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Towards integral utilization of grape pomace from winemaking process: A review

Carolina Beres [a], Gislaine N.S. Costa [b], Ignacio Cabezudo [c], Nina K. da Silva-James [b], Aline S.C. Teles [a], Ana P.G. Cruz [a], Caroline Mellinger-Silva [d], Renata V. Tonon [d,*], Lourdes M.C. Cabral [d], Suely P. Freitas [b]

[a] *Chemical Institute, Federal University of Rio de Janeiro, Rio de Janeiro, RJ, Brazil*
[b] *Chemical School, Federal University of Rio de Janeiro, Rio de Janeiro, RJ, Brazil*
[c] *Biotechnological and Chemical Process Institute, Faculty of Biochemical and Pharmaceutical Science, National University of Rosario, Rosario, SF, Argentina*
[d] *Embrapa Agroindústria de Alimentos, Rio de Janeiro, RJ, Brazil*

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ABSTRACT

Grape is the main fruit crop in several countries. Although many grape-based food products can be found in the market, studies have shown that around 75% of the world grape production is destined for the wine industry. Grape pomace is an abundant by-product from the wine industry, which consists of the remaining skin, seeds and stalks and represents around 25% of total grape weight used in the winemaking process. In countries such as Italy, France and Spain, where wine production is more relevant, the annual grape pomace generation can reach nearly 1200 tonnes per year. In order to reach a sustainable winemaking process there is a need of a waste reduction policy. Several studies explore this subject using grape pomace as a source of healthy and technological compounds that could be applied in animal feed, pharmaceutical, cosmetic or food industry to improve stability and nutritional characteristics, and in cosmetic industry, where grape seeds oil is widely used. This review aims to approach the recent winemaking scenario and the benefits achieved when a waste management policy is implemented, as well as to compare available extractive technologies and a wide alternative of uses for grape pomace.

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* Corresponding author at: Embrapa Agroindústria de Alimentos, Avenida das Américas, 29501, Postal Code: 23020-470, Guaratiba, Rio de Janeiro, RJ, Brazil.
E-mail address: renata.tonon@embrapa.br (R.V. Tonon).

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1. Introduction

Grape (*Vitis* spp.) is one of the most valued conventional fruits in the world (García-Lomillo and González-SanJosé, 2017). It can be consumed raw or can be used in the formulation of products such as wine, jam, juice, jelly, raisins, vinegar and seed oil. Grape crops are one of the main extended agro economic activities in the world with more than 50 million tons produced every year, of which more than 20 million tons correspond to European producers (FAOSTAT, 2014; Scoma et al., 2014). Taking into consideration the whole grape production, approximately 75% is utilized into wine-making (Zhu et al., 2015), being global wine production around 27 billion litres a year (Amienyo et al., 2014). The three main wine producer in 2014 were France (4,670,100 L), Italy (4,473,900 L) and Spain (3,820,400 L) (FAOSTAT, 2014) (Fig. 1).

The most commonly cultivated species for wine production is *Vitis vinifera* (Devesa-Rey et al., 2011). The wine health benefits were introduced in 1990s due to the theorized "French paradox", when the high consumption of red wine in France reduced the prevalence of coronary heart diseases even with a traditional consumption of large amounts of saturated fats and sugar. Studies believed that this paradox was due to the phenolic compounds present in wine (Renauld and Lorgeril, 1992).

From then on, wine consumption has increased over the years and, along with that, the concomitant increase in grape pomace production has been drawing attention. Grape pomace is the main solid organic waste from winery industries; resulting from the pressing and/or fermentation processes it is generated in large amounts in many parts of the world (Abarghuei et al., 2010; Christ and Burrit, 2013; Cuccia, 2015). The main components of grape pomace are seeds and skin. Studies have shown the potential of phenolics and antioxidant fibres recovery from skin (Chamorro et al., 2012; Duba et al., 2015; Beres et al.,2016), as well as oil recovery from the seeds (Bail et al., 2008; Fernandes et al., 2013; Fiori et al., 2014). However, there is still a long way to go until all these residues gains a factual recovery pathway, making the winemaking process a more sustainable activity. In this way, this review presents the main components of grape pomace, together with some extraction pathway and current applications for them, aiming to decrease the negative environmental impact of underutilized grape pomace.

2. Winemaking process and pomace generation

2.1. Sustainability issues into the winemaking process

A sustainable winemaking process consists of maximizing resources and decrease emissions generated by the production process (Castillo-Vergara et al., 2015; Cuccia, 2015). On a global scale, wine sector is responsible for around 0.3% of annual greenhouse gases (GHG) emission (Amienyo et al., 2014).

Carbon footprint is a worldwide standardized indicator of GHG emissions all over the life cycle phases of any goods, service or activity in accordance with the Kyoto Protocol and Life Cycle Thinking statements. The increase in the consumer interest concerning environmental profile of products, particularly those linked to the food and beverages sector, together with the pressures from local communities and governments, has started a race to propagate environmentally relevant results in order to improve consumer satisfaction. The concern regarding increases in GHGs with the potential to modify regional climate patterns has encouraged many firms to move towards sustainable grape culture and wine production practices (Rugani et al., 2013; Cuccia, 2015; Da Ros et al., 2016).

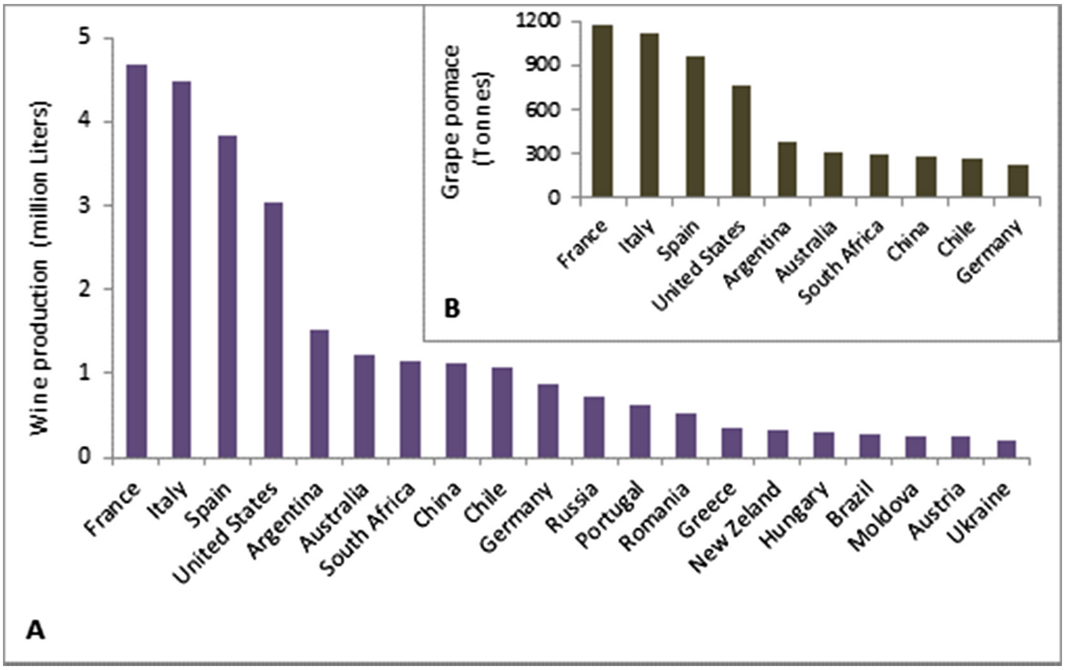

Fig. 1. World wine (A) and grape pomace (B) production by country in 2014, considering that 25% of wine production is pomace (Adapted from http://www.wineinstitute.org/resources/statistics) (Wine Institute, 2014).

