Unripe grapes: an overview of the composition, traditional and innovative applications, and extraction methods of a promising waste of viticulture

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Abstract

Unripe grapes (UGs) are a waste product of grapevine cultivation and an emerging source of several compounds, such as organic acids, phenolic compounds, vitamins and mineral salts, of great economic importance to the pharmaceutical, cosmetic and food industries. Traditionally, products made from UGs, such as verjuice and sour grape sauces, have been used as seasoning or acidifying agents. The health effects of grape compounds are described as anti-inflammatory, cardioprotective, anticancer and antidiabetic, as often demonstrated by both in vitro and in vivo studies. Recently, UGs have received renewed attention because of the innovative potential applications of their extracts in food and beverages for purposes of preservation and enrichment with healthy compounds, or for direct use in the human diet. The aim of this article is to review the composition and properties of UG products and their traditional and innovative application in food and beverages.

Keywords: *antioxidants, micronutrients, organic acids, phenolic compounds, thinning practice, unripe grapes*

Introduction

The grapevine (*Vitis vinifera*) is the most cultivated fruit crop in the world, with more than 75 million tonnes of grapes produced every year (Food and Agriculture Organization of the United Nations 2018). Approximately 75% of the grapes produced in the world are used to make wine (Beres et al. 2017), while the remainder is used for consumption as fresh fruit or in the form of juice or raisins (Teixeira et al. 2014).

The grape juice and wine industry generates a large amount of organic waste, consisting of industrial waste, mainly pomace and lees, and vine waste, such as stalks, leaves, vine canes and unripe grapes (UGs) (Teixeira et al. 2014, Beres et al. 2017). The exploitation of these waste products is an important challenge for the sustainability of the wine and juice industry. Indeed, the efficient use of these raw materials leads to the reduction of waste, hence minimising the environmental impact and increasing the profitability of these agro-industrial sectors. These waste products can be the source of bioactive compounds with the potential for use as ingredients in the cosmetic, pharmaceutical and nutraceutical industries (Balasundram et al. 2006, Salvador et al. 2019, Trigo et al. 2020). For these reasons, many potential solutions have been proposed for the extraction of bioactive compounds from waste with the aim of producing new marketable products (Beres et al. 2017).

Unripe grapes are a waste product derived from thinning, that is, the green pruning practice carried out to improve the size and composition of both tablegrapes and grapes for high-quality red wine production (Guidoni et al. 2008). Normally, the thinned grapes are abandoned in the field and left to rot. Unripe grapes are a promising waste product, however, because they have not already been exploited to make wine or juice and therefore still contain all their endogenous nutrients and biologically active compounds. In general, the composition of grapes varies according to several factors, such as cultivar, vintage and ripening stage (Adams 2006, Mattivi et al. 2006). Unripe grapes contain little simple sugar but are rich in organic acids, phenolic flavonoids, non-flavonoids, condensed tannins, stilbenes and glutathione (Adams 2006).

This review, in line with others that have recently dealt with the exploitation of agro-industrial waste and farm sustainability, aims to summarise the composition and properties of UGs, the traditional and potential innovative uses of this form of viticulture waste, as well as the methods used for the extraction of the biologically active compounds.

Thinning

To make good wines, the grapes need to be ripe enough from both the technological and the phenolic points of view. In regions with poor climatic conditions, however, it can be

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difficult to reach full maturity. In contrast, even where the climatic conditions are optimal, it is well accepted that high crop yields delay ripening and reduce fruit and wine quality (Bravdo et al. 1984). As a result, many production regulations set a limit on the grape yield (tonnes/ha) in order to guarantee a higher quality product. For these reasons, a series of cultural practices have been developed to improve grape ripeness. Factors, such as crop level and the ratio between leaf area and total fruit mass per plant (source/sink ratio), are considered essential in controlling and ensuring the correct development of berries (Kliewer and Dokoozlian 2005). Excessive canopy growth can be controlled by practices such as leaf removal and/or summer pruning. In addition, plant yield can be further controlled by winter pruning and grape thinning. There are two main forms of reducing crop load, namely bunch thinning, consisting of the elimination of complete bunches, and berry thinning, which involves the removal of the tips of the bunches. The first practice is the most widespread; however, the data reported in the literature have shown these practices to achieve contrasting results, with bunch thinning leading to improved fruit composition in some cases (Guidoni et al. 2008, Pastore et al. 2011, King et al. 2015, Xi et al. 2016), while having no clear effect in others (Keller et al. 2005). Selective berry thinning has been proposed as an alternative to traditional bunch thinning to improve grape maturity (Roberto et al. 2015) despite being even more labour intensive and less economically sustainable. This technique consists of removing the tips of the bunches just after flowering and is based on the observation that for some cultivars the berries located in the bunch tips ripen later than the others (Pagay and Cheng 2010, Figueiredo-González et al. 2012, Doumouya et al. 2014). The contrasting results regarding the effect of grape thinning depend on the large number of factors that can affect the vine's response to the treatment, such as the grape cultivar, weather conditions, and timing and degree of the thinning. For example, there are no specific rules to decide the optimal timing for bunch thinning (Gil et al. 2013), and veraison, when vegetative growth has stopped and all the sugars synthesised by the leaves are accumulated in the bunches, appears to be the most effective time to carry out bunch thinning. Thinning techniques represent an additional cost for winegrowers because of the workforce required and the lower final grape production. Despite its economic impact, grape thinning is a common practice applied to both table- and winegrapes, especially for coloured grape cultivars grown in cool climate regions and regions with a short growing season (Gil et al. 2013, Condurso et al. 2016, Wang et al. 2019). Grape thinning can also be used to bring forward grape ripening in white grape cultivars (Keller et al. 2005). In tablegrapes, it is also applied to reduce the compactness of the bunches and to increase the size of the berries (Roberto et al. 2017).

From the quantitative point of view, the bunches (or parts thereof) are usually left on the ground, which makes it difficult to have a clear idea of the effective waste mass. In a rough calculation, considering that at veraison the grapes reach about 60% of the final mass (Ollat et al. 2002), and supposing a mean thinning rate of 30% (Carmona-Jiménez et al. 2021), a vineyard with a total forecast production of 10 t/ha will generate at least 1.8 t/ha of UGs.

An additional case of grape thinning is the so-called 'green harvest'. Even though in many cases, this term can be used as a synonym of grape thinning, for the European Commission (EC) the term 'green harvest' means the complete elimination of the grapes before harvesting. Following this method, the total crop is left to rot on the ground and the UG recovery can be even greater than in the case of grape thinning (European Commission, https://ec.europa.eu/info/food-farming-fisheries/plants-and-plant-products/fruits-and-vegetables_en). This policy measure was expressly devised to help re-establish an equilibrium between wine supply and demand in those years that were forecast to produce a large harvest (2009–2013). Even recently, because of the excess from the 2020 vintage that remained unsold because of the pandemic, Italian producers requested government intervention with a new 'green harvest' policy.

Unripe grape products

Unripe grapes are traditionally used to produce different products [unripe grape products (UGPs)], such as acidic juices, sauces, digestive drinks and syrup, as well as being added to typical products as a dried or fresh ingredient (Karapinar and Sengun 2007, Nikfardjam 2008, Hayoglu et al. 2009, 2016, Öncül and Karabiyikli 2015, 2016). In the Mediterranean area, where the grapevine is one of the main crops, the most ancient use of UGs is to transform them into an acidic juice known as verjuice, its name differing depending on the country where it is produced, *vertjus* or *verjus* in France, *agraz* in Spain and Germany, *agresto* in Italy, *koruk* in Turkey and *abe-ghureh* in Persia (Öncül and Karabiyikli 2015). The verjuice can be boiled and seasoned with salt, vinegar and spices, according to traditional recipes, to obtain different types of sour grape sauces. These traditional UGPs are an alternative sour-taste seasoning and dressing to lemon or vinegar (Öncül and Karabiyikli 2015). Dried UGs are also used as an ingredient of *zahter*, a cream traditionally consumed for breakfast in Turkey (Hayoglu et al. 2016). Typical Turkish sorbets are made using UGs too (Ekici et al. 2018).

Recently, new applications of traditional UGPs in food and beverages have been proposed in response to the increasing consumer demand for natural and healthy products (Tinello and Lante 2017, Tinello et al. 2018, Dupas de Matos et al. 2019, Ozturk and Sengun 2019, Sengun et al. 2019).

The composition of UGPs

Juice yield

Unripe grape products can be made using grapes picked from the period of bunch closure to veraison. During the herbaceous growth phase, the berries are small, green and hard (Coombe 1995) and their acid content increases. After veraison, the berries begin to soften and sugars start to accumulate. Veraison is a crucial stage in the evolution of the grape, which coincides approximately with the start of the normal expansion in berry volume, accumulation of sugars and reduction in acidity. The structure, composition and hard consistency of the unripe berries account for the difficulty encountered in pressing this fruit and justify the low juice yield that can be obtained from this raw material.

In general, the juice yield from pressing UGs varies from 40% [mass(m)/v] to 60% (m/v) (Table 1**)**. Dupas de Matos et al. (2017) obtained a juice yield ranging from 54 to 60% (m/m) from several cultivars of grapes, picked at growth stages 32 to 34 (from bunch closure to early

Table 1. Grape characteristics, juice yield, chemical and physical parameters of different unripe grape products.

