions (Romero-Pérez et al., 1999; Toscano et al., 2017).

Volatile compounds are responsible for the aroma of grape juice. They can originate from the grape itself or from the fermentation process, as in the case of ethanol and acetic aldehyde. Methanol originates from the hydrolysis of pectins in the contact of the crushed grape film with the must (Ribéreau-Gayon et al., 2006).

Regarding preference, Europeans prefer juices with 13 to 16% sugar and acidity between 0.8 to 1.0%, expressed in tartaric acid (w/v), with small variations depending on the country considered. On the other hand, in Argentina, juices have 17 to 20% sugar and acidity between 0.6 and 0.7%. Therefore, variations in sugar content and acidity show the diversity of tastes of different peoples. For Brazilian standards, the preference is grape juice with approximately 15% sugar and 0.8% total acidity (w/v), and sugar/acidity ratio between 16 and 19.5 (Marzarotto, 2010).

4. Factors that Influence Grape Juice Quality

The quality of the juice is closely linked to the quality of its main raw material, that is, grapes. The obtaining of grapes with the desirable aspects for the preparation of juices, depends on several factors, such as the vine cultivar, the climatic and soil conditions of the region of cultivation, the care in the cultural treatments, especially in the stage of maturation of the berries, among others.

4.1. Grape Cultivars

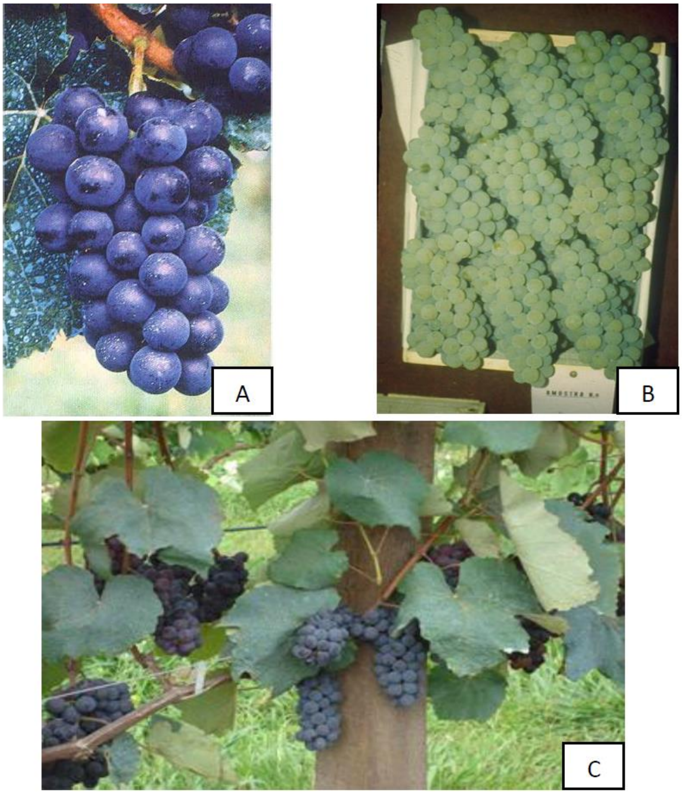
Commercial grape cultivars are selected for different purposes such as fresh consumption, processing in wine, juice, jellies, among others, according to their characteristics, such as flavor, color, sugars and acid content. Specially for production of juice, other important factors are considered, such as the ripening duration, the usual harvest date and the acidity level in the harvest (Boulton et al., 1996).

At first, juice could be made with any grape cultivar, as long as it reaches an adequate maturation and presents a good sanitary condition, a present good must yield, adequate sugar/acidity ratio, pleasant and well-defined aroma and flavor (Rizzon and Meneguzzo, 2007; Marzaroto, 2010; Gurak et al., 2012). In addition, the choice of a grape cultivar for the preparation of juice should also consider the consumer’s preference, since the diversity of habits leads to the use of grapes with very different flavor characteristics (Rizzon and Meneguzzo, 2007; Dutra et al., 2014). This diversity means that, in each region, grapes are used with very different flavor characteristics, which is evidenced by the fact that grapes of American, European and/or hybrid origin are used, according to the region (Marzarotto, 2010).

The juice produced in many countries with a wine tradition is made with *Vitis vinifera* grapes, from both white and red cultivars. Nevertheless, American grapes, such as 'Concord' (*Vitis labrusca*) have become the quality standard for red grape juice worldwide. For white juice, 'Niagara' grapes, along 'Delaware' and 'Catawba' and various hybrid grapes are gaining popularity (Bates et al., 2001; Gurak et al., 2012).

The practice of carrying out blends or mixtures between the different cultivars is quite common in order to have a quality juice, with adequate color, sweetness and flavor, in order to enhance the relevant characteristics of each cultivar (Maia et al., 2013). Thus, the selection of different cultivars for the production of juice can be favorable, as any imbalances can be corrected through blends during processing (Assis et al., 2011).

One of the main qualities of the grape for juice is the maintenance of the freshness of the flavor throughout the production and conservation process, which are presented in American grape cultivars, even after pasteurization. The "foxed" aroma of American grapes, which is not accepted by a large number of wine consumers, becomes a positive characteristic when present in grape juice. Thus, in United States of America, native varieties predominate in the juice industry, especially 'Concord' (Marzarotto, 2010). On the other hand, juice of European grape cultivars (*V. vinifera* L.) loses its freshness and takes on a stew taste during processing, justifying the lack of aroma of European grape juices, except for those made from Muscat family of grapes, causing many producers to mix grape juice with other fruits, such as orange, raspberry and strawberry (Marzarotto, 2010). In Central European countries, varieties of the species *V. vinifera* are used, such as 'Chasselas Doré' and 'Riesling', in addition to some French hybrids, whose freshness is maintained by the use of ultrafiltration. In Italy, the juice is prepared with 'Isabella' (*V. labrusca*) and 'Seibel 5455' (hybrid) grapes and with the white grapes, such as 'Seyve-Villard 5276' (hybrid), 'Cardinal' (*V. vinifera*) and 'Regina' (*V. vinifera*) grapes. These last have a special aptitude, due to their low sugar content, aromatic finesse and richness in pectic and colloidal substances (capable of stabilizing cloudy juices). In France, 'Aramon' (*V. vinifera*) is used, while in the United States, the grapes 'Concord' and 'Isabella' (*V. labrusca*) are predominant. In Spain, 'Moscatel', 'Macabeo', 'Airen' and 'Jaen' grapes, and in Argentina, 'Barbera d'Asti', 'Cereza' and 'Pedro Ximenez' (*V. vinifera*) grapes are used (Marzarotto, 2010).



Source: Authors.

Figure 2. Three different grapes varieties (*Vitis labrusca*) used for juice production: (A) Ives, (B) Niagara, (C) Isabella.

In Brazil, grape juice is made mainly with varieties from the American species and their hybrids, which have a special aptitude for making quality juices, such as 'Isabella', 'Ives' and 'Concord' (*V. labrusca*). To a lesser extent, white grape juice is produced from 'Niagara' (*V. labrusca*) (Figure 2) (Rizzon et al., 1998; Camargo, 2005; Marzarotto, 2010; Ritschel et al., 2018).

Therefore, which variety should be planted in a new area depends on many factors such as biology, climatology and economics. Not a single variety can be universally recommended, considering the value of diversity between products derived from grapes to maintain consumer interest (Boulton et al., 1996).

4.2. Grape Ripening for Juice Production

The traditional American or hybrid grape cultivars used for juice, add raspberry flavor to the most, and this a reference of the organoleptic quality of grape juices. This group of varieties used by the Brazilian juice industry has been complemented in the last years with the breeding of novel grape juice cultivars in order to increase the sustainability and the competitive edge of this segment, especially to obtain hybrid cultivars with different ripening periods. These new juice cultivars differ in the length of productive cycles, in the intensity of the juice color, in the sugar content, and also in the range of climatic adaptation. Six new grape juice cultivars were released in last years by the Grape Breeding Program maintained by Embrapa Grape and Wine Research institute. This group of cultivars has contributed to increase and diversify the options of grape juice cultivars in Brazil (Ritschel and Maia, 2012). Among them, 'BRS Magna' is a new grape used for juice making, with intermediate cycle and wide climatic adaptation, released as an alternative to improve the color, the sweetness and the flavor of grape juice (Ritschel et al., 2014). The juice made with 'BRS Magna' is intense violet, and can be taken pure or in blends with other juices. In comparison with the juice made with other cultivars released by the Grape Breeding Program. 'BRS Magna' anthocyanin and phenolic compounds contents were distinguished with high quality, especially when grown under semi-arid conditions, where ripening phases can be controlled in order to obtain full ripe any different seasons along the year.

In the cultivation of grapes for juice production, the ripening phase is fundamental in the quality of the final product, as it is the moment when the main qualitative aspects are defined. In this phase, there is a greater accumulation of carbohydrates by the berries, as well as a decrease in acidity. In addition, precursor substances for aromas, such as phenolic compounds are formed, giving rise to the typical characteristics of each cultivar (Abe, 2007).

During the ripening of the grapes, several changes occur in the bunches, among them the color change of the berries (Rosier, 2003). At this stage, all the carbohydrate produced by the grapevine, which is initially directed towards its vegetative growth, starts to be directed towards the berries, thus causing the accumulation of sugars, and the period of greatest accumulation lasts an average of 15 days. Close to harvest, the berries continue to accumulate sugar, but more slowly, and depending on climatic conditions, the sugar content may even decrease (Blouin and Guimberteau, 2004).

According to Chaves (1986), the concentration of sugar in the berries depends on the photosynthetically active leaf surface, on competition with other drains (trunks and roots) and on the translocation of assimilated leaves to the bunches. At the beginning of maturation, the organic acids of the grape are quite high, since their synthesis occurs in leaves and berries that are still green (Possner and Kliewer, 1985). However, with the evolution of maturation there is a reduction in acidity due to the entry of water in the berries and by the respiratory process that consumes acids as an energy source. High temperatures also contribute to the degradation of acids, as they increase the respiration rate of vines, which is why grapes grown in colder places tend to have a higher acid content than those produced in warmer places (Blouin and Guimberteau, 2004). The migration of bases and the consequent salinization of organic acids also contribute to the reduction in the content of its acidity (Rizzon et al., 2000).

The synthesis of phenolic compounds is closely related to sugar metabolism. When the vine starts to accumulate carbohydrates in the berries instead of consuming them, alternative metabolic pathways occur, which lead to the synthesis of phenolic compounds. Glycolysis via pyruvate is one of them and is also responsible for the main vital functions of the plant such as respiration, acid formation and vegetative development (Rosier, 2003). Another metabolic pathway is that of the pentoses, in which phenylalanine is found, which, commanded by the hormonal concentration, directs energy towards vegetative growth. When hormonal rates vary, metabolism via the pentose pathway causes phenylalanine to direct energy to two distinct points: the formation of lignin for plant reserves and chalcone, a common precursor to tannins, flavonoids and anthocyanidins, which without the competition of vegetative growth, receive their share of energy redoubled, via glycolysis and via pentose (Rosier, 2003).

For the synthesis of phenolic compounds, hormonal variation is a fundamental factor, caused by several factors linked to climatic conditions such as light, temperature and daily thermal amplitude (Favero, 2007). Usually in hot regions with lower thermal amplitude, the grapes are less colorful and have lower tannin content (Champagnol, 1984). The phenolic compounds are produced in the cytoplasm, stored in the Golgi complex and later migrate to the cell wall (Elias, 2008). They are defined as substances with one or more aromatic rings (benzene) and at least one hydroxyl, and because they have a strong ability to donate electrons (H^+), they are considered potent antioxidants (Ribéreau-Gayon et al., 2006). The presence of phenolic compounds occurs throughout the plant kingdom, and the grapevine is a great source of these compounds, being found mainly in the seeds and in the skins of berries (Blouin and Guimbereau, 2004). They are also responsible for pigmentation and much of the flavor of the grapes, and the differences in color and flavor between the cultivars are associated with the content and polyphenols profile of each variety (Abe et al., 2007).

4.3. Soil and Climate Conditions

For grape production, the climate is considered a major factor in the duration of the vine cycle, in the quality of the product, in the plant health and in the productivity of the vine; with solar radiation, air temperature, precipitation and relative humidity being the most important meteorological elements (Sentelhas, 1998; Van Leeuwen et al., 2004; Mandelli, 2009).

The vine, being a heliophile plant, is demanding in solar radiation, and the lack of light causes problems mainly during flowering and maturation, and this factor varies with latitude, time of year, hours of the day, exposure of the land, hygrometric degree and cloudiness (Sentelhas, 1998; Pedro Júnior and Sentelhas, 2003). The main effects of light on the metabolism of the grapevine are associated with the differentiation of bud fertility, the growth and composition of the berries, the gas exchange in the leaves and the metabolism of nitrogen (Moura et al., 2009). According to Williams et al. (1994), vines with clusters that are more exposed to light intensity, produce grapes with a higher sugar content and phenolic compounds, and reduced acidity.

Another factor that influences practically all the physiological processes of the vine is the temperature, since the photosynthetic activity involves biochemical reactions, whose catalysts are dependent on the temperature to express its maximum activity. Values below 20ºC result in less intense photosynthesis reactions; between 20 and 30ºC they come close to the ideal and, in temperatures above 45ºC, they fall again (Kishino et al., 2019; Teixeira, 2009). Therefore, temperature has an influence on all the phenological phases of the vines (Favero, 2007).

The vine is considered a drought-resistant plant, because its root system is capable of penetrating the soil at great depths and can grow, from regions where the annual rainfall does not exceed 200 mm, even in the most humid regions, with more than 1,000 mm, varying production technology and productivity levels (Pedro Júnior and Sentelhas, 2003). During vegetative growth, continuous rain favors infection by fungal diseases of the aerial part, as it increases the leaf wetting period, disseminating pathogens and washing applied fungicides, in addition to not allowing phytosanitary treatments (Kishino et al., 2019). Excessive rainfall also limits the production of quality grapes, given that their occurrence during flowering causes failure in fruiting, and during ripening causes fruit rot and loss of quality (Simão, 1998). Thus, the relative humidity of the air and the duration of leaf wetting by dew influence the development of the vine, as the constant presence of moisture in the vineyard provides conditions for the installation of pathogens of the main fungal diseases (Sentelhas, 1998).

Although excess moisture is a limiting factor in grape production, water deficit also affects vineyard production. In conditions where the loss of water by the plant is greater than its uptake, there may be limitations on the growth and development of the vines (Souza, 1999). The water demand varies according to the phase of the phenological cycle, and depending on this phase and physiological conditions, the water deficit can bring favorable or unfavorable consequences to the plant. For example, in the final stage of maturation, the lack of water can cause higher concentration of sugars and phenolic compounds in berries (Ojeda et al., 2004; Deloire and Hunter, 2005). There is a strong relationship between the quality of grape and water deficit before "veraison." An initial water deficit causes early growth of sprouts to stop and reduces the size of the berries. Under these conditions, the concentrations of berry sugar and anthocyanin increase due to the faster ripening process. Moreover, the total acidity is reduced, as the berries contain less malic acid (Van Leeuwen et al., 2004).

In relation to the soil, vines can be grown on a wide variety of soils. In deep and rich soils, the vines are vigorous and highly productive. The effect of the soil on the behavior of the grapevine and the composition of the grapes is complex, since the soil influences the mineral nutrition and the conditions of water relations of the grapevine, as well as the depth of the root system and the temperature of the root zone. To understand the effect of soil on viticulture, it is necessary to take into account the interaction between the soil and the vine (Van Leeuwen et al., 2004; Van Leeuwen and Seguin, 2006).

The edaphic-climatic conditions of the producing region can influence the vegetative development of the vines, as well as the physicochemical characteristics of the vines, influencing the quantity and quality of the grapes produced, as well as in the derived products, mainly wines and juices (Chavarria et al., 2011; Luciano et al., 2013; Granato et al., 2016). In this way, information about soil chemistry has the potential to be used to define the best adaptation of vine varieties, and guide the practices of soil management to obtain better juice quality, since it influences the composition of the grape (Mackenzie and Christy, 2005). According to Van Leeuwen and Seguin (2006) the supply of water and nitrogen to the vines must be moderate, because severe stress can negatively affect the grape's aroma potential.

The high quality of the grape can be obtained when a limiting factor reduces the vigor of the vine and the size of the berry, and increases the phenolics of the grape skin. In most terroirs known for their high-quality grapes, this limiting factor is a mild water deficit, either due to the dry climate or the low water holding capacity in the soil (Van Leeuwen and Seguin, 2006).

CONCLUSION

Grape juice is a product with a tendency of consumption growth worldwide, mainly driven by its organoleptic and nutraceutical attributes. Thus, the production of grape juice becomes a very promising economic activity for the development of different regions of the world. To this end, it is important to achieve scientific and technological advances, seeking to improve production both at the vineyard level and in industrialization; including the selection of vine cultivars adapted to each region, the proper management of the vineyard and the choice of suitable processing methods.

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Chapter 7

VALORIZATION OF VINE LEAVES FOR INFUSIONS PRODUCTION: CHEMICAL COMPOSITION AND SENSORY PROFILE

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ABSTRACT

In recent years, the consumption of teas and herbal infusions has increased in Europe and the United States of America and created a new market opportunity for new entries to the herbal tea market. Herbal infusions can be prepared from a great diversity of edible, aromatic, and medicinal plants. Vine leaves after grape harvest are often left on the vine itself or used as organic material for fertilization, animal feed, or energy production. The potential use of vine leaf infusions may be an interesting option for the habitual infusion consumers, opening up the range of options for this type of product and, at the same time, increasing the economical valorization of vine leaves. In addition, vine leaves infusion may be a potential alternative source of bioactive compounds for the human diet, besides being caffeine-free infusions, which may be a further advantage because some consumers have some sensitivity to this compound found in teas. Thus, this chapter describes the recent knowledge of the chemical composition of vine leaf infusions concerning different perspectives, such as their phenolic and mineral composition, amino acid profile, as well as a few examples of the sensory profile of these types of infusions.

Keywords: amino acid profile, infusions, phenolics, mineral composition, sensory profile, vine leaves

1. INTRODUCTION

Herbal infusions, usually named tisanes, are a good source of phytochemicals with health-promoting properties, consumed not only as herbal medicine but also consumed as a daily ready-to-drink hot beverage (Martins et al., 2001; Li et al., 2013; Xiao et al., 2017).

Due to the growing scientific evidence supporting the potential health benefits associated with herbal tea consumption, plants and herbal infusions have been used for traditional medicine as a beverage for centuries (Larkin, 1983; Poswal et al., 2019). In last years, there has been a resurgence of interest in “natural” products such as herbal teas with medicinal or nonmedicinal purposes (Manteiga et al., 1997). In fact, recently the rising consumer awareness of the role of a healthy diet in general well-being, quality of life, and disease prevention have been the main driver of choice for most herbal teas (Joubert et al., 2017). This has led to the expansion of the global herbal tea market, and the sales of these infusions increased progressively in Europe and in the United States of America (Smith et al., 2015).

Another important factor of infusions choice is the sensory attractive flavor and taste, beyond the comparatively low trade value for most herbal teas. However, for health aware consumers, the medicinal characteristics of herbal teas have become a decisive factor for the choice of herbal infusions. This trend in herbal infusion consumption created a new market opportunity for new entries to the herbal tea market (Joubert et al., 2017).

Infusions can be prepared from a great diversity of edible, aromatic, and medicinal plants. Herbal infusions are rich sources of natural bioactive compounds, such as alkaloids, carotenoids, coumarins, flavonoids, polyacetylenes, and terpenoids (Chandrasekara and Shahidi, 2018). Therefore, the World Health Organization pursues to exploit the use of herbal medicines in its 2014-2023 strategy, with the aim of keeping populations healthy through giving access to effective and affordable alternatives to medicine, and to give healthcare option coherent with people's cultural practices (World Health Organization, 2013).

Currently, the demand and use of plants to obtain infusions for medicinal purposes are increasing, and a great variety of these herbal products are available on the market. Several of them are obtained from plants that are familiar to the consumers, such as *Vitis vinifera* L. (*Vitaceae*). This crop is considered one of the most important in the world (7.5 Mha, nearly 80 million tons in 2018) concerning the position in the wine industry (FAO-OIV, 2016; FAOSTAT, 2020). There are around 2,000 different *Vitis vinifera* grape varieties grown all over the world (Lacombe et al., 2011). The vegetative parts, particularly leaves, are rich in bioactive compounds (such as, caffeic acid, catechin, kaempferol, quercetin, several phytosterols, and fatty acids) and are a disregarded by-product that is treated as waste in the wine industry (Maia et al., 2019).

A known herbal medicine practitioner Marušic (1990) points out the significance of the vine in his book Through herbal medicine to health, noting that the primary material for the preparation of herbal remedies should be grapes, flowers, leaves, and vine tendrils. Knowledge of the medicinal properties of grapevine (*Vitis vinifera* L.) can be traced far back in history. On the other hand, in Europe, the leaves of *Vitis vinifera* are documented in the literature of traditional medicine for their astringent and homeostatic properties where they are utilized in the treatment of diarrhea, bleeding, hemorrhoids, varicose veins, and other circulatory diseases (Lardos and Krauter 2000; Orhan et al., 2009; Nassiri-Asl and Hossein-zadeh, 2009; Pari and Suresh, 2009). In some European countries, *Vitis vinifera* leaves have traditionally been used as food (Dani et al., 2010), while in others they are considered waste and thus discarded, rather than valorized. However, grapevine leaves are a rich source of polyphenols and other therapeutic compounds (Schneider et al., 2008; Lacerda et al., 2016). The phenolic composition and biological activity of leaves were investigated in different grape varieties of *Vitis vinifera* (Fernandes et al., 2013; Katalinić et al., 2009; Labanca et al., 2020), as a promising source of bioactive compounds giving a new perspective for the use of this by-product and to develop a new value-chain. Torres et al. (2015) studied the antioxidant properties of vine leaves from *Vitis vinifera* cultivar Tempranillo and concluded that there is significant intra-varietal diversity in the response of Tempranillo to biotic and environmental factors to the presence of the antioxidant compounds.

The chemical composition of vine leaves is highly influenced by the grape variety of *Vitis vinifera* L., degree of maturation, climate condition, and the location in which the grapevines are grown (Krol et al., 2014; Taware et al., 2010; Teixeira et al., 2013). Studies for the identification and quantification of these phytochemicals in grapevine leaves were performed to optimize the harvest dates and leaves sampling position for the maximum phenolic compound’s concentration (Schoedl et al., 2012). Also, the changes in the phenolic profile and antioxidant activity of *Vitis vinifera* L. leaves due to the grape variety, sampling-time (Katalinić et al., 2009; Katalinić et al., 2013), powdery mildew infection (Taware et al., 2010), and drought stress (Krol et al., 2014) were investigated.

Thus, taking into account all of these points mentioned, this chapter describes the chemical composition of vine leaves infusion concerning phenolic composition, mineral composition, amino acid profile, as well as the sensory profile of vine leave infusion, especially showing several data obtained by the authors of the present chapter.

2. CHEMICAL COMPOSITION OF VINE LEAVES INFUSIONS

The vegetative organs of the vine include the roots and five parts extending from the root system to the visible aboveground: trunk, cordons, canes, stems, and leaves. These organs play a key role in light energy capture via photosynthesis, as well as water and nutrient absorption as regulated by transportation (Goufo et al., 2020). Specifically, leaves are the most visible parts of the canopy and consist of the blade and the petiole (the stem-like structure that connects the leaf to the shoot). Vine leaves after grape harvest are often left on the vine itself or used as organic material for fertilization, animal feed, or energy production. Thus, vine leaves valorization and consequent commercialization are not so developed as for wine and table grapes. Several authors have reported the antimicrobial properties (Jayaprakasha et al., 2003; Deliorman-Orhan et al., 2009; Ceyhan et al., 2012), antioxidant activity (Koşar et al., 2007; Fernandes et al., 2013), and phenolic composition (Xia et al., 2010; Fernandes et al., 2013) of *Vitis vinifera* L. leaves.

The potential use of vine leaves as herbal infusions are conditioned by their chemical composition and sensory characteristics. These properties are depending, namely on the different chemical components of the leaves used and the extraction process of these components during the infusion preparation. In the case of vine leaves, efficient discrimination tools can aid producers in optimizing and controlling the production process, namely harvesting time and drying process, and informing consumers concerning the infusion quality of the leaves. Fernandes et al. (2015) studied the volatile composition in vine leaves from two different Portuguese *Vitis vinifera* red cultivars (Touriga Nacional and Tinta Roriz) collected 30 and 60 days after the grape harvest (Figure 1) and in the respective vine leaf infusions. These authors observed that the volatile compounds present in vine leaves are dependent on the time of harvest with significant differences in the volatile composition of the leaves from the two grape cultivars, especially in the sample collected 60 days after the grape harvest. However, this is not reflected in the volatile composition of the vine leaf infusion made from these two cultivars, indicating that the harvesting date is more important for the volatile profile of vine leaf infusion than the vine leaf grape cultivar.

(A) (B)

Figure 1. Example of the visual appearance of vine leaves at 30 (A) and 60 (B) days after grape harvest of cv Touriga Nacional (photo: authors).

2.1. Phenolic Characterization

In *Vitis vinifera* L., many studies have been published reporting results of phenolics in grape berries and their impact on human health (Singh and Basu, 2102; Olas 2018; Marhuenda-Muñoz et al., 2019). According to several authors, grape phenolic compounds play an important role in human health, such as in oxidation inhibition of low-density lipoproteins (LDLs) (Ghiselli et al., 1998; Serafini et al., 2000; Xia et al., 2010), a decrease of inflammatory and carcinogenic processes (Tapiero et al., 2002) and inhibition of platelet aggregation (Gryglewski et al., 1987; Escarpa and

Gonzalez, 2001). In addition, during the last decades, a great number of studies reported the phenolic profile of the specific vine fractions, namely for grape bunch, which included skins (Jordão et al., 1998; 2001a; 2012; Costa et al., 2014; 2015a; 2015b), pulp (Costa et al., 2015b), seeds (Jordão et al., 2001a; 2012) and stems (Souquet et al., 2000; Jordão et al., 2001b). Also, for the other vine parts, several authors published numerous studies about the phenolic characterization, namely for canes (Gharwalová et al., 2018; Ferreyra et al., 2019; Moreira et al., 2020), roots (Weidner et al., 2009; Goufo et al., 2020) and leaves (Hmamouchi et al., 1996; Ramalhosa et al., 2013; Dresch et al., 2014; Harb et al., 2015; Aouey et al., 2016; Chitarrini et al., 2017). In addition, other study reported also the phenolic characterization of commercial dietary ingredients derived from *Vitis vinifera* L. grape skins, pomace, and leaves (Monagas et al., 2006). Nevertheless, during storage and after transformation and processing of each different fractions of the vine, the phenolic composition initially present will tend to undergo several changes, namely through its potential quantitative and qualitative reduction and also determine the composition of the final products (Monagas et al., 2006).

Several studies described the phenolic composition of several herbal infusions obtained from diverse plants, including from some grapevine fractions, namely skins and vine leaves (Table 1).

Tea, one of the major sources of phenolic compounds, is made up of processed leaves of a shrub known as *Camellia sinensis* from which a somewhat bitter, aromatic beverage is prepared by infusion in hot water. The most extensively studied infusions products for their phenol content and antioxidant activity are white, green, oolong, and black teas (Kilman and Hsu, 2003; Beknit et al., 2011; Costa et al., 2012; Veljković et al., 2013; Herrera et al., 2018), and chamomile (Veljković et al., 2013; Herrera et al., 2018) among others. For fruit tea infusions, also several studies have been published (Belščak et al., 2011; Celep et al., 2017).