Table 1
Correlation between wine making process and environmental concern.

Wine industry: process steps	Environmental risk
Grape culture	Pesticides, fertilisers, water supply and fuel
Packaging	Glass bottles and paper labels
Vinification	Electricity, water, sulphur dioxide and sodium hydroxide
Transport	Fuel
Waste management	Effluents, wastewater and grape pomace

Adapted from Christ and Burrit (2013) and Amienyo et al. (2014).

There are five main critical points in the wine industry that could be an environmental problem, as reported in Table 1.

Grape culture contributes on an average of 41% to the environmental impacts, mainly due to the life cycles of pesticides, fertilizers and fuels. Transport is the next largest contributors, adding an average of 32% to the impact (Amienyo et al., 2014; Da Ros et al., 2016). Evidence suggest that the production of wine might have a negative impact on the quantity and quality of local water resources (Christ and Burrit, 2013)

In this sense, there is an increased interest in a sustainable winemaking activity, since the application of a preventive environmental procedure for products and services that leads to a reduction of human and environmental risks, and costs (Castillo-Vergara et al., 2015; Martinez et al., 2016).

Knowledge is the first step to implement a cleaner production. Wine producers should know where the organic waste is produced, manage it properly and encourage the reuse of wine by-products for alternative purposes (Christ and Burrit, 2013; Cuccia, 2015).

2.2. Grape pomace: The main winemaking by-product

The amount of pomace generated from winemaking is dependent on the grape cultivar and the pressing process, as well as on the fermentation steps. Studies have shown that pomace represent, in general, 20–30% of the original grape weight (Dwyer et al., 2014).

Winemaking starts with grape harvesting, however, depending on the desired sensorial aspects of the final product, the production process to obtain it may vary as well. In general, approximately 1 kg of grape is required to produce 0.75 L of red wine. Stems have high tannins concentration and, depending on the desired wine composition, they can be removed or not. Must fermentation also depend on the desired wine colour (Amienyo et al., 2014). In the red wine processing, grapes are entirely involved in the fermentation and in this case, juice and pomace are fermented together. The presence of the skin during this stage provides pigments such as anthocyanins, necessary to create the red colour of wine. In the white winemaking process, pomace is not involved in the fermentation. In this case, only the juice is fermented after pressing (Dwyer et al., 2014). For this reason, pomace from white wine making process have more pulp and residual sugar when compare to red wine pomace (Mendes et al., 2013). Red wine pressing occurs only after fermentation, which is conducted at 28–30 °C, for one or two weeks, and consist on the conversion of sugar into alcohol by yeasts (Amienyo et al., 2014).

After fermentation, the wine is pumped off into tanks and the skins are pressed to extract the remaining juice and wine. An optional secondary fermentation can be carried out using bacteria to decrease the acidity and soften the wine taste of wine by converting malic to lactic acid. Prior to bottling, the wine must be settled, clarified and finally filtered. Most red wine is then matured in oak barrels for a few weeks to several years depending on the grapes variety and desired wine style (Amienyo et al., 2014).

During winemaking, grapes are crushed and pressed, which does not alter their chemical composition. Fermentation, in red wine processing, is the only significant step that occurs before the pomace is generated, which promote alterations in the carbohydrate composition. However, it does not induce large chemical changes in the bioactive compounds content. Therefore, in both red and white grape pomaces, a significant amount of bioactive compounds are retained. It has been reported that approximately 70% of the phenolic content is preserved in the grape pomace after processing (González-Centeno et al., 2010; Dwyer et al., 2014). The potential use of grape by-products can be a promising alternative, not only motivated by environmental issues, but also by the possibility of enhancing food quality and developing high added-value ingredients and products (Abarghuei et al., 2010; Martinez et al., 2016).

The main solid residues from winemaking are plant remains, sediments from clarification process, grape pomace from pressing, and lees which are basically dead yeasts (Devesa-Rey et al., 2011). As mentioned, grape pomace consists of skin, stem, residual pulp and seed (Christ and Burrit, 2013; Brenes et al., 2016). Seed and skin represent, on dry winemaking residue, 38–52% and 5–10% of grape pomace respectively (Brenes et al., 2016).

Over the decades, utilization of grape pomace has been inefficient. In the last years, it is estimated that 3% of grape pomace produced is reused for animal feed (Dwyer et al., 2014; Brenes et al., 2016), other applications are as waste-based compost (Santos et al., 2016) and a possibility to improve thermal insulation on building construction (Muñoz et al., 2014). Large amounts of pomace are produced during a short period of harvesting, which increases the concentration per area. Incineration or discard in land field may be detrimental to the environment, due to the phenolic compounds decreasing the pH of the pomace as well as increasing resistance to biological degradation. Other environmental problems include: surface and ground water pollution, foul odour, flies and pests attraction that may spread diseases and oxygen depletion in soil and ground waters by tannins and other compounds (Christ and Burrit, 2013; Dwyer et al., 2014).

Due to the increasing consumer demand for the use of natural over synthetic compounds, and because of the increased attention to sustainable of agricultural practices, there is a vast array of applications for grape pomace, such as functional food (dietary fibre and polyphenols), food processing (biosurfactants), cosmetic (grape seed oil and antioxidants), pharmaceutical and supplements (grape pomace powder) (Rózek et al., 2010; Dwyer et al., 2014; Shinagawa et al., 2015).

According to Dwyer et al. (2014), the market potential of grape pomace in Canada shows that if every gram of red pomace skin is sold, there is a profit of approximately 448 million euros, and if all grape seed were used to produce oil, each 750 mL bottle at a price of 4.7 euros, it would result in a final profit of more than 4 million euros. The market potential decreases when a large portion of the produced grape pomace is used to create compost which is than recycled back into the vineyard.

An obstacle considered by Brenes et al. (2016) for grape pomace utilization is its composition which can be different depending on grape variety, location, fertilization conditions, soil and harvest period. However, these differences should not be a problem, since they represent different application possibilities. A better knowledge of grape pomace composition enable to find industrial uses (Llobera and Cañellas, 2007) and to evaluate the importance of the raw material variability (Rondeau et al., 2013) on the final application. Despite a substantial number of studies using grape pomace for different applications, in reality they are often ineffective as they are not successfully implemented in larger scales (Christ and Burrit, 2013).

Countries have their own policy to manage agricultural waste in order to control the disposal and to prevent environmental injury. In Spain, one of the top ten world wine producers, the government gives wine companies three alternatives for managing grape pomace: recycle, valorise or dispose. Many companies choose waste disposal, however a disposal fee must be paid (e.g. 230 Euros/month/m^3/h) taxed by authorities. The waste disposal must be according to the country policy, if it is not done properly, a penalty is charged. In order to avoid disposal and to encourage companies to use other alternatives, the fine applied on company because of inappropriate waste disposal increased from 3000 euros to 30,000 euros in recent years. Besides the fine, the company will have other obligations such as to decontaminate affected areas (Devesa-Rey et al., 2011). This strict policy shows the importance of a proper waste management and the promotion of a integrated, sustainable and standardized alternative protocols for the valorisation of solid winery waste (Martinez et al., 2016).

3. Main grape pomace components

Despite all the environmental issues presented above concerning the winemaking process, this review focused on the two major fractions of grape pomace, namely the seedless pomace (residual pulp, skin and stem) and the seeds themselves, as shown in Fig. 2. Fibre and oil will be the main discussed components in grape seedless pomace and grape seed, respectively, as well as the most used extraction methods and potential applications found in the literature. Both fractions are also rich in bioactive compounds, such as phenolic compounds which will also be explored. The most abundant phenolic compound in wine pomace are anthocyanins concentrated in the skin, and flavonols more present in the seed (56–65% total flavonol) (García-Lomillo and González-SanJosé, 2017).

