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Potential for Use of the Residues of the Wine Industry in Human Nutrition and as Agricultural Input

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Abstract

The use of underutilized resources, with the aim of increasing productivity and creating wealth, will increasingly deserve the attention of the wine sector. The treatment of agricultural by-products will increasingly enter the priority agenda of the agribusiness sector, with a view to its use, the environment's re-cleanliness and, in many cases, whenever possible, for both purposes. Solid waste from the process of grape industrialization, when not adequately disposed, is aggressive to the environment. Such residues release significant amounts of liquid effluents when disposed in the soil, and this liquid contains high content of nutrients, organic matter, and other elements that can change the environment, especially of streams and sources, causing the death of aquatic beings. However, if properly used, they can be used as raw materials for other purposes. The solid residues of industrially processed grapes, which may have some potential economic interest, are pomace, seeds, liquid (lees), and other materials. In this context, this chapter presents the description of these by-products and their potential for use.

Keywords: *Vitis* spp., by-products, pomace, winery, flour, polyphenols, antioxidants, seed oil

1. Introduction

Approximately 75,100 million tons of grapes are produced annually in the world and are destined mostly to wine production or in natura consumption, with Italy, France, Spain, the United States, Australia, China, Chile, South Africa, Argentina, and Germany being the main producers. These countries produce about 275.7 million hectoliters of wine.

This results in approximately 13 million tons of residues, which are normally used as fertilizer or simply discarded [1].

Although not widely used, the residues from the wine industry have high fiber content and antioxidant substances that could be beneficial for use in food, but there are few reports about this potential. One of the best applications for grape residues, especially the pomace, could be to obtain flour, which can be used in the preparation of biscuits, breads, cereal bars, home-made pasta, and juices [2, 3].

The phenols are defined as the largest group of natural antioxidants, with about 8000 different compounds. They are distributed in several plant foods, being secondary metabolites of these and considered fundamental for the proper development of the plant, defense against environmental injuries, and infectious processes. Among the different vegetables, grapes are considered one of the major sources of phenolic compounds; however, it is known that there is considerable diversity among cultivars, and this results in grapes with different characteristics, such as flavor and color, which is certainly associated with the content and profile of polyphenols [4].

Grape seeds usually contain 8–20% of oil, which represent about 5% of the fruit weight, with about 3 million tons of grape seeds discarded annually in the world [5]. The seeds constitute about 20% of the gross weight of the fruit and calculated on dry matter, representing between 40 and 60% [6]. The complete use of grapes, including 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 have a considerable content of phenolic compounds (about 60–70% of their content), with smaller percentages found in other parts of the fruit such as 28–35% in the skin and approximately 10% in the pulp [6].

These compounds present in grapes are recognized for their role in modulating the expression of antioxidant enzymes [7], protection against oxidative damage in rat brain cells [8], and some anti-inflammatory effects. Some studies have shown anticholinergic effects of grape seed oil, with a proven reduction of low-density lipoprotein (LDL) and increases in high-density lipoprotein (HDL) levels, characteristics related to cardioprotective effects [9].

Some phenolic compounds were identified as the monomers, gallic acid, (+)-catechin, (+)-epicatechin, and epicatechin-3-*O*-gallate, and a large variety of procyanidins oligomers in skin and grape seeds [10, 11]. These high contents of bioactive compounds in both flour and grape seed oil characterize them as a functional food, widely disseminated in current nutritional practices.

Due to its abundance and its richness in compounds with bioactive properties, the study of the use of grape residues as an agricultural input, aiming at the management of plant cover, pests, and diseases, represents a great potential, especially considering the issues related to sustainability, impacts on the environment, and production costs.

In viticulture, intensive management practices and the use of agrochemicals are adopted on a large scale to control pests, diseases, and weeds. These practices tend to have significant impacts on agroecosystems, since they alter the characteristics of the habitat and the composition of the trophic chain. Thus, in recent years, there has been a growing demand for alternative management methods that reduce impacts on nontarget organisms and are satisfactorily effective against target organisms.