Table 1. Phenolic composition of several herbal infusions obtained from different plants and fruits

Herbal infusions	Total phenolics	Total flavonoids	Gallic acid	(+)-Catechin	Quercetin	Caffeic acid	Kaem-pferol	Rutin	*p*-Couma-ric acid	References
Fennel	127.86[2]	43.95[3]	1.76[1]	5.64[1]	n.d.	0.27[1]	n.d.	22.02[1]	9.65[1]	De Magalhães and Dos Santos (2020)
Anise	107.20[2]	31.15[3]	0.84[1]	9.11[1]	n.d.	0.44[1]	n.d.	4.76[1]	1.83[1]	
Peppermint	557.7[2]	155.60[3]	0.25[1]	0.66[1]	0.62[1]	4.84[1]	n.d.	4.84[1]	2.78[1]	
Lemon balm	496.63[2]	85.77[3]	5.04[1]	5.04[1]	n.d.	6.63[1]	0.79[1]	15.14[1]	3.99[1]	
Green tea	229-291[2]	84 - 87[4]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Costa et al.(2012)
Rooibos red leaves	219.0[2]	116.0[4]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Borututu roots	14.0[2]	3.4[4]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Red grape skins	1.2[5]	n.d.	0.09[6]	0.24-0.88[6]	n.q.	0.03-0.07[6]	n.q.	0.26[6]	n.q.	Beknit et al. (2011)
Green tea	6.0[5]	n.d.	0.60[6]	n.d.	n.q.	0.03[6]	n.q.	2.25[6]	n.q.	
Hibiscus	1.0[5]	n.d.	0.09[6]	n.d.	n.q.	0.10[6]	n.q.	0.30[6]	n.q.	
Black tea	21.5[7]	5.1[7]	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	Herrera et al. (2018)
Green tea	61.0[7]	2.9[7]	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	
Chamomile	6.0[7]	3.7[7]	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	
Thyme	40.3[7]	35.9[7]	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	
Black tea	164.6[8]	63.34[8]	1.34[8]	0.263[8]	n.q.	0.195[8]	n.q.	1.48[8]	n.q.	Veljković et al.(2013)
Green tea	240.7[8]	84.94[8]	1.98[8]	0.40[8]	n.q.	0.261[8]	n.q.	1.09[8]	n.q.	
Chamomile	36.3[8]	11.79[8]	0.11[8]	0.17[8]	n.q.	0.205[8]	n.q.	n.d.	n.q.	
Vine leaves	14.0-37.0[1]	8.1-27.5[1]	n.q.	n.q.	12.7-75.9[1]	n.q.	n.q.	11.5-43.7[1]	n.q.	Jordão et al. (2019)
	n.q.	n.q.	1.2-12.4[9]	31.3-49.5[9]	39.7-101.1[9]	2.1-88.2[9]	82.3-105.8[9]	n.q.	n.q.	Alejandro et al. (2020)

n.d. = not detected; n.q. = not quantified;[1] mg/L;[2] mg/L gallic acid equivalents;[3] mg/L quercetin equivalents;[4] expressed as (-)-epicatechin equivalents;[5] expressed as mg gallic cid equivalents based on 2 g of tea infusion per serve;[6] mg/g of extracts;[7] mg/g of dry weight;[8] g/g extract;[9] µg/g dry weight.

According to Potter (2012), there are a great number of polyphenols in tea. For black tea (resultant of a total fermented *Camellia sinensis* leaves) the most abundant phenolic compounds found include oxidized derivatives of catechins, namely thearubigins and theaflavins, quercetin, gallic acid, and caffeic acid (Lee et al., 2002). Bhebhe et al. (2016) reported higher total phenolic content (more than 50%) in aqueous organic solvents, particularly by the use of hot water, in the infusions from *Camellia sinensis*. This tendency was also detected by other authors by the use of other plant extracts (Tatiya et al., 2011; Yuxi and Xu, 2014). In general, when is compared total phenolic composition between tea infusions and other herbal infusions, tea infusions, especially green tea infusions, showing the highest total phenolic content (Celep et al., 2017).

Bekhit et al. (2011) reported the highest total phenolic content in green tea infusions at a concentration of 215.9 mg gallic acid equivalents per cup. However, according to these authors, grape skin may be a potentially interesting tea infusion since grapes are very aromatic fruits with wide flavor profiles and containing a high content of phenolic compounds. These authors reported values of total phenolic content in grape skin infusions from Pinot Noir and Pinot Gris between 1.3 and 1.5 mg gallic acid equivalents per cup. On the other hand, Gerardi et al. (2020) reported the phenolic composition of grape skin infusions from cvs Primitivo, Negramaro, and Verdica, and also from black tea. The combination of grape skins with black tea (1 g grape skins and 1 g black tea) produced the highest ratio of total phenol content. Previously, Limberger et al. (2018) studied Cabernet Sauvignon grape skins from wine by-product as a raw material for the production of infusions. This study analyzed the anthocyanin content of grape skins dried by different methods and their infusions. These authors concluded that the percentual of anthocyanins present in the infusions related to the anthocyanins content of their corresponding grape skins varied from 37.1 to 83.3%.

According to several studies, *Vitis vinifera* leaves extracts, can be also considered a rich natural source of polyphenolic compounds with good antioxidative properties. Vine leaves contain a wide range of polyphenol flavonoids including flavon (ol)-glycosides and glucuronides, quercetin-3-*O*-beta-D-glucuronide (most abundant of flavonoids), isoquercitrin, anthocyanins, oligomeric proanthocyanidins (Hmamouchi et al., 1997; Monagas et al., 2006; Jordão et al., 2019), catechin, epicatechin monomers and dimmers, caffeic acid, and gallic acid (Felicio et al., 2001; Alejandro et al., 2020). The phytoalexin trans-resveratrol, another polyphenolic substance belonging to the stilbene group, can also be found in grapevine leaves (Langcake et al., 1979). Moreover, $AlCl_3$ is a potent elicitor of resveratrol production also found vine leaves (Adrian et al., 1996). In vine leaves, also organic acids, mainly malic and oxalic acids but also tartaric acid could be found. Citric, fumaric, and succinic acids can be also detected in the leaves, however only in traces.

According to the French Pharmacopoeia, the dried leaves of grapevine should contain at least 4% of total polyphenols and 0.2% of anthocyanins (Laparra et al., 1989; Lardos and Kreuter, 2000). In order to evaluate sustainable sources of high-quality pharmaceutical starting material, a comparative study of 135 samples of red vine leaves of different origins was conducted by Schneider et al. (2008) to determine flavonol, anthocyanin, and polyphenol contents. According to these authors, total flavonol was found to be between 0.6% and 3.5%, anthocyanin between 0.2% and 1.45%, and polyphenol between 4.6% and 18.9%. In addition, as flavonol compounds are considered relevant for the vasoprotective effect of red vine leaves, their content in herbal medicines needs to be considered. Also, Radovanović et al. (2015) described for different leaves extracts obtained from five different grape varieties of *Vitis vinifera* (Vranac, Prokupac, Merlot, Gamay, and Italian Riesling), grown in southern Serbia, as an important natural source of phenolic compounds with good antioxidant properties. These authors reported values for total phenols ranged from 18.32 to 42.62 mg/g gallic acid equivalents and for flavanols values ranged from 10.12 to 15.82 mg/g quercetin equivalents. However, it must be in attention that in this work the phenolic extraction was carried out with methanol/water/formic acid solution and not by the use of water, as it is prepared to make infusions for human use.

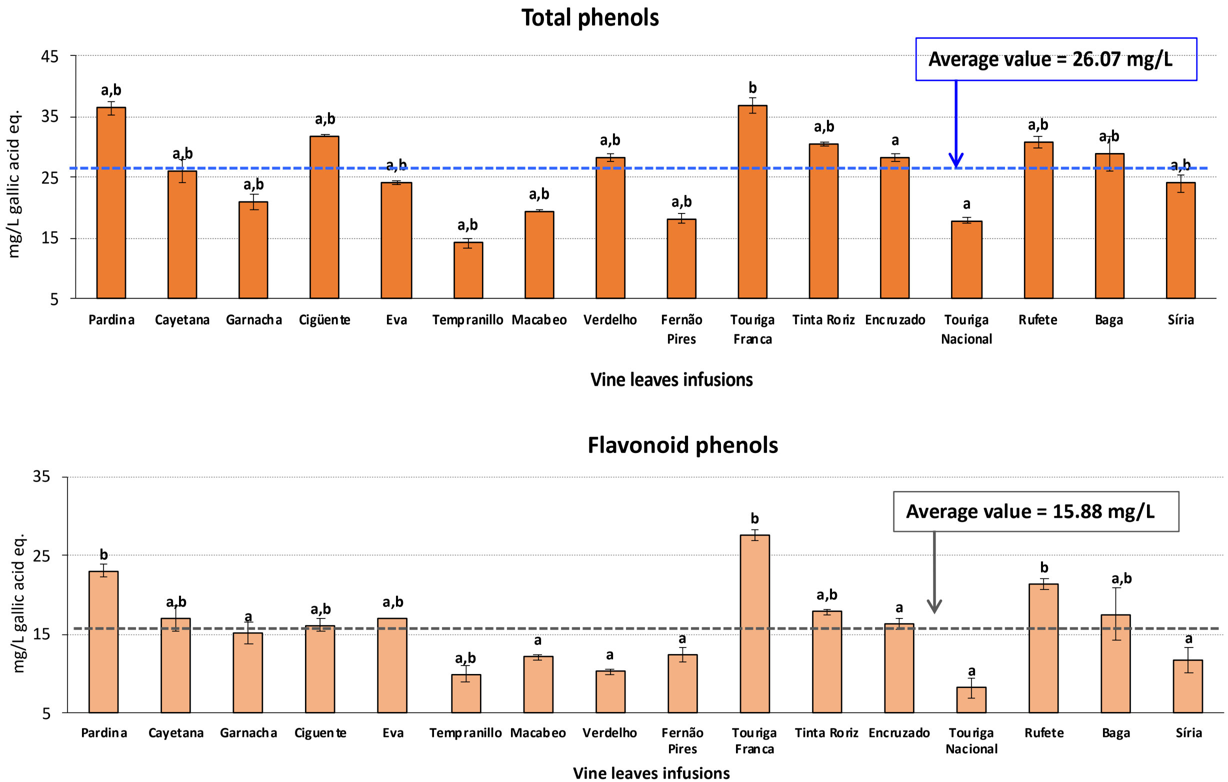

Figure 2. (Continued)

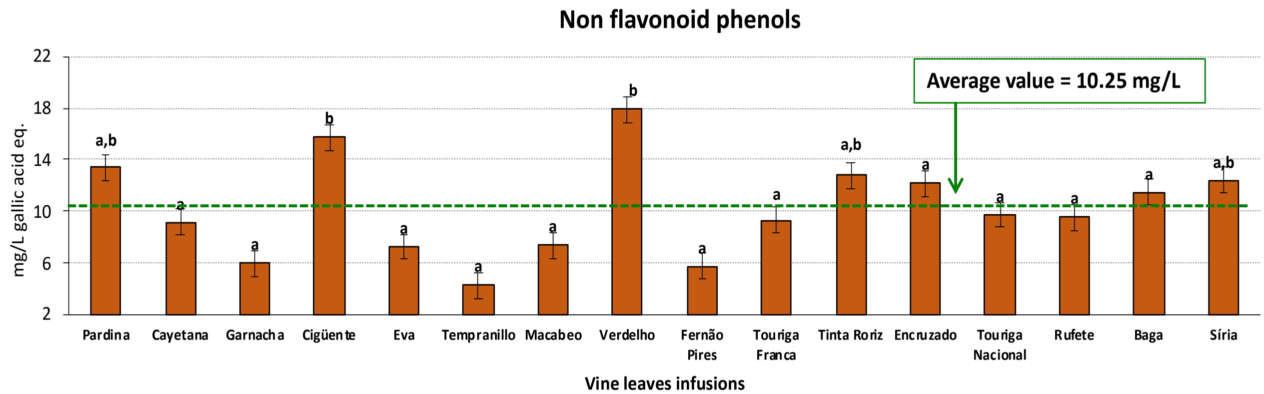

Figure 2. Total phenols, flavonoid, and non-flavonoid phenols quantified in the different vine leaves infusions produced from several *Vitis vinifera* L. varieties collected between 30 and 40 days after the grape harvest (adapted from Jordão et al., 2019).
White varieties: Cayetana, Pardina, Eva, Cigüente, Macabeo, Verdelho, Fernão Pires, Encruzado and Siria; *Red varieties:* Garnacha, Tempranillo, Touriga Franca, Tinta Roriz, Touriga Nacional, Rufete, and Baga.

Katalinić et al. (2009) reported for leaf ethanolic extracts of *Vitis vinifera* collected during lush vegetation period (May leaves) and after the harvest (September leaves) a high number of different phenolic compounds, such as phenolic acids (3-hydroxybenzoic acid, caffeic acid, gallic acid, and vanillin acid), flavonoids ((+)-catechin, (-)-epicatechin, apigenin, myricetin, quercetin, quercetin-4'-glucoside, and rutin), and stilbenes (*trans*-resveratrol and resveratrol derivatives). More recently, Jordão et al. (2019) considered that vine leaves infusion may be a potential alternative source of bioactive compounds for the human diet, besides being caffeine-free infusions, which may be a further advantage because some consumers have some sensitivity to this compound present in the teas. In this context, these authors investigated the phenolic composition of vine leaves infusions prepared from eight different Portuguese and Spanish *Vitis vinifer*a varieties and collected 30 days after grape harvest. For the production of these vine leaves infusions, dry leaves samples were placed in boiling water at a concentration of 1.5 g/L for 10 minutes. Figure 2 shows the results obtained for divers' global phenolic parameters (total phenols, flavonoid, and non-flavonoid phenols) quantified in the different vine leaves infusions produced from those red and white *Vitis vinifera* varieties. According to the results obtained, a high variation was observed for the values of the different phenolic parameters. Thus, for total phenolic content quantified in the different vine leaves infusions the values ranged from 14 to 37 mg/L gallic acid equivalents (with an average value of 26.07 mg/L), while for flavonoid phenols the values ranged from 8 to 28 mg/L gallic acid equivalents (with an average value of 15.88 mg/L).

Finally, for non-flavonoid phenols, the values ranged from 4 to 18 mg/L gallic acid equivalents (with an average value of 10.25 mg/L). Previously, Horžić et al. (2009) reported for flavonoid and non-flavonoid phenols values around 20 and 15 mg/L respectively, in chamomile infusions using a concentration of 1.5 g/L of this herb for infusion production. In addition, Katalinić et al. (2009) reported that the phenolic potential of vine leaves extracts is dependent on variety and picking-time. For these authors, vine leaves collected in September were the richest in total phenols, flavonoids, flavonols, and stilbenes.

2.2. Mineral Composition

Mineral elements are fundamentals in biochemical and physiological functions of the human body, as components of enzymes and hormones, for the synthesis of vitamins, and bone formation (Rashed, 1995; Biziuk and Kuczynska, 2007). For example, calcium is one of the essential minerals needed in the composition of bones and teeth in the activations of a large number of enzymes, having also a vital role in the functioning of muscles. On the other hand, magnesium is extremely relevant in the processes of the human body including activation of enzymes like myokinase, creatine kinase, and many others (Shapses, 2012; Vormann, 2012). Finally, iron is crucial to delivering oxygen to each cell of the body and is present in red blood cells, being in the liver, bone marrow, spleen, and muscles, and acts as an essential component of various processes that occur in the body and is also engaged in immune function and cognitive performance (Costa, 2002). However, high levels of minerals can be toxic for the human body (Silva and Williams, 2001; Razic et al., 2005). According to Fleming and Ponka (2012), iron-overload disorders are typically insidious, causing progressive and sometimes irreversible end-organ injury before clinical symptoms develop.

The level of minerals, which plants are able to absorb depends, for instance, on the chemical composition and fertility of the soil, accumulating them in the leaves, barks, and other parts (Razic et al., 2005; Kock et al., 2018; Koláčková et al., 2021). The analysis of the mineral composition of different herbal infusions is essential for assurance the safe use of these beverages. Thus, in the last years, a great number of researches have been published about the mineral composition of leaves from different herbal species and their infusions (Karak and Bhagat, 2010; Olivier et al., 2012; Pereira et al., 2017; Koláčková et al., 2021). Recently, Koláčková et al. (2021) studied mineral and trace mineral elements from tea infusions before and after *in vitro* digestibility. These authors reported K, Mg, Mn, Fe, Zn, and Na, as the main mineral components quantified in the different ice tea infusions. For walnut shell tea, Simsek and Süfer (2021) quantified 13 different elements and the amounts detected were in the following decreasing order of K > Mg > Na > Si > Mn > Cu, whereas Cr, Fe, Ni P, Pb, Se, and Zn were detected as trace elements. Previously, Pereira et al. (2017) studied mineral contents of infusions from stems, leaves, and flowers of *Crithmum maritimum* L. having detected Na as the most abundant mineral in all tisanes followed by Ca and Mg in leaves' infusions and K in flowers. Considering black and green tea as one of the most consumed beverages, Olivier et al. (2012) studied the mineral composition of dry tea leaves and their infusions. These authors reported that, in general, teas cannot be considered as a major source of dietary nutrients, however, K, Ca, Mg, P, and S are the most abundant minerals in the dry tea leaves.

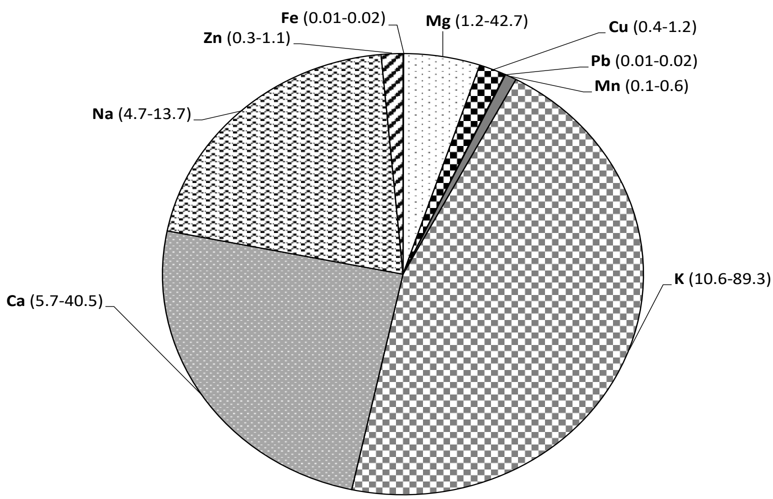

Figure 3. Mineral composition obtained in different vine leaves infusions produced from diverse *Vitis vinifera* L. varieties (results expressed in ppm values). Adapted from Jordão et al. (2019).

Taking into account the different parts of vines and grapes, such as leaves, seeds, skins, and pulp, several authors studied their mineral composition. Specifically, in vine leaves, Banjanin et al. (2020) reported their mineral composition of eleven different grapevine varieties collected from vineyards in Bosnia and Herzegovina. The results obtained by these authors showed a large variation depending on vine varieties. However, the results indicated that P, K, Ca, Mg and Na as the key elements on vine leaves. Gerardi et al. (2020) studied the value of grape skin pomace as a source of bioactive compounds with health properties and suggest its exploitation as an ingredient for functional beverages, including infusions productions. These authors reported that K is the most abundant metal in the infusions obtained from all varieties analyzed, followed by Ca and Mg. Previously, Pérez Cid et al. (2019) reported for grape skins isolated from the pomace of five Galician grape varieties similar tendency. However, there is very scarce information about the use of vine leaves for infusions and their respective mineral composition. Jordão et al. (2019) describes the mineral composition of vine leave infusions produced from different Portuguese and Spanish *Vitis vinifera* L. varieties (Figure 3).

These authors reported K, Ca and Na, as the three major mineral components quantified in the different vine leave infusions. For K the values ranged from 10.6 to 89.3 ppm, while for Ca the values ranged from 5.7 to 40.5 ppm, and finally, for Na, the values ranged from 4.7 to 13.7 ppm. The remaining mineral elements quantified (Mg, Cu, Zn, Mn, and Fe) showed very low values. Previously, also Lakatosová et al. (2015) reported K and Ca as the most abundant mineral elements quantified in vine leaves from Slovakia vineyards, while Ghaffari and Ferchichichi (2011) studying mineral composition in 30 different grapevine leaves from Tunisia founded Ca, P and Mg as the main elements quantified.

2.3. Amino Acid Profile

Amino acids (AAs) are constituent units of proteins and precursors for the formation of secondary metabolites in gene expression, homeostasis, hormone synthesis, and for transport and storage of all nutrients such as carbohydrates, proteins, vitamins, minerals, water, and fats (Kumar et al., 2015). Besides, AAs have antioxidant effects. Various disorders such as diabetes, insomnia, obesity, and arthritis are caused by metabolic disturbances and it is reported that the correct composition of AAs may be able to repair these metabolic deficiencies (Park, 2016).

AAs are categorized into essential and non-essential AAs. His, Iso, Leu, Lys, Met, Phe, Thr, Trp, and Val are considered as "essential", i.e., essential in the diet of humans and are unable to synthesize them endogenously. Dietary proteins are key sources of these essential AAs in mammals and humans. Non-essential amino acids such as Ala, Asn, Asp, Cys, Glu, Gln, Gly, Pro, Ser, Tyr, and β-Ala are synthesized by plants as well as by human beings (Kumar et al., 2015). Free AAs such as Cit, Gaba, and Orn are also found in plants.

Nitrogen (N) is an essential macroelement for plant growth and development. Plants mainly absorb inorganic N in the form of nitrate and ammonium from the soil, while organic N such as AAs, can also be taken up by plants (Näsholm et al., 2009). Free AAs are essential for secondary plant metabolism and biosynthesis of compounds, such as phenolics and glucosinolates, which play an essential function in the interaction of the environment and human health either directly or indirectly (Fu et al., 2002). According to Kumar et al. (2019), AAs are abundantly found in plants and their individual concentrations are of enormous importance in terms of human nutrition. These last researchers reported an overview of AAs composition in different plants: the data of 142 economically important plant species were collected from Google Scholar, Scopus, and Google by searching the keyword ''amino acids in food plants'' and "amino acids in economical plant species''. According their work, the average concentration of relative AAs is: Leu > Asp > Glu > Ala > Glu > Arg > Gly > Ile > Ser > Pro > Lys > Thr > Val > His > Phe > Tyr > Cys > Met > Trp. AAs in roots are transported mainly to source leaves in the xylem transpiration stream (Tegeder and Masclaux-Daubresse, 2018). Kumar et al. (2019) showed that the AAs content in leaves, flowers, and barks were higher than in seeds, fruits, underground storage organs, and roots.

Recently the authors of this chapter studied the amino acid composition of infusions prepared from *Vitis vinifera* L. leaves from four varieties: Cayetana, Eva (white cultivars), Merlot, and Tempranillo (red cultivars). All vine leaves were sampled between 30 and 40 days after the grape harvest. Afterward, vine leaves were dried at room temperature (22 ± 2°C) under totally dark conditions until a final humidity of 6-8%. Subsequently, the leaves were crushed (2-8 mm) and used to prepare the infusions. For the production of vine leaves infusions, leaves samples were placed in boiling water at a concentration of 1.5 g/L for 10 minutes. After this time, vine leaves infusions were filtered prior to aminoacidic analysis. The AAs and ammonia were separated and quantified by high performance liquid chromatography (HPLC) followed the methodology described previously by Valdés et al. (2019).

Table 2. Amino acidic profile (mg/L) of *Vitis vinifera* leaves infusions produced from four different cultivars

Amino acids	**Infusions/Cultivars**			
	Cayetana	Eva	Merlot	Tempranillo
Ala	2.68 [d*]	0.87 [c]	0.00 [a]	0.63 [b]
Asp	0.01 [c]	0.016 [b]	0.017 [b]	0.05 [a]
Gaba	1.23 [c]	0.90 [b]	0.82 [b]	0.50 [a]
Glu	0.85 [b]	0.00 [a]	0.00 [a]	0.00 [a]
Leu	0.72 [a]	0.74 [a]	0.69 [a]	0.27 [a]
Phser	0.81 [b]	0.35 [a]	0.30 [a]	0.32 [a]
Sarc	0.08 [a]	0.092 [b]	0.09 [b]	0.09 [b]
Ser	0.38 [c]	0.15 [b]	0.00 [a]	0.00 [a]
Taur	0.39 [b]	0.00 [a]	0.00 [a]	0.00 [a]
Thr	0.53 [b]	0.04 [a]	0.00 [a]	0.00 [a]
Tyr	0.29 [b]	0.00 [a]	0.00 [a]	0.00 [a]
Total	7.97 [c]	3.16 [b]	2.09 [a]	1.81 [a]

* Different lowercase letters indicate significant differences (in line) between infusions ($p \leq 0.05$) for a given aminoacid (Tukey test); Amino acids abbreviations: Ala: alanine; Asp: aspartic acid; Gaba: γ-aminobutíric acid; Glu: glutamic acid; Leu: leucine; Phser: phenilserine; Sarc: sarcosine; Ser: serine; Taur: taurine; Thr: threonine; Val: valine.

The average values (mg/L) of amino acids identified and quantified on monovarietal infusions of *Vitis vinifera* leaves are shown in Table 2. The highest total contents of free AAs on infusions elaborated was found in the infusion cv. Cayetana (7.97 mg/L) and the lowest in cv. Tempranillo (1.81 mg/L). The infusions from cultivars Eva and Merlot had intermediate contents (3.16 and 2.09 mg/L, respectively). However, it has been shown that the total metabolite contents in beverages prepared from leaves for each botanical family depend on a large number of variables such as the mode of preparation, solid-liquid contact time, and temperature of the liquid (Periche et al., 2013; Fotakis et al., 2016), in the case of tea on the fermentation of the leaves (Horanni and Engelhardt, 2013) and also the analysis method used (Wang et al., 2010).

The AAS Ala, Asp, Gaba, Phser, Leu, and Sarc, were identified and quantified in infusions prepared from leaves from cvs. Cayetana, Eva, Merlot and Tempranillo. Besides, Thr and Ser were found in Cayetana and Eva (white cultivars) and finally, Glu, Tau and Tyr, were only detected in the infusions cv. Cayetana. As reflects in Table 2, the infusion of Cayetana had the highest number of amino acids (11). In opposite, only 5 were identified in infusions made with leaves from cv. Merlot. Table 2 also exposes significant differences ($p < 0.05$) between the contents of all AAs with exception of Leu.

All AAs found in the infusions from *Vitis Vinifera* leaves were also found in other studies on the green, white, black, Oolong, and Pu-erh teas, besides Arg, Asn, Ile, His, Phe, Meth, and Thea (5-N-ethyl-glutamine) one of the main free amino acid found in teas (Alcazar et al., 2007; Yilmaz et al., 2020). The *stevia* leaf infusions contain Ala, Asp, Glu, Leu, Ser and Tyr, and Asn, Ile, Phe, Pro; however, Gaba, Phser, Sarc, either Thr were not detected on them (Periche et al., 2013). Lately, the metabolomics strategy based on NMR spectroscopy has been employed as a new analytical method for the stricter standardization, quality control, and authentication of phytomedicines. By means of this technique Fotakis et al. (2016), identified Val, Leu, Iso, Ala, Pro, Glu, Asn, Lys, iTyr, and Thr on infusions of *Matricaria chamomilla* and Val, Leu, Iso, Lys, Ala, Met, and Glu in the *Origanum majorana*. Therefore, these results show that the metabolic profile is a good indicator of the source of the infusion.

Table 3 indicates the percentage of each amino acid with respect to the total content for each vine leaf infusion. According to these results, AAs can be considered as good chemical descriptors to differentiate infusions of leaves from different *Vitis vinifera* leaves. Ala, Gaba, Leu, and Phser were the most important amino acids in infusions of *Vitis vinifera* leaves. Alanine (Ala) is a non-essential amino acid; thus, the body is capable of synthesizing it from other AAs or cellular compounds by means of enzymatic reactions. However, for the maintenance of human health, it is necessary to provide at least the minimum protein requirement of 0.8 g/kg/day, which in the case of athletes is increased to 1.6 g/kg/day and up to 2 g/kg/day in strength sports and bodybuilders.

Table 3. Distribution (%) of amino acids in monovarietal infusions of *Vitis vinifera* leaves from different cultivars

Aminoacids	Infusions/Cultivars			
	Cayetana	Eva	Merlot	Tempranillo
Ala	33.7	27.59	0.00	34.48
Asp	0.16	0.19	0.32	0.25
Gaba	15.48	28.46	39.46	27.82
Glu	10,61	0.00	0.00	0.00
Leu	9.19	23.51	33.23	14.86
Phser	10.10	11.17	14.15	17.72
Sarc	0.971	9.92	4.26	4.87
Ser	4.76	4.82	0.00	0.00
Taur	4.85	0.00	0.00	0.00
Thr	6.61	1.34	0.00	0.00
Tyr	3.63	0.00	0.00	0.00

Amino acids abbreviations: Ala: alanine; Asp: aspartic acid; Gaba: γ-aminobutíric acid; Glu: glutamic acid; Leu: leucine; Phser: phenilserine; Sarc: sarcosine; Ser: serine; Taur: taurine; Thr: threonine; Val: valine.

Ala is frequently provided in supplement form to ensure that the amino acid is available for protein synthesis. Adequate alanine intake also supports blood glucose balance to serve as a source of energy for muscles, the brain, and the nervous system. It can also support proper prostate health and detoxification of the body. γ-Aminobutíric acid (Gaba) is a non-proteinaceous amino acid and is one of the major inhibitory neurotransmitters in the central nervous system. Gaba could work effectively as a natural relaxant to diminish anxiety, and its administration could enhance immunity under stress conditions. Furthermore, Gaba has a physiological role in many systems outside the central system, such as regulation of cardiovascular functions, inhibition metastasis of cancer cells, and modulation of renal function (Sheng-Dun et al., 2012). Besides, as it is mentioned above, this substance plays a potent role in the decision process affecting our food preferences. Layman and Walker (2006) explained that leucine (Leu) improves glucose and insulin homeostasis (ability to maintain a stable internal condition) by balancing blood glucose levels. It may also increase endogenous growth hormone production and indirectly plays hormonal roles in male and female sex hormones, as well as in proper bile secretion. Thus, *Vitis vinifera* infusions could be considered a nutraceutical beverage in terms of human health.