3.1. Seedless grape pomace

The chemical composition of by-products generated by the wine industry can be influenced by environmental factors such as planting, harvesting, grape variety and also by the process to which it was subjected (Kammerer et al., 2004; Arnous and Meyer, 2009).

A summary of studies that reported a large variability in the chemical composition of grape pomaces are presented in Table 2, where it is possible to compare the variation in different cultivar and even in the same cultivar from different regions.

Seedless grape pomace has received increasing interest for being rich in phenolic compounds, which were not completely extracted during the vinification process. These compounds are known for their antioxidant capacity, as presented in the next topics.

3.2. Grape seed

Grape seeds represent between 2 and 5% of grape weight and constitute approximately 38–52% of solid wastes generated by wine industries (Brenes et al., 2016). In general, they contain about 40% fibre, 10–20% lipid, 10% protein, complex phenolics, as well as sugars and minerals (Rockenbach et al., 2012). Indigestible fractions, mainly cellulose and pectins, are the main constituents of grape seeds, accounting for about 80% of sugar-free dry matter (Goñi et al., 2005).

Grape seeds are mainly valued for the nutritional properties of the oil, which is rich in unsaturated fatty acids (oleic and linoleic) and phenolic compounds (Bail et al., 2008; Hanganu et al., 2012). After oil extraction, there is a rich-polyphenolic residue that

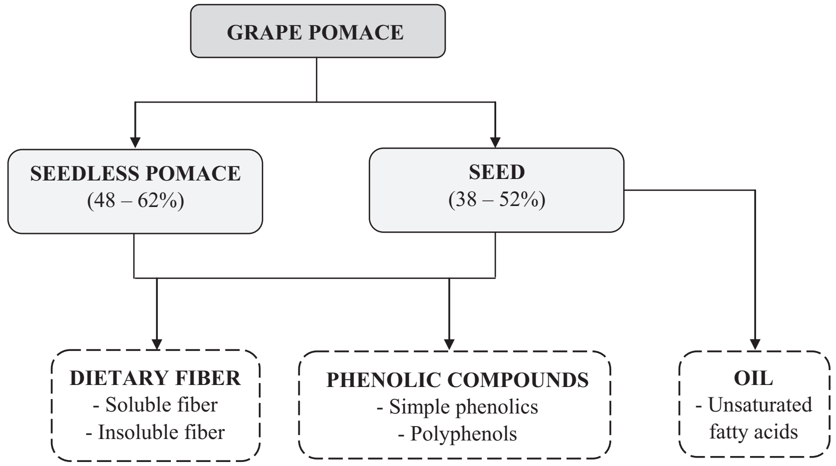

Fig. 2. Main fractions of grape pomace and the components obtained from them.

Table 2
Chemical composition of grape pomace from different varieties (g /100 g dry matter).

	Moisture	Fat	TDF	SDF	IDF	SS	Ash	Protein
Mario Mucato[a]	–	1.1	17.3	0.84	16.4	77.53	3.3	5.4
Merlot[a]	–	3.3	51.1	1.5	49.6	1.34	7.2	11.3
Pinot noir[a]	–	4.7	56.3	1.7	54.6	1.38	6.2	12.1
Marselan[b]	–	5.1	58.0	–	–	–	12.5	6.8
Pinot noir[c]	–	4.2	51.4	–	–	10.9	5.5	13.8
Cabernet S.[a]	–	4.7	53.2	52.4	0.81	1.71	7.6	12.3

Total dietary fibre (TDF), Soluble dietary fibre (SDF), Insoluble dietary fibre (IDF), Soluble sugar (SS).
[a] Deng et al. (2011).
[b] Bender et al. (2015).
[c] Beres et al. (2016).

corresponds, in dry basis, to about 77% of the whole seed (Luque-Rodríguez et al., 2005). Few studies reported the defatted seed residue composition, such as Prado et al. (2014) which suggested a composition of moisture (6.5%), ash (5.7%), protein (11%) and lignin (46%).

4. Main compounds recovered from winemaking by-products

4.1. Phenolic compounds

Phenolic compounds represent one of the most numerous, important and widely distributed groups of natural products in plant kingdom. They exhibit a wide range of physiological properties such as antiallergenic, anti-inflammatory, antimicrobial, antioxidant, antithrombotic, cardioprotective and vasodilatory effects. They are usually associated with health benefits derived from consuming high levels of fruit and vegetables (Haminiuk et al., 2012).

Red wine is a phenolic rich beverage, and its phenolic compounds are well known for their health protective effect towards consumers (Renauld and Lorgeril, 1992; Boussetta et al., 2012). Nevertheless, the whole residue left after fermentation still contains high levels of polyphenols. In fact, during vinification only 30–40% of phenolic compounds are extracted, depending on grape varieties, vineyard location and technological parameters of winemaking (de-stemming, crushing, maceration and pressing) (Ky et al., 2014).

Structurally, phenolic compounds contain an aromatic ring, bearing one or more hydroxyl substituents, and range from elementary single-phenolic molecules to highly polymerized compounds. Phenolics contained in grapes and wine can in general be classified into three main groups, as phenolic acids, flavonoids and tannins, as shown in Fig. 3.

Many phenolic compounds have been identified in grape pomace, where the most abundant are anthocyanins, hydroxybenzoic and hydroxycinnamic acids, flavan-3-ols, flavonols and stilbenes (Pinelo et al., 2006; Kammerer et al., 2004; Soto et al., 2015). Anthocyanins are pigments characteristic of red colour and produced during ripening (Castañeda-Ovando et al., 2009; Xia et al., 2010). They are highly susceptible to chemical transformations due to the action of agents such as light, temperature, oxygen, pH, solvents and metallic ions. Due to this characteristic, one of the great focus of investigations on this compound is its stabilization for use as a natural colourant in food industry. The main anthocyanins found in grape skin are: 3-O-glycosides of malvidin, petunidine, cyanidin, peonidin and delphinidine, however, factors such as variety, maturity and climate may alter the presence of these compounds (Souza et al., 2014; Xu et al., 2015a).

Phenolic acids have a carboxylic acid functional group and are divided into hydroxycinnamic acids and hydroxybenzoic acids. The latter includes the p-hydroxybenzoic acid, protocatechuic, syringic and vanillic acids, while hydroxycinnamic acids include gallic, caffeic, ferulic, p-coumaric, chlorogenic and sinapic acids, and aromatic compounds having a side chain of three carbons (Ignat et al., 2011; Yu and Ahmedna, 2013).

Flavan-3-ols (i.e. proanthocyanidins and catechins) are the most common group of flavonoids in human diet, being easily found in fruits and vegetables. They are of extreme importance in the sensorial characteristics of wine, being extracted from grapes during the vinification process, but not completely, remaining in great amount in the winemaking residue. The highest concentration of these compounds is found in the seed, but they are also present in the grape skin. However, seed and skin have different flavan-3-ol compositions, being catechins, gallocatechins and proanthocyanidins found in the skin, while seeds contain only catechins and procyanidins (González-Manzano et al., 2004).

Stilbenes are phytoalexins that occur in edible plants, especially in grapes. The main stilbene found in grape, wine and in the winemaking residue is resveratrol, and its quantification varies according to the maturation stage and grape variety. The most important stilbenes of grapes are resveratrol-3-O-β-d-glucopyranoside, cis and trans resveratrol, piceatanol and resveratrol dimers, being some glycosylated and isomeric forms also found (Flamini et al. 2013).