UGPs	Cultivar		Harvest time	Yield (%)	TA (g/L)	pH	Sugar (g/L)	TSS (°Brix)	TP (mg/L)	TAnt (mg/L)	AA (μmol TEAC/L)	References
Verjuice	France	–	–	–	28.7	–	56.6	–	315	–	–	Nikfardjam et al. (2008)
Verjuice	Germany	–	–	–	32.4	–	38.2	–	346	–	–	Nikfardjam et al. (2008)
Verjuice	Germany	–	–	–	31.4	–	22.8	–	786	–	–	Nikfardjam et al. (2008)
Verjuice	Germany	–	–	–	19.6	–	95.1	–	442	–	–	Nikfardjam et al. (2008)
Verjuice	Germany	–	–	–	29.4	–	40.3	–	200	–	–	Nikfardjam et al. (2008)
Verjuice	Iran	–	–	–	25.0	–	0.1	–	1330	–	–	Nikfardjam et al. (2008)
Verjuice	Iran	–	–	–	39.6	–	0.2	–	780	–	–	Nikfardjam et al. (2008)
Verjuice	Kabarcik	White	45 Days after flowering	47	24.8	2.98	–	7.47	6267.7	–	–	Hayoglu et al. (2009)
Verjuice	Yediversen	Red	45 Days after flowering	47	30.0	2.91	–	4.50	7538.0	–	–	Hayoglu et al. (2009)
Verjuice	Yediveren	Red	–	–	33.3	2.48	6.11	5.0	618.54	–	491	Öncül and Karabiykli (2015)
Verjuice	Margaz	White	–	–	32.5	2.47	13.56	5.0	659	–	721	Öncül and Karabiykli (2015)
Verjuice	Muskule	Red	–	–	29.8	2.35	7.88	4.2	672.74	–	540	Öncül and Karabiykli (2015)
Verjuice	Kalecik Karasi	Red	–	–	38.7	2.37	7.32	5.4	650.61	–	860	Öncül and Karabiykli (2015)
Verjuice	Narince	White	–	–	22.9	2.59	0.85	8.0	233.43	–	35	Öncül and Karabiykli (2015)
Verjuice	Glera	White	Early veraison growth stage 34§	59.04	17.85†	2.91	–	9.65	–	–	–	Dupas de Matos et al. (2017)
Verjuice	Chardonnay	White	Early veraison growth stage 34§	57.61	25.06†	2.90	–	7.88	–	–	–	Dupas de Matos et al. (2017)
Verjuice	Sauvignon Blanc	White	Early veraison growth stage 34§	54.40	26.44†	2.83	–	9.86	–	–	–	Dupas de Matos et al. (2017)
Verjuice	Merlot	Red	Early veraison growth stage 34§	57.76	27.07†	2.73	–	7.29	–	–	–	Dupas de Matos et al. (2017)
Verjuice	Cabernet Franc	Red	Early veraison growth stage 34§	54.76	30.15†	2.72	–	5.99	–	–	–	Dupas de Matos et al. (2017)
Verjuice	Cabernet Sauvignon	Red	Early veraison growth stage 34§	54.83	25.24†	2.82	–	7.31	–	–	–	Dupas de Matos et al. (2017)
Verjuice	Merlot	Red	End of July 2013	–	13.2	–	–	–	1600	–	–	Tinello and Lante (2017)
Verjuice	Barbera	Red	End of July 2013	–	14.0	–	–	–	1500	–	–	

(Continues)

Table 1. Continued

UGPs	Cultivar		Harvest time	Yield (%)	TA (g/L)	pH	Sugar (g/L)	TSS (°Brix)	TP (mg/L)	TAnt (mg/L)	AA (μmol TEAC/L)	References
												Tinello and Lante (2017)
Verjuice	Merlot	Red	End of July 2014	–	14.1	–	–	–	1000	–	–	Tinello and Lante (2017)
Verjuice	Barbera	Red	End of July 2014	–	14	–	–	–	1100	–	–	Tinello and Lante (2017)
Verjuice	*Vitis vinifera* cv.	Red	Summer 2017—before veraison	–	30.1	2.35	–	5.03	307	23.43	35.65 ‡	Shakir and Rashid (2019)
Verjuice	Pinot Noir	Red	Veraison 2016	–	12.25	3.10	129	–	–	–	–	Piccardo et al. (2019)
Verjuice	Tannat	Red	Veraison 2016	–	8.43	3.12	175	–	–	–	–	Piccardo et al. (2019)
Verjuice	Tfayfihi	Red	Early July 2017, before the onset of veraison	–	37.9	2.59	–	4.09	341.49	–	–	Salah Eddine et al. (2020)
Verjuice	Black	Red	Early July 2017, before the onset of veraison	–	36.6	2.56	–	4.91	492.92	–	–	Salah Eddine et al. (2020)
Verjuice	Baytamoni	White	Early July 2017, before the onset of veraison	–	34.5	2.53	–	4.38	445.94	–	–	Salah Eddine et al. (2020)
Verjuice	Obeideh	White	Early July 2017, before the onset of veraison	–	40.9	2.52	–	3.72	274.00	–	–	Salah Eddine et al. (2020)
Sour grape sauce	Mixed cultivars	White, red	–	–	32.72	2.84	–	17.30	–	–	–	Vasile Simone et al. (2013)
Sour grape sauce	Yediveren	Red	–	–	32.1	2.74	2.34	3.55	523.89	–	239	Öncül and Karabiykli (2015)
Sour grape sauce	Yediveren	Red	–	–	36.8	2.42	1.22	7.2	482.29	–	205	Öncül and Karabiykli (2015)
Sour grape sauce	–	–	–	–	42.8	2.27	9.71	5.1	652.13	–	885	Oncul and Karabiykli (2015)
Sour grape sauce	Cabernet Sauvignon, Shiraz, Merlot	Red	–	–	43.3	2.3	1.18	5.1	96.79	–	158	Öncül and Karabiykli (2015)
Sour grape sauce	Cabernet Sauvignon, Shiraz, Merlot	Red	–	–	70.9	2.14	17.04	7.82	150.22	–	70	Öncül and Karabiykli (2015)
Liquid extract	Sangiovese	Red	18 August 2015, growth stage 36§	40	11.09	2.97	153	–	1214.6	197	5346	Fia et al. (2018)
Liquid extract	Sangiovese	Red	21 August 2017	75	5.7	3.3	143	–	2522	132.9	8277	Fia et al. (2020)

–, not analysed. †Total acidity is calculated as malic plus tartaric acids. ‡Expressed as μmol/mL gallic acid equivalents (GAE). §According to the modified Eichhorn–Lorenz (E–L) system. AA, antioxidant activity; TAnt, total anthocyanins; TEAC, Trolox equivalent antioxidant capacity; TP, total phenols; UGP, unripe grape product.

veraison) in the Eichhorn–Lorenz (E–L) phenological classification (Coombe 1995), using a small-scale, stainless steel basket press. A lower juice yield of 47% was obtained from the Kabarcik and Yediveren cultivars using a mechanical hand press (Hayoglu et al. 2009). The low juice yield observed by these authors is consistent with the fact that early harvesting precedes the expansion that normally occurs in berry volume after veraison (Dupas de Matos et al. 2017). At a commercial scale, Fia et al. (2018) obtained a juice yield of 40% (m/v) from UGs (cv. Sangiovese) picked at growth stage 36 of the E–L system, which were crushed, destemmed and extracted by maceration, without pressing the pomace. Recently, a juice yield of 75% (m/v) was obtained from Sangiovese grapes collected at veraison, crushed, destemmed and macerated; after that the free run juice was collected with the juice derived from pressing the pomace (Fia et al. 2020). The differences in juice yield mainly appear to be related to the extraction method and, to a lesser extent, to the cultivar of grape and harvest date (Dupas de Matos et al. 2017).

Sugars

Grapes contain some simple sugars (mono- and disaccharides) and complex sugars, such as pectin, which are structural polysaccharides of the grape cell wall. Fully ripe grapes contain mainly glucose and fructose, in an almost equimolar concentration, because they derive from the conversion of the sucrose imported into the fruit. At the beginning of the ripening phase, however, glucose predominates. In UGs, Sidersky (1942) reported a glucose/fructose ratio of above 1, but he noted that this value varied with the cultivar. In another work, glucose was found to account for 85% of the total sugar content of green berries sampled at an early developmental stage while, during veraison, glucose was found to predominate over fructose (Seymor et al. 1993). This evolution determines a different glucose : fructose ratio in unripe berries depending on the harvest time and the cultivar. More recently, Dupas de Matos et al. (2017) compared six different cultivars and found glucose to be absent at an early picking time (bunch closure and 15 days later), while the fructose increased at the early veraison stage (with values from 3.21 to 39.95 g/L), reaching a glucose : fructose ratio of between 1.17 and 6.07.

The total sugar concentration of UGPs ranges from 0.1 to 175 g/L (Table 1). The majority of UGPs contain less than 50 g/L of sugar. Piccardo et al. (2019) detected the highest sugar concentration in the verjuice, cv. Tannat, obtained from grapes picked at the beginning of veraison, while the Iranian verjuice studied by Nikfardjam (2008) showed the lowest sugar concentration. Sour grape sauces have a total sugar concentration ranging from 1.22 to 17.4 g/L. The TSS of the UGPs ranges from 3.55 to 17.30°Brix (Table 1). The highest value was detected in a sour grape sauce made from mixed cultivars (Vasile Simone et al. 2013), while the lowest was observed in a sour grape sauce obtained from the Yediveren cultivar (Öncül and Karabiyikli 2015). The inclusion of a concentration step in the production process can result in an increase in the TSS. In general, at the early stage of grape development, the main soluble solids are glucose, fructose, tartaric acid, malic acid, citric acid and phenolic compounds (Sabir et al. 2010, Salah Eddine et al. 2020). In UGs, the concentration of organic acids and phenolic compounds can be as high as that of sugars or even higher. Therefore, their contribution to the TSS of verjuice is important. For this reason, when soluble solids are described, some authors consider these compounds together with sugars.