3. Sensory Profile of Vine Leaves Infusions

Few studies have been published about the sensory evaluation of infusions using different parts of the vine, namely grape skins (Bekhit et al., 2011), dehydrated grapes (Santos et al., 2011), and leaves (Jordão et al., 2017; 2019). According to Bekhit et al. (2011), grape skins may be a potentially interesting tea infusion since grapes are very aromatic fruits with wide flavor profiles that vary with the grape variety. Santos et al. (2011) evaluated the probability of producing dehydrated material from grapes from different grape varieties (Syrah, Alicante Bouschet, Isabella, Mourvedre, Crimson, Petit Verdot, and Red Globe) produced in the São Francisco Valley, Brazil, with the purpose of being used for infusions production. The infusions produced (3 g/100 mL of boiling water) were evaluated sensorially by a panel not trained using several sensory parameters (color, aroma, and flavor), as well as the buy intention. The results show that the infusions produced from Isabella, Mourvedre, and Syrah grape varieties showed higher values in terms of color intensity and flavor. However, all infusions had 100% acceptance essentially due to their innovative character, highlighting the importance of dehydration in sensory and nutritional characteristics, contributing not only to minimize losses but also to provide countless health benefits (Khan and Mukhtar, 2007).

Bekhit et al. (2011) investigated the potential use of grape skins from Pinot Noir and Pinot Gris as infusions. A sensory evaluation was carried out using infusions formulated from these grape skins alone or added with green tea. Thus, five formulations of tea infusions were prepared: 100% Pinot Noir skins; 100% Pinot Gris skin; 50% Pinot Noir skin + 25% green tea +25% hibiscus petals; 50% Pinot Gris skin + 50% green tea, and 50% Pinot Noir skin + 50% Pinot Gris skin. According to the results obtained by these authors, only color and bitterness were significantly perceived differently among the infusion samples produced. In addition, in terms of infusion perceptions, most of the consumers considered the infusion containing Pinot Noir to be more refreshing than calming, whereas those containing Pinot Gris to be more calming than refreshing. However, the purchase intention was moderate and the consumer did not show any preferences toward a particular infusion formulation. Recently, Jordão et al. (2019) studied the sensory profile of infusions of vine leaves made from different Portuguese and Spanish varieties. The infusions of vine leaves were prepared from eight *Vitis vinifera* L. Portuguese varieties (Fernão Pires, Touriga Franca, Tinta Roriz, Encruzado, Touriga Nacional, Rufete, Baga e Síria) and Spanish (Pardina, Cayetana, Garnacha, Cigüente, Eva, Tempranillo, Macabeo, and Verdelho). The general experimental leaves infusion preparation is described in Figure 4.

In this study, vine leaves collected 30 to 40 days after the grape harvest were previously dried at room temperature (22 ± 2ºC) protected from light until a final humidity of 6-8%. Subsequently, the leaves were crushed (2-8 mm) and used to prepare the infusions. In preparing the infusions, the leaves were placed in boiling water at a concentration of 1.5 g/L for 10 minutes. After this time, the leaves were removed, the infusions were filtered and the infusions samples were presented to a panel in white tea cups at a temperature of 45ºC. The sensory attributes evaluated were: visual aspect (color hue and color intensity), aroma (intensity and quality), flavor (sweetness, bitterness, astringency, and after taste), and overall assessment. Different sensory profiles were obtained in the vine leaves according to the varieties used. Thus, Figure 5 shows two examples of different sensory profiles obtained, corresponding to the infusions made from the leaves of the Spanish white variety Cayetana and the Portuguese red variety Touriga Nacional.

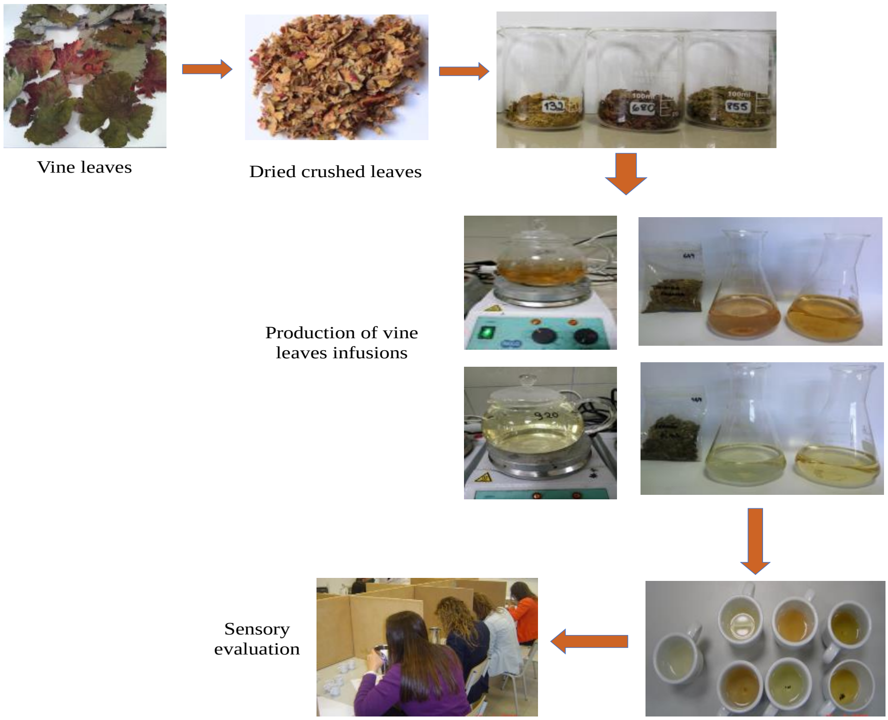

Figure 4. Experimental leaves infusions preparation made from different vine leaves and their sensory analysis (photo: authors).

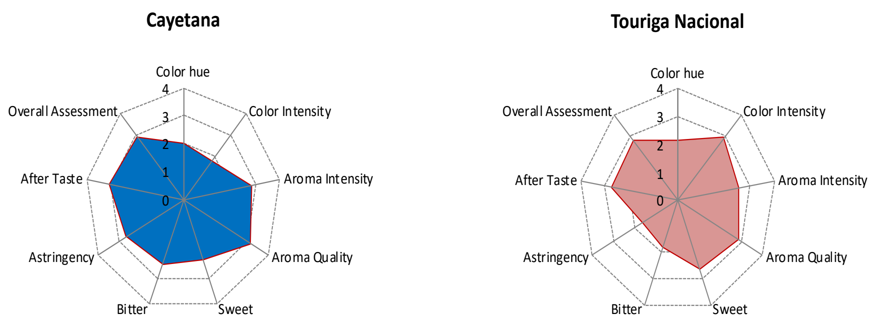

Figure 5. Sensory profile of grapevine leaf infusions produced from Cayetana and Touriga Nacional varieties (Adapted from Jordão et al., 2019).

By the analysis of the results shown in Figure 5, vine leaf infusion made from Cayetana variety was characterized by a lower average score associated with the color components (intensity and hue) compared to the other attributes. On the other hand, the sensory profile of vine leaf infusion made from Touriga Nacional variety was associated with low scores related to the astringency and bitterness, which reflects the fact that this infusion showed lower total phenolic content (Figure 2). Thus, it was clear that vine variety and its composition, namely phenolic composition, could play an important role in the sensory profile of the infusions. Previously, other authors (Coelho et al., 2016) described for *Cymbopogon citratus* leaves infusions that generally, consumers indicate a bitter taste in these infusions when the content of the phenolic compounds was higher, in particular for *p*-coumaric acid. In addition, according to Hara et al. (1995), amino acids have also an impact on sensory proprieties. These authors reported a correlation between the sensory properties of tea and the quality with its content of total nitrogen, free amino acids, and theanine. This last, theanine (5-N-ethyl glutamine) is the main free amino acid in teas, representing as much as 50% of the total amino acids in black tea and 1-2% of the dry weight of green tea.

Also, in vine leave infusions made from Touriga Nacional and Tinta Roriz varieties collected 30 and 60 days after the grape harvest, Jordão et al. (2017) reported a tendency for a clear influence of the vine leaves harvest date on the volatile composition and sensory profile of vine leaves infusions much higher than the influence of grapevine variety. Moreover, leaves collected 60 days after grape harvest showed the highest sensory scores for both red grape varieties used, in particular for aroma intensity and astringency taste.

4. Final Remarks and Perspectives

Products obtained from the vine, in particular grapes, have been deeply studied as important sources of phenolic compounds and other bioactive compounds. However, from vines, other plant parts could be harnessed, namely leaves. In that case, vine leaves may be potentially interesting for the production of herbal infusions. This is a potential alternative not fully exploited for vine leaves valorization after the grape harvest. Taking into consideration the chemical composition of vine leaves infusions and the respective data, the few research works published reported that, these infusions may be a potential alternative source of phenolic compounds, amino acids and some mineral compounds with relevant importance for the human diet. In addition, it is important to note that vine leave infusions are caffeine-free which may be a further advantage because some consumers have some sensitivity to this compound present in the teas. However, there are several factors that must be studied and deepened, such as the effect of vine cultivar, the moment of harvesting the leaves, the vine leaves drying process, and also the optimization of the processes for preparing the infusions themselves. On the other hand, all of these factors must be also studied taking into account the sensory properties of the wine leave infusions. Thus, all of these topics will be critical to improving the knowledge about the quality of vine leaves infusions, including the potential health benefits and consumer's preference and at the same time, to contribute to improving the economical valorization of vine leaves.

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Chapter 8

Fatty Acids, Vitamin E and Thermal Degradation of Grape Seed Oils from Different Cultivars

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ABSTRACT

Grape pomace derived from wine production includes peel and seeds, which can be used in the production of grape seed oil, obtaining a sustainable product with a high nutritional content. Our study performed an evaluation of the fatty acids profile, and content of vitamin E of different oils extracted from seeds of twelve different grape cultivars, and their thermal degradation resistance when submitted to high temperatures. Analysis of the fatty acid profile was performed by gas chromatography with mass spectrometry detection (GC-MS). Vitamin E (α-tocopherol) was analyzed by HPLC with fluorescence detection. The analyses of the thermal degradation events were carried out in thermogravimetric equipment with controlled atmosphere of synthetic air and heating between 30 - 600°C at a rate of 10ºCmin^{-1}. The chromatographic analysis of grape seed oils identified four fatty acids (oleic acid, linoleic acid, stearic acid and palmitic acid) for all the cultivars studied, with superior amounts of linoleic acid. Vitamin E indices was significantly higher for the oils obtained from seeds of grape cultivars Merlot and Malbec. Thermogravimetric analysis showed that the samples present similar curves, whose degradation point of fatty acids is higher than 280°C, representing good prospects of using this oil for cooking preparations that require high temperatures (oven or deep fryer), but with preservation of fatty acids that makes it up. Due to the nutritional enrichment and to add value to the agro industrial residue discarded by the wineries, the use of the oils extracted from the grape seeds is a viable alternative to the food industry and in the daily cooking.

Keywords: grape seed oils, termogravimetry, *Vitis vinifera*, *Vitis labrusca*, wine by-products

1. INTRODUCTION

World production of grapes for winemaking is about 77.8 million tonnes, resulting in approximately 292 million hectoliters of wine and generated about 13 million tonnes of residues (OIV 2019). The Brazilian production is quite expressive, with approximately 750 million tons of grapes destined to wine production, with an estimated 210 thousand tonnes of residues generated per year (MAPA 2019).

The grape pomace is a mixture of skin and seeds, and is one of the most abundant residues in the wine industry. This material is known to be rich in many compounds such as phenolic acids, flavonoids, tannins and saponins (Makris et al. 2007; Garavaglia et al. 2016; Karling et al. 2017). Seeds usually contain between 8 and 20% of oil, which represents about 5% of the fruit's weight (Choi and Lee 2009), and about 3 million tons of grape seeds are discarded annually in the world. The grape seeds constitute about 7 - 20% of the fruit weight, and calculated on dry matter, represents between 40 and 60% (Matthäus 2008). The complete use of the grapes, including the seeds, is considered an important economic and sustainability factor, since the oil has a pleasant and neutral taste, and has a high concentration of linoleic acid, and natural vitamin E, which provides considerable oxidative stability to the product. Grape seeds also present a considerable content of phenolic compounds (about 60 to 70% of their content), with smaller percentages found in other parts of the fruit, such as 28 to 35% in the skin and approximately 10% in the pulp (Davidov - Pardo and Mcclements 2015).

In relation to the fatty acids profile, studies have shown that the main component is linoleic acid, with contents varying in 60–75% for linoleic acid and 14–22% for oleic acid (Baydar et al. 2007). Especially these fatty acids have a great variation. Lutterodt et al. (2011) evaluated the fatty acid content for the seed oils of the grape cultivars Chardonnay, Concord, Muscadine, and Ruby Red. The cultivar Concord had the highest content of linoleic acid (75.3%), with Ruby Red containing the lowest amount (66.0%). The antioxidant vitamin profile, especially vitamin E (α-tocopherol), vitamin A (ß-carotene, lutein, zeaxanthin and cryptoxanthin) and phenolic compounds have also been characterized (Lutterodt et al. 2011). In this context, there are still few studies that characterizes the events of thermal degradation in grape seed oil and if different cultivars have similar properties, especially in the case of *Vitis labrusca* cultivares, produced in large quantities in Brazil.

Thus, considering the nutritional value added to grape seed oil, a product with significant importance as a by-product of the grape agroindustry and produced in a sustainable way, this study aimed to characterize the oil extracts of twelve cultivars, from residues obtained in Brazilian wineries.

Moreover, the thermal degradation events were also analyzed in four of these seed oils, in order to evaluate the viability of their use under high temperatures.

2. Materials and Methods

For analyzes of fatty acid profile and vitamin E contents in the oils, the grape seeds were separated from the pomace of nine *Vitis vinifera* cultivars (Cabernet Franc, Malbec, Tannat, Ancellotta, Pinot Noir, Sangiovese, Cabernet Sauvignon and Merlot); two *Vitis labrusca* cultivars (Ives and Niagara) and two complex hybrids (Seibel 2 and Seyval). Endothermic and exothermic degradation events in the grape seed oils extracted were evaluated for the cultivars Merlot, Cabernet Sauvignon, Sangiovese and Sauvignon Blanc. All experimental procedure is showns in Figure 1.

Immediately after the pomace removal from the fermentation tanks in the wineries, the samples were frozen and stored until analyses (-18°C). Next, the pomace samples for chemical analysis were placed in aluminum trays (750 mL), and submitted to drying in a stove with air circulation and air renewal model SL 102 (Solab, Piracicaba, São Paulo, Brazil) at 45°C. The samples for thermal events evaluation were dehydrated in freeze-dryer model LD 1500 (Terroni, São Carlos, São Paulo, Brazil).

All pomace samples had moisture content <14% w/w after drying (APHA 2001). Later, the samples were sieved in Tyler-type sieves with openings of 28 Tyler meshes (Bertel, Caieiras, São Paulo, Brazil) to obtain the seeds.

Posteriorly, these seeds were pressed in a hydraulic press model P1000 (Bovenau, Rio do Sul, Santa Catarina, Brazil). In this process, a sample of 70 g of seeds was placed in a steel extractor and squeezed in a hydraulic pressing equivalent to 10 tons. Each extracted oil was maintained for a period of decanting by 72 hours in the dark.

The saponification and subsequent reaction of esterification of the oils was done with methyl alcohol, based on the method of Hermann (1964).

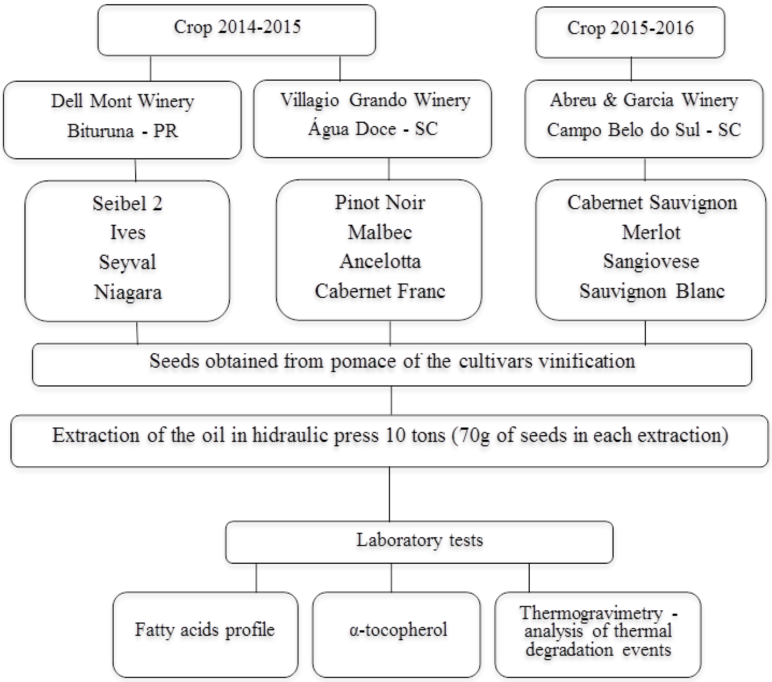


Figure 1. Flowchart of elaboration and analysis of the grape seed oils.

These analyses were performed with a gas chromatograph model GC-17A (Shimadzu, Kyoto, Japan) coupled to the mass spectrometry detector model 5050 - 17A (Shimadzu, Kyoto, Japan) with the Wiley 229 l. The ionization process in this equipment has electronic impact of 70eV. The capillary column used was OV-05 (methyl silicone with 5% phenyl groups) with 30m long, 0.25mm internal diameter and 0.25µm stationary phase thickness. Helium was used as the entrainment gas with a flow of 1mL/min. The injector was maintained at 280°C with heating at 2°C/min in split mode (1:10). The oven was maintained at the final temperature for 20 minutes, with operating system in SCAN mode.

For the quantitative analysis of the formed esters, ions that could be monitored by SIM (Single Ion Monitoring) mode and quantified separately were selected, according to the method previously described by Moretto and Fett (1998). Analysis of vitamin E (α-tocopherol) were performed with a HPLC UV/Vis detector (Waters 2487 Dual λ Absorbance Detector, Arcade, New York, USA) with detection at 292nm and isocratic mode analysis were used with the methanol: water (96: 4) as the mobile phase. The quantification of α-tocopherol was performed by the external standardization method from individual stock solutions of approximately 1000mg/ L. The mixtures of the standards of these solutions were made with different concentrations for the construction of the calibration curve (Freitas 2007). The thermogravimetric curves were obtained from samples with 1.0 mg masses in the TGA/SDTA851 model (Mettler Toledo, Beijing, China) adapted from the methodology described by Rampazzo (2015). The temperature range was 30 to 600°C at the heating rate of 10°Cmin^{-1}, in an open platinum crucible with a synthetic air atmosphere.

Data was submitted to analysis of variance (ANOVA), with the post-hoc SNK test for comparison using the software SISVAR version 5.6 (Ferreira 2011). For the chromatography data obtained, principal component analysis (PCA) was performed using the MINITAB R14 program (Tabachnik and Fidell 2007).

3. Grape Seeds Fatty Acids Profile

Among the fatty acids identified in the grape seed oils, linoleic acid had the highest content for all cultivars analyzed (Figure 2). Only two main components are required to explain more than 96% variability of the fatty acid content in the seed oils of the grape cultivars (Figure 3A). Seed samples that are located on the negative axis of CP-1 showed higher average levels of all the fatty acids in their seeds (Figure 3C). However, the cultivar Malbec differs from the other varieties by the higher content of stearic acid. The cultivars Seibel 2, Niagara and Seyval form a group due to similar contents of palmitic, oleic and linoleic acids, while the cultivars Ives, Malbec and Cabernet Franc had lower levels of almost all fatty acids. Niagara, Seibel 2 and Seyval cultivars had similar contents of the analyzed fatty acids (Figures 2 and 3B).

In Figure 3, data distribution is showed in the hierarchical analysis, which confirms the groups presented in Figure 3B.

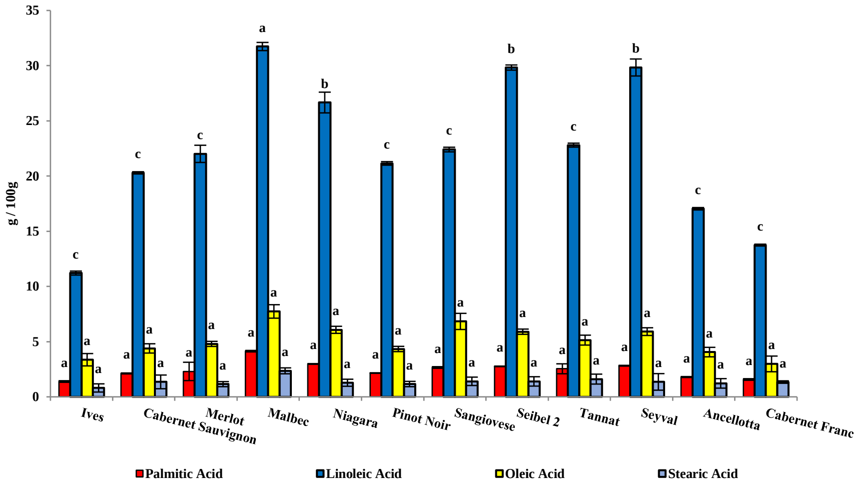


Figure 2. Content of fatty acids in the different grape seed oils. Means followed by the same letter for each fatty acid between different grape varieties did not differ among themselves (Student Neuman-Keuls test, $p \leq 0.05$). Vertical bars indicate standard deviation (n = 3).

By the Euclidean distance of 34, the grape seed oils are grouped into three distinct groups according to the fatty acid contents. The first is formed by Niagara, Seyval, Seibel 2 and Malbec. The second group is formed by Ancellotta, Sangiovese, Tannat, Merlot, Pinot Noir and Cabernet Sauvignon; and in the third group are Cabernet Franc and Ives.

Some studies have shown that the fatty acid profile is one of the determining factors for thermal stability of oils, for example, oleic acid esters are stable at temperatures about 175°C in air atmosphere, when they begin to degrade (Kim et. al. 2010). Crews et al. (2006) evaluated some grape seed oils from the major grape producing countries in Europe (France, Italy and Spain) in order to catalog the variations occurring in the fatty acids profile for the Codex Alimentarius database in 2004. These authors found that, out of 10 oil samples evaluated in each country, regardless of the region where they were grown and processed, the content of each fatty acid was within the ranges recommended by international legislation (58 to 78% of linoleic acid, 12 to 28% of oleic acid and 5.5 to 11% of palmitic acid) (Codex Alimentarius, 1999); which were also in agreement with what was observed in the results obtained by the present study.

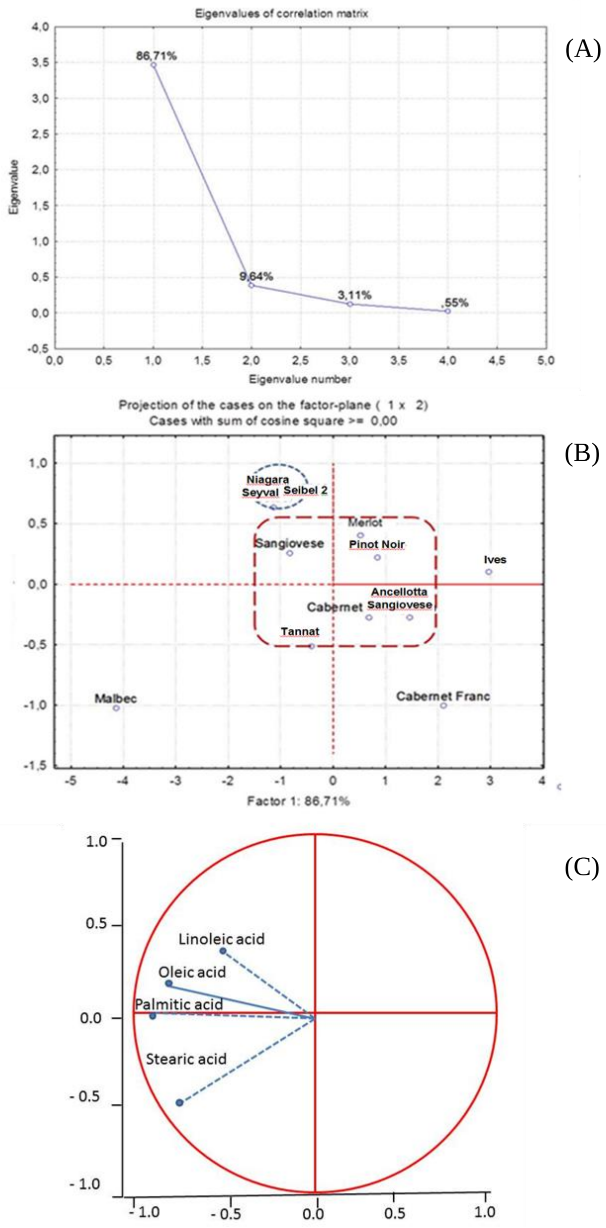


Figure 3. Projection of the main components and main variables observed for fatty acids in the samples of grape seed oils. (A) Eigenvalues of correlation matrix; (B) Projection of grape cultivares; (C) Projection of the main variables.

In Figure 4, data distribution is showed in the hierarchical analysis, which confirms the groups presented in Figure 3B. By the Euclidean distance of 34, the grape seed oils are grouped into three distinct groups according to the fatty acid contents. The first is formed by Niagara, Seyval, Seibel 2 and Malbec. The second group is formed by Ancellotta, Sangiovese, Tannat, Merlot, Pinot Noir and Cabernet Sauvignon; and in the third group are Cabernet Franc and Ives. Some studies have shown that the fatty acid profile is one of the determining factors for thermal stability of oils, for example, oleic acid esters are stable at temperatures about 175°C in air atmosphere, when they begin to degrade (Kim et al. 2010).

Crews et al. (2006) evaluated some grape seed oils from the major grape producing countries in Europe (France, Italy and Spain) in order to catalog the variations occurring in the fatty acids profile for the Codex Alimentarius database in 2004.

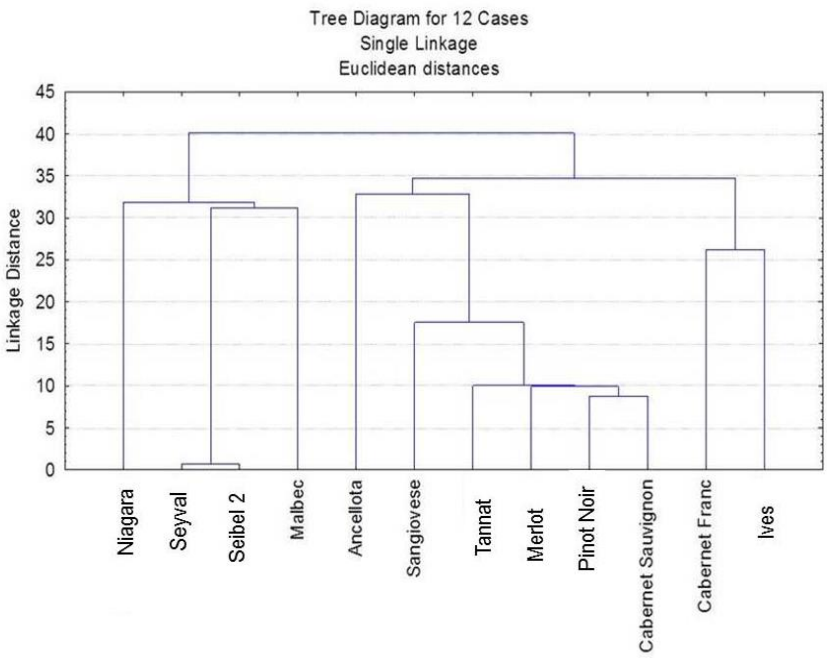


Figure 4. Hierarchical clusters analysis for the content of fatty acids present in grape seed oils comparing cultivars.

These authors found that, out of 10 oil samples evaluated in each country, regardless of the region where they were grown and processed, the content of each fatty acid was within the ranges recommended by international legislation (58 to 78% of linoleic acid, 12 to 28% of oleic acid and 5.5 to 11% of palmitic acid) (Codex Alimentarius, 1999); which were also in agreement with what was observed in the results obtained by the present study.