Flavonols originate from the same biosynthetic pathway that produces anthocyanins and condensed tannins in grapes, being associated with co-pigmentation, conferring stability to the colour form of anthocyanins, by altering or increasing colour intensity. Kaempferol, quercetin, myricetin and isoramnetin are its main representatives (Makris et al., 2006).

Phenolic compounds are broadly distributed inside grapes. When extracting a single grape variety, the phenolic composition depends upon whether the extraction is performed on whole grape

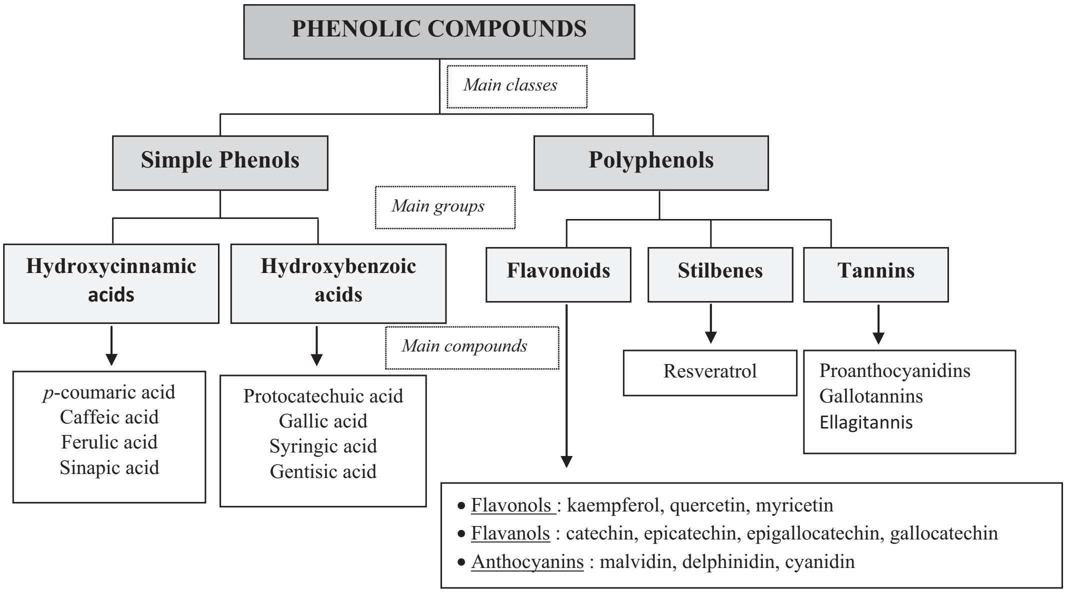

Fig. 3. Main phenolic compounds found in grape pomace.

pulp, skin or seeds. The total extractable phenolics in grape are present at only about 10% or less in pulp, 60–70% in the seeds, and 28–35% in the skin (Shi et al.,2003). The phenolic content of seeds may range from 5% to 8% by weight (Baiano and Terracone, 2011). Grape seed extracts were reported as a great source of proanthocyanidins, usually oligomers and polymers of polyhydroxy flavan-3-ols such as (+)-catechin and (−)-epicatechin, many in the form of gallate esters or glycosides (Brannan, 2008).

As phenolics compounds are the most important grape secondary metabolites with antioxidant properties, the total phenolic content of grape pomace extracts is usually well correlated to their antioxidant activity. The phenolic compounds content and antioxidant activity of seed and skin of different Brazilian grape varieties were investigated (Rockenbach et al., 2011). The authors observed that there was a greater concentration of phenolic compounds in the seeds than in the skins, for all the grape varieties, and the correlation with antioxidant activity was good. Spigno et al. (2007) and Jara-Palacios et al. (2014) also observed a high and significant correlation between antioxidant activity and total phenolic content in grape pomace samples.

4.1.1. Phenolics extraction

Phenolic compounds variability and yield extraction depends on grape cultivar, geographical location, climate, soil condition and process technology. Conventional solvent extraction using a mixture of water and organic solvent provides high yields (Schieber, 2017). Drosou et al. (2015) compared three solvents (water, water:ethanol (1:1) and ethanol) and three extraction methods (microwave assisted, ultrasound assisted and conventional Soxhlet extraction) and observed that the phenolic extraction yield varied from 2.82 ± 0.14 to 24.35 ± 0.34% in dry basis. The authors determined that both the extraction technique and solvent polarity influence in the extraction yield.

The most widely reported extraction technique for polyphenols from grape pomace is solid-liquid extraction by mechanical agitation. The extraction efficiency can be improved mainly by changes in the solvent type, particle size, temperature, and extraction time, as well as the presence of interfering substances in the matrix (Ignat et al., 2011). Although other factors have been reported, generally the most relevant to extraction are solvent, temperature and time. In the last years, traditional extraction with organic solvent have been gradually switched to novel methods with reduced extraction times and low consumption of organic solvents, aiming at increasing the process sustainability.

Due to the polar nature of polyphenols, they are easily solubilized in polar protic media such as hydroalcoholic solutions. In fact, pure acetone or methanol did not give the optimum level of antioxidants in the extracts from grape seeds (Jayaprakasha et al., 2001). On the contrary, water, methanol, acetone and ethanol were tested as Muscadine grape seed powder extractants. In that report aqueous solutions of ethanol, methanol or acetone extracted more than a single-solvent systems for total phenols (Yilmaz and Toledo, 2006). Moreover, aqueous mixtures of alcohols such as ethanol were preferred for the extraction of phenolics in the study of Spigno et al. (2007). In that case, the influence of extraction time and temperature, on phenolic yield was evaluated. Extraction was a slow process, with higher yields at 60 °C than at 45 °C, and with apparent thermal degradation of constituents beyond 20 h (Spigno et al., 2007). In another study, by Pinelo et al. (2006), grape by-products were subjected to an extraction process under various different experimental conditions such as solvent type (ethanol, methanol and water), temperature (25–50 °C) and time (30–90 min) in order to study the effect of these conditions on the yield of phenolic compounds and antiradical activity of extracts. In this case, highest values of time and temperature were preferred, using ethanol as solvent.

In spite of the large number of studies on phenolics recovery described using organic solvents (and their water mixtures), it is well known that phenolics can be covalently bound to complex polysaccharides in cell walls of food matrices (Anson et al., 2009). Traditional extractions methods such as mechanical agitation can be inefficient to extract part of the phenolic compounds. These “nonextractable phenolics” can be ester bound or trapped within proteins, polysaccharides, on cell walls (Saura-Calixto, 2012). A considerable amount of phenolics is left behind after extraction in some matrixes; as a consequence, huge amounts of potential health-promoting substances could remain in the pomace. Nonextractable phenolics recovery has already been studied in the alkaline hydrolysis of cranberry pomace (White et al., 2010) and cauliflower waste (Gonzales et al., 2014).

Supercritical Fluid Extraction (SFE) is a fairly novel technique to extract analytes of interest from solid matrices. A fluid is considered supercritical when it is both heated above its critical temperature and pressurized above its critical pressure. With the manipulation of the pressure and/or temperature within the critical range, the physical properties of the SFE can be modulated, adjusting their solvent selectivity for each target compound (Rombaut et al., 2014a; Brunner, 2005). Supercritical fluid has gas-like viscosity and diffusivity, liquid-like density, solvating power, and the solvent can be easily separated from the extracted product by simple depressurization (Duba and Fiori, 2016). Supercritical CO_2 extraction has emerged for natural products recovery, because it offers a number of advantages. CO_2 has moderately low critical point, it is non-toxic, non-flammable, non-polluting, cheap, and no traces of solvent remain in the extracted product (Mohamed et al., 2016; Ni et al., 2015). The effect of ethanol concentration (10, 15 and 20% w/w) and the flow rate (0.01–9.99 mL/min) were studied in relation to the antioxidant potential present in grape pomace extracts (De Campos et al., 2008). The experiment was conducted with CO_2 (99.9%) delivered at 6 MPa, and the extract conditions were 15 MPa, 40 °C and the solvent flow rate was 0.67 CO_2/min. Other features such as phenolics yields and lipophilic composition of extracts were also evaluated. The authors observed that the antioxidant activity and phenolic content of the extracts obtained by this technique were lower than those achieved by traditional extraction methods.