Organic acids

The organic acids of plants include several different compounds with technological, biological and sensory properties. They are responsible for the low pH of fruit juices and fermented beverages, influencing their microbiological and chemical stability. Excluding sugars, organic acids are the compounds in greatest concentration in grape juice. L-(+)-tartaric and L-(−)-malic acids are the most abundant organic acids in grapes, accounting for about 90% of the total acid content at maturity. Other less abundant organic grape acids are involved in grapes' metabolic pathways, such as glycolysis, the Krebs cycle and the shikimic acid pathway. The total acidity of grape juice increases during the herbaceous growth phase and then decreases during ripening. Malic acid accumulates rapidly in the berries, reaching a maximum value of up to 25 g/L of juice, while the accumulation of tartaric acid is slower, although its concentration can be as high as 15 g/L at the end of the vegetative growth phase (Sabir et al. 2010). Dupas de Matos et al. (2017) studied the organic acid content of UG juices obtained from different white (Glera, Chardonnay, Sauvignon Blanc) and red (Merlot, Cabernet Franc, Cabernet Sauvignon) cultivars collected at growth stages 32 to 34 of the E–L system. The concentration of malic acid was higher than that of tartaric acid in all of the juices analysed. The malic acid concentration ranged from 10.90 to 22.38 g/L and the tartaric acid concentration from 6.25 to 11.35 g/L. The UG acids in cvs Merlot and Barbera included citric, fumaric, malic, tartaric, succinic and oxalic acid, and the total concentration of organic acids of the two cultivars was statistically different independently from the vintage (2013 and 2014) (Tinello and Lante 2017). In general, UGPs are characterised by a high acidity and low pH values (Table 1). The pH value of verjuice and liquid extracts ranges from 2.35 to 3.3. The highest pH (3.3) value and lowest total acidity (5.7 g/L) have been detected in the liquid extract obtained from grapes picked at growth stage 36 of the E–L system (Fia et al. 2020). The highest TA (40.9 g/L) has been detected in the verjuice obtained from UGs (cv. Obeideh) picked before the onset of veraison (Salah Eddine et al. 2020). The pH of sour grape sauces ranges from 2.14 to 2.84 and the TA from 32.1 to 70.9 g/L (Öncül and Karabiyikli 2015). These authors ascribed the high value of TA (70.9 g/L) of the sour grape sauce sample to the use of acidifying agents during the commercial production process (Öncül and Karabiyikli 2015). The low pH value and high TA of the UGPs are consistent with the early stage of development of the berries used to make the UGPs.

Phenolic compounds

Phenolic compounds are ubiquitous secondary metabolites in plants that are essential for growth, reproduction and protection against pathogens and radiations. Phenolic compounds have important chemical and biological properties. They are widely studied for their potential health benefits due to their potent antioxidant and free radical scavenging activities. Phenolic compounds occur in a wide range of different structures and, in general, they are characterised by the presence of at least one aromatic ring linked to at least one hydroxyl group (—OH). Phenolic compounds have different names depending on the number of phenolic hydroxyl groups: the phenol structure has one phenolic —OH group, while catechol, resorcinol and hydroquinone have two —OH groups, and gallocatechol and phloroglucinol structures have three —OH groups (Chiorcea-Paquim et al. 2020). The redox-active phenol moiety is responsible for the antioxidant properties of phenolic compounds. All phenolic compounds have a common redox behaviour, namely, electrochemical oxidation occurring in the —OH groups. These reactions, however, are influenced by the number and position of the hydroxyl groups and the chemical substituents linked to the aromatic rings of the phenols (Balasundram et al. 2006, Hidalgo et al. 2010, Cosme et al. 2018). The in vitro antioxidant capacity of phenolic compounds depends on the phenolic hydrogens, which are hydrogen-donating radical scavengers and exhibit metal-chelating properties of bidentate phenolic functions as well as binding interaction with biologically active oxidoreductases (Procházková et al. 2011, Chiorcea-Paquim et al. 2020, Zeb 2020). In in vitro studies, the direct scavenging of reactive oxygen species (ROS) by phenol flavonoids has been seen to depend mainly on the B-ring hydroxyl configuration. The antioxidant capacity of flavonoids increased in tandem with their degree of polymerisation. For example, proanthocyanidins, the polymers of catechins, are excellent in vitro antioxidants because of the high number of hydroxyl groups in their molecules (Procházková et al. 2011). Some flavonoids are able to chelate iron and copper, which are the promoters of the redox reactions responsible for the formation of free radicals. Moreover, phenolic compounds are able to interact with biopolymers, having a particular affinity for proteins and polysaccharides, with some important consequences on the nutritional value of food and human health (Zhang et al. 2014). In humans and animals, these interactions can affect both the bioactivity and bioavailability of phenols and influence the functionality of proteins (Jakobek 2015).

The phenolic compounds of grapes include flavonoids (anthocyanins, flavonols and tannins), non-flavonoid (phenolic acids) compounds and stilbenes. Many different chemical structures belong to the phenolic compounds of grapes. The structure of phenolic compounds can be simple, with a low molecular mass, such as phenolic acids, or complex, with a high molecular mass, such as the tannins that derive from the polymerisation of flavan-3-ols (Adams 2006, Mattivi et al. 2006, Boido et al. 2011). In grapes, flavonoids are the most abundant class of phenolic compounds and they exhibit variable evolution during the development and ripening of grapes (Adams 2006, Boido et al. 2011, Liang et al. 2012).

Anthocyanins are the pigments of red grapes and, with few exceptions, they are located in the skin of the berries, within the vacuoles (Mattivi et al. 2006). Anthocyanins begin to accumulate in grape berries at veraison and their concentration increases up to a maximum value as a function of some factors such as the cultivar, seasonal conditions, production area and viticulture practices (Downey et al. 2006). In general, compared to ripe grapes, UGs have a lower concentration of anthocyanins; even so, the anthocyanin profile is quite stable alongside ripening (Downey et al. 2004, Adams 2006, Benbouguerra et al. 2020, Kurt-Celebi et al. 2020). Flavonol biosynthesis occurs in two distinct periods, the first around flowering, and the second after veraison and continuing throughout ripening in the skin of berries.

Tannins are found in both the skin and seeds of berries. In the seeds, tannin accumulation starts immediately after fruitset and reaches a maximum level around veraison, while tannin accumulation in the skins is high at flowering and continues from fruitset until 1 or 2 weeks after veraison (Kennedy et al. 2000, 2001, Harbertson et al. 2002, Downey et al. 2003, Downey et al. 2006, Adams 2006). The concentration of tannins in the skin declines during ripening in proportion to the berry growth (Harbertson et al. 2002, Adams 2006). During berry development and ripening, the mean degree of polymerisation of tannins in the skin has been shown to increase in some cases (Kennedy et al. 2001) while decreasing in others (Downey et al. 2003). Non-flavonoids are less concentrated with respect to flavonoids and located mainly in the grape pulp (Adams 2006). They include several structures, however, such as caftaric and gallic acids, with important biological and technological properties (Fia et al. 2016). Hydroxycinnamates are the major non-flavonoid compounds of grapes and, on a per-berry basis, they show a peak prior to veraison followed by a decline to a constant amount as the fruit ripens (Fia et al. 2016, Romeyer et al. 1983). Unripe grapes are a rich source of flavonoid compounds, mainly tannins from seeds and skins, flavonols and hydroxycinnamic acids, but a less rich source of anthocyanins than mature grapes. Nikfardjam (2008) studied the phenol composition of seven commercial and experimental verjuices, highlighting that the concentration of polyphenols was higher in those products with a lower sugar concentration, that is, made with grapes picked before sugar accumulation. This author noticed that the total polyphenol concentration obtained by the Folin–Ciocalteu assay was higher than the one measured by means of HPLC. Therefore, he hypothesised that most of the phenolic fraction of UGs could be polymeric in nature. Resveratrol is a stilbene found in grapes and has been intensively studied for its positive health effects (Auger et al. 2005). Resveratrol is positively correlated with grapevine disease resistance and it is mainly located in the berry skin. The amount of resveratrol is high in UGs while it drops to low concentration in the ripe fruit (Adams 2006, Mattivi et al. 2006). The concentration of other stilbenes such as the viniferins has been less studied in grapes because of their lower concentration compared with resveratrol. In one case (Corvina grapes), however, it has been reported that ε-viniferin is the predominant stilbene in berry tissues at pre-veraison stage (Toffali et al. 2011). Even though it is well known that both biotic and abiotic stresses can induce the stilbene synthesis, no data about the induction in UG tissues have been reported yet.

The total phenol (TP) concentration of grapes and their products is usually determined by the Folin–Ciocalteu reagent following the method described by Singleton and Rossi (1965), which is based on a redox reaction. The TP concentration of the UGPs is shown in Table 1. The UGPs show a wide range of TP concentration from 96.79 to 7538 mg/L. The variability of the phenol concentration in grapes depends on many factors, such as maturity level, sunlight exposure, temperature and water availability (Kennedy et al. 2002, Downey et al 2006). Tinello and Lante (2017) observed significant differences between the phenolic concentration in Barbera and Merlot UGs, independent of the vintage. The amount of phenols extracted in the juice also depends on their localisation in the berry structures (skin, pulp and seeds) and extractability (Hanlin et al. 2010), and it is strongly influenced by the extraction technique and process variables, such as temperature, time and use of solvents (Setford et al. 2017). The anthocyanin concentration in UGs and UGPs is low, ranging from 23.4 to 197 mg/L of the verjuice or liquid extract (Table 1).

Table 2 summarises the information available about the phenolic composition of different verjuices, and UG liquid and dry extracts. Unripe grapes contain hydroxycinnamic and benzoic acids, flavan-3-ols and flavonols (Nikfardjam 2008). Tinello and Lante (2017) observed that verjuices from Merlot and Barbera cultivars contained flavan-3-ols (mainly epigallocatechin gallate) and phenolic acids. Phenolic acids, flavonols, flavan-3-ols, procyanidins and resveratrol have been detected in the liquid extracts obtained from Sangiovese UGs, and caftaric and fertaric acid, (+)-catechin, (−)-epicatechin and quercetin-3-*O*-glucuronide were the most abundant phenolic compounds (Fia et al. 2018, 2020).