In this context, the use of winery residues is indicated as an important perspective in the management of grapevine, once the action of its components, such as phenolic acids and flavonoids, have already been reported as efficient against microorganisms [12] and also weeds [13]. The isolated effect of some compounds present in this residue has already been characterized on some insects, such as the flavonoids, which caused inhibited development of *Phyllotreta cruciferae* (Coleoptera: Chrysomelidae) [14].

2. Wine production and waste generation

The main by-products of winemaking are separated during the crushing and pressing stages of the grapes, and only small quantities of these residues are available. Recovery of compounds from the continuous waste produced by the wine industry could represent a significant step forward in maintaining the balance of the environment, as the large quantities of waste generated in the wineries present serious problems of storage, processing, or disposal in ecological and economic terms. This situation explains the growing interest in exploring the by-products of winemaking.

Solid residues from the grape industrialization process, when disposed outdoor, are aggressive to the environment, releasing significant amounts of liquid effluents, which contain high nutrient content, organic matter, and other elements that, in contact with the soil and sources of water, can cause death of living organisms. However, adopting some technologies, they can be used as raw material for other purposes. Solid residues of industrially processed grapes, which may have some potential economic interest, are stalks, pomace, seeds, liquid (lees), and other materials. Although many polyphenols are transferred from the grapes to the wine during the maceration process, the residual seeds have been the focus of studies that relate them as good sources of phenolic compounds [7].

The pomace consists of the skin, the seeds, and the remains of the pulp of the grape, resulting from the crushing of the berries through a process of separation of the juice or must. Under normal conditions, the pomace is equivalent to 15% of the weight of the berries.

Other solid wastes are lees and tartar. The sludge originates in the bottom of the kites, is dense, and comes from the processes of purification of the wine stored. The tartar is solid and deposits on the walls of the containers (pipes) used to age the wine. Liquid wastes result from washes and spills of raw material. These materials should be submitted to the treatment of effluents in canteens. Regulation (EC) No 1493/99 defines wine sludge as the residue which is deposited in receptacles containing wine after fermentation, or at the time of storage, or after authorized treatment, as well as the residue obtained by the filtration and/or centrifugation of this wine product [12]. Also considered as wine lees is waste that is deposited in containers containing grape must. The amount of lees obtained annually depends on several factors, namely those inherent to the constitution of the grape varieties, maturation stage and phytosanitary state of the berries, climatic factors, and the winemaking techniques adopted. In general, these represent about 5% of the wine volume. A quantity of 140 kg of grapes produces approximately 1 hL of wine, giving 5.5 kg of liquid lees with 4.5% alcohol.

Pomace is the main by-product of winemaking, not only because of its alcoholic and tartaric richness but also because of the economic interest of some of its physical components. Pomace,

as is well known, is the product resulting from the pressing of the wine masses, consisting of the solid parts of the grapes and the must or the wort/wine assembly that soaks them. Regulation (EC) No 1493/1999 defines it as the residue of pressing of fresh grapes, fermented or not. The pomace consists mainly of water, wines, and lees—these being dependent on the pressing; alcohols, especially ethanol, and also methanol and glycerol; aldehydes, esters, volatile acids, polyphenols, proteins, cellulose, pectins, mineral salts, and sugar residues [12].

3. Composition of grapes pomace and its potential for use

Botanically, the grape can be classified as a fruit of the vine, belonging to the family Vitaceae and to the genus *Vitis*, with the following main species: *Vitis vinifera*, *Vitis labrusca*, *Vitis rupestris*, *Vitis aestivalis*, *Vitis riparia*, *Vitis cinerea*, and *Vitis rotundifolia* [15]. In this sense, the existence of numerous grape varieties causes differences in their chemical composition, which allows to select the most suitable cultivars for both industrialization and in natura consumption.

The composition of the grape berry is generally formed by 6–12% of skin, 2–5% of seed, and 85–92% of pulp. The pulp, which constitutes the main part of the grape, is composed of the following constituents: 65–85% water, 12–25% reducing sugars, 0.6–1.4% organic acids, 0.25–0.5% of mineral substances, and 0.05–0.1% of nitrogenous compounds, besides several water-soluble and fat-soluble vitamins [16].