Accelerated Solvent Extraction also known as pressurized fluid extraction or pressurized liquid extraction, takes advantage of the differential properties of conventional solvents at elevated temperatures and high pressures (up to 20 MPa). It affects solvent, sample, and the interactions between them, and enhances the extraction of organic analytes from solid samples with the selected solvents. The extraction of several galloylated and nongalloylated flavan-3-ol compounds and condensed products of catechin with acetaldehyde, were reported using a mixture of acetone/water (70:30), at 25 °C, in two cycles and 100% flush volume (Rockenbach et al., 2012). Two alternative extraction methods by ASE for procyanidins were studied by the Mauromoustakos group (Monrad et al., 2009) who found a mixture of 50:50 ethanol/water (v/v), under the pressure of 6.8 MPa, with one extraction cycle at 40–140 °C, as the more suitable for the extraction of procyanidins from red grape pomace.

Other non-conventional method that has been used for phenolic compounds recovery from grape pomace is ultrasound-assisted extraction. It consists in sound waves above human earring, but below microwaves frequencies (20 kHz–10 MHz). When a sound wave passes through an elastic medium, it induces longitudinal displacement of particles. A cavitation bubble can be generated close to the material surface, then the bubble collapses during the compression cycle and a micro jet is created towards the raw-material. The high temperature and pressure involved in the process will destroy the plant cell walls and release its contents into the bulk. The ability to cause cavitation depends upon the characteristics of the parameters used in ultrasound (e.g. frequency and intensity of waves, temperature and pressure) and the medium properties (viscosity and surface tension). Ultrasonic baths and ultrasonic probes are the most common equipment used for assisted extraction. Ultrasonic assisted extraction have being incorporated to other extraction techniques as they are reported to enhance efficiency of the conventional system. The main advantages of this technique is the extraction time reduction, low energy consumption and enhanced extract quality when compared to conventional maceration. In this case, the use of solvent can be drastically reduced (Awad et al., 2012; Azmir et al., 2013; Chemat et al., 2011; Rombaut et al., 2014a; Tiwari, 2015). Several works reported in the literature used the ultrasound-assisted extraction for phenolics recovery from grape skins, achieving high yields in short periods of time (González-Centeno et al., 2015; González-Centeno et al., 2014; Drosou et al., 2015).

4.1.2. Bioactive compounds applications

Grape pomace extracts can be applied in food, pharmaceutical, cosmetics and others products in the form of liquid extracts, concentrate or powder (Prodanov et al., 2005). Studies used grape pomace extracts as food protectors due to their antioxidant ability to prevent lipid oxidation in fish-based products (Pazos et al., 2005) and antibacterial capacity against different bacterial spectrum: *Staphylococcus aureus*, *Bacillus cereus*, *Campylobacter coli*, *Escherichia coli O157:H7 and Salmonella infantis* (Katalinić et al., 2010); *Listeria monocytogenes* ATCC 7644 and *Staphylococcus aureus* ATCC 29213 (Xu et al., 2016). Grape pomace flour exhibited high antioxidant capacity and delayed lipid oxidation, while seedless grape pomace products showed also bactericidal effects against total aerobic mesophilic bacteria, lactic-acid and Enterobacteriacea (García-Lomillo et al., 2014). In this sense, whole grape pomace was used in miced fish frozen successfully to lipid oxidation prevention (Sánchez-Alonso et al., 2007a).

Grape pomace extracts can be used as functional supplement in food production, to enrich beverages, or even as ingredient of osmotic solution to obtain dehydrated fruit incremented in phenolic content (Rózek et al., 2010). Grape pomace extracts were also successful incorporated into chitosan edible films (hydrophobic and hydrophilic), providing antioxidant properties and promising shelf life extension (Ferreira et al., 2014).

In the food industry, phenolic extracts from grape pomace can also be used as replacers to synthetic antioxidants. Garrido et al. (2011) used red grape extract as a natural antioxidant in pork burgers. The study evaluated lipid oxidation, colour stability and product overall acceptability and concluded that grape pomace extracts had the potential to be used as preservatives in meat products. Guerra-Rivas et al. (2016), applied grape pomace seed extract with vitamin E as a control, to evaluate the shelf life of lamb meat. The authors observed that both the grape seed extract and the vitamin E were effective in reducing lipid oxidation (20%) after the 7th day of storage.

Zhu et al. (2009) and Xu et al. (2015b) used grape seed polyphenol extracts to reduce acrylamide formation during Maillard reaction. In the first work, a chemical asparagine/glucose model was used to study the effect of extracts of different plants on the reduction of acrylamide in this system. In the second study, a model of potato chips and a simulated physiological system were used. As a result in these two studies, a reduction in the acrylamide content of 54% and up to 90% were found, respectively.

Grape pomace extract presented protective vascular and antioxidant properties (Rodriguez-Rodriguez et al., 2012), and antioxidant and anti-postprandial hyperglycemic activities *in vitro* and *in vivo*, suggesting its use as a functional ingredient (Hogan et al., 2010). Grape seed extract administrated to hamsters during 12 weeks reduced 25% of plasmatic cholesterol (Auger et al., 2004), and also had anticancer actions to different cancer types (skin, prostate, breast) (Kaur et al., 2009).

Wang et al. (2016) neutralized the production of reactive oxygen induced by tert-butyl hydroperoxide after intestinal cells treatment with grape pomace extract. Ferri et al. (2016) reported another biological effect of grape pomace phenolics, the regulation of two enzymes (7α-hydroxylase (CYP7A1) and sterol 27-hydroxylase (CYP27A1)) involved in the production of the intracellular cholesterol. The authors observed that the presence of high concentrations of polyphenols, tannins, flavonoids and anthocyanins reduced cholesterol levels, lowering the enzymatic activity.

A cosmetic application was tested using grape pomace as an inhibitor of the activity of proteolytic enzymes such as collagenase and elastase, related to skin aging. The best results for enzyme inactivation were obtained with hydrophilic polyphenols, such as low molecular weight phenolic acids, especially gallic acid (Wittenauer et al., 2015).

Despite the potential health benefits of resveratrol, its employment as a nutraceutical ingredient within the food industry is currently narrow. Some of the main reasons are its poor water-solubility, chemical instability and limited bioavailability. Delivery systems in the form of emulsions are a promising encapsulation approach; lipophilic bioactive ingredients can be protected from degradation during storage by encapsulation inside the hydrophobic core of the lipid droplets and then liberated after ingestion. A nanoemulsion combining grape seed oil and grape skin extract to encapsulate resveratrol creating a stable delivery system proved to be effective in protecting resveratrol against UV-light isomerization and degradation (Davidov-Pardo and McClements, 2015).

Another example of the versatility of grape pomace polyphenols application is the study by Da Rocha et al. (2012), which evaluated the inhibitory activity of steel corrosion in HCl solution in presence of this extract. This study used different hydroalcoholic concentrations of grape pomace and observed that the corrosion inhibition was proportional to the concentration of the extracts.

Nowadays, there are commercialized cosmetic products with grape polyphenols such as day or night cream, and face serum from Pure Super Grape® (Marks and Spencer – United Kingdom), mattifying fluid, anti-wrinkle and protect fluid from Caudalíe® (France), which declare to use polyphenols from grape seed. In the food supplementation field there are few brands claiming to use polyphenols, mainly resveratrol, from grape. For exemple: 100 Natural®, Nature's Way®, Maximum Strength®, GrapeSeedRich®. Those products confirms the commercial potential of bioactive compounds extracted from grape, or grape by-products.