Santos et al. (2011) studied different parts of the grape berry, such as epidem, pulp and seed of two varieties of *Vitis vinifera* (Benitaka and Brazil) and two *Vitis labrusca* (Isabella and Niagara), comparing the fatty acid profile. According to these authors, considerable differences were observed in their compositions, mainly in relation to the high content of polyunsaturated fatty acids presents in the grape seed, constituted mainly by linoleic acid (C18:2). Sabir et al. (2012) evaluated the grape seed oils extracted from 21 different grape genotypes and noted a range of 53.6 to 69.6g/100g for linoleic acid, followed by oleic acid (16.2 to 31.2g/100g) and palmitic saturated fatty acid (6.9 to 12.9g/100g).

The results of vitamin E (α-tocopherol) content analyzes in grape seed oils (Figure 5) indicate that cv. Malbec and Merlot had higher values, followed by the cvs. Cabernet Franc, Cabernet Sauvignon, Pinot Noir and Seibel 2, which differed statistically from cvs. Ancellotta, Cabernet Sauvignon, Sangiovese and Tannat. The lowest contents were identified in the cvs. Ives, Niagara and Seyval. The American cultivars (*Vitis labrusca),* with the exception of Seibel 2, presented the lowest contents of this antioxidant compound. The daily consumption recommendation for vitamin E is 15mg (Institute of Medicine 2000), and for a food classification as a source of this nutrient, it must present at least 10% of the daily recommendation in 100g, that is, 1.5mg/100g (Anvisa 2012). According to our results, none of the samples could be matched in this classification, since the highest value found was 1.08mg/100g (cv. Malbec).

The main components analysis for grape seed oils in relation to fatty acid contents by adding the vitamin E index, shows that it is possible to explain 95% of data variability using the first two main components.

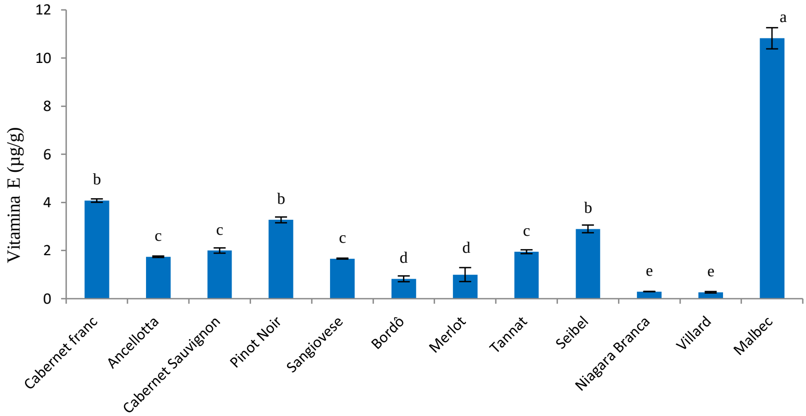


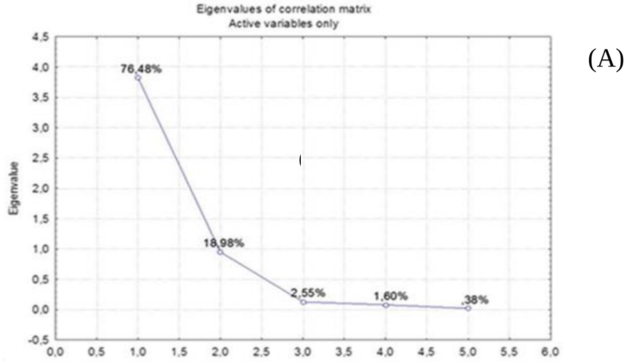
Figure 5. Vitamin E content in grape seed oils. Means followed by the same letter do not differ by the Student Newman-Keuls test ($p \leq 0.05$). Vertical bars indicate standard deviation ($n = 3$).

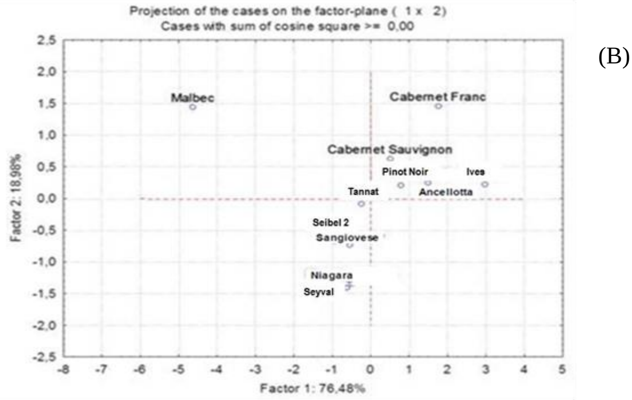
Once more cv. Malbec was separated from the other samples due to the higher levels of stearic acid and vitamin E (Figure 6).

Shinagawa (2015), evaluating seven commercial samples of grape seed oils, obtained α-tocopherol values ranging from 1.33 to 1.76mg/100g. The legislation for vegetable oils establishes values between 1.6 to 3.8mg/100 g for α-tocopherol (Codex Alimentarius, 1999). Beveridge et al. (2005) reported α-tocopherol contents in different grape varieties, though in a smaller range (3.58 - 30.9mg/100g). Crews et al. (2006) also reported α-tocopherol contents of grape seed oils from Europe, with values ranging from 14 to 229mg/100g.

4. Endothermic and Exothermic Degradation in Grape Seed Oils

The use of thermogravimetry (TGA) can be an important factor to determine the quality of vegetable oils for industrial processes use. Due to the characteristics of this analysis, such as its high reliability of results and data supply in a relatively short time, this technique has been increasingly adopted.





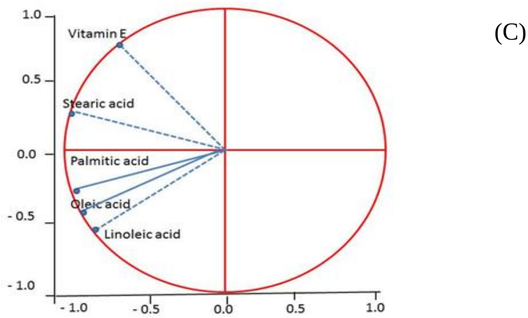


Figure 6. Projection of the main components and the main variables observed for vitamin E (α-tocopherol) and fatty acids in the grape seed oil samples. (A) Eigeinvalues of correlation matrix; (B) Projection of the grape cultivars; (C) Projection of main variables.

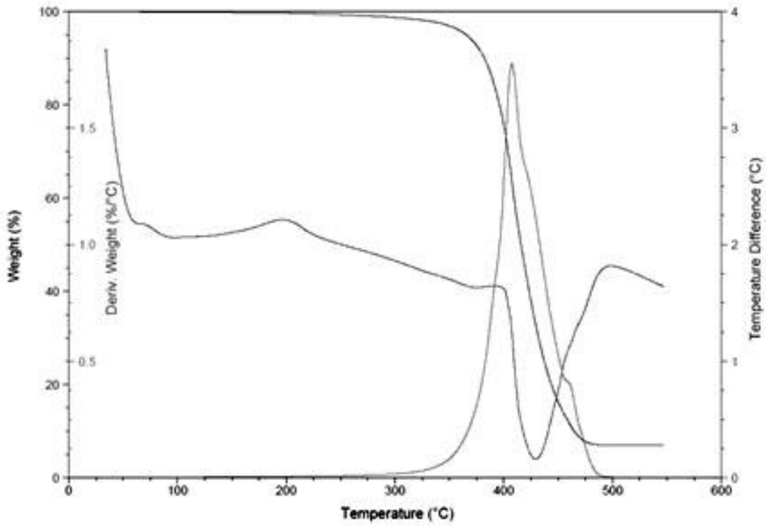


Figure 7. Thermogravimetric curve of endothermic events in 'Merlot' grape seed oil.

In our study, no significant differences were verified between the cultivars in relation to the thermal degradation of the seed oils. The thermogravimetric curve of the endothermic events of the seed oil of cv. Merlot is show on Figure 7. The results showed that the samples remained stable to decomposition until the temperature of 280°C and; the end of the decomposition, which represents the stability temperature, was achieved at 500°C.

Table 1 shows the main events identified for each of the grape seed oil samples.

Seed oils lost about 1% of their weight at temperatures between 196.2 (Sauvignon Blanc) and 283.0ºC (Cabernet Sauvignon). Moreover, losses in oil mass greater than 10% was observed at temperatures between 382.2 (Merlot) and 196.2°C (Sauvignon Blanc). The temperatures, which the degradation stabilized, ranged from 432.4°C (Sauvignon Blanc) to 546.9°C (Merlot).

However, the percentage of remaining mass was 0.17% for cv. Sauvignon Blanc, 6.98% for cv. Merlot, 7.59% for cv. Cabernet Sauvignon and 13.51% for cv. Sangiovese.

Table 1. Thermal events identified in the thermogravimetric analysis of grape seed oils

	Stability Temperature		Final Decomposition temperature	
Cultivar	TR (°C)	WL (%)	TR(°C)	WL (%)
Merlot	282.9 - 382.2	89.0	382.3 - 546.9	7.0
Cabernet Sauvignon	285.1 - 365.1	90.0	365.3 - 545.3	7.6
Sangiovese	246.1 - 372.1	90.0	372.2 - 546.5	13.5
Sauvignon Blanc	196.2 - 366.0	90.0	366.1 - 432.3	0.17

TR: Temperature range of the thermal event;
WL: Weight loss.
(Guarapuava-PR, Brazil, 2017).

Santos et al. (2007) studied the composition of soy, corn, canola and sunflower oils, and they verified that mass losses of each sample were related to the composition of fatty acids and their susceptibility to decomposition.

According to the authors, this decomposition was related to the loss of mass of polyunsaturated fatty acids that occurred in a range of 200 - 380°C, monounsaturated in a range of 380 - 480 °C and saturated between 480 and 600°C, in function of their structures being more or less resistant to high temperatures.

In the study of Rampazzo (2015), grape seed oil also presented two events of significant mass loss in the thermogravimetric evaluation, with the first loss being 85.28% and the second loss being 11.46%. The results obtained allow to include the oils of grape seeds next to the group of vegetable oils with greater thermal stability, such as soybean, canola, sunflower (Santos et al. 2007), and olive oils (Chiou and Kalogeroupolos 2017), traditionally used under high temperatures without showing significant losses, mainly in the profile of fatty acids.

FINAL REMARKS AND PERSPECTIVES

Chromatographic analyses of grape seed oils identified four fatty acids (oleic acid, linoleic acid, stearic acid and palmitic acid) and higher rates of vitamin E in cultivars Merlot and Malbec. These results showed the important nutritional value of grape seed oil and its potential for commercial explotation of these products. Moreover, the oil composition is strongly cultivar dependent, what should be consider for future studies and development of new commercial products based in grape seed oil.

Thermogravimetric analyses showed that the oil samples present similar curves, whose degradation point of fatty acids is higher than 280°C, and this loss is slow and gradual, until the temperature of 540°C, representing good perspectives for use these oils to cooking preparations that require high temperatures (oven or deep fryer). Thus, considering the nutritional enrichment and the add value to the residue discarded by the wineries, the oils extracted from the grape seeds is a viable alternative in the food industry and in the daily cooking.

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Chapter 9

A Review of Polyphenols Extraction Technologies from Grapes and By-Products

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Abstract

Phenolic compounds or polyphenols are secondary metabolites that are synthetized by grapes and are extracted into wines during the process of vinification. These compounds present a wide variety of chemical structures and diverse biological activities. These compounds are also found in the by-products (grape pomace and lees) after vinification. The

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main challenge remains in the extraction of phenolic compounds from grapes and by-products.

Traditionally, maceration with heat-treatment is a very effective method for polyphenol extraction from grapes but the use of heat potentially results in polyphenols degradation depending on time/temperature parameters. Also, extraction using chemical solvents as methanol and acetone is very common for by-products polyphenols. This type of extraction has several drawbacks, mainly being toxic, not ecofriendly, flammable and/or expensive.

Therefore, the aim of this chapter is to review the non-thermal ecofriendly processes used to extract polyphenols from grapes and by-products. These processes include grape pomace and lees (pulsed electric fields - PEF and high voltage electrical discharges - HVED).

Keywords: grape and by-products, high-pressure assisted extraction, microwave assisted extraction, polyphenol, pulsed electric fields, supercritical fluid extraction

1. Introduction

Grapevine (*Vitis* spp) is one of the most cultivated fruit crops in the world, with an area dedicated to viticulture of 7.45 million hectares. In 2019, 261 million hl of wine were produced (http://www.oiv.int/public/medias/7033/en-oiv-point-de-conjoncture.pdf).

Grapes are a major source of polyphenols. Phenolic compounds are secondary metabolites synthetized in response to stress conditions. These compounds are divided into two groups: non-flavonoids and flavonoids. The non-flavonoid compounds include phenolic acids divided into hydroxybenzoic acids (vanillic, syringic, gentisic and gallic acid) characterized by a C_6-C_1 skeleton and hydroxycinnamic acids (caffeic, coumaric and ferulic) with a C_6-C_3 skeleton, but also other phenol derivatives such as stilbenes (resveratrol). Flavonoids are characterized by a basic structure of 15 carbon atoms including 2 aromatic rings bound through a 3-carbon chain. Different subclasses of flavonoids exist due to differences in the oxidation state and substitution on C ring. The major classes of grape flavonoids are the anthocyanins, flavanols ((+)-catechin and (-)-

epicatechin), flavonols (quercetin) and flavanones (astilbin) (El Rayess, 2014).

Polyphenols are the principal compounds related to the wine consumption benefits due to their antioxidant and free radical scavenging properties. Both flavonoids and non-flavonoids compounds exhibit anti-inflammatory, antibacterial, antifungal, antiviral, neuroprotective, antiproliferative and antiangiogenic activities by reducing reduce harmful low-density lipoprotein (LDL) cholesterol oxidation, modulating cell signaling pathways, reducing platelet aggregation, inhibiting the growth of some tumor types (Guilford and Pezzuto, 2011).

On the other hand, phenolic compounds play an important technological role by constituting a decisive factor in red wine quality and contributing to wine organoleptic characteristic such as color, taste, astringency and bitterness. The wine aging capacity is also referred to wine.

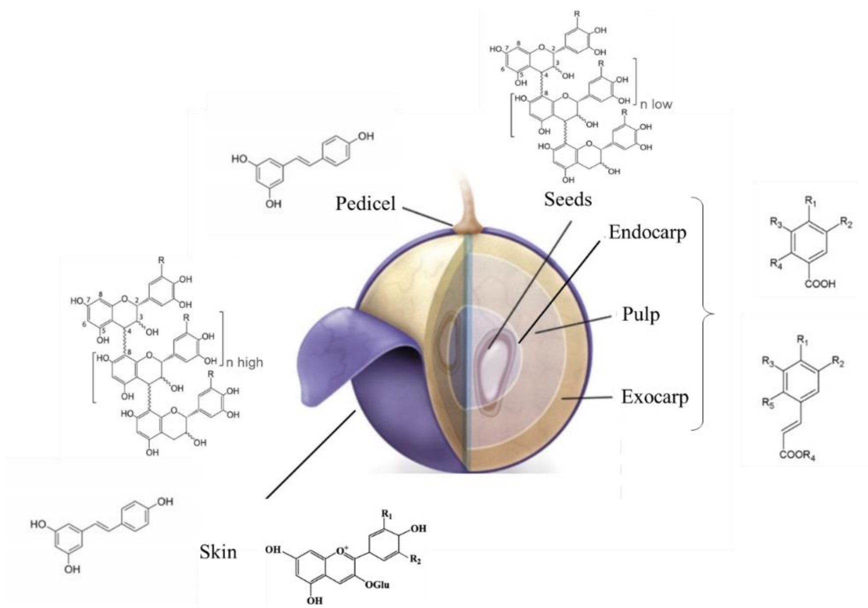

Figure 1. Phenolic compounds distribution in the different grape berry fractions.

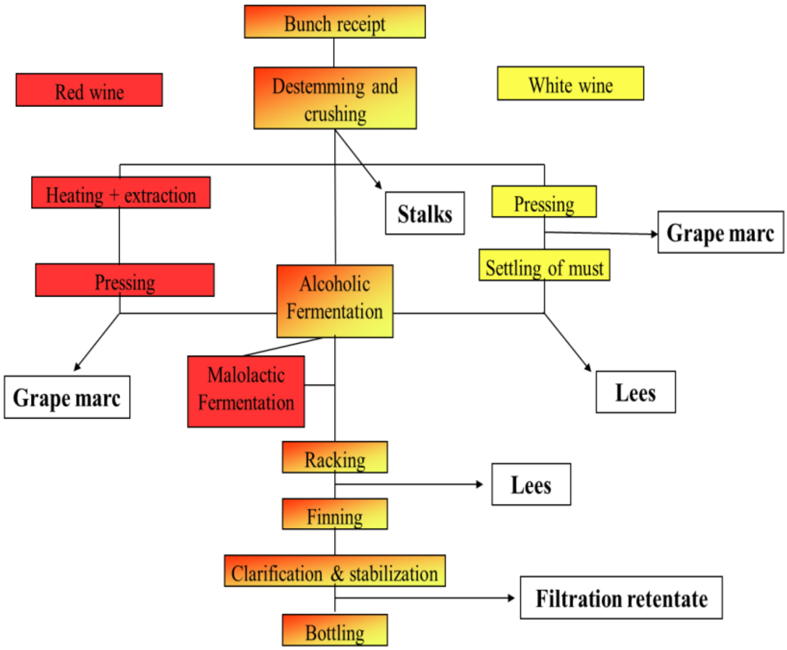

Figure 2. Wine industry waste production during winemaking process. (bold balck color indicates residues and by-products)

Different parts of grapes (i.e., pulp, skin and seeds) contain different polyphenols in variable amounts. As seen in Figure 1, the skin is rich in anthocyanins, stilbenes and proanthocyanidins with high polymerization degrees. The pulp contains only non-flavonoids phenolic compounds while seeds are rich in flavanols and proanthocyanidins with low polymerization degrees.

During winemaking, the extraction of phenolic compounds and other compounds contained in the grape and their transfer to the wine are done by diffusion through the contact between the juice and the solid part of grapes. This step of diffusion is called maceration and it can occur before (pre-fermentation maceration), during (conventional maceration) and after (post-fermentation or extended maceration) fermentation. The rate and amount of phenolic compounds extraction are affected by several factors as time, temperature, ethanol concentration, enzymes, etc. (Ghanem et al., 2019).

Winemaking process generates different residues and by-products characterized by high contents of phenolic compounds. As seen in Figure 2, several types of residues and by-products) are produced in white and red winemaking. The main solid wastes and by-products from winemaking production are grape stalk, grape marc and wine lees. The requirements as regards waste management due to environmental issues incited researchers and wine industrials to develop different strategies for the valorization of wine industry wastes and by-products. These strategies within the concept and methodology of circular economy and bio-economy consisted into compost, animal feed, recovery of tartaric acid and ions, seed oil production, anaerobic digestion and distillation. However, the recovery of phenolic compounds remains the main strategy for valorization.

2. Phenolic Compounds Extraction

2.1. Conventional Extraction Methods

During winemaking, the extraction of phenolic compounds from grapes occurs during the first stages of maceration and fermentation. Hilgard in 1887 was the first to note that the maximum of color extraction is attained before tannins at high temperatures. This type of extraction is governed by diffusion law by which a compound moves from a region of high concentration toward a region of lower concentration. The nature and concentration of phenolic compounds extracted are affected by several factors, such as grape variety and maturity, temperature of must or wine, dioxide, use of enzymes and the frequency of pump overs (Ghanem et al., 2014).

Anthocyanins are compounds exhibiting chromatic properties in red wines. These compounds are located in the vacuoles and cell breakdown is needed for their extraction and diffusion. Due to their water-soluble character, anthocyanins diffusion result in a peak of extraction within the third to fifth day of maceration (Habertson et al., 2009; Casassa et al., 2013). The concentration of anthocyanins decreases after several days of maceration due to oxidation, copigmentation reactions and adsorption by yeasts and grape cell walls (Boulton, 2001; Zanoni et al, 2010; Bautista-Ortin et al., 2016; Bimpilas et al., 2016). The diffusive process of anthocyanins is well described by a two-term extraction model with an initial fast extraction followed by a slower decrease to its final value (Setford et al., 2017). Ghanem et al. (2019) showed that during the pre-fermentation heat maceration of red grapes, the maximum amounts of anthocyanins were obtained when heating at 70°C for 8 hours. When exceeding the 8 hours, a decrease in anthocyanins amounts were observed. Cold maceration technique (10°C) is not favorable for the extraction of anthocyanins where slow rate of extraction was observed (Lukic et al., 2017; Ghanem et al., 2019). Geoffrey et al. (2018) claimed that the reduction of the heating temperature in some vintages can be compensated for through an extension of the heating period to obtain the same amounts of phenolic compounds.

Flavan-3-ols compounds are constituted of 4 major monomeric units: (+)-catechin, (-)-epicatechin, (+)-epigallocatechin and (-)-epicatechin-3-O-gallate. They are located in skins, seeds and stems. Like anthocyanins, these compounds have water-soluble nature and are extracted within the first 3 days of maceration (Gambuti et al., 2009). The seeds contribute almost 90% of the total flavan-3-ol content suggesting that skin flavan-3-ols are extracted at a slow rate (Casassa and Harbertson, 2014). Ghanem et al. (2019) showed that monomeric flavan-3-ols extraction is favored by high temperature (70°C) for 24 hours of maceration.

Proanthocyanidins or condensed tannins are constituted of oligomeric (degree of polymerization ≥ 2) and polymeric (degree of polymerization ≥ 5) flavan-3-ols. These compounds are found in both skin and seeds. Most skin proanthocyanidins are extracted together with anthocyanins in the first days of fermentative maceration while the extraction of seed proanthocyanidins require longer maceration times and favored by the presence of ethanol. The rate of extraction and the quantities of proanthocyanidins are influenced by the grape variety and temperature (Bautista-Ortin et al., 2016, Ghanem et al., 2019, Piccardo et al., 2019). Cerpa-Calderon and Kennedy (2008) showed that the extraction of skin proanthocyanidins fit to a Boltzmann sigmoid model.

This model is constituted by a slow lag phase of extraction which is followed by a plateau concentration characterized the maximum concentration of proanthocyanidins.

Another process replacing the heat maceration in wine industry is the flash release. This process consists in heating the grapes quickly at high temperature (>95 °C) with biological vapor at atmospheric pressure and then placing them under a strong vacuum (pressure closed to 60 hPa) which causes instant vaporization fragilizing the cells walls which favorites the polyphenol extraction. It is generally coupled to fermentation in liquid phase (Ghanem et al. 2014). Moutounet et al. (2000) showed that grapes treated with flash release possessed an increase 50% in total phenolic compounds. Larger amounts of flavonols, anthocyanins, catechins and proanthocyanidins in wines were observed after flash release treatment when compared to control wines. Also, Samoticha et al. (2016) demonstrated that the flash release expansion improved the extraction of polyphenol compounds from Pinot Noir grapes, especially anthocyanins, as well as color properties and antioxidant activity. Not all the cited techniques are efficient. Some of them modify the quality of the finished wine; others are costly in terms of energy and time consumption, which is an aberration in terms of present-day environmental issues.

The conventional extraction method of polyphenols from grape by-products is the low-pressure extraction using organic solvents. Due to the polar nature of polyphenols, the used solvents are therefore of polar nature. The most used organic solvents are methanol, ethanol and acetone. Traditionally, solid−liquid or Soxhlet extractions techniques have been extensively used for many decades, but they are time-consuming and require relatively large quantities of not eco-friendly solvents. Also, due to steps like heating, boiling, or refluxing, a loss of polyphenols was remarked due to ionization, hydrolysis, and oxidation occurs during the procedure.

Table 1. Literature review of solid/liquid extraction of phenolic compounds from grape by-products

Grape by-product matrix	Operating variables	Targeted phenolics and biological activities	Reference
Fresh seeds from Riesling grape pomace	Binary mixtures of ethyl acetate and water (from 3.3 to 20% of water).	Proanthocyanidins	Pekic et al. (1998)
Cabernet Sauvignon and Tempranillo grape marc	Mixture of ethyl acetate and water; liquid/solid ratio 10:1 (v/w); 5, 10, 20 and 30 min.	Anthocyanins, flavonols, phenolic acids, flavanols and antioxidant activity	Bonilla et al. (1999)
Dried powdered defatted seeds from fresh red grape (Bangalore blue)	Solvent: acetone, ethyl acetate, methanol and binary mixtures of ethyl acetate and water (from 10 to 20% water); temperature: 60 - 70°C; Soxhlet extraction for 10 h.	Monomeric flavanols, procyanidins and antioxidant activity	Jayaprakasha et al. (2001)
Dried powdered defatted seeds from fresh red grape (Bangalore blue)	Solvents: acetone: water: acetic acid (90:9.5:0.5) and methanol: water:acetic acid (90:9.5:0.5); extraction time: 8h..	Monomeric procyanidin antioxidant activity and antimicrobial activity	Jayaprakasha et al. (2003)
White Garnacha grapes byproducts	Particles smaller than 5.5, 3 and 0.5 mm; continuous extraction with ethanol; temperature: 50°C.	Total phenolics and antioxidant activity	Pinelo et al. (2006)
White Garnacha grapes byproducts	Solvent: ethanol, methanol, water Liquid-to-solid ratio (from 1 to 5 (v/w) Extraction time (from 30 to 90 min) Temperature (from 25 to 50°C).	Total phenolics and antioxidant activity	Pinelo et al. (2005)
Merlot, Chardonnay and Muscadine grape seed powders	Solvents: water, methanol, acetone and ethanol; liquid/solvent ratio of 1:10 (w/v); sonication for 15 min and shaking for 30 min at room temperature.	Total phenolics, antioxidant activity	Yilmaz and Toledo (2006)
Roditis and Agiorgitiko by-products	Solvent 0.1% HCl in methanol/acetone/water (60/30/10, v/v/v).	Total flavonols, total polyphenols, total flavanols and antioxidant activity	Makris et al. (2007)
Refošk, Merlot and Cabernet grape marc	Solvents: acetone (20%, 40%, 60%, 80% and 100% (v/v)); ethanol (50%, 70% and 100% (v/v)) mixtures with water at temperatures 20˚C, 40˚C and 60˚C. pH = 2, 4, and 6.	Total phenolic compounds, total monomeric anthocyanins, total quercetin, catechin, epicatechin and *trans*-resveratrol	Vatai et al. (2009)
Two white wine grape pomace (Morio Muscat and, Muller Thurgau), three red wine grape pomace (Cabernet Sauvignon, Merlot and Pinot Noir)	Solvent: 0.1% HCl/70% acetone/29.9% water (v/v/v); solid/ liquid ratio 1:4 (w/v); Sonication for 1h at room temperature.	Total phenolic, total flavanol, anthocyanin content, proanthocyanidins and antioxidant activity	Deng et al. (2011)
Red and white grape by-products after distillation	4 g with 100 mL of solvent (water/acetone/acetic acid, 29.5/70/0.5) during 2 h at 50°C under stirring.	Total phenols, flavanols content, anthocyanins content	Brahim et al. (2014)
Cabernet Sauvignon grape by-products	93 minutes at 94˚C and in 66% ethanol/water solvent.	Total phenolic compounds, flavonoid content, total monomeric anthocyanin composition and tannin concentration	Rajha et al. (2014b)

Grape by-product matrix	Operating variables	Targeted phenolics and biological activities	Reference
Agiorgitiko grape pomace	Air drying, accelerated solar drying; water, water:ethanol (1:1) and ethanol; 3 g extract/ 100 ml solvent; 2 to 6 hours extraction time.	Total polyphenols, anthocyanins, flavonoids, flavonols and antioxidant capacity	Drosou et al. (2015)
Red grape pomace (Touriga Nacional, Touriga Franca, Tempranillo and Tinta Toriz)	Solvent: ethanol/water 80% v/v; 20 g/100 ml, agitation at 300 rpm 48h.	Total phenolics and antioxidant activity	Tournour et al. (2015)
Merlot skins and seeds	0.3 g of grape pomace/20 mL of 50% aqueous ethanol (v/v); Acidity: 1 N HCl (0, 0.5and 1%); time: 30, 45 and 60 min. Temperature: 80°C.	Total phenolics, hydroxycinnamic acids and antioxidant activity	Putnik et al. (2016)
Red grape pomace	Solvent: water, ethanol (8-92%); solid/liquid ratio (1:3 and 1:17); agitation at 200 rpm and 30°C, for 1 hour.	Total phenolics, anthocyanins profile, phenolic acids profile, flavonol profile and antioxidant activity	Caldas et al. (2018)
Cabernet Sauvignon pomace	5 g of freeze-dried pomace/100 ml of solvent; particle size 420 µm; extraction temperatures (25˚C, 35 ˚C and 45 ˚C); solvent types: Ethanol, water, water/ ethanol (3:1, 1:1, 1:3) and ethyl acetate.	Total phenolic compounds, total flavonoid content, total flavonols and antioxidant activity	Nayak et al. (2018)

Figure 3. Green processes advantages for polyphenols extraction from grapes and their by-products.