Like the other nutrients presented, the mineral composition of the grape may vary according to the conditions provided for growth, such as the composition of the soil and the use of fertilizers and herbicides. The nutritional relevance of the juice is mainly due to the high content of potassium, calcium, iron, magnesium and phosphorus, and low levels of sodium. Thus, fresh grape juice presents from 2.5 to 3.5 g L⁻¹ of mineral substances [17].

Pomace (a mixture of grapes skin and seed) accounts for about 16% of the total processed grape and is one of the most abundant residues in the wine industry, and this material is known to be rich in many compounds such as phenolic acids, flavonoids, tannins, and saponins and, therefore, has a great utility potential for a variety of purposes, including pests, diseases, and weed control in agricultural crops, and the use of grape extract as a corrosion inhibitor by the metallurgical industry due to its high antioxidant capacity. The pomace contains another coproduct with high added value: the seed, which generates vegetable oil [4, 5].

In a research carried out in Brazil [17], it was analyzed for the mineral content (N, P, K, S, Ca, Fe, Mg, Mn, Fe, and Zn), anthocyanins, and phenolic compounds in flours produced from residues of different grape cultivars from different wineries (**Tables 1 and 2**). Mineral analysis showed a significant difference for all grape cultivar, with the exception in phosphorus content. Residues from cv. Seibel showed higher levels of N, Cu, and Mg. The cultivars Ancelotta, Tannat, and Ives present higher contents of K, Zn, Mn, Fe, and Ca. For the concentration of anthocyanins, cultivars Cabernet Sauvignon (114.7 mg/100 g), Tannat (88.5 mg/100 g), and Ancelotta (33.8 mg/100 g) had the highest concentrations. The cultivars Pinot Noir (7.0 g AGE/100 g), Tannat (4.3 g AGE/100 g),