In general, the phenolic compounds of grapes may act as antioxidants and the TP concentration is highly correlated with the grapes' antioxidant capacity (De Beer et al. 2004). Hagen et al. (2008) observed that both the composition of the juice and the antioxidant activity were strongly influenced by the grape cultivar and the extraction technique. Unripe grape products display a wide range of antioxidant activity (AA), varying from 35.65 to 8277 μmol of Trolox equivalent antioxidant capacity (TEAC)/L, which was detected in a Sangiovese liquid extract (Fia et al. 2020). Differences in the antioxidant activity of traditional UGPs have been observed as a function of the development stage of the grapes (Öncül and Karabiyikli 2015).

Glutathione

Glutathione is a key antioxidant in the biological system. It is involved in the so-called antioxidant network that provides a sophisticated defence mechanism against the attack of free radicals (Serafini 2006). Indeed, antioxidants do not act alone in vivo but oxidised antioxidants can be recycled in interplay with other antioxidants such as ascorbate and glutathione (Procházková et al. 2011). Glutathione is an endogenous antioxidant of grapes involved in the prevention of enzymatic oxidation of the juice. When the reduced glutathione (GSH) acts as an antioxidant, it is enzymatically oxidised into glutathione disulfide (GSSG). 2-*S*-Glutathionil caftaric acid [grape reaction product (GRP)] is also formed when the grapes are broken, the juice is exposed to oxygen and the *o*-quinones, derived from the enzymatic oxidation of phenolic acids, are in the presence of GSH (Motta et al. 2014). In grape berries, GSH accumulates at the onset of ripening and its concentration is correlated with sugar accumulation during grape ripening. At maturity, the GSH concentration ranges from 0 to 100 mg/L, according to several factors, such as grape cultivar and environmental conditions (Pons et al. 2015). Different forms of glutathione (reduced, oxidised and GRP) have been detected in UG extracts (Table 2) (Fia et al. 2018, 2020, Bucalossi et al. 2020).

Fibres

Dietary fibres (DFs) 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 Food and Agriculture Organization/World Health Organization of the United Nations 2010).The main effects related to the consumption of DF are the reduction of the risk of cardiovascular diseases, protection against cancer, the prevention of diabetes due to a lower absorption of glucose, improvement of the digestive process, the reduction of blood cholesterol and the prevention of obesity (Llobera and Cañellas 2007, González-Centeno et al. 2010, Deng et al. 2011). The intake recommendation guidelines state 25–30 g/day of DFs (The United States Food and Drug Administration 2013), which is normally obtained from cereals, vegetables and fruit. Dietary fibre is divided into soluble and insoluble fibre; the first category includes pectin, gums, β-glucans, while cellulose, hemicellulose and lignin are insoluble fibres (Beres et al. 2017). The physiological effects of total DF, that is, both the insoluble and the soluble fractions of foods, have an important role in human nutrition. Like most of the fibre derived from cereals, the skin and seeds of grapes contain a high level of good-quality DF (Deng et al. 2011). Polysaccharides, cellulose and polygalacturonans are the major constituents of the cell wall in mature grape berries, accounting for 30–40% by mass of the polysaccharide component of the walls (Nunan et al. 1997). During the ripening process, however, the molecular mass, solubility and degree of substitution of individual cell wall polysaccharides may change drastically. Upon extracting different polysaccharide classes from berries picked at several developmental stages, Yakushiji et al. (2001) found a significant decrease in soluble polysaccharides and pectin content as well as a reduction in the content of hemicellulose and cellulose. No data are available on the polysaccharide content of verjuice or other UGPs; however, it can be assumed that they contain more polysaccharides than juice made from fully ripe grapes because of the limited activity of the cell wall-degrading enzymes. Most of the studies on DFs from by-products of the wine sector have focused on the chemical composition of grape pomace (González-Centeno et al. 2010, Deng et al. 2011). For example, González-Centeno et al. (2010) studied the DF content of the stems and pomace of ten cultivars of grape. They observed that the Tempranillo red grape cultivar contained the highest amount of DF in the grape (5.1 g/100 g FM), stem (34.8 g/100 g FM) and pomace (36.9 g/100 g FM). Recently, Shakir and Rashid (2019) studied the fibre concentration of unripe black grape juice and they observed a crude fibre value of 4.5 g/100 g (DM), indicating it as a good source of DF.

Mineral elements

Minerals are defined as micronutrients because small amounts are required in the human diet. However, as minerals have diverse functionalities in the metabolism and homeostasis, the deficiency of these constituents can result in the incidence of disorders and disease symptoms (Gharibzahedi and Jafari 2017). Minerals are divided into major minerals (Ca, Mg, K, Na, Cl, P and S) and trace minerals (I, Zn, Se, Fe, Mn, Cu, Co, Mo, F, Cr and B). The main sources of both vegetable and animal minerals and their functions are reviewed by Gharibzahedi and Jafari (2017).

Grapes contain major minerals, such as potassium, calcium, sulfur and phosphorus, and trace minerals, such as iron and copper. Panceri et al. (2013) identified 15 elements in Cabernet Sauvignon and Merlot grapes. Mineral concentration in the grapes can vary in relation to many factors, such as the stage of maturity, grape type, ability to absorb inorganic minerals, temperature, soil, fertilisation, sunlight exposure and rainfall (Etchebarne et al. 2009). Potassium is the most abundant element within the grape berry, accounting for about 80% of the cations, at all stages of development, and it has a higher rate of accumulation after veraison compared with the other elements (Rogiers et al. 2017). Potassium ions

Table 2. Phenolic composition of unripe grape products, verjuice, liquid extract and dried extract.

	Concentration (mg/L)						Concentration (mg/kg)		
	Verjuice				Liquid extract		Dried extract		
Compound	**M1†**	**M2†**	**B1†**	**B2†**	**S1‡**	**S2¶**	**S3‡**	**V1§**	**M3††**
Phenolic acids									
Caffeic acid	21.62 ± 0.2	14.54 ± 0.5	18.83 ± 0.6	15.37 ± 1.8	0.43 ± 0.16	n.d.	0.8 ± 0.0	1.1 ± 0.11	11.0 ± 0.4
Cumaric acid	–	–	–	–	n.d.	n.d.	0.5 ± 0.1	1.1 ± 0.26	19.6 ± 0.6
Ferulic acid	–	–	–	–	0.14 ± 0.00	n.d.	29.4 ± 4.7	110.4 ± 28.3	4.63 ± 0.59
Caftaric acid	–	–	–	–	27.15 ± 1.7	135.3 ± 3.36	191 ± 5.0	1190 ± 252	704 ± 33
Coutaric acid	–	–	–	–	9.40 ± 0.1	74.41 ± 3.49	27.6 4.4	81.0 ± 14.66	34.3 ± 1.1
Fertaric acid	–	–	–	–	30.10 ± 3.3	33.06 ± 0.96	291 ± 73	147.4 ± 6.17	52.0 ± 2.0
Gallic acid	6.5 ± 0.2	0.5 ± 0.2	0.6 ± 0.1	0.5 ± 0.1	9.40 ± 2.1	0.06 ± 0.00	9.5 ± 0.3	3.0 ± 0.05	1.63 ± 0.03
Chlorogenic acid	21.9 ± 0.2	10.7 ± 0.2	19.7 ± 0.2	9.3 ± 0.2	–	–	–	–	–
Flavonols									
Quercetin	–	–	–	–	0.29 ± 0.00	0.05 ± 0.00	1.3 ± 0.0	1.6 ± 0.0	14.0 ± 0.4
Quercetin-3-*O*-hexoside	–	–	–	–	19.8 ± 0.8	12.33 ± 0.46	11.8 ± 0.8	27.7 ± 1.88	1.32 ± 0.08
Quercetin −3-*O*-gluconoride	–	–	–	–	27.0 ± 1.2	23.54 ± 0.69	56.6 ± 3.1	–	–
Rutin					0.40 ± 0.03	0.86 ± 0.03	0.4 ± 0.0	0.2 ± 0.00	–
Myricetin	–	–	–	–	0.03 ± 0.00	0.04 ± 0.02	n.d.	n.d.	3.79 ± 0.11
Isorhamnetin	–	–	–	–	n.d.	n.d.	0.7 ± 0.0	0.7 ± 0.0	1.41 ± 0.03
Kaempferol	–	–	–	–	n.d.	n.d.	0.5 ± 0.0	0.6 ± 0.01	0.78 ± 0.04
Kaempferol 3-*O*-glucoside	–	–	–	–	n.d.	2.43 ± 0.14	–	1.1 ± 0.05	0.54 ± 0.03
Flavan-3-ols									
(+)-Catechin	5.1 ± 0.2	9.3 ± 0.8	4.3 ± 0.6	12.1 ± 0.5	38.4 ± 1.3	156.31 ± 1.29	327 ± 19	91.4 ± 0.78	13.6 ± 0.8
(−)-Epicatechin	2.8 ± 0.1	5.5 ± 1.0	2.0 ± 0.1	5.3 ± 0.7	39.5 ± 1.6	17.21 ± 0.42	64 ± 12	9.3 ± 0.84	8.23 ± 0.29
Epicatechin gallate	20.9 ± 0.1	24.2 ± 0.9	32.4 ± 0.1	80.9 ± 0.1	–	0.15 ± 0.01	–	1.9 ± 0.11	–
Epigallocatechin	13.8 ± 0.3	54.4 ± 3.4	17.0 ± 0.5	77.7 ± 1.3	–	–	–	–	–
Epigallocatechin gallate	212.6 ± 3.0	683.4 ± 16	238.9 ± 6.8	660.1 ± 13	–	–	–	–	–
Procyanidins									
Procyanidin B1	–	–	–	–	23.9 ± 0.9	10.30 ± 0.15	19 ± 1.5	12.9 ± 1.51	4.55 ± 0.19
Procyanidin B2	–	–	–	–	2.0 ± 0.1	17.71 ± 0.5	10.1 ± 1.0	2.5 ± 0.18	9.74 ± 0.37
Stilbenes									
trans-Resveratrol	–	–	–	–	0.01 ± 0.00	n.d.	0.2 ± 0.0	2.7 ± 0.07	31.3 ± 1.6
Glutathione									
GSH	–	–	–	–	–	n.d.	–	5.9 ± 0.01	–
Grape reaction product (GRP)	–	–	–	–	–	6.39 ± 0.75	–	125 ± 12.55	16.8 ± 0.6
GSSG	–	–	–	–	–	1.14 ± 0.09	–	n.d.	n.d.