Many parameters are influencing the extraction process as solid/liquid ratio, time, temperature, pH, particle size and solvent nature and mixture (Yammine et al., 2017). The literature works aimed to the extraction of phenolic compounds from grape by-products are presented in Table 1.

2.2. Alternative Green Extraction Processes

In the last two decades, numerous alternative processes have emerged in order to displace conventional solvent extraction methods. In fact, many drawbacks of conventional solvent extraction make its application quite uneconomical due to excessive consumption of time, energy, and polluting solvents (Cravotto et al., 2011). These facts have pushed scientists to explore more cost-effective and greener techniques for the extraction of polyphenols in grapes and their byproducts. The aim of these new techniques is to reduce significantly solvent consumption as well as to increase the rate of the extraction with less energy consumption (Delsart et al., 2012; Ortero-Pareja et al., 2015). Figure 3 illustrates the advantages of the use of green technologies to extract polyphenols from grapes and their byproducts. The new processes include: Pulsed Electrical Fields (PEF), High Voltage Electrical Discharges (HVED), Microwave-Assisted Extraction (MAE), Ultrasound-Assisted Extraction (UAE), High-Pressure Assisted Extraction (HPAE) and Supercritical Fluids Extraction (SFE).

2.2.1. Pulsed Electrical Fields (PEF)

PEF began to be used in the food industry in the 1960s. However, the first trials in wine industry have been applied at early 2000s (Boussetta et al., 2015). The principle of the PEF is based on electroporation. This phenomenon is induced by the application of an external pulsed electrical field which will cause the formation of pores on the cell membrane (Figure 4). During PEF treatment, an electrical field ($E \neq 0$) is applied causing the accumulation of charges on both sides of the membrane. A transmembrane potential (V_m) appears due to the membrane polarization. When V_m exceeds the dielectric constant of the membrane, membrane permeability drastically increases and pores are simultaneously formed in the membrane. After PEF treatment, the pore formed can be either reversible or irreversible. A PEF system, in general, consists of three basic components: a high voltage pulse generator, a treatment chamber, and a control system for monitoring the process parameters.

Nowadays, PEF is used in wine industry for polyphenol extraction and inactivation of spoilage microorganisms. The last application will not be discussed in this chapter.

In the literature, several researches have been realized on grapes PEF treatment in order to replace maceration step and enhance polyphenol extraction. Comparing to traditional maceration step, PEF treatments have been proven to enhance polyphenol extraction through increasing intracellular substance transfer. Praporscic et al. (2007) and Anderson et al. (2009) showed that PEF treatments on white grapes accelerate the juice expression and increase yields (20-50%) for all the experimental conditions.

Comuzzo et al. (2018) demonstrated that the PEF treatment of white grapes (22 Kj/Kg) increased the extraction of varietal aroma precursors with a limited color evolution and phenolic compounds extraction. Puertolas et al. (2010b) investigated the PEF treatment on whole grapes (Merlot, Syrah and Cabernet Sauvignon). They showed an increase in anthocyanins and total phenols extraction rate while increasing in the electric field from 2 to 7 kV/cm. Also, Delsart et al. (2012) studied the influence of PEF treatment (0.5 – 0.7 kV/cm with a short duration 40- 100 ms) on wine characteristics of grapes cv. Evolution of color intensity, anthocyanins and total phenolic content during the alcoholic fermentation and seven months after bottling were noticed. No significant differences were identified during sensory evaluation of PEF treated wines and untreated wines. PEF treatments on Cabernet Sauvignon grape berries showed that treatment with low intensity (0.7 kV/cm) for a long duration (200 ms) profoundly modified the organization of skin cell walls leading to an improve in polyphenol extraction and wine quality (Cholet et al., 2014).

Ricci et al. (2018) recently reviewed the studies concerning grape treatments by pulsed electrical fields. All the mentioned studies showed an improvement in the extraction of phenolic compounds measured by different methods as total polyphenol index (Puertolas et al., 2010a,b,c; Delsart et al., 2012; Delsart et al., 2014; Luengo et al., 2014; Delsart et al., 2016), polyphenol content (Puertolas et al., 2010; El Darra et al., 2013a,b), anthocyanin content (Puertolas et al., 2010 a,b,c; El Darra et al., 2013a; Delsart et al., 2014; 2016; Lopez-Giral et al., 2015) and color intensity (Puertolas et al., 2010 a,b,c; Delsart et al., 2012; El Darra et al., 2013a,b; Delsart et al., 2014; 2016; Luengo et al., 2014,). Maza et al. (2019) tested the impact PEF treatment on phenolics of Garnacha grape variety. They found that PEF treatment resulted in high amount of tannins which was the consequence of a higher degree of tannins extraction from grape skins rather than from seeds. PEF processing at high-intensity electric field strength (≥ 30 kV/cm) was tested on Merlot grapes. Results showed a maximal anthocyanin extraction with intense must color (Leong et al., 2020).

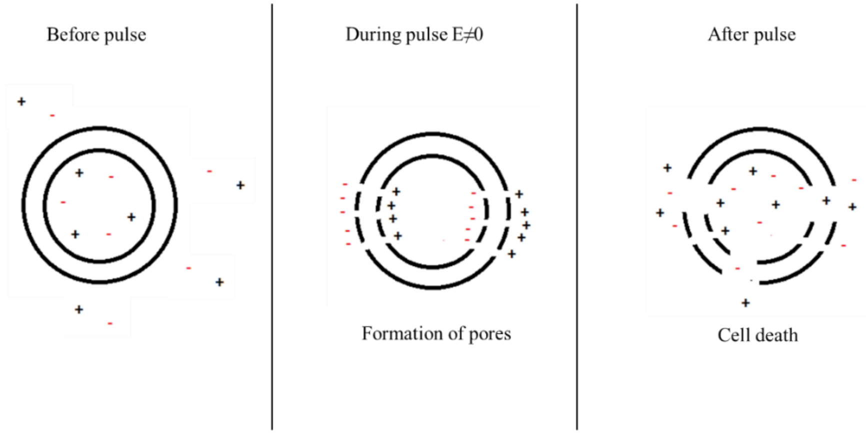

Figure 4. Irreversible electroporation of cell membrane during PEF treatment.

Nowadays, researches are focused also on the biological activities of the wines or extracts obtained by grapes PEF treatment. In fact, PEF treatment of Merlot grapes allowed a higher extraction of anthocyanins amount and types providing the obtained juice a higher activity against Caco-2 cells oxidative damage (Leong et al., 2018). In 2016, same authors evaluated the capacity of Pinot Noir grape juice to protect Caco-2 cells against H_2O_2-induced oxidative stress. PEF treatment enhanced the release of anthocyanins and total phenolics which improved the radical scavenging activity of the juice and the bioprotective capacity. Shree et al. (2018) indicated that grape extract obtained after PEF treatment induced more cell death of HeLa cell line (cervical cancer) claiming the potential used of PEF-treated grape extract as a possible anti-cancer drug.

PEF technique was also studied for the extraction of phenolic compounds from grape byproducts especially in seeds and pomace. These types of materials required a submersion into water in order to improve electrical contact between electrodes (Yammine et al., 2018). Also, high electric field strength ($E \geq 13$ kV/cm) is required for an effective extraction of polyphenols. Boussetta et al. (2012) tested the PEF treatment to extract polyphenols from grape seeds. Grape seeds (50 g) were introduced between the electrodes with an extraction solvent at 20°C or 50°C. The liquid was either distilled water or an ethanol/water (v/v). The tested electric field strengths E were 8, 10, 13.3 and 20 kV/cm and the applied time varied from 1 to 20 ms. Results showed that PEF was an effective technique for the extraction from grape seeds. The efficiency is improved when the treatments were performed at 50°C (E = 20 kV/cm) in the presence of ethanol. Brianceau et al. (2015) treated Dunkelfelder fermented grape pomace with PEF (E = 13.3 kV/cm). Anthocyanins recovery with PEF treatment was 3.4 times higher than the reference extraction of grinded pomace in water. Same authors showed that PEF treatment combined with densification of wet pomace can be realized at low electric field strengths (E = 1.2 kV/cm). This process allowed an increase 15% in total phenol content compared to untreated samples (Brianceau et al., 2015).

2.2.2. High Voltage Electrical Discharges (HVED)

Comparing to PEF technology, HEVD uses several tens of kilojoules for few microseconds to induce the electrical breakdown of water leading to the formation of gas bubbles. Cavitation processes and high amplitude pressure shock waves that are responsible for fragmentation of particles (Yammine et al., 2014). Thus, the application of this technology allows the recovery of intracellular compounds. Boussetta et al. (2009) tested the HEVD technology on the aqueous extraction of polyphenols from fresh, frozen-thawed and sulphured grape pomace for 160 s at constant temperature in the range 20-60°C. HVED technique increased the yield of polyphenols. Highest temperature (60°C) with the addition of Sulphur dioxide were the best conditions to obtain the highest yields. This technology was also studied for polyphenol extraction from grape seeds. The maximal concentration of extracted polyphenols reached 8.3 g GAE/100 g dry grape seed after 300 discharges (Liu et al., 2011). Brianceau et al. (2015) used HEVD to extract stilbenes from grape stems (cv. Cabernet Franc). They showed that HEVD treatment (4 ms) followed by a diffusion with 50% ethanol in water was a positive combination for piceatannol and piceid recovery. Same authors showed that HEVD in the same conditions increased the total phenolic content, flavan-3-ols and flavonols extraction from grape stems compared to conventional hydro-alcoholic extraction (Brianceau et al., 2016).

Rajha et al. (2014a) showed that HVED treatment of vine shoots (Grenache Blanc) in water at 50°C increased the polyphenol content by 3.1 times compared to the control extraction. However, Delsart et al. (2016) compared PEF and HVED treatment on red wine characteristics. They showed that HVED technology showed less polyphenol extraction than PEF technique at same treatment times. In fact, phenolic compounds were degraded after HVED treatment and the quality of wine was modified. Barba et al. (2015) proved that at equivalent cell disintegration indexes, HEVD was less selective than PEF regarding the amounts of anthocyanins recovered.

2.2.3. Microwave-Assisted Extraction (MAE)

MAE technique uses non-ionizing radiations with a range of frequencies between 300 MHz and 300 GHz. These radiations activate the rotational energy levels of the molecules. Electromagnetic energy is converted to heat following ionic conduction and dipole rotation mechanisms (Moret et al., 2019). The process involves disruption of hydrogen bonds, as a result of microwave-induced dipole rotation of molecules, and migration of the ions, which enhance penetration of the solvent into the matrix, allowing dissolution of the components to be extracted. Many parameters should be considered in this technique as solubility, dielectric constant and the dissipation factor. Many factors influence MAE extraction efficiency as matrix nature, particle size, solvent type, loading ratio, microwave power, application time and temperature (Routray and Oursat, 2012; Kala et al., 2016).

MAE was investigated by several researchers in order to recover polyphenols from grapes and byproducts. Liazid et al. (2011) studied the MAE for the anthocyanins extraction from grape skins. Six different extraction variables were tested as: microwave power, extraction volume, stirring, solvent (mixtures of methanol and water), extraction time and temperature (50°C up to 150°C). They found that the best extraction was allowed in 5 minutes using 100°C and 40% methanol in water.

Al Bittar et al. (2013) demonstrated that MAE constitutes an efficient technique in order to produce grape juice rich in polyphenols. Li et al. (2011) developed the MAE technique to extract polyphenols from grape seeds of several grape varieties (Cabernet Sauvignon, Shiraz, Sauvignon Blanc and Chardonnay). The optimal extraction conditions were ethanol concentration (47.2%), liquid:solid ratio (45.3:1) and time (4.6 min). They conclude that MAE provides better extraction with shorter time than other extraction methods. Regarding grape polyphenol extraction, MAE allows to obtain just in 10 minutes twice the amount of polyphenols that is extracted in 3 hours by a conventional solid liquid extraction (Brahim et al., 2014). Álvarez et al. (2017) employed MAE as a pretreatment for grape pomace polyphenol extraction, improving by 57% the efficiency of polyphenols extraction. The anthocyanin content in the final dry product was 85% higher than the control extraction. Also, the antioxidant bioactivity was improved between 83% and 133% compared to the conventional extract. Moreira et al. (2018) explored MAE technique to extract natural antioxidants from vine shoots (cvs. Touriga National and Tinta Roriz), obtaining higher total phenolic content and total flavonoids content and improving the antioxidant activity compared to those achieved by the conventional extraction. Garrido et al. (2019) employed the MAE technique to extract phenolic compounds from 'Chardonnay' grapes marc testing different extraction conditions. They found that the optimal parameters were 10 minutes of extraction time, 48% ethanol and 1.77 g for solid mass. High antioxidant activity (87% DPPH inhibition) was also registered.

2.2.4. Ultrasound-Assisted Extraction (UAE)

Ultrasounds are mechanical waves with frequencies range from 20 KHz to 10 MHz. The major effects of UAE for extraction in liquid medium are attributed to the cavitation process. This process is the result of the creation, the expansion and the implosion of microbubbles formed from gases initially dissolved in the liquid. This generates several effects such as surface peeling, erosion and particle breakdown. According to Chemat et al. (2016), UAE doesn't only act with one mechanism but through combined mechanisms as: fragmentation, erosion, capillarity, detexturation and sonoporation. Several parameters influence the efficiency of UAE technique, such as, ultrasound power and frequency, ultrasonic intensity, shape and size of the reactors, solvent type, temperature, presence of dissolved gases, external pressure and matrix type.

UAE is widely studied in the literature for the extraction of polyphenols from grapes and by-products. Ghafoor et al. (2009) showed that the better extraction condition of polyphenols from grape seeds (Campbell Early) using UAE were 53.15% ethanol, 56.03°C temperature, and 29.03 min time for the maximum total phenolic compounds (5.44 mg GAE/100 mL); 53.06% ethanol, 60.65°C temperature, and 30.58 min time for the maximum antioxidant activity (12.31 mg/mL); and 52.35% ethanol, 55.13°C temperature, and 29.49 min time for the maximum total anthocyanins extraction (2.28 mg/mL). The effects of acoustic energy density (6.8–47.4 W/L) and temperature (20–50°C) on the extraction yields of total phenolics during ultrasound-assisted extraction (25 KHz) from grape marc was studied by Tao et al. (2014). It was found that the initial extraction rate and final extraction yield increased with the increase of acoustic energy density and temperature. Gonzalez-Centeno et al. (2014) showed that the optimal parameters for polyphenols extraction from grape pomace (cv, Syrah) were 40 KHz, 150 W/L and 25 minutes. The same authors explored the use of UAE (40 KHz, 48 W/L) for the extraction of polyphenols of wine lees. The optimal parameters were 60 minutes, 60°C, 50% ethanol and 50:1 solvent to solid ratio.

Pineiro et al. (2016) optimized and validated a rapid extraction of stilbenes from grape canes using UAE. The techniques allowed extraction in 10 minutes at 75°C with 60% ethanol. Mazza et al. (2019) also showed that the most suitable conditions chosen for polyphenols extraction from 'Syrah' grape skin using UAE were 3000 W/L of power, 2.5% citric acid and 1:15 solid:liquid ratio. Milella et al. (2019) aimed to determine the optimum parameters of UAE for polyphenols extraction from grape skin for each dependent variable. Optimized extraction conditions for UAE from grape skin were: 59.5% ethanol, 113.6 min and 66.8°C for TPC extraction; 61.1% ethanol, 99.4 min and 66.1°C for TPC-280 extraction; 57.1% ethanol, 99.5 min and 66.8°C for DPPH radical-scavenging activity; 60.2% ethanol, 82.4 min and 66.8°C for ORAC value. For the same purposes, Dranca and Oroian (2019) showed that according to optimization tests and in order to achieve the highest yield of total phenolic content, the following conditions were necessary: 2-propanol as solvent type at a concentration of 50% and 50°C and 29.6 minutes as temperature and extraction time, respectively.

Drevelegka and Goula (2020) investigated recently the UAE extraction conditions for polyphenol recovery from grape pomace. The optimum extraction yield (48.76 mg GAE/g dry pomace) was achieved using ultrasound extraction at 56°C, a solvent/solid ratio of 8 mL/g, an amplitude of 34%, and a time of 20 min with 53% v/v ethanol, after pretreatment with cellulase, at a concentration of 4% w/w, time of 240 min, and water/pomace ratio of 2 mL/g. Natolino and Da Porto (2020) applied six mathematical models in order to describe kinetics of UAE of polyphenols from fresh and distilled defatted grape marc and its main components. The two-site kinetic model showed the best agreement with the experimental results obtained with the optimum conditions (ethanol-water mixture (57:43 v/v), 200 W, 26 KHz and 30 minutes).

2.2.5. High-Pressure Assistant Extraction (HPAE)

The principle of HPAE is to use water as solvent instead of organic solvents at temperature between 100 and 374°C under high pressure (1 to 6 MPa). These conditions keep water under its liquid state. Superior mass transfer properties of subcritical water lead to high diffusivity and hence higher extraction efficiency. The solubility and diffusivity of water at moderate pressure is, therefore, comparable with organic solvents (Yammine et al., 2014). The pressurized solvent at high temperature increases the solubility of the analyte and also the desorption kinetic rate of the analyte from the sample matrix. HPAE technology could also be designated as subcritical water extraction (SWE), superheated liquid extraction (SHLE), and pressurized liquid extraction (PLE) or pressurized liquid extraction (ASE). Many parameters affect the efficiency of HPAE technology as: solvent, temperature, pressure, extraction time and number of cycles, and the matrix nature (Khan et al., 2018)

HPAE is widely studied in the literature for the extraction of polyphenols from grapes and by-products. Several temperatures (100 – 160°C) were tested for the extraction of anthocyanins from dried red grape pomace. The highest levels of anthocyanins were obtained at 110°C (Ju et al., 2003). Garcia-Marino et al. (2006) showed that temperature of 150°C was necessary for the optimal recovery of catechins and proanthocyanidins from grape seeds. Monrad et al. (2010) demonstrated that adding solvent to water as ethanol (50 – 70% v/v) can accelerate the recovery of anthocyanins from grape pomace. Casazza et al. (2012) showed that HPAE conditions for the highest yields in polyphenols from grape skin (total polyphenol content 60.7 mg gallic acid equivalent g^{-1}DM) and total flavonoids (15.1 mg catechin equivalent. g^{-1}DM) were 150°C for 270 min and 150°C for15 min, respectively. Same observations were also done by Vergara-Salinas et al. (2013) while extracting antioxidants from grape pomace. They found that increasing temperature (150°C) allowed an increase in total antioxidants extraction and antioxidant activity, while using higher temperature and longer extraction resulted in sharp decrease of polyphenol yield.

Duba et al. (2015) optimized the polyphenols extraction from grape skins and defatted seeds using HPAE. The highest polyphenol yield was obtained at 120°C, 10 MPa and 2 ml/min flow rate for 2 hours. Two-site kinetic model described better the extraction kinetic of polyphenols. The extraction of resveratrol from grape seed was optimized by Tian et al. (2017). The most significant factor influencing resveratrol yield was extraction temperature. The optimal conditions were temperature of 153°C for 24.89 min at 1.02 MPa with a solid:solvent ratio of 1:15 g/ml. Pereira et al. (2019) showed that the solvent was the most influencing parameter for the extraction of monomeric anthocyanins (ethanol-water pH 2.0 (50% w/w)) and the temperature (100°C) for the total polyphenol content. Furthermore, the three-line Spline model and two-site kinetic desorption model fitted the experimental date of the monomeric anthocyanin and total phenolic compounds extraction.

However, Todd and Baroutian (2017) showed in a techno-economic analysis of the polyphenols from grape marc that the cost of manufacture by HPAE (89.60 NZ$/Kg product) approached that of current solvent techniques (87.0 NZ$/Kg product). They also claimed that HPAE is high energy consuming techniques which offset many of its environmental advantages.

2.2.6. Supercritical Fluid Extraction (SFE)

A fluid is at its supercritical state, when it is forced to a pressure and temperature above the critical point. This state confers to the fluid many properties as gas-like low viscosity and high diffusivity. When used as a solvent, a supercritical fluid can easily penetrate into the matrix with a rapid mass transfer rate. By increasing the pressure to four times that of the critical pressure of a given supercritical fluid, the density can be approximately doubled maintaining values as a liquid. This technique offers many advantages as: rapid extraction, inexpensive, small amount of organic solvent or no solvent, selective extraction and preserves bioactive compounds. Many parameters can influence the SFE process as: solvent selection, pressure, temperature, solvent type and ratio, co-solvent use, time, flow rate, particles size and the moisture of the material (da Silva et al., 2016). One of the main used solvent in SFE is carbon dioxide (CO_2) which has relatively low critical temperature of 31.1°C and low critical pressure of 7.4 MPa. Supercritical CO_2 properties facilitate mass transfer and yield to a solvent-free extract (Yammine et al., 2018). To extract polar compounds, a co-solvent as ethanol is often added to CO_2 to enhance the solubility of polar compounds, resulting in a higher yield of the targeted material.

Several authors studied the application of SFE to grape and by-products for polyphenols extraction. Murga et al. (2000) studied the feasibility of application of mixtures of carbon dioxide and alcohol under supercritical conditions for the extraction of low molecular weight phenolic compounds from grape seeds. It was found that the solvent capacity tends to increase with pressure and the amount of alcohol. The operating conditions were 30 MPa, 55°C, 20 minutes and 20% v/v methanol/water. Pinelo et al. (2007) compared polyphenol extraction from white grape pomace by using SFE and conventional extraction. They found that SFE yielded higher phenolic concentrations. SFE efficiency was enhanced when increasing temperature (up to 50°C) and contact time (up to 90 min), decreasing solvent to solid ratio (1:1) and adding ethanol as co-solvent (8%).

Casas et al. (2010) found that optimum conditions for resveratrol extraction from grapes seeds, stems, skins and pomace by supercritical CO_2 were 400 bar for pressure, 35°C for temperature and the use of 5% v/v ethanol as co-solvent. Ghafoor et al. (2010) optimized SFE process for the extraction of phenolic compounds from grape peel by using response surface methodology. Optimal SFE conditions were identified as 45-46°C temperature, 160-165 kg.cm^{-2} pressure and 6-7% ethanol as modifier. Da Porto et al. (2014) investigated the effect of ethanol-water mixture for phenolic compounds recovery from grape pomace. The highest yield were obtained at 6 ml/min CO_2 and 10% ethanol/water. Also in 2015, Da Porto et al. showed that combining UAE and SFE increased polyphenols yield compared to controls. Finally, Da Porto and Natolino (2017) optimized the polyphenol extraction from white grape seeds using supercritical carbon dioxide with ethanol-water mixture (57% v/v) as co-solvent. The optimum extraction conditions were a pressure of 80 bar, CO_2 flow rate of 6 kg/h and 20% (w/w) co-solvent at 40°C.

2.2.7. Membrane Processes

Over the last 30 years, membrane technologies have been widely applied in the food-processing industry. Nowadays, they are commonly used in the processing of several beverages such as wine, but also for the separation, recovery and concentration of polyphenols from grapes, wines and byproducts (El Rayess and Mietton-Peuchot, 2016; Yammine et al., 2018). The membrane is defined as a barrier separating two phases and restricting the transport of various molecules in a selective manner. The mean pore diameter of the membrane plays an important role in determining the transport phenomena and thus can define the type of pressure driven membrane processes as: microfiltration (0.1 µm-10 µm), ultrafiltration (0.005 µm-0.1 µm), nanofiltration (around 0.001 µm) and reverse osmosis (< 0.001 µm). These processes have low environmental impact as they utilize mild temperatures, little amounts or no solvents and low pressures.

Microfiltration (0.22 and 0.45 µm) was shown to purify the polyphenols while treating an aqueous ethanolic extract from grape seeds (Nawaz et al., 2006). Same technique allowed a recovery rate of 21% of the total polyphenol content from wine lees after several dilutions (Giacobbo et al., 2015). Diaz-Reinoso et al. (2009) aimed to obtain polyphenols enriched fractions by treating aqueous extracts from pressed distilled grape pomace by ultrafiltration (1 kDa) and nanofiltration (250, 300 and 350 Da). The 250 Da nanofiltration membrane allowed the concentration of total phenolic compounds up to 6.3 times. The polyphenols rejection of 87-91% were achieved with ultrafiltration (150 and 50 Kda) of HVED grape seeds extracts (Liu et al., 2011).

Galanakis et al. (2013) used ultrafiltration with different membrane types (100 kDa- and 20 kDa-polysulfone, 1 kDa-fluoropolymer) for the fractionation of phenolic compounds recovered from winery sludge. It was found that the fluoropolymer membrane separated successfully hydroxycinnamic acid derivatives from anthocyanins and flavonols. Fernández et al. (2015) studied the impact of operating conditions (transmembrane pressure and tangential velocity) on the permeate flux in the purification of a grape seed extract by ultrafiltration. The authors concluded that the UF optimum conditions for obtained the highest permeate flux (10-kDa membrane, 5 bar and 1.3 m/s) reduced the mean degree of polymerization of the extracts from 7.15 up to 1–3 units of flavan-3-ols, corresponding to dimmers and trimmers in the permeate.

Giacobbo et al. (2017) demonstrated that ultrafiltration membranes make possible the separation of polyphenols (permeate) from polysaccharides (retentate). Yammine et al. (2019b) tested 11 ultrafiltration membrane with molecular weight ranging from 2 to 100 KDa for the extraction and separation of polyphenols from subcritical water grape pomace extract. They found that solutes retention was not affected by size exclusion but by membrane fouling. Polysulfone membranes were able only to separate polymeric and monomeric proanthocyanidins but no other phenolic classes. Same authors showed that nanofiltration membranes with molecule weight cut-off between 500 and 1000 Da are able to recover polymeric proanthocyanidins from grape pomace extracts while membrane between 300 and 600 Da could partially fractionate monomeric phenolic substances (Yammine et al., 2019a).

CONCLUSION

Phenolic compounds are a diversified group of phytochemicals extracted from grapes during winemaking but also found in abundancy in by-products of the winemaking chain. Numerous methods of extraction have been developed such as the case of traditional extraction with organic solvents. These traditional methods have several drawbacks as being not ecofriendly, toxic, flammable and expensive. New alternative processes have been studied as pulse-electric fields, ultrasound-assisted extraction, pressurized liquid extraction, microwaves assisted solvent extraction, supercritical or subcritical fluid extraction, and high voltage electrical discharges. Several of these emerging technologies have showed their effectiveness. However, the scale-up of these techniques still hindering their application in the field. Also, the large number of phenolic compounds and their chemical structures and properties in grape and by-products add more difficulties in their extraction especially concerning the yields.

In the future, more studies are needed in terms of yields and energy balance of the alternative processes. Further studies are required for comparison of energy consumption in all extraction technologies. As for replacing the maceration, more studies are needed on the impact of these technologies on the final quality of wines. Very few sensorial studies are found in the literature. As for purification and solidification of phenolic extracts, it is very important to compare the existing technologies in terms of energy consumption and phenolics loss during these stages.

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Chapter 10

ECONOMICAL CHARACTERIZATION OF SMALL WINE PRODUCERS FROM THREE WINE REGIONS FROM CHILE: CHALLENGES FOR THE FUTURE

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ABSTRACT

Chilean wine production underwent significant changes due to the trade liberalization policy implemented in the country, becoming an impulse for the export volume to grow 20 times between 1990 and 2019. To achieve this success, the national wine industry developed different

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strategies such as an increase in vineyard area, increase in production efficiency, viticultural zoning and adoption of technologies, among others. All this action allowed Chile to position itself in eighth place in the area of vineyards, in sixth place in the production of wine production, and in fourth place in the volume of wine exported. However, this development of exports has not covered all the wine producers in the country. On the contrary, it has affected the sustainability of small rural winegrowers and traditional production areas, as has happened in part in the South Maule, Bío Bío and Ñuble regions. The main objectives of this chapter are to contrast both realities and determine the factors that drove the uneven progress of the national wine sector to suggest development policies and plans to face sustainability problems. In this sense, complementing the incorporation of technology and knowledge without losing the identity of the wine and the territories could be one of the key factors to improve the sustainability of small and medium wineries.

Keywords: Chile, small and medium-sized enterprise (SME), wineries, wine sector

1. Introduction

Currently, Chile has 146.341 hectares of vineyards for wine (SAG, 2018), which are located from north to south in six wine regions: Atacama, Coquimbo, Aconcagua, Central Valley, South Region and Austral Region which are further divided into subregions, zones and areas (Ley N°18.455).