4.2. Dietary fibres

Dietary fibres (DF) are defined as "carbohydrate polymers that present ten or more monomeric units, which are not hydrolysed by the endogenous enzymes in the small intestine of humans" (Joint FAO/WHO, 2010). The main effects related to DF consumption are the reduction of risk for cardiovascular diseases, protection against cancer, diabetes prevention due to glucose absorption attenuation, improvement of food transit through digestive system, blood cholesterol decrease, constipation and obesity prevention (Deng et al., 2011; González-Centeno et al., 2010; Llobera and Cañellas, 2007).

The intake recommendation guidelines consumption is 25–30 g/day of dietary fibre (ANVISA, 2001; FDA, 2013), which are normally obtained from cereals, vegetables and fruits. However, this ingestion is not easily achieved and a need for alternative sources has promoted the development of commercial fibre-rich products

Table 3
Monosaccharide composition (mol%)[a] of grape pomace.

Grape variety	Rha	Ara	Xyl	Man	Gal	Glc	GalA
Pinot noir[b]	2.0	20.4	3.0	11.8	8.8	37.0	17
Chardonay[c]	4.6	29.8	3.5	8.5	14.5	39.1	–
Chardonay[d]	0.1	6.4	14.1	4.8	3.9	29.8	40.7
Mix of white grapes[e]	0.43	1.49	4.59	2.66	2.04	0.24	4.13
Red grape[f]	2.5	10.2	9.6	10.8	5.3	61.1	–
Vitis vinifera L.[g]	1.7	5.5	20.4	4.8	4.9	62.7	–
Cabernet Sauvignon[h]	3.8	21.2	7.7	19.9	15.5	10.7	21.2

[a] Alditol acetates analysed by gas chromatography, coupled to ESI-MS identification. Rhamnose (Rha), Arabinose (Ara), Xylose (Xyl), Mannose (Man), Galactose (Gal), Glucose (Glc), Galacturonic acid (GalA).
[b] Beres et al. (2016).
[c] Ferreira et al. (2013).
[d] González-Centeno et al. (2010).
[e] Rondeau et al. (2013).
[f] Mendes et al. (2013).
[g] Prozil et al. (2012).
[h] Corbin et al. (2015).

and supplements (Llobera and Cañellas, 2007; González-Centeno et al., 2010).

The cereal industry is the usual source of fibre components, however by-products obtained from fruits processing are also potential sources of them, with a higher soluble DF content, better insoluble/soluble fibre ratio, low caloric content, and better functional properties than those obtained from cereal processing (González-Centeno et al., 2010). The winemaking industry by-products have those characteristics (Deng et al., 2011) as grape skin is a complex lignocellulosic material containing large amounts of hemicellulosic sugars that, after hydrolysis, produce solutions containing a wide variety of xylose and glucose monomers (Devesa-Rey et al., 2011).

Monosaccharide composition of grape pomace is widely distributed and consists generally of Rhamnose (Rha), Arabinose (Ara), Xylose (Xyl), Mannose (Man), Galactose (Gal), Glucose (Glc) and Uronic acid, mainly Galacturonic acid (GalA) (Beres et al., 2016; Ferreira et al., 2013; González-Centeno et al., 2010). Table 3 shows monosaccharide composition from different grape pomaces.

Chamorro et al. (2012) suggested the following composition of grape pomace cell wall: 30% of neutral polysaccharides (cellulose, xyloglucan, arabinan, galactan, xylan and mannan), 20% of acidic pectin substances, 15% of insoluble proanthocyanidins, lignin, structural proteins and phenols, these two latter crosslinked to the lignin–carbohydrate framework. This distribution is in accordance with other authors (González-Centeno et al., 2010; Deng et al., 2011).

Grape skins contain a large amount of homogalacturonan and a small amount of pectic polysaccharides, (rhamnogalacturonan I and rhamnogalacturonan II), which consists of a backbone of rhamnogalacturonan with clusters of four different side chains that might contain up to ten different sugar units (González-Centeno et al., 2010; Deng et al., 2011).

Pectin is a high-value functional food ingredient widely used as gelling and stabilizing agent, and also an abundant component of plants cell walls. The molecular weight and the degree of esterification of pectic polysaccharides affect their commercial use as gelling and thickening agents (Minjares-Fuentes et al., 2014). As reported by González-Centeno et al. (2010), pectins with a low degree of methylesterification were the main cell wall polymer type in grape pomaces, whereas cellulose was the predominant cell wall polysaccharide in grape stems.

Studies have correlated dietary fibre content and antioxidant capacity, and these combination results in the so-called "antioxidant dietary fibre", defined by Saura-Calixto (1998) as a product that is composed of more than 50% of dietary fibre on a dried matter basis and presents a natural antioxidant capacity equivalent to at lest 50mg of vitamin E when measured by DPPH method.

Recent studies have been investigating the properties and benefits of such compounds for the cosmeceutical and neutraceutical areas of applications (Soto et al., 2015).

4.2.1. Dietary fibres extraction

The main extraction method used to recover polysaccharides from vegetable cell walls, raw materials and agricultural residues is hot water extraction (Zhu and Liu, 2013; Ferreira et al., 2013; Prado et al., 2014; Beres et al., 2016; Maran et al., 2016). In general, the extraction of dietary fibre and sugar from vegetable raw materials can be conducted by conventional solid-liquid process, which can be assisted by microwave or ultrasound technologies or by applying enzymes as an alternative to help disrupting the cell wall ultra structure (Zhu et al., 2015).

The optimization of soluble dietary fibre extraction from grape pomace was conducted by Du et al. (2011), using hydrochloric acid as solvent. The best extraction efficiency was obtained with hydrochloric acid at 0.4 mol L^{-1}, with a substrate:solvent ratio of 1:12 (m:v), under 75 °C, and extraction time of 90 min. Under these conditions it was possible to achieve a yield of 47% of soluble fibre.

The ultrasound-assisted extraction, previously described, has also been used for dietary fibre extraction. The ultrasound-assisted extraction of pectin from grape pomace was optimized and the best yield (32%) was obtained when the process was performed at 70 °C, for 60 min, using hydrochloric acid solution at pH 2.0, suggesting that the extraction assisted by ultrasound can be a good alternative for the extraction of pectin from grape pomace on an industrial scale (Minjares-Fuentes et al., 2014).

Enzyme-assisted extraction is gaining increasing attention because of the need for eco-friendly extraction methods (Puri et al., 2012). However, enzymatic treatment and/or pretreatment can disrupt the grape pomace cell wall, by breaking glycosidic linkages from polysaccharide chains into mono and oligosaccharides (Chamorro et al., 2012).

Hot water extraction was used to recover simple sugars and polysaccharides from *Pinot noir* grape pomace (Beres et al., 2016). The authors evaluated different temperatures, particle sizes and solute:solvent ratios and observed that the best condition for sugars recovery were achieved at 100 °C, using the smallest particle size (approximately 300 nm) and solute:solvent ratio of 1:12.

The extraction of soluble dietary fibre from white grape pomace *Chardonay* using water, alkali solution and enzyme was evaluated by Ferreira et al. (2013), which reported that the maximum sugar recovery was achieved with 2.5% alkali solution, while sugar yields of 1% and 0.7% were found for aqueous and enzyme extractions, respectively.