Data are reported as mean ± SD ($n = 3$); n.d., not detected; –, not analysed. †Tinello and Lante (2017). ‡Fia et al. (2018). §Fia, pers. comm., 2019. ¶Fia et al. (2020). ††Bucalossi et al. (2020). B1, verjuice cv. Barbera 2013; B2, verjuice cv. Barbera 2014; GSH, reduced glutathione; grape reaction product, GRP, 2-*S*-glutathionyl caftaric acid; GSSG, oxidised glutathione; M1, verjuice cv. Merlot 2013; M2, verjuice cv. Merlot 2014; M3, freeze-dried extract cv. Merlot 2016; S1, liquid extract cv. Sangiovese 2015; S2, liquid extract cv. Sangiovese 2017; S3, spray-dried extract cv. Sangiovese 2015; V1, freeze-dried extract cv. Viognier 2016.

have an important role in regulating the membrane potential of the cell, and consequently it is critical for the uptake of other ions and sugars. It is an important element for plant signalling, osmoregulation, maintaining the cation–anion balance, cytoplasmic pH regulation, enzyme activation, and protein and starch synthesis (Rogiers et al. 2017). The second major cation of grapes is calcium and its content is linked to pathogen resistance (Etchebarne et al. 2009). The concentration-per-berry basis of potassium, calcium and magnesium increases during the entire berry development period (Doneche and Chardonnet 1992). The mineral elements of grapes can be separated into two categories according to their accumulation pattern in the berry. The first group of elements continues to accumulate throughout berry growth and ripening, and comprises phloem-mobile potassium, phosphorus, sulfur, magnesium, boron, iron and copper. The second group of elements accumulate mostly prior to veraison and include the xylem-mobile minerals calcium, manganese and zinc (Rogiers et al. 2006).

Recently, Shakir and Rashid (2019) evaluated the minerals in a juice from UGs, finding a higher potassium concentration compared with that of the other minerals tested, such as magnesium, sodium and calcium, while iron was detected at a concentration of 0.39 mg/mL.

Vitamins

Liposoluble vitamins such as vitamin E and carotenoids have been identified in grapes (Evers et al. 2021). Vitamin E consists of four tocopherols (α-, β-, γ- and δ-forms) and the corresponding unsaturated forms, such as the tocotrienols. Tocopherols are concentrated in grape seeds and the alpha form, generally recognised as most active in humans, is predominant (Aubert and Chalot 2018). In *V. vinifera*, tocotrienols are only present in the endosperm of seeds (Horvath et al. 2006). Tocopherols decrease while tocotrienols accumulate during seed development (Horvath et al. 2006). As they are powerful antioxidants, tocopherols prevent oxidation of the fats and oil contained in the seeds, ensuring their longevity and healthy germination (Munné-Bosch and Alegre 2002). Grape carotenoids have two main functions in the photosynthetic pathway: photoprotection, exerted by the channelling of photochemical energy away from chlorophyll to avoid damage of the photosynthetic apparatus, and light harvesting, through the collection and transfer of light to the chlorophyll via photochemical transduction (Kamffer et al. 2010). The most common carotenoids of ripe grapes are β-carotene and lutein, representing almost 85% of the total carotenoid content. The remaining proportion of the total carotenoids consists of neoxanthin and violaxanthin, lutein-5,6-epoxide, zeaxanthin, neochrome, flavoxanthin and luteoxanthin. From veraison to harvest, the concentration of carotenoids decreases (Kamffer et al. 2010). Carotenoids are natural pigments and precursors of vitamin A, which is an essential vitamin for human growth, reproduction and vision (Aubert and Chalot 2018).

The water-soluble vitamins in grapes include vitamin C, pantothenic acid, niacin, riboflavin, thiamine and biotin (Hagen et al. 2008, Aubert and Chalot 2018, Andrade et al. 2019). In the human diet, more than 90% of vitamin C is supplied by fruit and vegetables, and unripe fruit normally contains a higher vitamin C content than ripe fruit (Melino et al. 2009). The vitamin content of some red and white cultivars of grapes picked at maturity is reported by Andrade et al. (2019), according to the United States Department of Agriculture Food Composition Database (United States Department of Agriculture Food Database). The water-soluble vitamins identified in some UGPs are reported in Table 3. Fia et al. (2020) identified pantothenic acid (452 μg/L), choline (782 μg/L), niacin (62 μg/L) and pyridoxine (100 μg/L) in the liquid extract obtained from UGs of Sangiovese. The vitamin C in verjuices obtained from different grape cultivars has been found to vary from 15 to 20 mg/L (Hayoglu et al. 2009, Shakir and Rashid 2019). Data on vitamin C content in ripe grapes are scarce. Evers et al. (2021) reported a concentration range of vitamin C in grape must from 30 to 572 mg/L. The same authors indicated that these data derived from experiments performed many years ago when the sensitivity of the methods employed was low. Therefore, they concluded that it can be assumed that ascorbic acid concentration does not actually reach such a high maximal value. Other authors demonstrated that grapes accumulate vitamin C in the green berries reaching a maximum concentration before veraison. The accumulation then slows down before restarting during the ripening phase (Melino et al. 2009). Hagen et al. (2008) observed that pantothenic acid and biotin do not vary significantly depending on the stage of ripening, while the cultivar appears to have a great effect on the content of these vitamins. Over 3 years, Hagen et al. (2008) analysed many samples of white and red grapes and reported that the concentration of biotin varied from about 1–5 μg/L while that of pantothenic acid varied from 179 to 1260 μg/L.

Lipids and other minor compounds

Some bioactive compounds of grapes, with a lower concentration compared to that of phenolic compounds, have been little studied. Among them, triterpenic compounds, fatty acids, long-chain aliphatic alcohols and sterols were recently evaluated in dichloromethane extracts of shoots, canes, stalks, leaves and UGs (Salvador et al. 2019). The UGs contained a higher concentration of saturated than unsaturated fatty acids and triacontanoic acid [21 mg/100 g dry mass

Table 3. Water-soluble vitamin composition of unripe grape products.

		Water-soluble vitamins					
UGPs	**Cultivar**	**Pantothenic acid (B5) (μg/L)**	**Ascorbic acid (mg/L)**	**Choline (μg/L)**	**Niacin (μg/L)**	**Pyridoxine (μg/L)**	**References**
Verjuice	Kabarcik	–	20.0	–	–	–	Hayoglu et al. (2009)
Verjuice	Yediveren	–	19.0	–	–	–	Hayoglu et al. (2009)
Verjuice	Black grape (*Vitis vinifera*)	–	150.0 ± 0.64	–	–	–	Shakir and Rashid (2019)
Liquid extract	Sangiovese	452.0 ± 82.5	n.d.	782.3 ± 29.3	62.0 ± 2.6	100.7 ± 8.4	Fia et al. (2020)

n.d., not detected; –, not analysed; UGP, unripe grape product.

(DM)] is predominant. Long-chain aliphatic alcohols, mainly octacosanol (32.5 mg/100 g DM) and hexacosanol (42.3 mg/100 g DM), were components of UGs. Stigmasterol (7.0 mg/100 g DM), β-sitosterol (21.1 mg/100 g DM) and stigmastanol (11.9 mg/100 g DM) were the sterols identified in unripe berries that were also a source of ursolic acid (653.5 mg/100 g DM), a triterpenic compound connected with a range of biological activities (Salvador et al. 2019). The lipids in grapes were recently characterised by Della Corte et al. (2015) and Pérez-Navarro et al. (2019). The concentration of total free fatty acids in grape skins varied from about 27 to 81 mg/kg fresh mass (FM) and from 62 to 153 mg/kg FM depending on the cultivar. Among triterpenoids, uvaol and oleanolic acid were quantified only in skins (1.5–3.9 and 38.6–57.6 mg/kg FM, respectively) (Pérez-Navarro et al. 2019). The evolution of the triterpenoids during grape development has been investigated by Pensec et al. (2014). The study revealed a characteristic evolution of triterpenoid concentration during fruit development, with a high concentration of total triterpenoids in young grapes that gradually decreased with a slight increase in the level of neutral triterpenoids. Oleanolic acid, the most abundant triterpenoid present in grape cuticular waxes, ranged from 406 ± 22 μg/mg of wax extract in Muscat d'Alsace to 782 ± 58 μg/mg in Sylvaner; this concentration subsequently decreased during fruit maturation to 309 ± 12 μg/mg in Muscat d'Alsace and 440 ± 30 μg/mg in Sylvaner (Pensec et al. 2014). In general, lipids contained in the grape waxes were influenced by the cultivar and grape development stage, with a high level of total triterpenoids in young grapes which decreased gradually during ripening. Recently, Nasser et al. (2020) evaluated the total alkaloid content (5.7% DM) in a green grape juice. These compounds are deemed to be protective against the risk of cancer and are largely present in cruciferous vegetables (Rochfort and Panozzo 2007).