Chile is a relatively small country with a population of approximately 17.574.003 (INE, 2017), highly dependent in international trade. Chilean wine plays a key role in the international wine trade (OIV, 2019). Wine exports represent approximately 3.41% of total exports with a value of US$2.17 billons (The Growth Lab at Harvard University, 2017). While several medium and big companies are part of this story of success, many others, mainly small and medium-sized wineries, are struggling and might not be able to adapt to be successful at the national and international wine market that has been observed in other countries (Alonso and Liu, 2012). Thus, the main aims of this chapter are to contrast both realities and determine the factors that drove uneven progress of the national wine sector to suggest development policies and plans to cope with sustainability issues.

2. METHODS

2.1. The Context of the Study

The study was focused on South Maule, Ñubleand Bío Bío Regions, which included three wine valleys: Tutuvén (zone within Maule Valley), Itata and Bío Bío, respectively (Figure 1). These three valleys are located in the center-south of Chile and are characterized by having most of the small and medium-sized wine enterprises (SMEs) in Chile. Most of the information related to these three valleys were collected by the “Centro de Extensión Vitivinícola del Sur” (CevdelSur) funded by Corfo (a governmental economic development agency, Ministry of Economy). CevdelSur is a Centre for extension in viticulture and enology conformed by UC Davis Chile Life Sciences Innovation Center, University of Concepción (UdeC) and National Agricultural Research Institute (INIA).

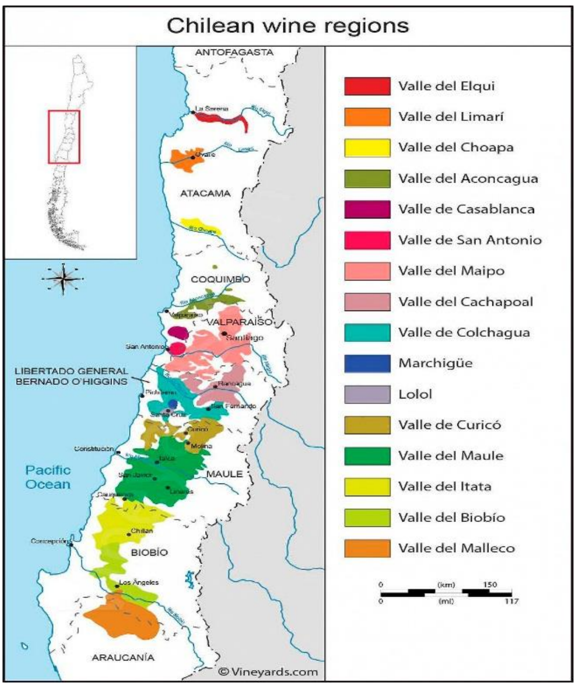


Figure 1. Chilean wine regions.

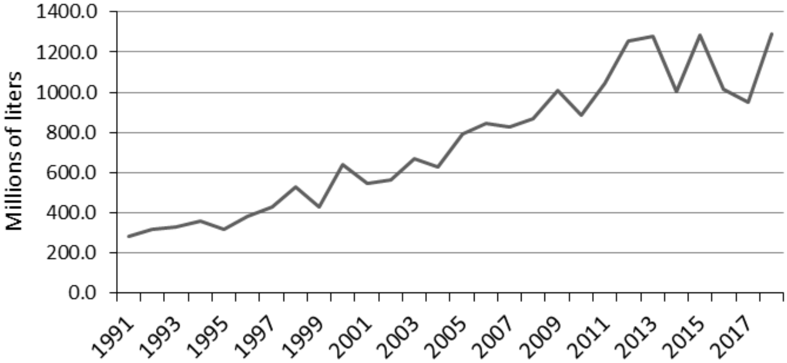
2.2. Methodology

A survey by CevdelSur was performed on 144 SMEs from Itata and Bio Bio valleys, collecting information related to grape and wine production, commercialization and business management. To put in context the distinct features of these three valleys in comparison with the rest of Chilean valleys, viticultural and enological data was analysed from the "Agricultural and Livestock Service" (SAG) and Agrarian Policy and Studies Office" (ODEPA), both services dependant of the Ministry of Agriculture and Trade Map (https://www.trademap.org/Index.aspx).

3. Results and Discussion

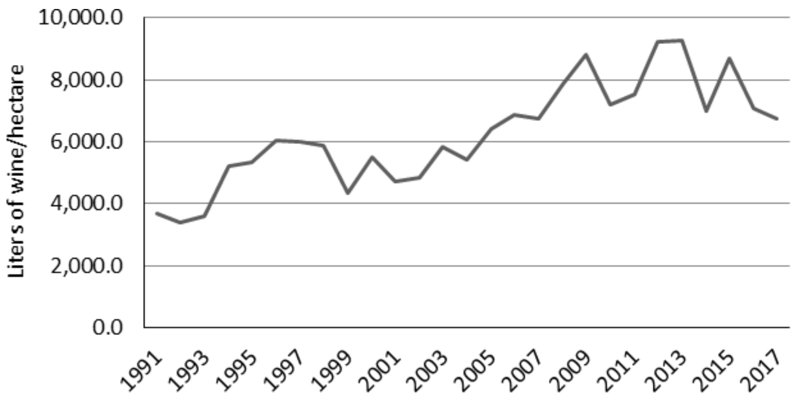
3.1. Performance of the National Wine Production

Chilean wine production has experienced a quite relevant increment during the last 25 years, ranging from around 300 million liters, at the beginning of the nineties, to over 1.000 millions of liters during the current decade. Currently, this strong growth during the past decades has been slowed at around 1.000 to 1.200 millions of liters per year (Figure 2).



Source: Own elaboration from ODEPA data. Includes wine made from table grapes.

Figure 2. Evolution of total wine production in Chile in millions of liters during the period between 1991 and 2018.



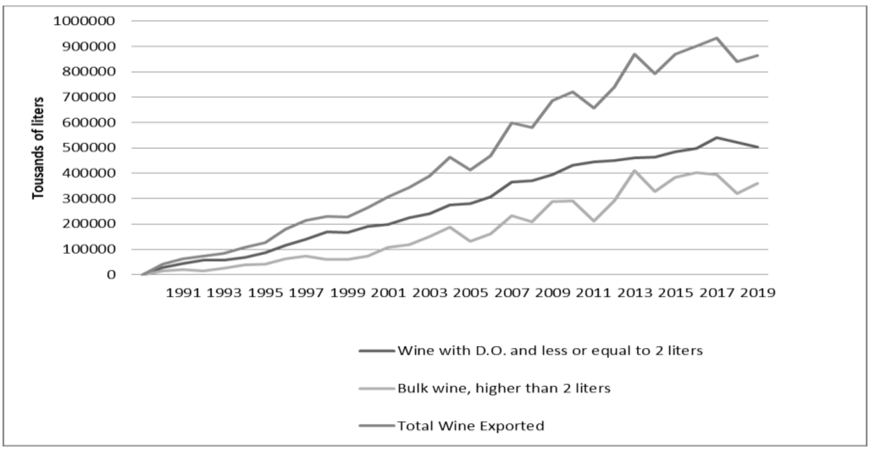
Source: Own elaboration with ODEPA data.

Figure 3. Evolution of mean productivity of wine per unit of surface (in liters per hectare) during the period between 1991 and 2017.

The explanation for this higher wine production has two components. In one hand, the higher growth in the vine area, which in the period between 1991 and 2017 growth 109.6%. Besides, ODEPA recognizes that a huge number of hectares were not declared to the SAG because they correspond to microexplotations (lower than 0.5 hectares of planted vineyards), located mainly in Ñuble and Bío Bío regions (Lima, 2015). Nevertheless, another reason to explain the higher production efficiency, generating higher wine production per unit of soil, is due to the incorporation of technology, mainly in irrigation and fertilization. This trend of a sustained increase in Chilean wine production has been driven since the beginning of the 1990s by the opening of the country to international markets and by the convenient price-quality ratio of its production. Figure 3 shows this improvement in productivity even though relevant climatic variations exist.

The productive trend, whether in production volume, vine area and production efficiency, shows a sharp increase in previous decades; afterwards, lower growth rates or stagnation persist. This behavior can also be visualized in Chile's wine exports. Figure 4 shows wine exports between 1990 and 2019, which increased from 42 million to 863 million liters. However, this volume of wine exported in 2019 is slightly lower than what was exported in 2015, 2016 and 2017, which might prove that the exports reach a level where a greater effort is required to place the wines in the different target markets.

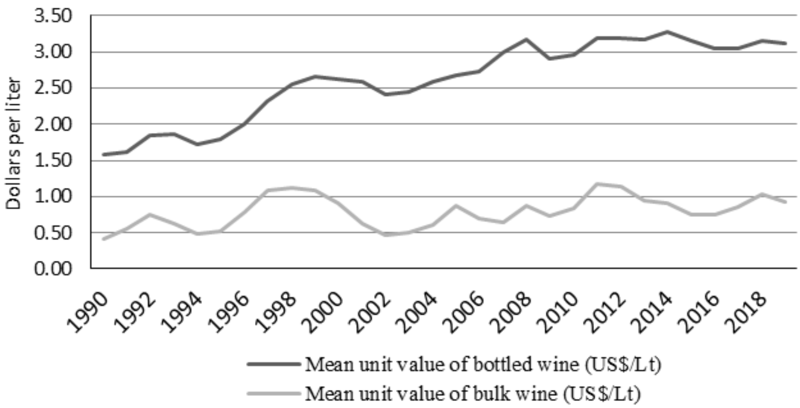
One of the strategies used to improve the exports was to stimulate the export of bottled wines less than 2 liters with a designation of origin (D.O.), over bulk wine or in containers over 2 liters. Since 2013, bulk wine, except small variations, has maintained its exported volume, while wine with D.O. only in 2018 and 2019 has stabilized at around 500 million litres (Figure 4). This strategy, which is based on the quality and typicity of the wine produced, generates an appreciation by the consumer market, which is reflected in the price paid for each type of wine, as shown in Figure 5. Thus for wine with D.O. in packs less than 2 liters, the average value varied from US$/Lt 1.6 to just over US$/Lt 3.0 since 2010, while for bulk wine the values fluctuated between US$/Lt 0.5 and 1.1 and with a very slight upward trend.



Source: Own elaboration with ODEPA data.

Figure 4. Evolution of volume of exported wines, in thousands of liters during the period between 1990 and 2019.

The data shows that the Chilean wine industry is reaching a plateau, with stabilized growth rates and a worldwide positioning among the world's leading exporters. Faced with this reality the industry is modifying its structure and processes to adapt to the demands of the market. Examples of this line are the initiative National Code of Sustainability of Wines of Chile, the incorporation of biotech and production processes, social responsibility and the rescue of the country's diversity and winemaking tradition. These are some of the initiatives driven by the national wine industry.



Source: Own elaboration with ODEPA data.

Figure 5. Evolution of export unit value of wine, in dollars per litre during the period between 1990 and 2019.

These and other strategies to position Chilean wine on the international market will be necessary considering the volumes and unit values obtained by countries that dominate the international market, which is well above Chile's performance, especially in the obtained unit values, as shown in Table 1.

When considering Argentinean wines as a close competitor, it is possible to see that, while it has exported volumes well below Chile, its unit values are above Chilean wines. Regarding the structure of wine production, in 1995 Chile established wine zoning, with 5 major wine regions consisting of: 1) Atacama Region; 2) Coquimbo Region; 3) Aconcagua Region; 4) Central Valley Wine Region and 5) South Region. Austral Region has added afterwards. Thus, the Central Valley Wine Region, which owns 67% of the country's vineyard area, is made up of the Maipo, Rapel, Curicó and Maule valleys.

Table 1. Volume and average unit value of exported bottled and bulk wines during the period 2015-2019

Countries	Bottled wine (<= 2 Lts)		Bulk wine (> 2 Lts)	
	Exported quantity (ton)	Unit value (US$/Lt)	Exported quantity (ton)	Unit value (US$/Lt)
Italy	1.193.052	3,9	483.436	0,8
France	1.061.677	5,9	195.855	1,4
Spain	792.902	2,5	1.233.495	0,5
Chile	501.407	3,1	375.256	0,9
Australia	357.669	4,2	397.759	0,9
Argentina	189.258	3,9	63.320	1,1

Source: Own elaboration with TRADE MAP data.

Table 2. Area of vineyards, number of wine properties and average area per vine property in different Valleys (year of 2017)

Valleys	Vineyards area (ha)	Proportion of national vineyards area (%)	Number of wine properties	Average area per vine property (ha)
Maipo	8.460,0	6,2	264	32,0
Colchagua	33.063,1	24,3	1.396	23,7
Cachapoal	5.943,9	4,4	259	22,9
Rapel	39.007,0	28,7	1.655	23,6
Curicó	11.070,5	8,1	760	14,6
Maule	32.361,6	23,8	2.725	11,9
Total of Rapel, Curicó y Maule	82.439,1	60,7	5.140	16,0
Itata	10.099,9	7,4	4585	2,2
Bío Bío	1.634,2	1,2	222	7,4

Source: Own elaboration from SAG data.

3.2. Commercialization of Small Wine Producers

Chilean wine production is concentrated in the central area of the country, with 81.3% of the area of wine vines and with an average area per wine estate of 17.1 hectares, higher than the national average of 11.3 hectares. When carrying out an analysis by wine-growing areas, specifically by Valleys, it is possible to see more clearly the concentration of small wine producers in the Itata Valley and in the Bío Bío Valley corresponding to the Southern Wine Region, who have an average area per vineyard ownership of 2.2 and 7.4 hectares, respectively (Table 2).

As a counterpart, the Maipo Valley, located in the Metropolitan Region is the one that has the highest average area per wine property with 32 hectares, followed by the Rapel Valley which in turn is made up from Colchagua and Cachapoal valleys. Curicó, Maule, Itata and Bío Bío valleys are located to the south of the country, showing a decline in the average areas per vineyard ownership, confirming the geographical concentration of small vineyard ownership in the regions of Itata and Bío Bío, with a low share of the area of vineyards at the national level (Table 2). This data support that to characterize the country's small wine producers, it is valid to study the wine production of these two valleys (Itata and Bío Bío).

3.3. Commercial Background of Small Wine Producers

The history of the Itata and Bío Bío Valleys has been associated with wine production since the 16th century, with the introduction of the vine by Spanish colonization and evangelization, specifically through Friar Francisco de Carabantes who, in 1548, would have introduced the grapevine through the port of Talcahuano (Pszczólkowski, 2015). From this milestone and considering the wine development that transformed Chile and Argentina already in the eighteenth century in the most important wine region of America (Lacoste et al., 2009), the wine production of Concepción and Chillán (Bío Bío and Itata valleys, respectively) developed strongly, ensuring that in the time of Independence and until the middle of the nineteenth century, they gained fame for their quality, which would be explained by the lower yield of the grapevines obtained from drylands (Couyoumdjian, 2006).

In general, in Latin America, the viticultural practices of the conquest remained virtually immutable during the colony and the first decades of the Republican period, highlighting two grape cultivars: País (synonymies in Latin America: Listan Prieto, Missionary, Criolla Chica, Black of Peru, etc.) and Muscat of Alexandria (synonymies in Chile: Italy), both cultivars, are still prevalent today in the Itata and Bío Bío valleys (Pszczólkowski, 2015). The changes occurred with the arrival of new vine cultivars, mainly French during the twentieth century and the opening to the international market since the 1980s, which generated a boom in wine exports in the 1990s. In this context, traditional cultivars, mainly oriented to the domestic market, coupled with a decrease in national consumption, faced an adverse scenario due to a decrease in demand for this type of wine.

The modality in which they make up their productive activity is individual (65%) over associated forms (25%), which implies difficulties in accessing of certifications, product and process innovations, access to irrigation water, strategic alliances, use and application of the internet and social networks and also access to services. A study performed in Itata Valley showed that wine producers have an average of 58.9 ± 11.7 years old (Serra et al., 2017) which hinder access to new technologies. About 75.6% of the interviewers have a vineyard area of fewer than 5 hectares, a value that is consistent with the low average area per vineyard property for the Itata and Bio Bio valleys shown in Table 2. Muscat of Alexandria, País and Cinsault are the main wine cultivars, representing 70% of the total surface area of vines in both valleys, with a tendency to decrease, while Cabernet Sauvignon, Pinot Noir, Chardonnay and Sauvignon Blanc, recently introduced in both valleys, show an upward trend in their surface.

Regarding their income, 67% of those interviewed indicated that the vineyard contributes over 50% of their family income and 70% indicates wine production as the destination for their grape production. As for the sale of grapes for wine production, the price paid in 2019 presents higher variation, being higher in cv. País (Mission, Criolla), followed by cv. Cinsault variety and finally cv. Muscat of Alexandria. The main grape buyer is a collection center that acts as an intermediary between the producers and the winemaking company (Table 3).

This wide range in the paid grape price is also appreciated in the price paid for bottled wine (Table 4), which would show high differences in the capacities of wine producers to access the market. It is also possible to appreciate the higher average prices obtained by the wines made from new cultivars introduced in these valleys.

Table 3. Price and grape buyers in small wine producers attended by CevdelSur (year of 2019)

Cultivar	Pricing range US$/kg	Mean $/kg	Collection center (%)	Winery (%)	Collection center and winery (%)
País	0.1-0.4	0.22	93.0	7,0	0
Cinsault	0.1-0.3	0.21	91.7	8.3	0
Muscat of Alexandria	0.1-0.3	0.19	85.0	12.5	2.5

Source: Own elaboration with data from CevdelSur.

Table 4. Price paid for bottled wine in small wine producers attended by the CevdelSur (year of 2019)

Bottled wines	Price ranging paid (US$)	Mean (US$)
País sweet, 750 mL	1.2 – 6.1	3.9
País dry, 5 L	1.8 – 6.1	3.8
Cinsault dry	1.8 – 9.7	4.8
Cinsault dry, 5 L	2.4 – 6.1	4.3
Muscat dry, 750 mL	1.6 – 9.7	4.6
Muscat sweet, 750 mL	3.0 – 7.3	4.5
Muscat sparkling, 750 mL	3.0 – 12.1	6.5
Cabernet Sauvignon dry, 750 mL	2.1 – 9.7	5.4
Cabernet Sauvignon dry reserve, 750 mL	3.0 – 6.7	5.4
Malbec dry, 750 mL	4.2 – 12.1	8.0
Blend red dry, 750 mL	1.1 – 7.3	3.3

Source: Own elaboration with data from CevdelSur.

As for the volumes of bulk wine produced by small wine producers, these range from small quantities to high quantities (Table 5), and their main buyers are the big wineries followed by the final consumer. Regarding the prices paid, red cultivars get higher prices and even more than new cultivars introduced in the Valley.

The factors that small producers consider to determine the price of their products are the quality of them and the price of the competition, followed by their production costs. However, the availability of the product in the market and the type of buyer are not relevant aspects, which shows that when marketing their products, the background market information is not sufficiently considered and it is subordinated by internal aspects of the production process (cost and quality). This vision agrees with the commercial strategies used by the small winegrowers to position their products in the market, which are mainly differentiation and cost. The opening of new markets, associativity and focus on segments or market niches, are strategies considered marginally.

The promotion of its products in the market is the result of casual actions such as conversations with friends, family and acquaintances, participation in fairs and traditional parties, among other social activities. Advertising through different means and techniques is practically not considered, only when occasional potential buyers are visited, samples are sent or they participate in commercial tours. Finally, the main point of sale is the property or warehouse, occasionally it is delivered to a third party on consignment and/or commission, as well as delivering to a place defined by the buyer.

In general, small wine producers, from the wine regions studied, of the Bio Bio and Itata Valleys have serious deficiencies in the marketing and/or commercialization of their products. They do not develop strategic marketing, that is, they do not adjust the product-market combination according to their competitive advantages and the requirements and needs of the market. This disconnection has implied a loss in the market positioning of its wine production. Maintaining grape varieties and ancestral production processes has not been a distinguishing feature that could generate a competitive product and the few commercial strategies used have been insufficient to ensure the sale of their production.

As it is possible to appreciate, there are fundamental deficiencies in positioning the wine generated by the small wine producers of the Bío Bío and Itata Valleys, which go beyond production.

Examples of this loss of competitiveness of some wines made from traditional cultivars are Pipeño wine, which has a deep historical root, but despite this, its current permanence in the market would be limited to particular segments and uses (Lacoste et al., 2015). In the same sense, the wine “Vino Asoleado” from Cauquenes and Concepción, which was the first Chilean wine to acquire an appellation of origin in 1953. Nevertheless, currently is irrelevant for the industry (Lacoste et al., 2016). Based on these negative experiences and the difficulties in placing their products in the market, some wine producers from Itata Valley have looked for strategies to increase the value of these cultivars and generate a product according to market requirements. In this sense, highlights the production of sparkling wines, the production of organic wines and the heritage stamp. The results are still incipient, but they open a path for the sustainability of the country’s small wine producers.

Table 5. Bulk wine and prices paid, produced by small wine producers attended by CevdelSur (year of 2019)

Wines	Volume ranging (liters)	Mean volume (liters)	Price ranging paid (US$/liter)	Mean price paid (US$/liter)
País	650 - 200.000	16.584	0.2 - 1.0	0.5
Cinsault	500 - 150.000	22.960	0.3 - 1.0	0.6
Muscat of Alexandria	200 - 300.000	24.676	0.2 - 1.0	0.5
Cabernet Sauvignon	2.000 - 250.000	79.000	0.4 - 0.8	0.6
Red blend	2.000 - 200.000	44.500	0.2 - 0.7	0.5

Source: Own elaboration with data from CevdelSur.

3.4. Comparative Analysis of Commercialization between Small and Large Wine Producers

From the information collected in the previous sections, it is feasible to carry out a comparative analysis between the wine production from small and large producers (Table 6). This analysis highlights seven areas in which the greatest differences between both types of producers are visualized. They address different aspects of the wine production chain, from the production of raw materials to sale in the destination market. Certain differentiating aspects are transversal since they affect various stages of the chain, such as associativity, and there are others specific to some critical stage, such as the grape varieties used. Without detriment to the above, the seven highlights can be classified into three large groups. A first group related to the production function. Here, we must highlight the active search for technology in all productive processes, the innovation of both products and processes and the introduction of improvements in grape varieties in large wine producers versus the passivity, tradition and dependence on state services of small wine producers. A second group related to the commercialization function, which includes the use of techniques, tools and strategies to position their products in the destination markets by large wine producers, versus the low importance of these issues in small winegrowers. Finally, a third group related to policy issues understood as a collective action and the definition of common goals and objectives. In this aspect, the association of large wine producers to strengthen their productive activity and enter the international market is very different from the segmentation and poor integration of small wine producers. In these seven outstanding aspects, it is possible to appreciate the main differentiating aspects that explain the different paths that the great wine producers followed from the small wine producers.

3.5. Barriers of Small Winegrowers to the Marketing of Their Products

From the previous data it is possible to infer that the main barriers for small producers to get into the marketing circuits are as follows:

Table 6. Comparative analysis in commercialisation between small and large wine producers in Chile

Area of analysis	Big wineries	Small wine producers
Associativity	They have promoted different national associations, currently having an organization called “Vinos de Chile” to improve the access to the market, manage innovation and to deal with the different challenges of the industry. It is funded by the wine producers and partially by the State.	They have few associations and generally segmented into particular interests of the respective partners, in general, they do not achieve significant territorial integration.
Main destination market	International.	National.
Top competitive strategies	Differentiation, targeting and Vertical Integration.	Costs and differentiation.
Productive processes	Innovation seeking quality and efficiency.	Traditional and natural to lower the costs and maintain quality.
Technology	They carry out technological surveillance and adopt one that allows them to achieve their objectives.	They take it from state services and adopt the one that according to their reality can implement.
Marketing	Perform competitive and market intelligence to match their products to their chosen target markets.	In general, there is a disconnection from the market and its trends, which would not affect their productive decisions.

Source: Own elaboration with data from CevdelSur and ODEPA.

3.5.1. Combination Product - Market

Currently, small wine producers have as target market the national market with a product that is a traditional wine. The potential size of this market, assuming a percapita of 17 liters per habitant wine consumption is around 300 million liters, which is approximately 25% of the domestic production. That is, it is a market that has an oversupply, which is not clearly shown, due to domestic wine exports, but which when the international market contracts it has a strong impact on the domestic market. Faced with this reality, small wine production must explore different combinations of product-market to increase the options for its sustainability.

When a product meets the needs and/or requirements that society and/or market demands, efforts to place and sell such product are ostensibly diminished. On the other hand, if the product is not what society demands, the efforts and costs that must be borne for the consumer to buy it are high. Small wine producers find themselves in the latter situation with the product they generate for the domestic market and in the face of this situation, the solution will hardly come by forcing the market to change its tastes and requirements.

3.5.2. Access and Adoption of Technology

The current society went from an information society to knowledge society, turning knowledge a key resource for the new economy. A globalized world imposes challenges on issues that might not necessarily seem close to wine producers (safety, climate change, environmental conservation, among others), but which in target markets are valued. In this context, small wine producers could develop and incorporate technologies (knowledge) based on their reality, which can contribute to global challenges. An example could be to rescue and improve heritage and/or natural processes that could strengthen clean and/or organic production. This knowledge may require systematization or improvements for implementation, which would add a differentiating feature to the generated product.

3.5.3. Association

Many of the challenges facing small wine production require a community effort. What the country's big wine producers have done in confronting an even larger international market shows that progress must be made in partnership to deal with it successfully. Associativity does not involve addressing all aspects of the business in a community. In general, when opting for this horizontal integration strategy, a study is conducted to identify what aspects are needed to address together. Access to services, innovation and technology, promotion and marketing are usually some of the aspects that are done in an associative manner.

The diagnosis made showed that associativity was an aspect considered marginally by small wine producers, prioritizing their activity individually. Cultural and cognitive aspects may affect this response, so it is advisable in these situations to strengthen the social capital before implementing an associative structure.

CONCLUSION

The development of Chilean winemaking is impressive, as in a few years it was able to position its products in international markets, however, small winemakers did not participate in this growth. The causes of this marginalization are multiple and the barriers that must be overcome to improve the positioning of its products in the market go beyond the production aspects.

Thus, what to do to have an inclusive wine development? A first step would be to recognize that they are different production systems and therefore can have different development strategies. Small agriculture has ancestral different productive objectives, its main motivation being the subsistence of its family group. His relationship with the market was the sale of his surplus production, with whose income he could access those goods that he was not able to produce. This allowed it to survive as a system for many years, by configuring an autarkic system, quite independently of the society in which it was inserted. However, the context has changed and this autonomy becomes difficult to sustain. Today it is indicated to him that he must completely change his production system, that the main objective of his production should be to satisfy the needs of society, that he must associate with other producers and that he must change his ancestral form of production. This break for small winemaking requires a more detailed study, which allows progress with change but on what has been built for years, rescuing those bases that can sustain a better future.

A second step would be to develop support actions so that the small winegrowers can adjust their wine production system to the demands of the market. In general, support programs for small agriculture have focused on technological improvements to increase their production (Graziano da Silva et al., 2008), as a way to increase their income and therefore decrease their poverty. However, given the difficulty of placing their products on the market, initiatives have been implemented to incorporate them into food supply chains (Danse and Vellema, 2005; Egorov et al., 2019).

Specifically, in the wine sector, the obstacle to innovation would not lie in the role of wine production, but marketing. Thus, Lanfranchi et al. (2019) highlight the knowledge of technological innovations and their willingness to incorporate them in wine producers in the Sicilian district of Valle del Mela, Italy, while Medina-Albaladejo and Planas (2018), in their study "The role of the Spanish Cooperative Wineries in the wine trade" highlights their difficulties in adapting to changes in wine consumption patterns since the 1970s. In this same sense, Kubícková and Peprný, (2011) in their study on the internationalization of the small and medium-sized wine cellars of the Czech Republic, pose difficulties in the face of strong competition, which requires having capital and effective promotion, recommending direct exports and high-quality wines with special attributes.

Finally, a third step would be to recognize that it is possible to complement ancestral knowledge and techniques with the development of an internationally competitive production system, including using part of that knowledge and techniques as distinctive characteristics of wine production. In this sense, the experience acquired by CevdelSur working with small producers from the Bío Bío and Itata Valleys has not only improved the quality of their wine production but has also worked to maintain a wine identity (traditional cultivars and heritage cultural). Wine products have also been diversified with the production of sparkling wines and articulation with the national market.

Along this same line, it is possible to advance in wine tourism, which offers the opportunity to further diversify the possibilities of a sale. Rüdiger and Hanf, (2017) show in German viticulture a direct relationship between wine tourism and the acquisition of new consumers, thus being a direct sales instrument. On the other hand, the experience studied by Dentoni and Reardon, (2010) for small Italian producers of olive oil, of using social networks to carry out transactions with international buyers and build global niche brands, can be a comparable alternative to the wine industry of small winegrowers from the Bío Bio and Itata Valleys.