4.2.2. Dietary fibre applications

In recent years, research has evaluated the use of grape pomace and seed flours in different products such as popsicles (Ishimoto et al., 2009), cereal bars (Balestro et al., 2011), biscuits and cookies (Mildner-Szkudlarz et al., 2013; Piovesana et al., 2013; Acun and Gül, 2014), extruded snacks (Bender et al., 2016.), and *muffin* (Bender et al., 2015), obtaining products rich in fibre with antioxidant capacity potential and good acceptances by consumers. There is a tendency that new applications in this area arise in the coming years.

Pinot Noir grape fibre can be used as an alternative source of antioxidants and dietary fibre when added to yogurt and salad dressings, not only for increasing the fibre and phenolic content, but also for delaying lipid oxidation during storage, extending the shelf life of these products (Tseng and Zhao, 2013).

The application of fibre from grape pomace has also been performed in non-conventional products, such as codfish and seafood, where the addition of these compounds has been shown to be a promising tool in minimizing flavor changes, colour, texture and lipid oxidation during freezing storage (Sánchez-Alonso et al., 2007a,b, 2008). Antioxidant dietary fibre is of great interest for food applications. Studies added grape antioxidant dietary fibre on chicken breast hamburger (Sáyago-Ayerdi et al., 2009) and on fish muscle (Sánchez-Alonso et al., 2007b) and the result showed an improvement on the oxidative stability and on the radical scavenging activity of the products.

Due to their ability to absorb tannin, a study suggested that grape fibre addition in red wine production would be able to remove up to 38% of tannins generated during the process (Guerrero et al., 2013), besides also representing a promising adhesive application for wood particle board (Ping et al., 2011).

The development of biodegradable products using white and red grape pomace fibre has been reported as a feasible process. The high amount of soluble sugars in grape skin enable them to form innovative biodegradable packaging materials with excellent flexibility (Deng et al., 2011; Jiang et al., 2011).

Dietary fibre of grape pomace has potential to be used in different food products such as bakery products, beverages and meat products, in cosmetics and pharmaceuticals industries, offering a range of health benefits. Grape pomace skin is also a good source of lignin, cellulose and hemicellulose, and hence have great potentials as environmental-friendly supporting materials (Deng et al., 2011; Zhu et al., 2015). The chemical composition varies according to the grape variety, however there is a the presence of a lignocellulosic material, being an alternative for constructive field. Muñoz et al. (2014) showed that the use of 5% of grape pomace to clay improve the thermal transmittance in construction.

4.4. Grape seed oil

Grape seed oil is well known and already widely commercialized in some countries, being used for decades in several applications, particularly in cosmetics formulation. However, recent reported data has confirmed its bioactive properties promising new specific uses for bio products manufacturing (Soto et al., 2015; Garavaglia et al., 2016). Nutraceutical effects of grape seed oil have been reported in several studies due to its fatty acids composition, total phenolics and antioxidant capacity. Phenolic compounds are more concentrated in the seeds than in other parts of the grape and its distribution is about 70% in seeds, 20% in skin and 10% in the pulp (Shinagawa et al., 2015).

Grape seeds contains 8–15% (w/w) of oils with high levels of unsaturated fatty acids namely oleic and linoleic acids (Choi et al., 2010b), which represents more than 89% of the total oil composition with high level of essential fatty acids (Davidov-Pardo and McClements, 2015).

Linoleic acid is the most abundant fatty acid, representing around 60–78% of total oil composition, followed by oleic acid, with 10–24%. However, trilinoleoyl and trioleoyl ratio is dependent of climatic conditions, varying between 8 and 32%. Among the saturated fatty acids, palmitic and stearic acids are the major ones and appear as 7–9% and 3–6%, respectively. The β-sitosterol is the major sterol and α-tocopherol is the main tocopherol, reaching values of 62%–77%, corresponding to 3.8 mg. 100 g^{-1} of oil (Bada et al., 2015; Fiori et al., 2014; Pardo et al., 2009). Linoleic acid is an essential fatty acid, and together with its isomers known as conjugated linoleic acids is receiving much attention due to its biological effects (Yang et al., 2015; Bada et al., 2015; Hanganu et al., 2012; Wijendran and Hayes, 2004).

4.3.1. Grape seed oil extraction

Vegetable oil extraction from oleaginous seeds is generally carried out by solid-liquid extraction using hexane as solvent. It is a technique with high yield (above 95%), but with some disadvantages such as solvent losses during processing, mainly in the oil-solvent separation step. This solvent has been identified as air pollutant, since it can react with other contaminants to produce photochemical oxidants (Hanmoungjai et al., 2000). Furthermore, due to the solvent's toxicity the process needs further refining steps. Moreover, the solvent extraction process brings concerns to contemporary consumers, about the origin of what they are in fact consuming (Mohamed et al., 2016; Rombaut et al., 2015). Safeness, environmental and health concerns have increased the interest for alternative solvents to hexane in order to reduce the emissions of volatile organic compounds to the atmosphere as well as potential traces of hexane in edible oils.

Mechanical pressing is a classic method of oil recovery. In general, the product quality is superior to that obtained by solvent extraction, but the yield is relatively low. The oil content in grape seed together with the high lignin content are limitations to mechanical processes extraction. The manipulation of pressing parameters associated with enzymatic pre-treatment of seeds can improve the mechanical process. In this case, enzymes hydrolyze seeds cell walls, releasing bounded compounds and enhancing the oil yield (Azmir et al., 2013).

Rombaut et al. (2015) have used expeller pressing for grape seed oil extraction at three different waiting times (from harvesting until use), different pre-heating temperatures (90–120 °C), screw rotation speeds (40–70 rpm) and die diameter (10–15 mm) and found oil yields varying from 48.9% to 73.0%. The highest yield was the one with the higher screw rotation speed and larger die diameter. The pre-heating temperature had no significant effect on oil yield.

Conventional liquid solvent process uses petroleum ether (Fernandes et al., 2013), hexane, acetone, methanol and chloroform among others (Fernández et al., 2010). However, there is a growing number of studies aiming to insert eco-friendly technologies in the edible oil processing, and several papers are dedicated to improve non-conventional extraction methods to turn them into competitive green substitutes. Some of these techniques are already used for bioactive compounds extraction. The common advantages are the decrease or elimination of organic solvent used. But more research is needed for these techniques to be economically attractive for industries.

Supercritical fluid extraction (SFE), as defined previously in Section 4.1.1, gave good results for the extraction of non-polar compounds such as fatty acids like capric, lauric (low chain fatty acids), palmitic and linoleic acids; also phytol, a natural diterpenic alcohol, and ethyl linoleate (De Campos et al., 2008). Rombaut et al. (2014a) and Duba and Fiori (2015) extracted grape seed oil with SFE method, the yield obtained was higher than pressing techniques, however total phenolic content decreased more than 50%.

Subcritical Water Extraction occurs when water is pressurized to a temperature and pressure under its critical level conditions (100–374 °C and up to 22 MPa), known as subcritical region, and the motion of water molecules increases, changing their properties. The operation pressure is kept constant above the vapor pressure to hold the water in liquid state at subcritical conditions. The highly hydrogen-bonded structure at subcritical conditions slowly starts to dissipate, resulting in a decrease of polarity, increase of diffusion rate and decrease in viscosity and surface tension. The increase in dielectric constant and decrease in density result in nonpolar compounds becoming more water-soluble. In this condition, insoluble cell materials, normally complex polymeric structures (proteins, polysaccharides) can be simultaneously hydrolyzed during extraction, producing various water soluble products and increasing the overall yield. It is a promising green technology, since the only solvent is water and it is starting to be used for oil extraction, with the advantage of enhancing the antioxidant capacity of the oil. However, this technique still has its limitations once it also hydrolyses triglyceride to free fatty acids and glycerol. The hydrothermal degradation of vitamins and tocopherols naturally present in the oil also compromise the oil oxidative stability (Thiruvenkadam et al., 2015; Ravber et al., 2015; Yedro et al., 2015). Studies successfully extracted grape seed oil by this method, however further research is needed to find the parameters that make this process feasible (Duba et al., 2015; Duba and Fiori, 2015).