Properties of UGs

Nutraceutical and pharmaceutical properties

Grapes are a source of non-nutritive compounds, including phenolic compounds, but are also a source of nutrients such as sugar, and micronutrients such as minerals. In addition, grapes contain vitamins, a high concentration of DFs and a low concentration of lipids. Moreover, recent evidence has shown that grapes contain several phytochemicals including a lipophilic component, such as triterpenoids and fatty acids, and alkaloids. Overall, these compounds may have a synergistic and multifactorial effect on human health (Olas 2018). The consumption of fruit and berries may be associated with a reduced incidence of disorders resulting from ROS, including cardiovascular disorders, cancer and inflammatory processes (Rasines-Perea and Teissedre 2017, Olas 2018). The current knowledge on the beneficial effects of grape compounds acting as antioxidants in in vitro and in vivo models has been reviewed by Olas (2018). In in vivo studies, extracts from red grapes, grape seeds and grape pomace have shown positive effects, such as the inhibition of lipid peroxidation, an increase in total antioxidant status and an increase in the activity of antioxidant enzymes, and negative effects such as an increase in lipid peroxidation (Olas 2018). Phenolic compounds are recognised to have many biological effects, for example, anti-allergic, anti-inflammatory, antimutagenic, anticancer and anti-ischemic, and they are modulators of the enzymatic activity of antioxidant enzymes and oxidases (Xia et al. 2010, Guilford and Pezzuto 2011, Procházková et al. 2011, Rasines-Perea and Teissedre 2017,Olas 2018). The pharmacological activity of phenolic compounds is due to the different mechanisms of action, which include antioxidant effects through the inactivation of ROS, the binding of electrophiles, the induction of protective enzymes, the inhibition of lipid peroxidation, increasing the apoptosis rate, the inhibition of cellular proliferation, angiogenesis inhibition, H-donation and the inhibition of DNA oxidation (Procházková et al. 2011, Chiorcea-Paquim et al. 2020). Moreover, the ability of phenolic compounds to interact with macronutrients, such as proteins, carbohydrates and lipids, and the consequences of this interaction on the activity and bioavailability of phenols, digestibility of nutrients and enzyme activity have been reviewed by Jakobek (2015). An interesting aspect of dietary polyphenols concerns their potential role in controlling hyperglycemia. Diabetes is an important concern worldwide, and there is some evidence that grape polyphenols can contribute through different mechanisms to reduce the risk of type-2 diabetes (Guilford and Pezzuto 2011, Rasines-Perea and Teissedre 2017).

Anti-browning properties

The anti-browning activity of UGs is related to their phenolic concentration, high acidity and acidic composition. Some phenolic compounds, such as catechins and epigallocatechin gallate, found in the UGs, are known to be strong competitive inhibitors of polyphenol oxidase (PPO) or tyrosinase (TYR) (EC 1.10.3.1), and depigmenting agents, respectively (Bonesi et al. 2018). Polyphenol oxidase is a copper-containing oxidoreductase that catalyses two different reactions: the hydroxylation of monophenols to *o*-diphenols and the oxidation of *o*-diphenols to *o*-quinones, which polymerise with the subsequent formation of brown pigments (Seo et al. 2003). These reactions lead to colour alteration, reduction of the nutritional and sensory quality of food products, and degradation of the phenols (Rapeanu et al. 2006, Tinello and Lante 2020, Trigo et al. 2020). Even caftaric acid, one of the most abundant phenolic compounds in UGs, has proven to be an inhibitor of tyrosinase and is more potent than the related caffeic and chlorogenic acids (Honisch et al. 2020). The anti-browning activity of UGs is also strongly related to the composition of their organic acids and pH (Tinello and Lante 2017, Tinello et al. 2018, Moon et al. 2020). The organic acid profile of UGs includes some known inhibitors of PPO. In addition to oxalic acid, a strong anti-browning compound, tartaric, malic and citric acids provide a highly effective anti-browning performance in the catechol–mushroom PPO system (Son et al. 2001). The low pH of the juice deriving from UGs can help control the enzyme browning by reducing the activity of the tyrosinase (Rapeanu et al. 2006, Zhou et al. 2016). Moreover, the pH influences the redox behaviour, antioxidant capacity and formation of oxidation products of polyphenols (René et al. 2010, Chiorcea-Paquim et al. 2020).

Antimicrobial properties

The antimicrobial activities of UGs are related to their phenolic content, high acidity and acidic composition. Both organic acids and phenolic compounds from different origins, such as pomegranates, grapes, lemons, rosemary, oregano, cranberries and garlic, have antibacterial properties and plant extracts are used as potential natural preservatives in foods (Miron and Dima 2012). Phenolic compounds present many different antimicrobial action mechanisms: induction of acidification of the cytoplasm and coagulation of the cytoplasmic constituents; disruption of the membrane function and structure; modification of the membrane potential; interference with the metabolic intermediates; induction of leakage of the cellular content; and interruption of the DNA, RNA and protein synthesis and function. For instance, condensed tannins may cause damage to the cell membrane and inactivate the metabolism by binding to the enzymes (Silva et al. 2018, Ma et al. 2019). Phenolic acids are able to disrupt membrane integrity with the consequent leakage of the intracellular constituents. Quercetin increases membrane permeability and disturbs its potential, while several flavonoids, such as (−)-epicatechin gallate and (−)-epigallocatechin gallate, induce a reduction in membrane fluidity. Some of these antimicrobial effects are related to the direct pro-oxidant function of the flavonoids, which appears to be related to the phenolic structure and concentration (Procházková et al. 2011). The pro-oxidant behaviour of phenolic compounds is stimulated under those conditions that favour autoxidation, such as a high pH and a high concentration of metal ions and oxygen molecules (Olas 2018). Moreover, small molecules (i.e. quercetin and gallic acid) are easily oxidised and have a pro-oxidant effect, while phenolic compounds with high molecular mass (i.e. condensed tannins) have little or no pro-oxidant effect. Juice and sauces from UGs have shown antibacterial activity against *Escherichia coli*, *Listeria monocytogenes*, *Salmonella typhimurium*, *Bacillus cereus* and *Staphylococcus aureus*, which are responsible for food-borne diseases (Karapinar and Sengun 2007, Öncül and Karabıyıklı 2016, Ozturk and Sengun 2019, Sengun et al. 2019). This is a promising property, offering a potential natural alternative to the synthetic preservatives normally used to ensure the safety and extended shelf life of food products.

Sensory properties

Among the wine chain by-products, little investigation has been made of the sensory properties of UGs and their derivates (e.g. verjuice and sour grape sauce). The sensory attributes characterising UGs are mainly associated with their phenolic compounds and acid concentration. Phenolic compounds contribute to specific sensations, such as bitterness, astringency and sourness (Hufnagel and Hofmann 2008). In this context, previous studies conducted on red wine suggested that monomeric flavon-3-ols, procyanidin dimers and trimers are partly responsible for bitter taste and the perception of astringency (Peleg et al. 1999). Moreover, several reports have indicated that verjuice is characterised by a sour taste, since it is obtained from grapes that are harvested approximately 45 days after flowering, thus it displays a high amount of organic acids and a low sugar concentration (Nikfardjam 2008, Hayoglu et al. 2009, Salah Eddine et al. 2020). These data were also confirmed in a recent study where phenol-rich extracts obtained from UGs dissolved in water solutions were subjected to sensory descriptive analyses (Bucalossi et al. 2020). Phenolic acids were the most abundant and they accounted for 89% of the total amount of phenolic compounds. Caftaric acid accounted for 85% of the phenolic acid concentration, whereas flavonols, flavan-3-ols, procyanidins, *trans*-resveratrol and 2-S-glutathionyl caftaric acid accounted for the remaining 11% of the phenolic compounds identified in the UG extract. In this study, the perception of sourness increased significantly as the concentration of phenolic compounds increased (range 0.41–1.93 g/L), whereas the other sensations (bitterness, astringency and saltiness) showed limited increases in intensity.

Recent findings highlighted that the taste of UG juices obtained from grape cultivars, such as Merlot, Chardonnay and Sauvignon, was described mainly by the terms sour, astringent and to a lesser extent salty and sweet (Dupas de Matos et al. 2017). The most common terms used to describe odour perception were herbaceous, cooked or green apple, pear and floral (Dupas de Matos et al. 2017). The same authors found that the harvest date (three different dates) had no influence on the aromas whereas it did have an effect on taste, while the opposite results were found according to preservatives (sulfite or sorbate). It has also been shown that the use of different grape cultivars in verjuice production affects both the physicochemical and sensory properties, with some cultivars being more suitable to obtain a juice with higher concentration of antioxidant compounds and a more appreciable colour (Salah Eddine et al. 2020).

Unripe grapes have also been used to obtain red wine with a low alcohol concentration and pH, an intense colour and high concentration of phenolic compounds (Piccardo et al. 2019). Must from mature grapes was partly substituted with UG juice (about 31% of the mass of the destemmed and crushed grapes) and then was subjected to a pre-fermentative hot maceration. A strong, positive effect on colour (due to the high proportion of the flavylium form of anthocyanins aided by the low pH), chemical composition and sensory characteristics was observed.

Besides being used to produce juices, extracts rich in pro-healthy compounds can be obtained from UGs for use as new sustainable food ingredients in the development of functional food or beverages. The addition of UG extracts to food matrices (beetroot puree, tomato puree and bean puree) was found to increase sourness intensity as a function of the UG phenolic concentration and the type of food model (i.e. with different macro-components) (Bucalossi et al. 2020).

The specific above-mentioned sensory characteristics of UGs could lead to negative hedonic consumer responses, as also demonstrated using other wine chain by-products in food products. Indeed, for example, the addition of grape skin powders to soft cow's milk cheeses or apple purees was found to decrease liking scores, especially at higher powder concentration (Torri et al. 2016, Lavelli et al. 2017). Recent data demonstrated that the liking of beetroot puree samples with an added UG phenol extract decreased slightly as the concentration of phenolic compounds increased; however, all the experimental samples were considered acceptable by the consumers involved (Proserpio et al. 2020). It should be considered that health and sustainability-related information concerning the reuse of wine chain by-products as a source of value-added food ingredients could be used to influence consumer responses. It is well established, however, that people are generally not willing to compromise perceived taste for healthiness (Verbeke 2006). As regards functional food models with the addition of phenolic compounds from UGs, it has been shown that among specific segments of consumers pro-healthy and sustainable information could positively affect their expectations and hedonic responses (Proserpio et al. 2020).