In summary, Chile's wine development shows two very different faces, one inserted in international markets that faces the challenge of competing in a global market and the other that must migrate from a traditional activity focused on its self-sufficiency to the multifunctional wine industry, enhancing its ancestral history and culture, as a path to its sustainability.

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Chapter 11

CONTEMPORARY WINE CONSUMPTION: ROLE OF INTRINSIC AND EXTRINSIC ATTRIBUTES IN SHAPING CONSUMERS' PREFERENCES AND BEHAVIOR

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ABSTRACT

Wine can be produced from many different grape varieties, which strongly influence the quality and style of wine. Since ancient times, wine has been traditionally produced by different technologies, depending on local or regional traditions. It seems the reasons for the popularity of this alcoholic drink all over the world lie not only in its delicious aroma/flavor, but also in the belief that a moderate intake of wine is recommended since it has potential health-promoting and disease-preventing effects. As global

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wine consumption is constantly increasing, winemaking has spread across the world to novel wine-producing areas. Therefore, an upward trend is to protect the geographical origin and other aspects of wine production in order to avoid fraud. The purpose of this chapter is to investigate the influence of different factors that shape consumers' wine consumption patterns and to provide insight into the most important aspects of purchasing decisions and behavior on different consumption occasions. Special attention is placed on extrinsic (e.g., labeling, packaging, brand, price, and country of origin (COO)) and intrinsic (e.g., color, flavor, smell, and appearance) attributes of wines, and also on the influence on consumption patterns (perceived quality of the wine, willingness to pay, and purchasing intention). By identifying the most important drivers of wine consumption, wine producers should be able to segment wine consumers based on their preferences and consumption habits and define the most effective marketing strategies and promotional programs for their products.

Keywords: wine classification, extrinsic attributes, grape varieties, intrinsic attributes, organic wine, wine consumption, wine regulation

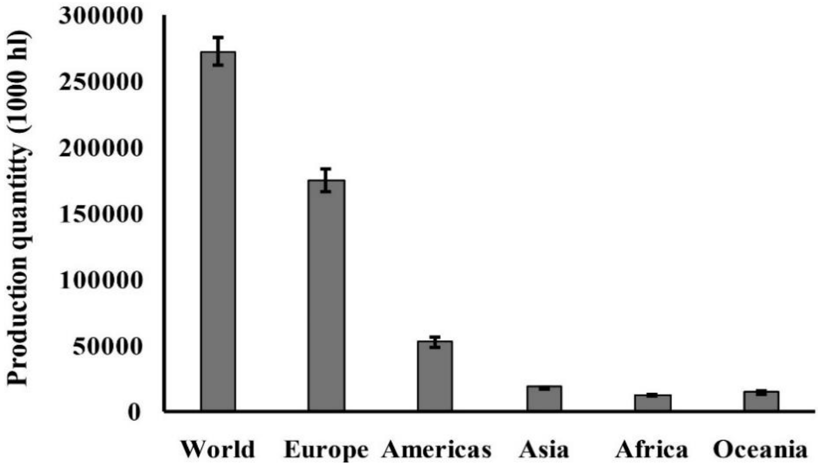
1. Introduction

Wine is one of the oldest and most popular alcoholic beverages in the world. The chemical composition of wine is very complex and even shows a certain mystique, since there are no two bottles of wines with the same composition from two vineyards, regions, or countries (Munsie, 2002). The sensory quality and chemical composition of wine depend on a wide variety of factors, such as geographic origin, viticultural practices, and the winemaking process. This famous alcoholic beverage is produced from different grape varieties. The previous trend in the global wine industry was that wines were mainly produced from a limited number of international grape varieties, mainly particular *Vitis vinifera* varieties, such as Cabernet Sauvignon (Munsie, 2002). Conversely, the current trend in the global wine industry is the increasing number of different grape varieties utilized for wine production, which is generally introducing native grape varieties (OIV, 2017). In many countries, besides grapes, different raw materials are used for wine production, and these beverages are widely known as non-grape wines (Davidović et al. 2012). According to European Union (EU) regulations, wine is defined as "the product obtained exclusively from the total or partial alcoholic fermentation of fresh grapes, whether or not crushed, or of grape must from vines of *Vitis vinifera*" (EU Commission, 2013).

The consumption of wine in today's world has gained socio-cultural characteristics and has become part of consumers' lifestyles (Ritchie, 2007; Mora and Moscarola, 2010). Wine is considered to be a predominantly hedonic product, and in the contemporary market, wine is perceived more as "a sophisticated, classic, sacred, pleasant, and quality product", and therefore, having a more symbolic meaning for consumers (Marinelli et al. 2014). Personal values attached by consumers to the consumption of wine are hedonism, benevolence/care, stimulation, achievement, joy, and happiness (Castro et al. 2019). Furthermore, many studies also confirmed the potential health benefits of moderate wine consumption (Majkić et al. 2019).

Wine is highlighted as an important agro-food product for many countries' economies (FAOSTAT, 2020). During 2018, the global area planted with vines destined for the production of wine grapes, table grapes, or dried grapes, also including that not yet in production or not yet harvested, was estimated at 7.4 million ha, whereas the vineyards in just five countries (Spain, China, France, Italy, and Turkey) stand at 50% of the overall world vineyard area (OIV, 2019). In recent decades, the great majority of vineyards (almost half) were situated in the EU (Meloni and Swinenne, 2013). However, present data shows wine regions are widespread throughout the world. In 2018, world grape production was 77.8 million tons, of which wine grapes made up 57% (OIV, 2019).

Although wine is produced in more than 60 countries all over the world, the largest wine production is still concentrated in Europe. During 2018, world wine production was 292 million hectoliters, while European countries produced more than half of this amount (Figure 1) (OIV, 2019). Furthermore, almost all European production of wine is situated in EU countries, which produce 180 million hl (61.4% of world production) (OIV, 2019).



Note: Vertical bars indicate standard deviation of the mean.

Figure 1. Average production of wine by world regions in the period 2011–2016 (in 1000 hl) (OIV, 2019).

Although wine is popular throughout the world, based on the aforementioned presented data, it is evident that the European region is the dominant world producer of wine. According to Trade Map data, world wine exports were estimated at more than 37 billion dollars in 2018, and the EU was the world's export leader (Trade Map, 2020). Although all EU member states produce wine, only three European countries (France, Italy, and Spain) contributed 54.9% of world wine exports in 2018 (OIV, 2019). Interestingly, Spain (21.1%) and Italy (19.7%) both export significantly higher quantities of wine than does France (14.1%), but the value of France's exports is more than one-third of the value of world wine exports (9.3 billion dollars) (OIV, 2019). Overall, France is the creator of all great wine styles, and produces the most respectable wines that are primarily sold in bottles. Furthermore, in 2018, the EU was the world's leading importer of wine, followed by the United States (US) (17.0%), China (7.5%), Canada (4.4%), and Japan (4.0%) (Trade Map, 2020).

Based on their wine traditions, countries are divided into the categories "Old World" (European countries) and "New World" (Defrancesco et al. 2012). Winemaking knowledge has been expanded to the New World by European settlers mainly from mainland European countries (Munsie, 2002). In the last centuries, the New World countries have become more involved in wine making, because of their more consistent climates, extended growing seasons, and the increasing effects of climate change. Overall, the New World countries of Australia, Chile, the US, New Zealand, and Argentina were among the ten top-rated exporters in 2018 (Trade Map, 2020). Furthermore, wine trade between the Old World and the New World has increased (Correia et al. 2019; Kustos et al. 2019). According to data from the world's largest online wine market, in 2018, the average cost of red wine was 15.66 dollars, while white wine 14.41 dollars (ViVino, 2020). Unlike other consumers of other alcoholic beverages, wine consumers have belonged to the ruling elite since the late Bronze Age. The price of extraordinary and unique wine can be extremely high, but generally depends on wine's scarcity or abundance. The price of the most expensive bottle of Bordeaux red wine, a Chateau Lafitte from 1787, was sold at auction in 1986 for 160,000 dollars (Hall and Mitchell, 2008). There is a general conclusion that most wine consumers live in countries with the highest purchasing power. Additionally, the structure of wine consumers has not significantly changed over the centuries. In the majority of New World countries, wine is still a status symbol and consumed on extraordinary occasions, while in the Old World, wine consumption is part of the daily diet (Hall and Mitchell, 2008).

2. The Most Common International Grape Varieties Used for Wine Production

White and red grapes grown in different regions create various wine styles and flavor profiles. The flavor of wine, a combination of smell (or odor) and taste, is directly influenced by the entire vinification process and originates primarily from the grapes, secondly from the treatment of the must (grape juice) and its fermentation, and tertiary from the maturation process of the wine. Concerning the varietal flavor and aromas, relatively minor variations in the ratios of the aroma compounds of the grape cultivars lead to the obvious perceptual differences in these sensory parameters in fermented wines (Styger et al. 2011; Bakker and Clarke, 2011). Although there are over three thousand varieties of *Vitis vinifera* grapes, some, the most familiar, have spread across the globe, constituting the backbone of the wine industry as the most commercially successful varietals (LaVilla, 2009). Some of the most common international grape cultivars, and their areas of cultivation and distribution across the world, according to OIV (International Organization of Vine and Wine, Paris, France) estimates from 2015, are presented in Table 1. The following section of this chapter will be devoted to these international grape cultivars used for wine production, with respect to their influence on the flavor profile of corresponding wines.

Table 1. Cultivation area and distribution across the world of some common international grape varieties in 2015 (OIV, 2017)

Grape Variety	Color	Vineyard area (ha)	Countries and areas
Cabernet Sauvignon	Black	341 000	China, France, Chile, the United States, Australia, Spain, Argentina, Italy, and South Africa
Merlot	Black	266 000	France, Italy, Spain, Germany, Switzerland, Austria, Bulgaria, Moldova, Croatia, Romania, Slovenia, Hungary, Ukraine, Russia, Portugal, Greece, United States, Canada, Mexico, Chile, Argentina, Oceania, South Africa, and Asia
Chardonnay	White	210 000	France, Italy, Spain, United States, Australia, and Chile
Syrah	Black	190 000	Australia, Argentina, South Africa, the United States, and Chile
Sauvignon Blanc	White	123 000	France (Loire Valley, Bordeaux), Australia, Chile, Brazil, New Zealand, North America, South Africa, California, Iran, and Ukraine
Pinot Noir	Black	112 000	Germany, Italy, Switzerland, Romania, Hungary, Spain, United States, New Zealand, Australia, Chile, Argentina, and South Africa

2.1. White Grape Cultivars

Thanks to its ability to grow well under diverse climatic conditions and its appealing fruity flavor, resembling citrus, apple, peach, or melon, Chardonnay is the most cultivated white grape that produces the vast majority of white wines. It originates from Burgundy, France, but its favorable characteristics have resulted in its global cultivation today, across 41 countries, covering an area of 210 000 ha in 2015 (OIV, 2017). Besides France, Italy, and Spain, the US, Australia, and Chile are among its main producers. In addition to producing fine table wines, it is an important component in the blending of one of the most well-known sparkling wines, champagne (Jackson, 2017).

Sauvignon Blanc originated from the Bordeaux region, where it is blended with Sémillon. However, the best and the most characteristic qualities are shown in the Loire Valley, where it is rarely blended and is responsible for the distinctive aromas of some white wines. It is grown in all major wine-producing countries of the world, with a total of 123 000 ha of cultivation area in 2015. It has become particularly popular in California and New Zealand. It is New Zealand's most commonly cultivated grape variety, with almost 20 500 ha of vineyards (OIV, 2017). Since it is particularly susceptible to environmental influences, this cultivar shows regional distinctiveness. The aromatic profile of Sauvignon Blanc is typically influenced by the presence of several volatile thiols, responsible for the marked odors of box tree and cat urine, but also grapefruit zest and passion fruit (Darriet et al. 1995). The well-known blending partner of cultivar Sauvignon Blanc in the Bordeaux region is Sémillon. Due to its richness of flavors and full body, Sémillon increases the body of the wine and also masks some of Sauvignon Blanc's acidity in dry white wines (LaVilla, 2009).

Riesling is a cool-climate grape variety that was presumably cultivated directly from wild vines in Germany, where it has always been considered a top-quality grape. Besides Germany, Riesling has been produced in Alsace (France), California and Washington (the US), Australia, New Zealand, Canada, Austria, Slovenia, Italy, Luxembourg, etc. The unique varietal character of Riesling is acidity and complex floral aromas, commonly reminiscent of roses and pine. Monoterpenes such as linalool, geraniol, nerol, citronellol, and α–terpineol are reported as key odorants of Riesling, contributing to floral, fruity, and citrus attributes (Strauss et al. 1986). The aroma of Riesling wines is delicious when young, but after several years in-bottle, it enhances significantly. Rieslings can be made in a variety of styles. Some regions produce dry Riesling, whereas others leave some residual sugar after fermentation and create off-dry Riesling, with a slight sweetness. When botrytized, it is possible to create a syrupy, sweet dessert-style wine, which has the lowest in alcohol content among the botrytized wines from other grape varieties. Riesling is sometimes suitable for producing sparkling wines (LaVilla, 2009; Jackson, 2017).

2.2. Red Grape Cultivars

Cabernet Sauvignon is used for the production of most Bordeaux wines. It is a small, thick-skinned grape, so the final wines are full-bodied, rich in tannins and coloring matter, and very suitable for oaking. Since it can be grown successfully in different climates, it has become one of the most widely planted grape cultivars, covering an area of 341 000 ha in 2015 (4% of the world's vineyards) and is typical for China, France, Chile, the US, Australia, Spain, Argentina, Italy, and South Africa (OIV, 2017). As a result, it produces a range of different wines. However, one particular flavor of wines, 'blackcurranty', seems to be characteristic, regardless of origin. A somewhat woody flavor, often described as 'cigar box', 'pencil shavings', or 'cedar', occurs when the wine is aged in casks, together with vanilla. Under less-favorable conditions, the presence of green bell pepper herbaceous note is evident in the descriptions (Bakker and Clarke, 2011). Merlot is popular for blending with Cabernet Sauvignon, since it moderates the tannin content in the resulting wine, which matures more quickly.

Pinot Noir is considered a cool-climate red varietal that originated in Burgundy, France, and is widely grown in Europe (Germany, Italy, Switzerland, Romania, Hungary, and Spain). The first association of New

World's Pinot Noir in the US is Oregon. New Zealand is becoming popular as a region for Pinot Noir production, but it is also grown in Australia, Chile, Argentina, and South Africa. It covered 112 000 ha of the world's total vineyards in 2015 (OIV, 2017). This varietal is very environmentally sensitive, producing its typical fragrance (beets and cherries) only under ideal conditions. Since it is an old vine cultivar, it is particularly prone to mutations. This cultivar is known for its thin-skinned grapes, so production of still, red table wine from Pinot Noir grapes is demanding, particularly in terms of extracting color, tannins, and flavor. Due to its low levels of phenolic compounds, the resulting wine is one of the lightest red wines seen in commerce, with transparent color, often a ruby or garnet red, if young, to light mahogany during aging. It is among the most aromatic of red wines, with complex aroma and flavor, resembling cherries, raspberries, and strawberries, when young. During aging, vegetal aromas tend to develop, with descriptors like mushrooms or beetroot, gamy, earthy, as well as floral notes like violets. The wine is medium-bodied with low to medium acidity levels and low tannin levels. Pinot Noir is the most commonly planted red variety in Champagne, France, and, along with Chardonnay and the red grape cultivar Pinot Meunier, it is the backbone of the sparkling wine, Champagne (LaVilla, 2009; Jackson, 2017).

Syrah (Shiraz in Australia) is the only red grape grown in its home area, the northern Rhône. As one of the most common international grape varieties, Syrah can be found throughout the world from France to New World wine regions such as Australia, Chile, South Africa, New Zealand, and the US (California and Washington states), with vineyard area of 190 000 ha in 2015 (OIV, 2017). Wines made from Syrah can vary significantly in style depending on the cultivation climate. The wines are pronouncedly flavored and full-bodied with a deep garnet red color, with some variation to the rim. Although no aroma can be regarded as typical, primary aroma notes usually are reminiscent of violets and carnations, berries, chocolate, coffee, and black pepper. There are also smoky and meaty (salami or bacon fat) aroma characters in Syrah wine, which is more pronounced in French than in Australian varietals. Due to their concentrated flavors and high tannin and acidity contents, the premium quality of Syrah wines is achieved after some considerable bottle aging. For wine production, Syrah can be used as a single varietal or as a blend. Lower quantities of Syrah are also used in the production of other wine styles, such as rosé wine and sparkling red wine (LaVilla, 2009; MacNeil, 2015).

Merlot originates from Bordeaux, France, and vines are high-yielding with thin skinned grapes. Merlot is one of the most popular and high-quality grape cultivars in the world, is grown in 37 countries, and covered 3% of the world's total vineyards in 2015 (266 000 ha) (OIV, 2017). Due to its low tannin content, Merlot wines are commonly smooth, easy-to-drink and acceptable to many consumers, although they vary in style a lot. The wine is of medium acidity and body, and is bright in color with red-ruby hue and medium to high intensity. The aroma is intense, fruity, and spicy, reminiscent of cherries, currants, plum, fig, prune, baking spices (such as clove, nutmeg, and cinnamon), chocolate or cocoa powder. In the case of unripe grapes, the herbaceous character can be noticed. In the New World, Merlot is often used as a single varietal for wine production. However, in Bordeaux and in some other regions around the world, it is used for blending and softening the strict nature of its well-known partner, Cabernet Sauvignon (LaVilla, 2009).

3. Organic Wines

A new trend on the global wine market is organically produced wine, since today's consumers are more convinced of environmental protection and the health benefits of consuming organic products (Vitali Čepo et al. 2018). Today, there is no unique definition for organic wine, since the regulatory law for organic wine is very different at the national level (Cravero, 2019). Beside the many differences, the production of all organic wine starts with growing a wine grape variety according to organic practice, without the utilization of synthetic chemical pesticides, fertilizers, and genetically modified organisms; this is in order to protect the environment from pollution and preserve biodiversity. Hereafter, the vinification of organic vines is regulated with particular restrictions, but mostly includes limited use of SO_2 during vinification. Organic wine certification has been regulated since 2000 in some New World countries (the US, Canada, and Australia), while in Europe, certification is regulated and resulting wines are labeled with the "Organic logo of the EU" (EU 203/2012). Special categories are allowed when wine is produced from organic grapes, and when wine is labeled as "wine made from organic grapes", but the vinification methods utilized are classified as conventional.

European countries, with an organic grape cultivation area amounting to almost 90% of global organic vineyards, are the leaders in organic grape production. Global organic wine grape production is estimated at only 5% of the total wine-growing area (Willer and Lernoud, 2019). In Australia between 2010/11 and 2014/2015, the production of organic grapes used for wine production increased by 15% (Willer and Lernoud, 2019). Expansion of the area in organic wine grapes is expected, since demand for organic, as well as conventionally produced wine is increasing, especially in the non-traditional markets, such as China (Mitry et al., 2009).

Organic production demands constant education of producers and more labor than conventional production; an additional disadvantage is decreased yields in comparison with conventional production. Taking into account all circumstances, organic wines are somewhat more highly priced than conventional products. Consumers are willing to buy more expensive organic products, but the quality difference must be recognizable. Recently, many studies have been conducted to compare the quality of organically and conventionally produced wines. Vitali Čepo et al. (2018) compared the content of sulfite, pesticide residues, ochratoxin A (OTA), and metal content between fourteen organically and twelve conventionally produced Croatian wines. The study showed that, although both the organically and conventionally produced wines contained all investigated contaminants, the levels of contaminants in organic wines were significantly lower than in the conventional wines produced from the same grape/wine varieties from same locations and with similar processing techniques. The organic wine analyzed contained significantly lower levels of pesticide residues and heavy metals (Pb and Mg) than did the conventional wines. In a similar study, where the influence of the production process on the phenolic profile was investigated, no significant differences in the phenolic profiles between organic and conventional wines were found, with the only exception being the higher anthocyanin content of conventionally produced wine (Dutra et al. 2019).

4. Health Benefits of Wine

Knowledge of the beneficial influences of wine on health has accumulated since at least 2200 BC, as suggested from the ancient Babylonian Nippur tablet (made before 2200 BC), considered as the oldest pharmacopeia in the world. Specifically, this tablet is inscribed with recipes for preparations mixed with wine against skin diseases. Throughout history, wine has been used for different health purposes, such as for refreshment of the body, and treatment of wounds, asthma, constipation, dyspepsia, etc. (Fehér et al. 2007). There is plenty of documentary evidence for this, in the form of recipes that have accumulated over time. Some of these recipes specify that wine can be used alone or as a base for other natural ingredients, such as herbs, leaves, spices, and roots, while others evoked magic and superstition. Wine was common to thousands of medicines that were prescribed by various sources for many health issues and conditions, among which were scorpion stings, fevers, leprosy, hemorrhoids, late menstruation, and kidney stones. Moreover, wine was an aid to promote overall health and to provide protection from illness, which was pointed to in the title of a 1638 book by the English physician, Tobias Whitaker: *The Tree of Human Life, or, The Blood of the Grape.* Proving the possibility of maintaining human life from infancy to extreme old age without any sickness by the use of wine (Phillips, 2018).

Long after, the health-promoting effects of wine were scientifically examined and explained. The notion of the therapeutic effect of wine was particularly popularized when epidemiological studies showed a lower incidence of coronary heart disease in France than in the US, despite the French diet being rich in saturated fats (especially animal fats, butter, and cheese). Researchers claimed that wine is responsible for this apparent contradiction, named the "French Paradox" (Phillips, 2018). The first scientific observation of the French Paradox seems to have been reported by Ducimetiere et al. (1980) in the Parisian protective study on 7 434people. This phenomenon was later confirmed by the MONICA project (WHO, 1989), a worldwide monitoring system for cardiovascular disease organized by the World Health Organization. In the following decade, other scientists aimed to research this connection between wine drinking and improved health, with studies performed in animals and humans. Renaud and Gueguen (2007) proposed the moderate daily consumption of red wine in France is associated with a low mortality rate, specifically from cardiovascular diseases. Also, epidemiologic studies, with different populations included, have revealed that individuals who consume moderate amounts of wine daily experience lower all-cause mortality, particularly cardiovascular mortality, when compared to individuals who abstain or who drink alcohol to excess (German and Walzem, 2000). Wine's antioxidant activity appears to be one of the factors possibly contributing to the French Paradox. Also, the health benefits of wine could be more pronounced when combined with a healthy diet. For example, the Mediterranean diet, rich in fruits, vegetables, and whole grains, combined with moderate wine consumption, can contribute to the synergistic effects of wine polyphenols and compounds found in other foods (Guilford and Pezzuto, 2011).

In addition to positive cardiovascular effects, there is a great deal of literature data related to other beneficial influences of wine on human health. For example, wine can help prevent high cholesterol by increasing high-density lipoprotein (HDL) cholesterol. It is believed that wine consumption with a meal allows cholesterol to be cleared before it is deposited in critical sites in the body. Moderate and regular red wine consumption is suggested to prevent type 2 diabetes, chronic obstructive pulmonary disease, lung cancer, acute respiratory distress syndrome, and high altitude pulmonary edema. The antibacterial activity of red and white wine has been also suggested against *Helicobacter pylori* and oral streptococci (Guilford and Pezzuto, 2011). Aromatized wines seem to exert special health benefits, since wine has been used from ancient times as a base for the addition of medicinal herbs and spices, and has long been considered a medicine. These wines are traditionally consumed after meals or after dessert. Also, bitter herbs aid food digestion by enhancing gastric acid secretion, so aromatized wines can be consumed as aperitifs before meals (e.g., fino sherries and vermouths). Bitter beverages are generally known for their aperitive and digestive effects, thus having a positive influence on human metabolism (Tonutti and Liddle, 2010; Petrović et al. 2019). Biological activity, such as the strong antioxidant and antimicrobial potential of some medicinal plants, reported in many studies (Katalinic et al. 2006; Tajkarimi et al. 2010; Petrovic et al. 2016; Veljović et al. 2019), might be responsible for the therapeutic effect of any alcoholic beverages containing herbs and spices.

There is much discussion in the literature on which components of wine are actually responsible for health-promoting effects, especially for cardiovascular health. Both the alcohol and the polyphenol components have been extensively studied in that regard (Saremi and Arora, 2008). Although polyphenolic antioxidants in red wine were initially considered mainly responsible for beneficial health effects, according to subsequent studies, moderate intake of alcoholic beverages, regardless of type (red and white wine, beer, spirits), appears to be the most related to cardiovascular benefits (Krenz and Korthuis, 2012). Whereas some studies claim that the impact of wine on cardiovascular health is primarily due to the effect of ethanol (Hansen et al. 2005), others reported that wine demonstrates health-promoting properties independently of the presence of ethanol, and so attributed the positive effect to wine's polyphenol content (Ruf, 2004). On the other hand, some researchers linked the health effects of red wine mainly to the synergy between ethanol and grape polyphenols (Chan et al. 2000). Although similar therapeutic effects have been ascribed to grapes and wine, it is believed that these benefits could be more pronounced in wine, probably due to enhanced bioavailability of polyphenols after the fermentation process, and due to synergistic effects of ethanol and polyphenols (Guilford and Pezzuto, 2011).

The phenolic composition of wines is mainly dependent on the grape variety, but other factors, such as geographical location, soil, weather, and conditions during the winemaking process, are also important variables (Giovinazzo and Grieco, 2019). Polyphenols occurring in grapes and wine can be divided into two main groups: flavonoids and nonflavonoids. Among flavonoids, the anthocyanins and proanthocyanidins are the most important red wine quality contributors, responsible for the main sensory properties of this beverage, such as color, bitterness, astringency, and chemical stability toward oxidation (Buglass, 2011). The primary nonflavonoids in wine are derivatives of hydroxycinnamic and hydroxybenzoic acids. Also, lignins in wood can release various cinnamaldehyde and benzaldehyde derivatives (Pecić et al. 2012; Smailagić et al. 2019). Although grape nonflavonoids do not have strong aromas or tastes, they can synergistically contribute to the mouthfeel and aroma of the wine (Buglass, 2011).

Phenolic compounds are secondary antioxidants included in the category of free radical terminators. Their antioxidant nature is closely related to their chemical structure. Namely, phenolics easily donate hydrogen or electrons, thus forming phenoxy radical intermediates, which are relatively stable due to resonance delocalization of unpaired electrons around the aromatic ring and lack of target sites for potential binding of molecular oxygen (Dávalos and Lasunción, 2009).

Consumers find the health benefits of wine to be especially important (Balestrini and Gamble, 2006; Boban et al. 2016). Some health benefits of wine polyphenols are shown in Figure 2. It should be noted, though, that some of these therapeutic effects could be closely intertwined. For example, much literature data suggests that wine polyphenols, especially those from red wine, have a protective cardiovascular effect. Specifically, some *in vivo* studies show the antioxidant effects of red wine polyphenols are linked to the prevention of low-density lipoprotein (LDL) oxidation, which leads to atherosclerosis (Nigdikar et al. 1998; Estruch et al. 2011). Furthermore, in a study in people with high cardiovascular risk, blood pressure lowering effects were attributed to red wine polyphenols and not to ethanol (Chiva-Blanch et al. 2012). Besides, the anti-inflammatory properties of polyphenols could be responsible for their protective role against cardiovascular diseases. As reviewed by Liberale et al. (2019), anti-inflammatory effects are linked to the antioxidant activity of plant polyphenols, but also to their ability to stimulate immune responses by directly modulating cytokine expression in rats fed a high-fat diet. According to a randomized clinical trial on sixty-seven men at high cardiovascular risk, red wine polyphenols are also suggested as responsible for the beneficial effects on glucose metabolism (Chiva-Blanch et al. 2013). As reviewed by He et al. (2008), red wine polyphenols have also been linked with cancer prevention. However, among all wine polyphenols, resveratrol has received the greatest attention regarding its cancer-preventing effects. Although the majority of studies on this topic have been conducted *in vitro* or using animal models, the suppressing effects of resveratrol on the proliferation of a wide variety of tumor cells, including lymphoid, myeloid, breast, prostate, stomach, colon, pancreas, thyroid, skin, head and neck, ovarian, and cervical, has been observed (Bianchini and Vainio, 2003; Guilford and Pezzuto, 2011). Due to it displaying various bioactivities (antioxidant, anti-inflammatory, antimutagen, etc.), resveratrol can successfully discourage several *in vitro* stages of carcinogenesis: carcinogen activation, tumor initiation, tumor promotion, and tumor progression (Jang, 1997).