Grape variety	Phosphor (mg/100 g)	Nitrogen (mg/100 g)	Sulfur (mg/100 g)	Potassium (mg/100 g)	Zinc (mg/100 g)
x ± DP					
Cabernet Sauvignon	39.59 ± 1.3 ^{ns}	21.83 ± 0.99 ^a	52.27 ± 1.64 ^{ab}	13.77 ± 2.02 ^a	NS
Tannat	33.05 ± 0.99	22.09 ± 1.31 ^a	38.53 ± 2.5 ^b	23.52 ± 3.14 ^b	16.35 ± 0.44 ^d
Ancelotta	43.88 ± 1.33	22.09 ± 1.06 ^a	85.4 ± 4.32 ^c	25.82 ± 0.01 ^b	33.59 ± 1.66 ^e
Pinot Noir	49.76 ± 9.81	22.45 ± 0.59 ^a	56.49 ± 2.69 ^{ab}	13.44 ± 1.49 ^a	6.7 ± 0.50 ^b
Malbec	42.43 ± 2.01	26.17 ± 0.87 ^b	53.94 ± 3.07 ^{ab}	19 ± 0.94 ^c	9.84 ± 0.81 ^c
Merlot	39.96 ± 3.42	3.92 ± 0.72 ^c	54.92 ± 1.46 ^{ab}	10.84 ± 0.56 ^a	0.08 ± 0.02 ^a
Seibel	44.1 ± 1.77	30.93 ± 1.45 ^e	67.47 ± 0.58 ^{ab}	5.96 ± 1.12 ^d	6.29 ± 0.35 ^b
Ives	35.65 ± 0.86	25.05 ± 0.91 ^b	87.88 ± 0.98 ^c	25.15 ± 0.69 ^b	17.47 ± 0.24 ^d
Cabernet Franc	45.14 ± 5.3	17.77 ± 0.74 ^d	63.12 ± 1.25 ^{ab}	18.66 ± 0.56 ^c	NS
Variety	Copper (mcg/100 g)	Manganese (mg/100 g)	Magnesium (mg/100 g)	Iron (mg/100 g)	Calcium (mg/100 g)
x ± DP					
Cabernet Sauvignon	86.52 ± 11.8 ^{ad}	24.87 ± 5.3 ^{abc}	62.21 ± 1.96 ^b	209.78 ± 7.02 ^{ab}	284.22 ± 3.59 ^b
Tannat	63.97 ± 19.18 ^{ac}	36.64 ± 0.26 ^d	104.32 ± 3.03 ^a	286.5 ± 6.05 ^c	429.5 ± 4.74 ^d
Ancelotta	89.94 ± 0.71 ^{ad}	32.27 ± 1.25 ^{bd}	86.93 ± 1.75 ^{ac}	212.89 ± 8.48 ^{ab}	357.02 ± 4.2 ^c
Pinot Noir	52.95 ± 1.44 ^{abc}	25.84 ± 1.37 ^{abc}	105.51 ± 3.62 ^a	164.84 ± 4.71 ^a	362.84 ± 1.67 ^c
Malbec	125.06 ± 2.57 ^d	19.91 ± 3.15 ^c	75.49 ± 1.95 ^c	250.06 ± 18.54 ^{bc}	312.13 ± 1.21 ^b
Merlot	9.25 ± 0.22 ^b	9.02 ± 1.25 ^e	58.73 ± 2.94 ^b	169.26 ± 11.66 ^a	158.04 ± 4.63 ^a
Seibel	296.42 ± 44.61 ^e	30 ± 6.58 ^{abd}	154.7 ± 20.42 ^d	166.36 ± 10.37 ^a	356.21 ± 13.68 ^c
Ives	36.38 ± 1.11 ^{bc}	29.26 ± 2.32 ^{abd}	102.87 ± 5.70 ^a	241.54 ± 19.81 ^{bc}	308.8 ± 3.96 ^b
Cabernet Franc	42.64 ± 1.64 ^{abc}	21.09 ± 0.78 ^{ac}	101.36 ± 1.73 ^a	155.3 ± 9.05 ^a	296.21 ± 7.84 ^b
Means followed by different letters on the same column are significantly different according to NSK at <i>P</i> < 0.05. NS, not significant.					

Table 1. Mineral content in grape pomace flour in southern Brazil [18].

Grape variety	Phenolic compounds (g AGE/100 g)	Anthocyanins (mg/100 g)
Cabernet Sauvignon	1.7 ± 0.29 ^a	114.7 ± 0.15 ^f
Tannat	4.3 ± 0.18 ^e	88.5 ± 2.02 ^e
Ancelotta	3.8 ± 0.04 ^d	33.8 ± 2.4 ^d
Pinot Noir	7.0 ± 0.17 ^f	3.48 ± 0.35 ^{bc}
Malbec	2.3 ± 0.31 ^b	12.89 ± 0.51 ^{ac}
Merlot	1.7 ± 0.02 ^a	15.78 ± 0.38 ^a
Seibel	5.9 ± 0.39 ^c	18.35 ± 2.1 ^a
Ives	2.4 ± 0.10 ^b	19.86 ± 6.46 ^a
Cabernet Franc	1.5 ± 0.12 ^a	0.9 ± 0.96 ^b

Means followed by different letters on the same column are significantly different according to NSK at $P < 0.05$. NS, not significant.

Table 2. Anthocyanin content and phenolic compounds in grape pomace flour in southern Brazil [18].

and Ancelotta (3.9 g AGE/100 g) had the highest content of phenolic compounds. Considering these results, the potential of using the residue of winemaking to produce flour for human consumption became evident, highlighting the grapes 'Tannat' and 'Ancelotta'.

The main phenolic compounds presented in the pomace of 'Pinot Noir' grapes were (1) flavonoids: flavan-3-ols (catechin, epicatechin, epicatechin gallate, procyanidins A and B), flavonols (quercetin and quercetin methyl glucoside), and anthocyanins (delphinidin-3-glucoside, 3-glucoside cyanidin-3-glucoside, petunidin-3-glucoside, peonidin-3-glucoside, malvidin-3-glucoside, vitisin) and (2) non-flavonoids: hydroxybenzoate (gallic acid) [5].