Traditional and innovative applications

Applications in food and beverages

In recent years, the accumulation of evidence on the properties of UGs and UGPs has led to the investigation of innovative applications beyond their traditional use for seasoning and flavouring foods. Verjuices have been tested as preservatives and as acidifying and antioxidant agents to extend the shelf life of food products and reduce the oxidation of dried fruits. Unripe grape juice has also been used to produce low-alcohol wines and beverages and to prevent wine and Kilka oil oxidation. Extracts have been used to enrich plant-based food with UG phenols. Table 4 shows the traditional and innovative UGPs and their applications in food and beverages. The antimicrobial properties of verjuice were highlighted for the first time by Karapinar and Sengun (2007) who studied the antimicrobial effect of a traditional verjuice (*V. vinifera* cv. Koruk) used as a flavouring and acidifying agent on cucumber and parsley inoculated with *S. typhimurium*. The authors observed an immediate reduction of the initial population, with the extent of the reduction varying depending on the strain tested. Hence, they proposed the Koruk verjuice as a potential alternative antimicrobial agent at the household level for salad vegetables. The antibacterial effect of traditional UGPs has been confirmed by Öncül and Karabiyikli (2016) who studied the survival of several pathogens (*E. coli, L. monocytogenes, S. typhimurium* and *S. aureus*) directly inoculated into five verjuices and five sour grape sauces. In this experiment, both gram-positive and gram-negative pathogens were inhibited after a period of 5 and 15 min of treatment depending on the dose of inoculated bacteria. The inhibitive effect of UGPs was ascribed to a combined effect of organic acid and phenolic compounds, and the authors concluded that UGPs have a self-protection system against inoculated pathogens. Other authors have tested the efficiency of marination liquids prepared with verjuice on the safety of meat products, indicating that verjuice has an antibacterial effect towards some of the common food-borne pathogens that could contaminate meat and poultry (Ozturk and Sengun 2019, Sengun et al. 2019).

In 2017, Tinello and Lante (2017) studied the anti-browning and antioxidant activity of verjuice obtained from Merlot and Barbera. The verjuices had different PPO activity inhibition capacities, antioxidant capacities and bleaching effects depending on the grape cultivar and vintage. The effect on browning of pretreating dried Golden Delicious apple slices by dipping in Merlot UG juice was studied by Tinello et al. (2018). Eighteen hours after drying at mild temperature of 45°C, the apple slices pretreated with verjuice showed both an improvement in antioxidant capacity and reduction in enzymatic browning. The increase in lightness and smaller colour change was ascribed to the inhibition of PPO activity.

More recently, Dupas de Matos et al. (2018) used a verjuice obtained by pressing UGs (cv. Sauvignon Blanc) as an acidic salad seasoning ingredient and evaluated consumer liking by comparing the salads seasoned with verjuice, lemon juice and white wine vinegar. Although the overall liking was significantly higher for salad seasoned with vinegar, the verjuice resulted in a viable alternative to lemon juice as a salad seasoning as it gave the salad similar sensory characteristics. Furthermore, the lack of the pungent acetic acid smell could make verjuice the preferred salad seasoning for those consumers who dislike the smell of vinegar. Due to its particular sensory properties, Dupas de Matos et al. (2019) proposed verjuice as a novel acidifying agent for pickled cucumber and compared it with traditional vinegar-pickled samples. Despite the chemical and sensory differences, the pickles preserved with verjuice and vinegar obtained similar overall liking scores for the visual, olfactory and gustatory aspects, suggesting that verjuice could be a potential alternative to vinegar for pickle production.

Among the different strategies to reduce the alcohol concentration and pH of wine, some authors have tested the use of UGs. Kontoudakis et al. (2011) used thinned UGs (cv. Grenache) for the production of an acidic and low-alcohol wine that was blended with a red wine produced with overripe grapes to reach a simultaneous decrease in pH and alcohol. Similarly, a mixture of must obtained from early and delayed harvest grapes (cv. Chardonnay) has been used to reduce the alcohol and pH of wine (Teslić et al. 2018). This alternative approach to moderate the effect of climate change on Chardonnay wine composition was effective, but it highlighted the risk of an excess of acidity and the perception of bitterness. Lemos Junior et al. (2019) investigated the innovative use of natural grape must obtained from unripe Glera grapes to produce low-alcohol beverages. The authors used a non-*Saccharomyces*, low alcohol-tolerant and high glycerol-producing yeast, *Starmerella bacillaris* and *Saccharomyces cerevisiae* in sequential fermentation. In this way, the authors observed an improvement in quality of the low-alcohol beverages by means of increasing the glycerol concentration and malic acid degradation, two properties with a great impact on the sensory quality of the product.

The effect of a microwave extract obtained from Ghure UG marc with the addition of methanol on Kilka oil oxidation was evaluated by Golmakani et al. (2017) in comparison with that of a common antioxidants such as α-tocopherol and butylated hydroxytoluene (BHT). Antioxidants were added to the Kilka oil at a concentration of 10, 100 and 1000 mg/L. The Ghure marc extract was more effective than α-tocopherol in reducing oxidation of the Kilka oil and similar to BHT. The incorporation of Ghure marc extract into Kilka oil can retard the oxidation of polyunsaturated fatty acids and the formation of oxidation by-products that can negatively impact the flavour of Kilka oil. The inhibitory effect of the Ghure marc extract against Kilka oil oxidation can be attributed to the presence of a high concentration of natural antioxidants such as phenolic and flavonoid compounds. An extract from UGs (cv. Sangiovese) was produced by maceration and, after spray drying, used as an anti-browning agent in different white wines (Fia et al. 2018). The extract was added to the wine at the dose of 2 g/L and the resistance to oxidation was tested after 1 h at 60°C, with the addition of 60 μL of a 3% hydrogen peroxide solution. Under these conditions, the addition of the Sangiovese UG extract to the white wines improved their antioxidant capacity with respect to that of the control wines and the UG extract displayed a similar effect to that of sulfur dioxide. The anti-browning effect of the UG extract can be attributed to the natural antioxidant complex of UGs that normally includes phenolic compounds, vitamins and glutathione. These compounds can protect wine colour through different mechanisms (Motta et al. 2020). More

Table 4. Traditional and innovative products obtained from unripe grape, production scale, and their application and effect in food and beverages.

UGP (No. of products tested)	Type of UGP	Production scale		Application	UGP effect	References
Verjuice (1)	Traditional	Experimental	Laboratory	Cucumber/Parsley	Antimicrobial	Karapinar and Sengun (2007)
Verjuice (7)	Traditional	Experimental/ commercial	Commercial	–	–	Nikfardjam (2008)
Verjuice (2)	Traditional	Experimental	Laboratory	–	–	Hayoglu et al. (2009)
Verjuice (4) Sour grape sauce (5)	Traditional	Experimental	Laboratory/commercial	–	Antioxidant	Öncül and Karabiyikli (2015)
Verjuice (5) Sour grape sauce (5)	Traditional	Experimental/ commercial	Laboratory/industrial	–	Antibacterial	Öncül and Karabiyikli (2016)
Dried unripe grapes	Traditional	Experimental	Laboratory	Cream zhater	Antioxidant	Hayoglu et al. (2016)
Verjuice (6)	Traditional	Experimental	Laboratory	–	Antioxidant	Dupas de Matos et al. (2017)
Verjuice (4)	Traditional	Experimental	Laboratory	Fruit	Antibrowning and antioxidant	Tinello and Lante (2017)
Verjuice (1)	Traditional	Experimental	Laboratory	Salad	Acidifying (seasoning)	Dupas de Matos et al. (2018)
Verjuice (1)	Traditional	Experimental	Laboratory	Fruit	Antibrowning and antioxidant	Tinello et al. (2018)
Sorbet (1)	Traditional	Experimental	Laboratory	–	Antioxidant	Ekici et al. (2018)
Verjuice (1)	Traditional	Experimental	Laboratory	Pickled cucumber	Acidifying (preservative)	Dupas de Matos et al. (2019)
Verjuice (1) with dried pomace	Traditional	Experimental	Laboratory	Meat	Antibacterial (preservative)	Ozturk and Sengun (2019)
Verjuice (1)	Traditional	Experimental	Laboratory	Poultry meat	Antibacterial (preservative)	Sengun et al. (2019)
Verjuice (4)	Traditional	Experimental	Laboratory	–	–	Salah Eddine et al. (2020)
Very acidic and low alcohol wine (1)	Innovative	Experimental	Pilot scale	Wine	pH and alcohol reducing	Kountodakis et al. (2011)
Marc extract (1)	Innovative	Experimental	Laboratory	Kilka oil	Antioxidant	Golmakani et al. (2017)
Very acidic and low alcohol wine (1)	Innovative	Experimental	Laboratory	Wine	pH and alcohol reducing	Teslić et al. (2018)
UG extract (1)	Innovative	Experimental	Commercial	Wine	Antioxidant	Fia et al. (2018)
Very acidic and low alcohol wine (8)	Innovative	Experimental	Pilot scale	Wine	pH and alcohol reducing	Piccardo et al. (2019)
Low alcohol beverage (1)	Innovative	Experimental	Laboratory	–	–	Lemos Junior et al. (2019)
UG extract (1)	Innovative	Experimental	Commercial	Vegetable food prototypes	Phenol enrichment	Bucalossi et al. (2020)
UG extract (1)	Innovative	Experimental	Commercial	–	–	Fia et al. (2020)
UG extract (1)	Innovative	Experimental	Commercial	Beetroot purée	Phenol enrichment	Proserpio et al. (2020)

UG, unripe grape; UGP, unripe grape product.

recently, a dried extract from UGs (cv. Merlot) was used to enrich three plant-based food models, mainly containing carbohydrates, starch and proteins, respectively, with phenolic substances. As expected, the inclusion of UG phenolic substances in plant-based food models increased the phenolic concentration and antioxidant activity of these foods. The phenolic concentration and antioxidant activity, however, in phenol-enriched foods varied as a function of their macro-composition. This indicates that the interaction of phenolic compounds with different macronutrients can influence both recovery of phenolic compounds and antioxidant activity (Bucalossi et al. 2020). It is well known that the formation of aggregates between phenolic substances and proteins lowers the extractability from raw material and the antioxidant activity of phenols (Ozdal et al. 2013). Moreover, phenolic compounds can interact with polysaccharides and the consequences of these interactions on phenolic antioxidant activity and extractability depend on the chemical characteristics of both phenolic compounds and polysaccharides (Zhang et al. 2014).