Ultrasound assisted extraction (UAE), as previously defined in Section 4.2.1, is recently being associated with conventional processing of oleaginous raw material, solvent extraction or mechanical pressing, aiming to enhance efficiency of oil recovery due to extraction intensification. Sicaire et al. (2016) estimated a solvent reduction of one third to extract oil from rapeseed cake press, compared to conventional extraction with hexane. Da Porto et al. (2013) compared grape seed oil extracted by soxhlet and UAE. The authors observed that the oil yield by UAE increased with higher ultrasonic power, though obtained with a lower solvent consumption and a shorter extraction time. Malićanin et al. (2014) reported similar results and also verified that the phenolic compound content in the oil was increased with UAE, even though they used a lower solvent/sample ratio (2/1). These studies show that UAE can be considered environmentally friendly since the solvent amount and time extraction can be significantly reduced.

4.3.2. Grape seed oil applications

Demand for plant oils in pharmaceutical, cosmetic, food and biodiesel industries is increasing since they are valuable natural sources of lipophilic compounds (Górnas and Rudzinska, 2016). Vegetable oils are part of human diet, and the search for new sources has increased since there is a need to replace animal fats. There are also components in seed oil with biological importance due to their antioxidant activity, such as phytosterols, tocopherols, tocotrienols, flavonoids, phenolic acids and carotenoids. A study have shown that a consumption of 45 grams of vegetable oil per day demonstrated an increase in HDL-cholesterol and reduced LDL-cholesterol level in 13 and 7% of treated patients, respectively (Shinagawa et al., 2015).

Recent reported data has proved beneficial effects of grape seed oil, such as hepatoprotective, neuroprotective and reducing liver cholesterol. In the studies of Ismail et al. (2015, 2016), rats had their liver and brain injured after γ –irradiation induction by carbon tetrachloride. In both cases, rats were feed with grape seed oil and were compared to a control group. The studies showed a protective effect on acute liver injury attributed to the oil potent antioxidant, anti-inflammatory and antiapoptotic activities. The protective mechanisms of grape seed oil against oxidative damage and inflammatory cascades in the brain represents a neuroprotective effect, which is related to its ability to scavenge free radicals, improve the activity of antioxidant enzymes, down-regulate the gene expression levels of xanthine oxidase and inducible nitric oxide synthase and suppress the inflammatory responses (Ismail et al., 2015). Wistar rats treated with grape seed oil for 10 weeks showed a good acceptability, significant decrease in feed intake, and beneficial effects on the liver cholesterol values (Asadi et al., 2010).

In the food industry, grape seed oil can promote lower production costs being more competitive than others and represent a new food source for human consumption (Shinagawa et al., 2015). Generally, meat products contain up to 30% fat, which are responsible for stabilizing the meat emulsion, reducing cooking loss, improving water holding capacity and providing flavor, juiciness and desirable mouth feel. However, animal fat provides significant amounts of saturated fatty acids and cholesterol, and a high animal fat intake is associated with obesity, hypertension, cardiovascular diseases and coronoray heart diseases (Choi et al., 2010a).

Modifications in the formulation of meat products have been made in order to attend an increased interest from consumer for healthier and functional foods (Choi et al., 2010a,b; Özvural and Vural; 2014). A basic modification is the reduction of some compounds such as fat, saturated fatty acids, and the addition of ingredients such as fibre, unsaturated fatty acids and antioxidants into products. Grape seed oil is a rich source of polyunsaturated fatty acids and can be utilized in meat products (Özvural and Vural, 2014). Vegetables oils in meat products improve their nutritional quality by reducing caloric and cholesterol contents without adversely affecting the products palatability (Choi et al., 2010a,b). Choi et al. (2010a) used pre-emulsified grape seed oil to replace pork back fat in frankfurter; and reported that the fat content was significantly lower, and closer to the target value of 20% (fat content). There was also an increase in gumminess and chewiness, improving textural properties. Vegetable oil affected fatty acid composition, and reduced fat frankfurters had acceptability similar to regular fat frankfurters. Özvural and Vural (2014) used Bogazkere grape seed oil, in different concentrations, to replace animal fat in frankfurters sausage. The decrease in the lipid oxidation was not significant, however it was well accepted by panelists.

In addition, grape seed oil presented a high smoke point and can be considered a potential biodiesel feedstock. The development of grape seed ethyl esters is under consideration, not only because of the good properties of this biodiesel, but also because bioethanol can be obtained from winery, resulting in a suitable solution for wineries waste management (Fernández et al., 2010; Górnas and Rudzinska, 2016). Fatty acid composition of the potential biodiesel feedstock has a significant impact on the physicochemical properties of biofuel. Biodiesel quality depends on the fatty acid composition of the raw vegetables oils. Plant oils characterized by higher monounsaturated fatty acids content present better biodiesel properties. Moreover, some properties of fatty acids methyl esters have disadvantageous association, for instance, high saturation and low unsaturation favour good oxidative stability but lead to poor low temperature performance (Górnas and Rudzinska, 2016).

Raw materials for biodiesel production are vegetable oils with a high proportion of monounsaturated acids, such as oleic acid. Two critical parameters for grape seed methyl esters were the oxidation stability and the cold filter plugging point, and two conventional transesterification processes using methanol and bioethanol were carried out to produce biodiesel with the extracted grape seed oil. Biodiesel based on fatty acid ethyl esters has the advantage of being entirely based on renewable raw materials and moreover it displays a higher specific energy, better lubricity, and enhanced cold behaviour because of the lower melting point of ethyl esters (Fernández et al., 2010).

Different from biodiesel, the most valuable plant oils for the pharmaceutical and cosmetic industries are those rich in polyunsaturated fatty acids, phytosterols and squalene (Górnas and Rudzinska, 2016). Consumers have widely expressed their interest in natural products, and one of the most significant reasons to search for alternative sources and raw materials is the appearance of allergies and skin irritations caused by synthetic preservatives (e.g. parabens), colourants, stabilizers, that have not still been fully evaluated in the long run for their consequences on consumers' health. Formulation of cosmetic emulsions with grape seed oil and diluted wine in the aqueous phase presented advantages such as direct inclusion of natural antioxidants, aroma and colour compounds that could enhance their organoleptic characteristics (Glampedaki and Dutschk, 2014).

5. Conclusion and future perspectives

Environmental issues are a mandatory concern in agriculture and agroindustrial processes. Several countries have agriculture as a main business, and an appropriate control policy is important in terms of maintaining the sustainability of these practices. The wine industry is responsible for a considerable part of the environmental problems as they dispose large amounts of grape pomace.

Together with that, natural functional compounds have been an industrial requirement, either to attend to strict laws or consumers demand. Those compounds can replace synthetic additives, adding multifunctional concepts by combining health benefits to technological use. This trend became stronger when residues from food industries started to be the raw materials for new developments, as the costs reduced on operational basis and the environmental legislation were attended. Wine industry residues are rich in bioactive compounds and, in this case the utilization of grape by-products for alternative uses has been a focus of research.

The traditional methods are still the most used for the extractions of compounds of interest. However, alternative technologies are emerging to recover bioactive compounds from grape pomace, in order to promote a faster and "greener" technology.

The utilization of grape pomace as a source of functional ingredients is a promising field. In this context, the recovery of bioactive compounds, dietary fibre and oil from grape pomace, can still be an interesting alternative of environmental and economic approaches.

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