Grape pomace also showed a great wealth of biologically active substances in the study that were developed to determine the chemical composition of seeds and skin of grape pomace of different cultivars of *V. vinifera* grapes both white and red in Italy and in California [19]. These authors verified that in the seeds and in the skin, the Italian samples presented higher content of organic matter—lignin and copper. In addition, the contents of K, Fe, and Zn were higher in grapes from California. The Italian white grapes had a higher content of saponins in the pell and tended to have a higher phenolic content in both the skin and the seeds.

A study with grape pomace extracts (GPEs) of the grapevines 'Niagara' and 'Isabella' (*V. labrusca*) was carried out to evaluate their effects on oxidative stability and quality of chicken meat. The use of the grape pomace extract was efficient to maintain the lipid stability of the chicken meat, presenting results compatible with those exhibited by the synthetic antioxidant butyl hydroxytoluene (BHT) [14].

Due to the richness of bioactive components, the use of grape pomace flour has been tested in different food product such as biscuits [3], muffins [20], and cookies [21]. These studies showed that, in general, the addition of flour does not negatively affect the preference for food. Moreover, the presence of bioactive compounds was verified, indicating the possibility of adding nutritional value to the food with the supplementation of flour of grape pomace.

A study with grape pomace of the cv. Marselan (*V. vinifera*) was carried out to evaluate the effect of its inclusion in extruded snack with respect to nutritional, technological, and sensory parameters [22]. The microbiological determinations of coliforms at 45°C and *Salmonella* in the flours were also performed. The centesimal composition presented fiber (58.01%), carbohydrates (17.62%), and ashes (12.46%) as the main constituents. Resveratrol (6.14 mg g⁻¹), luteolin (5.16 mg g⁻¹), and kaempferol (3.01 mg g⁻¹) were the phenolic compounds detected in greater quantity in the flour. The fiber formulation containing 9% (5% fiber) of flour presented better acceptance results with regard to color, aroma, and texture attributes compared to the standard snack formulation. According to these authors [22], for the nutritional enrichment (fibers and phytochemicals) and for adding value to the agro-industrial residue discarded by the wineries, the addition of pomace flour in extruded snacks is viable and quite interesting.

Grape pomace is known to be rich in many compounds such as phenolic acids, flavonoids, tannins, and saponins presenting a high potential for pests, diseases, and weed control in agricultural crops, including vineyards. The antimicrobial effect of 'Pinot Noir' grape pomace extracts against *Staphylococcus aureus* and *Candida albicans* was already reported [18].

Considering the composition of the grape pomace, one of the possibilities is the induction of resistance of plants to pathogens. In this context, a study was carried out to evaluate the effect of autoclaved grape pomace extract (GPE) in the induction of phytoalexin deoxyanthocyanidine in sorghum [23]. To obtain the extract, ground dry pomace was macerated in water at 70°C for approximately 12 h in the dark. The GPE was sterilized by autoclaving for 20 min at 120°C under a pressure of 1.1 kgf cm⁻², followed by fractionation in the tested doses. These authors reported the effect of GBE on the deoxythyanocyanidine synthesis, with a higher accumulation at the 3% dose.

The downy mildew (*Plasmopara viticola*) is responsible for qualitative and quantitative losses in grapevines production. In this context, a study was carried out aiming to verify the action of grape pomace extract (GPE) on sporangia germination of *P. viticola* and the severity of mildew on grapevines cv. Carmen [24]. These authors verified reduction of germination of the pathogen and incidence of mildew in grapevines. The highest dose of the extract (12%) controlled mildew severity at 36%, demonstrating the potential of the residue extract for the organic system.

4. Composition of grape seeds oil

Pomace represents approximately 16% of the grapes, of which about 20–26% are seeds [25]. Although winemakers have traditionally considered these wastes an economic and environmental problem, they are gradually being considered as a potential to add value to the products. Grape seeds usually contain 8–20% oil, with about 3 million tons of grape seeds being discarded annually worldwide [26].