Applications in the human diet

In the literature, there are few studies on the beneficial effects of UGs in the human diet. Unripe grapes were cited among herbal remedies for oral and topical diseases in a recent review on traditional Persian medicine (Parvizi et al. 2020). This ancient use of UGs in folk medicine and the high concentration of condensed tannins in UGs induced some researchers to test UG juice as a natural remedy for lipid disorders to control hypertension (Zibaeenezhad et al. 2012) and to reduce the risk of atherosclerosis (Mousa-Al-Reza et al. 2011, Alipour et al. 2012), cancer (Yıkmış et al. 2020) and diabetes (Rasines-Perea and Teissedre 2017). The effect of UG juice on the lipid profile and blood pressure of human volunteers has been investigated with promising results by Alipour et al. (2012) and Zibaeenezhad et al. (2012).

Other applications

Other unusual applications of verjuice include its use as a biocatalyst. The synthesis of various organic compounds traditionally involves the use of catalysts which are often corrosive, hazardous or polluting. Due to its high concentration of organic acids, which can activate the carbonyl group of aldehydes, verjuice has been proposed as a green and cheap alternative to classical catalysts in the synthesis of pyranopyrazole derivatives and hexahydroquinoline-3-carboxamides (Mokhtary 2019) or 5-arylmethylenepyrimidine-2,4,6-trione, pyrano[2,3-*d*] pyrimidinone and pyrimido[4,5-*d*] pyrimidinone derivatives (Safari et al. 2019). In both cases, verjuice proved to be an efficient catalyst with good to excellent yields, and in one case (Safari et al. 2019) it proved to be reusable up to five times following regeneration with charcoal. The solid waste produced after verjuice extraction has also been proposed as a natural adsorbent to remove unwanted chemical compounds from wastewater. In particular, the dried and powdered solid UG waste was used to efficiently remove from water methylene blue, a cationic dye commonly used for dyeing fabrics, leather, plastics and paper (Ansari and Mosayebzadeh 2011). The UG powder demonstrated a high affinity for the dye, removing up to 100 mg of methylene blue per gram of powder. Moreover, it also proved to be partially regenerable (75–80%) upon washing with 0.1 mol/L HCl.

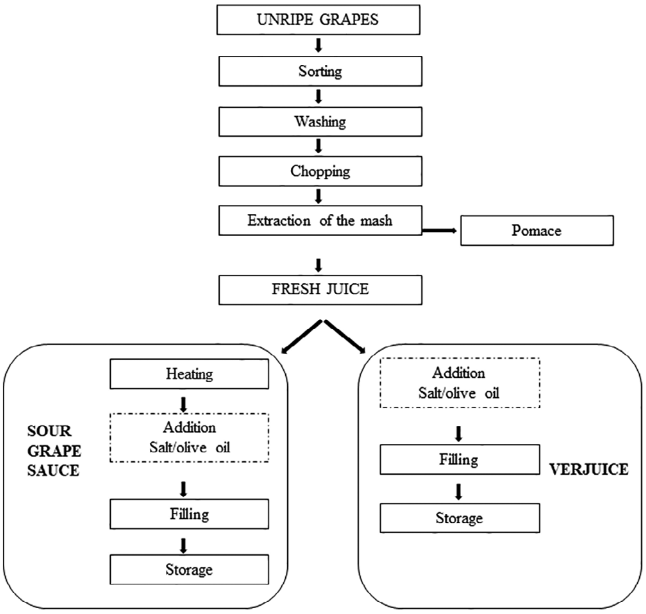

Figure 1. Flow diagram for the production of verjuice and sour grape sauce based on the traditional) method [adapted from Oncul and Karabiyikli (2015)].

Traditional production and emerging extraction techniques

Traditional techniques

The processing methods for the production of traditional UGPs consist of some steps common to both verjuice and sour grape sauce preparation (Figure 1). Öncül and Karabiyikli (2015) described the processing technique applied for laboratory production. The UGs are washed, chopped, the juice is extracted by squeezing and the pomace is discarded. Then, salt and/or olive oil are added to the verjuice and the product is bottled and stored. For the sour grape sauce production, the addition of salt and/or olive oil is also required. The main difference between verjuice and sour grape sauce is the heating step. There are three heating steps in the production of the commercial samples. First, fresh juice was concentrated and stored. Then, this concentrate was diluted and re-heated and the final heat treatment was applied after bottling (Öncül and Karabiyikli 2015).

Emerging techniques

Extraction techniques for UG have received scarce attention in the literature and the majority of the published research has been undertaken with juice obtained by pressing the UGs at laboratory scale. Recently, a green technique for production of UG extract at a commercial level was proposed by Fia et al. (2018) and improved by introducing a pomace pressing step (Fia et al. 2020) (Figure 2). The innovative maceration system and operating procedure to produce UG extracts were described by some authors (Fia et al. 2016, 2018, 2020). The proposed technique to improve the extraction was conducted with the aid of a patented tank that was coated with insulating material on 75% of the surface and equipped with an efficient internal movement system. The grapes were cooled by adding dry ice and the gaseous CO_2 developed was recovered. The liquid extracts were analysed step by step during production, and the final values of the total phenolic compounds and antioxidant activity were higher with respect to most of what was observed for other

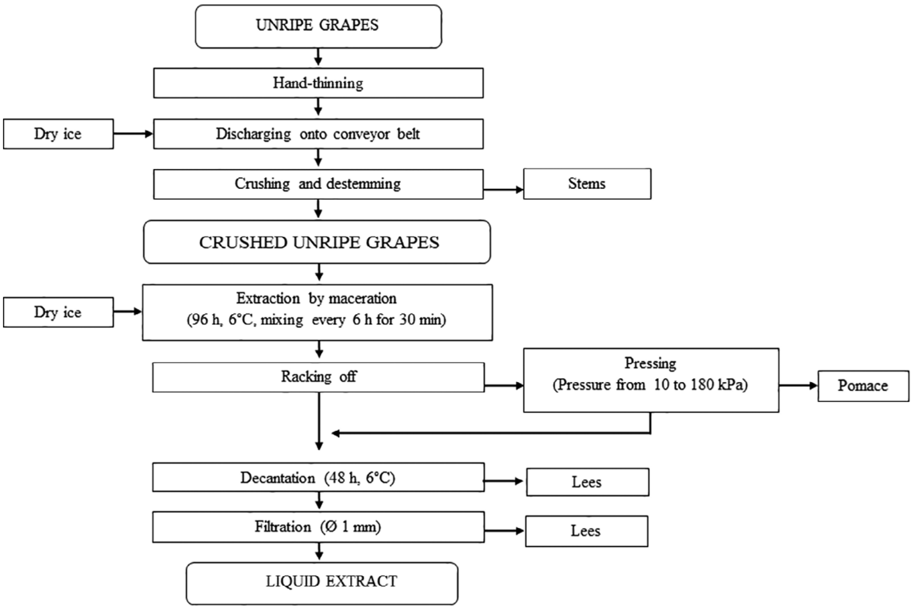

Figure 2. Flow diagram for the production of the extract from unripe grapes [adapted from Fia et al. 2020].

UGPs (Table 1). This production technique is thought to aid the reuse of residues inside the winery. It requires a low temperature that protects the extract from oxidative damage. Moreover, no solvents or preservatives are used during production or storage. The liquid extract can be dehydrated by spray drying or lyophilisation. In this way, the powder maintains its antioxidant activity during storage for approximately 1 year (Bucalossi et al. 2020).

Owing to the complexity of the matrix and considerable economic interest, there has been wide investigation into the extraction techniques to obtain a high recovery of valuable natural compounds from the by-products of grape transformation, that is, pomace and lees. Traditional extraction techniques have gradually been replaced by novel, efficient and green extraction methods to increase the sustainability of the process (Barba et al. 2016, Castro-Muñoz et al. 2016). There has been little application, however, of these novel extraction techniques to UGs, although ultrasound treatment has been applied to increase the extraction of bioactive components in verjuice vinegar (Yıkmış et al. 2020).

The non-extractable polyphenols (NEPs) in UGs are another aspect that deserves to be investigated. The group of NEPs includes polyphenols that are bound in plant matrices; they make up a high proportion of the total phenolic compounds of these raw materials. The NEPs can provide as much as 70–90% of the total antioxidant activity of some vegetable matrices (Dzah et al. 2020). The NEPs from by-products have high potential for use in industry, especially in pharmaceutical, nutraceutical and cosmetic applications.

Conclusion and future perspectives

In conclusion, UGs appear to be a promising waste product, containing several compounds with important biological activity that could be exploited in food and beverages, including wine. There is still a dearth of data, however, on the composition of UGs during the berry development mainly in relation to some active compounds such as vitamins and polysaccharides. It would be interesting to have more information about the in vitro and in vivo bioavailability of UG compounds in comparison with ripe grapes and their effect on human health. The UG extracts could be used as natural antioxidant alternative to chemical products. In the future, depending on the results obtained, the wine and grape industry could adopt appropriate strategies to exploit these valuable residues from viticulture.

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Author Contributions

All the authors have contributed significantly and are in agreement with the manuscript.

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