5. Regulation of the Wine Sector

The wine sector is very broad, profitable, and occupies an important place in the economy of many regions of the world. Taking into account its importance, establishing regulations for wine production is of extraordinary relevance to protect producers and consumers. National authorities establish wine production laws in order to regulate various aspects of production and trade. Meloni and Swinnen (2018) classified wine regulation into four different types: market regulation; vineyard regulation; winemaking regulation, and; bottle and labeling regulation, which differ greatly within and between countries. The first attempt to regulate wine production was during the reign of the Roman emperor Domitian (in AD 90), with an edict to ban vineyards spreading in Italian provinces (Unwin, 1996). During many centuries, strict rules have been established in very broad areas crucial for the wine sector. In EU countries, the main focus was to establish basic regulation for vines and vineyards, including the protection of geographical origins, since wine culture is part of the specific cultural identity and heritage of individual regions.

Although wine is not a potential source of significant health hazards, wine buyers demand information on the origin and quality of particular labeled wines. Since the quality of wine is strongly linked with its geographical origin, consumers are willing to pay more for products with protected geographical origins (Sotirchos et al. 2017).

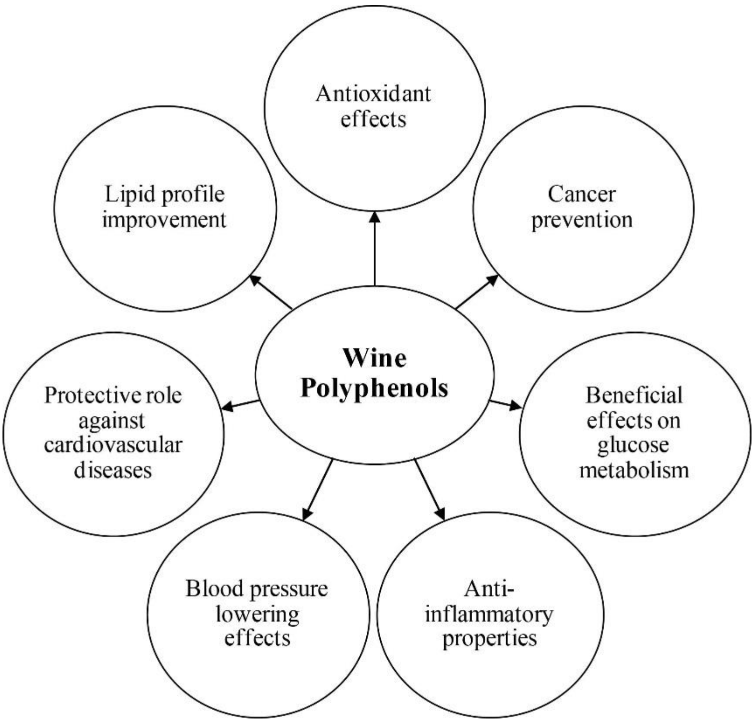


Figure 2. Health benefits from wine polyphenols.

Geographical indication (GI) is defined as "a sign used on products that have a specific geographical origin and possess qualities or a reputation that are due to that origin" (WIPO, 2020). GI has been recognized as covering intellectual property rights since the 1883 Paris Convention, but has applied in the wine sector since 1963. In the wine industry, GI often preserves from oblivion traditional knowledge and skills, which are the typical heritage passed down through generations and which have a strong link with the underlying geographical territory. GI provides *sui generis* protection, so a GI mark encompasses all wine producers found on the defined territory (country, region, or location), provided they respect the product specification. This collective protection has a lot of advantages, including greater influence on the international market than single producers, which is particularly proven in the case of some Italian wine brands, Prosecco PDO, Chianti Classico PDO, and Barolo PDO brands (Qualita, 2017).

In order to be competitive in the most important EU market, the concept of GIs has been accepted by most countries with significant wine production, including South Africa, the US, Argentina, and Australia (Meloni et al. 2019). According to the Trade-Related Aspects of Intellectual Property Rights (TRIPS) Agreement, the member countries are free to regulate the protection of GIs at the national level, provided the GI complies with the minimum standards set by TRIPS. As a result, some countries, such as the US, argued that GIs are sufficiently protected under existing trademark laws, but the EU demanded *sui generis* protection and the establishment of a multilateral register (Jovanović et al. 2012).

Article 93 of the relevant EU legislation (EU Commission, 2013) defines the terms and specific requirements that must be fulfilled in order to label wine with protected designation of origin (PDO) or protected geographical indication (PDI), which were initially introduced in the wine sector under Article 34 of Regulation 479 (European Commission, 2008). PDO covers wines that are produced, processed, and prepared in a given geographical area (region, a specific place or, in exceptional cases, a country) using recognized know-how. PGI covers wine closely linked to the geographical area. At least one of the stages of production, processing, or preparation takes place in a particular area. In Table 2, the particular requirements for wine to be labeled with PDO and PGI signs, which are strictly defined by legislation, are presented (Sotirchos et al. 2017). PDO provides a stronger protection level than PGI since all PDO winemaking steps must take place in the defined region, which is clearly stated on the bottle label.

According to data presented in the EU GI register (eAmbrosia) (EU Commission, 2019), 1607 wines had PDO protection in 2019, and the first wine was protected in 1973. As Sotirchos et al. (2017) previously reported, only two wine PDO regions are in non-EU countries, Vale dos Vinhedos in Brazil and Napa Valley in the US.

Besides regulation, simple, fast, and inexpensive methodology for approving the authenticity of wine, primarily its geographical origin and grapevine varietal identification, is necessary for implementing legal protection on wine's origins (Pereira et al. 2018). For this purpose, various analytical methods/techniques are applied, mostly based on profiling various metabolites, including volatile compounds, amino acids, proteins, phenolic compounds, mineral composition, and isotope ratios (Pereira et al. 2018). The quality and quantity of wine and grape metabolites used as markers for approval of geographical origin are strongly influenced by very different factors (environmental conditions, cultural practices, climate change, production systems, and processing methods). The development of new techniques with increased levels of detection broadens the spectra of analyzed compounds and improves the possibility of tracing the production area of wine. In the case of minerals, the location can be specified to as little as 1000 km^2 (Coetzee et al. 2014). This advantage can be useful especially in identification and approval of the uniqueness of wine as caused by the terroir – a special case of GI regulated by the French wine appellation d' origine contrôlée (AOC) system.

The growth of trade in high-quality agricultural products, including wines, demands defining restrictive product specifications/regulations in order to effectively protect and valorize products. In fact, the importance of GIs is based on the economics of information and reputation in order to produce added value protected products (FAO, 2018). Besides the relevance of GIs in the global wine trade, country of origin (COO) is an important information cue from the consumer point of view, even though as a category, it is not regulated by law. Since, in general, consumers do not possess a high level of knowledge of wine quality indicators, COO is a more commonly used indicator of production location that is taken into consideration when making a purchasing decision. Besides COO, the grape variety is an additional choice criterion with a significant impact on wine consumers with limited knowledge of wine quality. Because of that, the influence of COO and grape variety on consumer behavior is the subject of research in the vast majority of studies in this field.

Table 2. Differences between protected designation of origin (PDO) and protected geographical indication (PGI) of wines

Requirements	**Protected designation of origin**	**Protected geographical indication**
Quality characteristics	Essentially or exclusively due to a particular geographical environment with its inherent natural and human factors.	Wine possesses a specific quality, reputation or other characteristics attributable to that geographical origin.
Grape origin	The grapes from which the product comes are exclusively from this geographical area.	At least 85% of the grapes used for production come exclusively from this geographical area.
Production location	Production takes place in this geographical area.	Production takes place in this geographical area.
Grape variety	Vine variety belongs to the species *Vitis vinifera*.	Vine varieties belong to the species *Vitis vinifera* or are a cross between *Vitis vinifera* and other species of the genus *Vitis*.

Source: Regulation (EU) No. 1308/2013 (EU Commission, 2013)

6. Wine Consumption – Current Trends and Consumer Profiles

Since the worldwide consumption of wine has recorded a slight decline, it is necessary to apply marketing strategies that more effectively address changing consumer expectations and preferences (Castellini et al. 2014; Castellini et al. 2017; Rodríguez-Donate et al. 2019). Therefore, it is crucial to investigate the influence of different factors that shape wine consumption patterns and provide insight into the most important aspects of consumer purchasing decisions and behavior in different consumption occasions. By identifying the most important drivers of wine consumption, wine producers should be able to more accurately segment wine consumers, based on their preferences and consumption habits, and define the most effective marketing strategies and promotional programs for wine products.

6.1. Attribution Theory and Wine Purchasing

In accordance with attribution theory, consumers make evaluations of products in terms of available attributes, which serve as cues, to make a judgment about other characteristics that are not visible to them and to predict the purchase outcome (Heslop and Armenakyan, 2009). Informational cues have special importance for experiential products like wine, whereas actual evaluation of quality can be obtained solely at the time of consumption. There are two categories of cues – intrinsic and extrinsic. Extrinsic attributes of wine (e.g., COO, brand, price, and labeling) together with intrinsic attributes (e.g., color, flavor, aroma, appearance, grape variety, and production method), influence consumption patterns (perceived quality of the wine, willingness to pay, and purchasing intention) (Figure 3). In addition to this general typology of cues, there is a slightly different view. For example, Taylor et al. (2018) consider the factors that influence wine purchase and consumption can be divided into two general groups: intrinsic motivational factors (e.g., personal attributes), those that "push" consumers, and extrinsic motivational product attributes (e.g., situational attributes), which "pull" consumers toward purchasing.

In contemporary consumption of wine, as a highly hedonic product, consumers are more interested than in the past in gaining better information about wine ingredients and the production process and in becoming more skilled to evaluate the quality and enhance their enjoyment (Castellini et al. 2014; 2017; Latour and Deighton, 2019). However, an average consumer is still in the category of "passionate consumer", the person "who consumes and enjoys a hedonic product regularly but has failed to obtain product experience from his/her many experiences" (Latour and Latour, 2010). This indicates that consumers use various available cues to estimate wine quality. For many consumers with no sophisticated knowledge of wine, information cues act as heuristics that help decision making. Consumers with more sophisticated taste are also concerned about the ability to accurately judge the quality of wine due to the rising number of producing regions, the great number of brands on the market, new wine types and grape varieties, different practices in wine production, new channels for promotion, etc. (Barber et al. 2006).

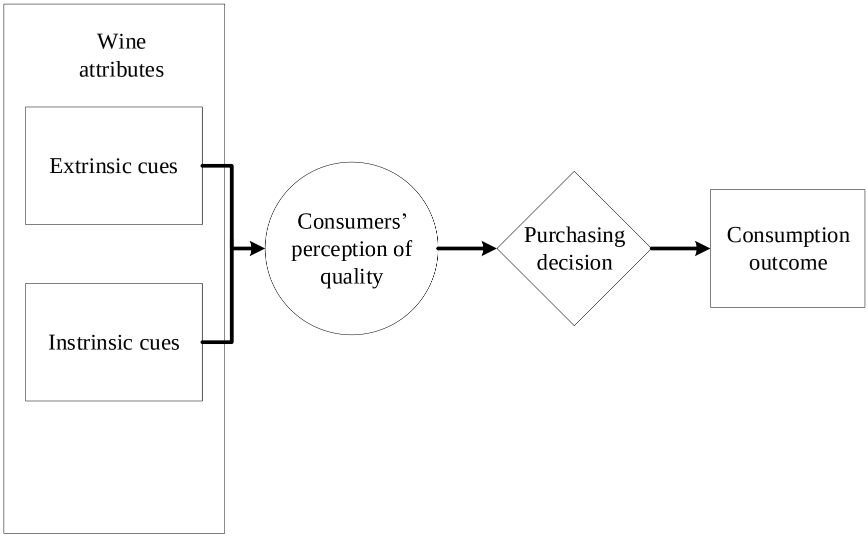


Figure 3. The influence of wine attributes on consumption patterns.

The approach related to the most pronounced cues in wine differs between traditional wine producers, the Old World wine countries, and New World wine countries. Old World wine countries, like France, Italy, and Spain, utilize COO labeling to differentiate their products based on the traditional locations of production and grape varieties used. This is based on the assumption that this attribute conveys information regarding unique heritage and quality.

6.2. Consumption Profiles and Characteristics

Wine is rarely purchased for individual consumption, but is more often purchased for consumption during different social interactions. Wine is considered to be a traditional gift in many cultures, so consumers often make decisions on their own behalf, but also on behalf of others when social occasions demand the chosen product will be consumed jointly or be offered as a present (Balestrini and Gamble, 2006; Wu et al. 2019). In a social context, consumers display different consumption patterns that depend on situation and occasion (Ritchie, 2007). When consumers make decisions for smaller groups of people, their choices represent a balance of personal and others' preferences, while choices made for larger groups more strongly reflect their personal preferences (Wu et al. 2019). Bruwer et al. (2019) concluded that consumers who dine out in larger groups are often the main decision-makers since they more often possess greater knowledge of wine taste and grape varieties and are ready to spend more on wine. Larsen et al. (2010) also found evidence that people tend to imitate the alcohol consumption of others in social encounters.

In a survey conducted by Müller (2006), participants needed to evaluate the following attributes of wine: flavor, brand, price, the winemaking process, vine variety, the country of origin of the base wine and regional origin of the producer. The results indicated six homogeneous consumer groups, based on wine attributes that are considered to be most relevant for making a purchase decision (Table 3). Undemanding consumers value flavor type and price, while ignoring other cues. Brand-conscious consumers evaluate brand as the second most important attribute, after flavor. Ambitious consumers were mostly young but interested consumers, with a low level of knowledge on wines, who observe COO as the most important cue. Region-of-origin-conscious consumers valued this information, while vine-variety-conscious consumers valued that piece of information as very important, after flavor type, price and brand. Expert consumers possess the greatest interest in and subjective knowledge of wine, and they observe all seven attributes as almost equally important (Müller, 2006).

Table 3. Types of wine consumers identified by different authors

Author	**Publication year**	**Types of consumers**
Müller	2006	Undemanding
		Brand-conscious
		Ambitious
		Region-of-origin-conscious
		Vine variety-conscious
		Experts
Bernabéu et al.	2008	Consumers led mainly by price
		Consumers led by origin
		Consumers led by price and wine type
Mora and Moscarola	2010	Individualistic
		Hedonic
		Collaborative
Cicia et al.	2013	Consumers of high-quality and highly-priced Italian and French wines
		Consumers of medium-quality Spanish wines
		Consumers of lower quality wines
Cuomo et al.	2016	Enjoyer
		Wannabe
		Wine victim
		Prophet
Hlédik and Harsányi	2019	Ordinary wine consumers
		Unsophisticated wine consumers
		Wealthy wine experts
		Open-minded consumers

Bernabéu et al. (2008) identified three consumer segments based on the most important cues – the first segment led mainly by price, the second led by the origin and the third, which evaluates the combination of price and wine type. Mora and Moscarola (2010) also defined three consumer groups based on emotions that accompany wine purchase and consumption: individualistic customer (demands customization of products, independence), hedonic customer (emotions above functionality) and collaborative customer (co-creates product offer). Segmentation of Hungarian wine consumers (Hlédik and Harsányi 2019) determined four segments: ordinary wine consumers, unsophisticated wine consumers, wealthy wine-experts and open-minded consumers. The last two segments were target groups for sales of high-quality wine. Additionally, empirical findings indicated three consumer segments in the Russian wine market: a segment demanding only high-quality and highly-priced Italian and French wines, the segment for medium-quality Spanish wines, and segment for lower quality wines (Cicia et al. 2013). Cuomo et al. (2016) defined the “map of identity” for consumers who express their liking of wine (“wine lovers”) via Instagram and defined the following clusters: “enjoyer” (consumes wine as a way to feel happiness and joy), “wannabe” (consumes wine as a way to express an aspiration to reach a better social status), “wine victim” (consumes wine in a manner to affirm social status), and “prophet” (consumes certain types of wine as an act of responsibility toward the environment).

When it comes to demographic characteristics, results indicate that adult men are the most probable consumers of wine, while women and younger individuals consume wine sporadically and in smaller amounts (Rodríguez-Donate et al. 2017; Rodríguez-Donate et al. 2019). While men more often order wine in restaurants and for consumption in a group, women rarely accept responsibility for buying in restaurants but often take responsibility for purchasing wine in more private situations (Ritchie, 2007). Also, Rodríguez-Donate et al. (2017) found that consumers with higher educational levels have a greater probability of occasionally consuming wine. Müller (2006) reported that consumers who are wine “experts” are characterized by higher age, education and income. On the other hand, younger consumers, from the group of under 35s, are more concerned in maintaining a healthy lifestyle and, therefore, perceive wine consumption as something to be reserved only for special occasions (Garcia et al. 2013). Similarly, Vecchio et al. (2017) and Gregory-Smith and Manika (2017) confirmed the tendency of consumers to value the healthy effect of moderate wine consumption.

7. Extrinsic Cues

The existence of a large number of wine brands, as well as their lack of knowledge about quality traits of different wine varieties and products, often makes it difficult for consumers to reach a meaningful decision when purchasing wine. This stimulates consumers to underpin their purchase decisions by relying on wine's extrinsic cues, which include a variety of intangible attributes that are not directly related to the performance of the product and do not include its physical characteristics. These cues include COO, brand name and price, and they are made visible on bottle labels and advertisements (Heslop and Armenakyan, 2009).

7.1. Country of Origin

COO is the most important extrinsic cue of wine, since it is often used as the main predictor of purchasing behavior. It is especially important for first-time purchasers of certain wine brands, who are more likely to use this information as a guideline. For this reason, wines are often displayed by countries in stores, in order to simplify wine choice (Chancy, 2002). COO affects the purchasing decision of wine since "growing country and region have been regarded as important bases for differential advantage" (Felzensztein et al. 2004). This means that consumers could be more likely to choose a wine from countries that are known for products due to their geographical and climate conditions and that have a long tradition of wine production. COO image can be also built based on socio-economic, demographic, political, and other factors. Nevertheless, sometimes, this can lead to avoidance due to the perception of inferior quality, or can lead to greater valuation of products due to the perception of superior quality, and it can change over time. COO is often taken to imply other product attributes, and therefore, it is considered when doing product evaluations and in decision-making processes (Heslop and Armenakyan, 2009).

The influence of COO has been confirmed in a great number of studies. For example, by examining the effect of an image of selected California wine regions on the perception of the quality of wine, Johnson and Bruwer (2007) found COO is the most important information about and predictor of wine quality. In addition, Orth et al. (2005) concluded that the wine region leads to six consumer motivational factors: quality, price, social acceptance, emotional, environmental value, and humane value, which are strong predictors of consumer preferences when it comes to wine. A study that focused on Spain also indicated that destination-of-origin (DO) is the main factor for wine purchase decisions (Martinez-Carrasco et al. 2005).

Guidry et al. (2009), studying French and Texan wines, also reported that the COO strongly influences consumers' preferences and perceptions of quality and price (Guidry et al. 2009). By analyzing the North American market, Arias-Bolzmann et al. (2003) found the perceived quality and price of the wine was favorable toward traditional wine-producing countries like France (Arias-Bolzmann et al. 2003).

Consumers in China are more likely to use extrinsic than intrinsic cues when evaluating wine quality. COO appears to be a more important quality cue than the price for Chinese consumers, even though it is equally as important as the brand name (Balestrini and Gamble, 2006). Other research related to the purchasing behavior of consumers in China also confirmed that COO, used as a single cue, is the most important factor in decision making. The impact of COO on consumers in China is even higher in cases when they purchase wine as a gift or consume it on public occasions, and results indicate that, in these situations, they are more prone to choosing foreign or imported wine (Hu et al. 2008). Research by Agnoli et al. (2014) also confirmed the significance of COO cues in the Chinese market.

Hamlin and Leith (2006) found the four COO cues (New Zealand, Australia, Chile, and France) studied are used as a common evaluation heuristic for wine purchases. Also, Veale and Quester (2008) confirmed the key impact of COO and price as extrinsic cues on evaluations of wine quality by consumers, even when intrinsic cues are experienced through consumption.

Some research focused on differences between novices and experts in using of COO as a quality cue. For example, the results of D'Alessandro and Pecotich (2013) showed that extrinsic cues are, in general, important for both novices and experts, even though they are used in a different manner. Since novices were unable to evaluate wine quality due to their lack of knowledge and experience, they relied mainly on COO as a cue, and used brand name limitedly. On the other hand, experts relied on physical quality and price evaluations, while using the COO and brand cues consistently. Other research that focused on European wine purchasers (from France, Austria, Germany, and the United Kingdom) also confirmed the significance of the region of origin, but revealed that its influence is significantly moderated by other attributes of wine, especially in the case of consumers who regard themselves as experts (Perrouty et al. 2006).

In addition to preferences toward wines from countries known for their production, some consumers can experience preference toward locally produced wines based on patriotic values, or even ethnocentrism or animosity toward foreign wines (Brown and O'Cass, 2006). The findings of Alonso (2012) demonstrate the preferences of consumers based on the local aspect of Muscadine wines in the southern US.

7.2. Brand Name and Labeling

The brand name is another extrinsic cue which enables identification of products in the market and guarantees the consistency of consumption experiences and expected quality. In relation to COO, there is less research related to the impact of the brand name on wine consumers, since it is less important to occasional purchasers and those without a high level of subjective knowledge on wines. However, with increased promotional activities by wine sellers, more distinctive labeling, and strong symbolic meanings, brand name could gain greater significance. Thomas and Pickering (2003) found that brand name, along with price and grape variety are the most important cues used in making purchase decisions. In their research, Barber et al. (2006) reported that brand name was the second most important cue visible on the label. On the other hand, Balestrini and Gamble (2006) stated that COO and brand name are equally important extrinsic cues for consumers in China when evaluating the quality of the wine. Also, D'Alessandro and Pecotich (2013) showed that while novices are less likely to use the brand name for evaluation, experts use COO and brand cues consistently, in addition to price and physical quality.

Labeling is especially important for wine (Thomas and Pickering, 2003). The label actually serves as an efficient channel of communication since it conveys a message on the heritage and winery tradition, production method, grape variety, year of production, brand name, COO, etc. Therefore, it can significantly contribute to consumers' perceptions of wine quality and provide information for decision making (Heslop and Armenakyan, 2009). Also, the label can convey information on the product's healthful properties and environmental suitability. For example, research by Vecchio et al. (2017) showed that consumers consider wines that possess an eco-label to be better for health than conventional wines.

7.3. Price

Price is considered to be a significant quality cue since a high wine price is most often perceived as a clear cue of its high quality. In research, price is often considered to be joined with or determined by other cues, mainly COO and brand name. For example, some research showed that French wines raise price expectations and consumer willingness to pay a higher price (Arias-Bolzmann et al. 2003; Heslop and Armenakyan, 2009; Guidry et al. 2009). Similarly, Brooks (2003) found an Italian origin on the label can significantly raise price expectations.

Price was, together with COO, a more important cue regarding the perception of quality than the taste of wine (Veale and Quester, 2009). On the other hand, Bruwer and Buller (2012) found price, taste, and grape variety to be the most important cues. Hu et al. (2008) determined that COO and price are equally important extrinsic cues. Price is also a significant factor in the US consumption of imported wine (Sam and Thompson, 2012). D'Alessandro and Pecotich (2013) concluded that in relation to novices, experts rely more on physical characteristics and price than on COO and brand name when making purchasing decisions. Also, Skuras and Vakrou

(2002) reported that non-qualified wine consumers are willing to pay double the price for a wine with guaranteed origin.

7.4. Media and Reviews

There is empirical evidence that prior advertising and marketing exposure of alcoholic beverages stimulates subsequent consumption (Smith and Foxcroft, 2009). Wine consumption has gained increasing attention in media, from traditional to social media, and wine-related content is becoming more directed toward the general public, instead of connoisseurs (Castellini and Samoggia, 2018). Sam and Thompson (2012) provided evidence that advertising of imported wines significantly increases the quantities imported. On the contrary, on examining four decades of data, Wilcox et al. (2015) determined advertising has no significant impact on sales of three types of beverages, among which was wine, in the US.

Aqueveque (2008) reported that expert reviews have a crucial impact on consumers' perceptions of quality and value, even more so than price and COO. Horverak (2009) identified the significant influence of wine critics on wine sales in Norway. Additionally, in their research, Williamson et al. (2016) established that quality ratings of wine in articles are the most important cues that influence the choice of consumers in China. Friberg and Grönqvist (2012) determined that neutral expert reviews have a small impact on enhanced wine demand in Sweden, while negative effects were not detected in the case of negative reviews.

8. Intrinsic Cues

Intrinsic cues are sense-related and they include: taste, color, aroma, grape variety, production method, alcohol level, etc. There is also an opinion that COO and region-of-origin, since they are significant determinants of wine taste and quality characteristics (ground and climate), can also be considered as intrinsic cues (Heslop and Armenakyan, 2009).

The influence of intrinsic cues is generally regarded less in the literature on consumer behavior since they are rarely used by average consumers without expert knowledge. D'Alessandro and Pecotich (2013) showed that since novices were unable to evaluate wine quality due to their lack of knowledge and experience, they relied mainly on extrinsic cues, while experts relied on physical quality and price evaluations. In research with Japanese wine consumers, those with higher levels of knowledge regarding wine use intrinsic cues (especially taste and variety) more often than extrinsic cues when making purchase decisions (Bruwer and Buller, 2012). Vrontis et al. (2011) reported grape varieties and production methods to be the most critical factors for purchase decisions when it comes to wine from Cyprus. The importance of the production method as an intrinsic cue is obvious in the case of organic wines. The belief that organic production will preserve and improve the taste of wine is an important factor that stimulates the production of organic wine (Pagliarini et al. 2013; Kim and Bonn, 2015). Recent studies showed consumers' preference toward organic wine in comparison with conventionally produced wines (Pagliarini et al. 2013; Araujo et al. 2017; Willer and Lernoud, 2019). However, despite the fact that the market share of organic wine is constantly increasing, it is still less than 10% of the global wine market (Schäufele and Hamm, 2018). A notable study was conducted by Janssen and coauthors (2020) to analyze the wine preferences of organic food consumers in Germany. The results showed that only 15% of survey participants buy organic wine exclusively, while the great majority of participants (60%) buy wine produced organically as well as conventionally.

The importance of taste and changing consumer preferences has led to the development of innovative wine flavors (e.g., mocha or vanilla), attractive to certain consumer groups (Castellini and Samoggia, 2018). Also, changes in wine consumption trends and greater expectations of consumers regarding health and sustainability means wine with lowered alcohol levels is now marketed (Saliba et al. 2013).

CONCLUSION

Wine is one of the most popular alcoholic beverages in the world, produced from hundreds of grape varieties that grow in different regions. The modern wine industry has increased the number of grape varieties used to satisfy present consumer demand for wine with non-traditional sensory profiles. Besides grape varieties, the flavor of the wine, which is an important sensory quality parameter, is directly influenced by the entire vinification process. Wine is considered as a predominantly hedonic product with unique flavor, while moderate intake of wine has proven health-promoting effects, especially protective cardiovascular effects. Although wine is popular throughout the world, including in both the Old World and New World production areas, the EU is the dominant world producer, exporter, and importer of wine. Taking into account wines' broad diversities, establishing wine regulation has extraordinary importance in protecting producers and consumers from fraud. National authorities establish wine laws in order to regulate various aspects of production and trade. Looking at the factors affecting wine quality, choosing a perfect wine is a very difficult decision for those consumers who do not possess a high level of knowledge of wine quality indicators. Considering that the intrinsic cues of wine cannot be assessed prior to purchase, conditions of high uncertainty surround the purchasing of wine, and therefore, consumers often take extrinsic cues as surrogate proofs of quality.

The identification of various information cues that are used in consumer decision making, as well as the characteristics and purchasing and consumption behavior of different target groups with different levels of knowledge and interest in wine, can help both Old and New World wine producers to identify the most appropriate sales and communication channels, bottle and packaging design, as well as innovative ingredients to make wine aroma more appealing to consumers. Besides producers, who are able to adjust their products to contemporary consumer preferences, identification of the most significant wine attributes is relevant for the foodservice industry in general, since it enables better customization of the wine offer.

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The book "*Vitis Products: Composition, Health Benefits and Economic Valorization*" highlights the nutraceutical value of juice and wine and brings new perspectives to the sustainable use of the byproducts of grape processing. The raw materials generated from the grape processing, including seeds, skins, and leaves have, in addition to many nutrients, bioactive compounds that can be used in the food, cosmetics, and pharmaceutical industries - and thus provide important income sources as well as contribute to the reduction of processing wastes.

Luís António Biasi, Full Professor
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This important book presents an overview about the chemical and sensory composition, health beneficial aspects and economic implications of the several *Vitis* products throughout a considerable number of chapters. This book is focused on recent scientific and technical advances of a wide group of grape derived products and by-products, all of them performed by important international researchers. This book will be quite useful for academic staff, but also for different students, as well as for specialized professionals from the grape and wine sector.

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