The complete use of grapes, including 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 oxidative stability to the product.

These properties are related to the reduction of low-density lipoprotein (LDL) and increases in high-density lipoprotein (HDL) levels—characteristics related to cardioprotective effects [26].

The oils present in grape seeds have numerous health benefits, especially vitamin E and essential fatty acids. These fatty acids are considered as protectors of cardiovascular diseases, while vitamin E has antitumor and neuroprotective properties, is able to lower cholesterol levels, and has antioxidant activity [26]. Additionally, in the extraction of the oil, part of it still remains in the residue and could be used for animal nutrition.

Seeds are rich sources of polyphenol components and have been widely studied by several groups [27–29]. Oils that are not refined may contain tocopherol and other active compounds with antioxidant properties [10].

The mineral content of grape seeds prior to the winemaking process and wine manufacturing residues has been shown to be an important source of nutrients and essential elements. In some grape seeds collected from different locations in Turkey, the mineral contents (Al, B, Ca, Co, Mo, Cr, Fe, K, Mg, Mn, Na, P, S, Se, and Zn) were determined [28]. Ca, K, Mg, Na, and P were the main minerals contained in grape seeds. While the contents of vitamins A and B1 and of the minerals Fe, Mn, and Zn were elevated in all seeds, Cu, Mo, and Cr contents were very low.

A trial was carried out to study the composition of fatty acids, oxidative stability, and antioxidant and antiproliferative activity of cold pressed oils and flours extracted from the pomace of grape cultivars Chardonnay, Concord, and Rubi [29]. In the seeds, the phenolic profiles were also measured. The most abundant fatty acid in the oils was linoleic acid, which ranged from 66.0 g 100 g⁻¹ of total fatty acids, in cv. Rubi; to 75.3 g 100 g⁻¹ in 'Concord' grape seed oil. The oils also had high levels of oleic acid and low levels of saturated fat. Seed oil of cv. Rubi had the highest oxidative stability index. The total phenolic content was up to 100 times lower in oils than in flours. Lutein, zeaxanthin, cryptoxanthin, β -carotene, and α -tocopherol levels were also measured. The antioxidant activity evaluated by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical elimination capacity ranged from 0.07 to 2.22 mmol Trolox (TE) g⁻¹ oil equivalents and 11.8 to 15.0 mmol TE g⁻¹ flour. In this study, the antiproliferative activity against HT-29 colon cancer cells was also tested. Seed meal and grape seed oil recorded significant ($p < 0.05$) inhibition of cancer cell growth, demonstrating the potential for the development of value-added applications for these seed oils and flours as dietary sources of natural antioxidants and anti-proliferative agents for health.

Studies on vitamin E extractions with oil of seeds of different grape varieties showed variations in concentrations. In the study with grape cultivars Barbera, Malbec, Gamay, Cabernet Sauvignon, Pinot Noir, Merlot, Cabernet Franc, and Syrah extracted with supercritical fluid, CO₂ and petroleum ether, the authors found values between 3.58 mg 100 g⁻¹ and 30.9 mg 100 g⁻¹ of vitamin E [29]. The result of the analysis of grapes grown in Brazil presented as results the oil of the 'Isabella' grape seed containing values lower than 1 mg of tocopherol in 100 g of oil. The best results were obtained for the cvs. Cabernet Sauvignon and Merlot (5.67 and 7.03 mg 100 g⁻¹) [30].

5. Conclusions

Considering the aspects presented in this chapter, it was evident to the innumerable nutritional and pharmaceutical properties of the residues of the wine industry. Both pomace and grape seed are materials that are considered as industrial waste but are rich in vitamins, polyphenols, unsaturated fatty acids, and other important components for nutrition and with positive effects on human health. Considering the increasing need for sustainability of agricultural and industrial activities, the use of these wine by-products may represent an advance in the production chain from an economic, social, and environmental point of view.

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