Wine lees from the 1st and 2nd rackings: valuable by-products

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Abstract Phenolic compounds of the first and second racking wine lees, including anthocyanins, were qualitatively and quantitatively analyzed by HPLC–DAD–MS. Wine lees from both rackings displayed similar chromatographic profiles. Therefore, it was impossible to differentiate the qualitative results regarding phenolic compounds. On the other hand, those from the second racking presented, on average, concentration of polyphenols twice as high. While the ones from the first racking displayed ca. 1600 mg phenolic compounds and 400 mg anthocyanins per kg of dry matter, those from the second racking have shown ca. 3300 mg phenolic compounds and 700 mg anthocyanins per kg of dry matter. These outcomes indicate that, although the wine lees from the first racking can be employed as a resource for phenolic compounds recovery, those from the second racking are more appropriate for this purpose.

Keywords Wine lees · Anthocyanin · Phenolic compounds · First racking · Second racking · Polyphenols

Introduction

In 2017, the production of wine throughout the world was estimated in 250 million hectoliters (OIV 2018), making the wine industry stand out as one of the main agro-industrial business in the world, especially in countries from the Mediterranean region (Ruggieri et al. 2009). During the winemaking process, a huge amount of wastes are generated (Devesa-Rey et al. 2011), representing more than 20% of the total wine produced, i.e., thousands of tons of winery wastes are generated, annually. In fact, although grape pomace is the most produced organic waste in wineries, representing around 62% of the total waste, wine lees, stalks and dewatered sludge are also generated in large quantities, representing ca. 14%, 12%, and 12%, respectively (Ruggieri et al. 2009). Other authors state that wine lees account for 25% of the total solid wastes (Oliveira and Duarte 2016).

Indeed, these wastes are characterized as highly polluting, presenting a high organic charge and also phytotoxic and antibacterial phenolic substances that are resistant to biological degradation (Devesa-Rey et al. 2011). On the other hand, winery wastes are rich in phenolic compounds, mainly phenolic acids, flavonoids, flavanols, stilbenes, and flavonols (Ramirez-Lopez and DeWitt 2014), being a cheap source for the recovery of these compounds. In addition, phenolic compounds have strong antioxidant properties, being important to the production of phytochemicals or food supplements (Rockenbach et al. 2011).

Grape pomace and wine lees are the most generated winery wastes. Up to now, researches are mainly addressed

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to grape pomace (Iora et al. 2015; Kammerer et al. 2014; Rockenbach et al. 2011). There are only a couple of works employing lees as a source for the recovery of antioxidants (Dimou et al. 2016; Giacobbo et al. 2017; Pérez-Serradilla and Luque de Castro 2011). This fact is entirely related to the scarcity of information about lees, since only a few studies displaying the chemical characterization of wine lees were found (Barcia et al. 2014; Delgado de la Torre et al. 2015).

Lees are separated from the wine in an operation called racking, which siphons the wine from one container to the next, to separate it from the sediment, i.e., from the lees. The lees from the 1st racking are derived from the alcoholic fermentation, while the ones from the 2nd racking resulted from the malolactic fermentation. In the studies from Alonso et al. (2002) and Barcia et al. (2014), no distinction was made between from which racking, the first or the second, the wine lees are derived. In fact, wine lees have been disregarded or have acquired much less attention than other wastes and they are still considered an under-valued by-product. In this sense, the present work aims to provide additional information through the determination of the phenolic compounds of the 1st and 2nd racking wine lees by high-performance liquid chromatography coupled to photodiode array and mass spectrometry detectors (HPLC–DAD–MSⁿ), in order to add value to these wastes, transforming them into inputs that can be used in the cosmetic, pharmaceutical or food industry, which already use polyphenol-rich extracts as feedstock (Beres et al. 2017).

Materials and methods

Chemicals

Catechin, epicatechin, quercetin, myricetin, kaempferol, gallic acid, *t*-resveratrol, *p*-coumaric acid, *m*-coumaric acid, 5-caffeoylquinic acid, ferulic acid, caffeic acid, tyrosol and cyanidin-3-glucoside were purchased from Sigma–Aldrich (Brazil). The solvents used for extraction and HPLC analyzes were analytical/HPLC grade and purchased from J. T. Baker (USA) or Merck (Brazil). Folin–Ciocalteu reagent, 2,4,6-tris(2-pyridyl)-1,3,5-triazine, was acquired from Fluka Chemie AG (Switzerland). Ultrapure water was produced through a Milli-Q system from Millipore (USA). Millipore membranes (0.45 µm pore size) were applied to the filtration of solvents and samples.

Samples

Wine lees generated in 1st and 2nd racking of red wine-making using Merlot grapes, harvested in 2013, were

supplied by a winery from Vale dos Vinhedos Region (Bento Gonçalves, Brazil). The lees were stockpiled at $-20\text{ }^{\circ}\text{C}$ and brought up to room temperature prior to use. The 1st and 2nd racking wine lees presented a total solids content of 204 and 11 g L⁻¹, respectively. All the wine lees were lyophilized at $-50\text{ }^{\circ}\text{C}$ below 40 mbar in a freeze dryer (Thermo Fisher Scientific, USA) to obtain a powder.

Extraction of phenolic compounds

Lyophilized samples, in amounts of 100 mg of wine lees, from both rackings, were extracted with 10 mL of a mixture 80:18.5:1.5 (V/V/V) of methanol/water/formic acid, helped by vortex, during 5 min and then centrifuged at 7000 rpm (5038 g) at room temperature (25 °C) for 5 min. Up to five extractions of the samples pellets resulted in approximately 99% of the phenolic content, as confirmed by the Folin–Ciocalteu method (Singleton and Rossi 1965) of successive extractions (up to seven). The extracts were concentrated in a rotary evaporator (IKA-Werke GmbH, Model RV-05 ST, Germany) at 30 °C and re-suspended in 5 mL of methanol. Each experiment was performed in triplicate.

HPLC–DAD–MSⁿ analysis

HPLC–MS was applied to determine the phenolic compounds on the solutions. The HPLC equipment (Shimadzu, Japan) was equipped with two LC-20AD pumps, an online degasser, an auto-injector, and a photodiode array detector (DAD). This chromatography system was coupled, in series, to an ion trap mass spectrometer, model Esquire 6000 from Bruker Daltonics (Germany), with an electrospray ionization (ESI) source.

The separation of phenolic compounds was performed based on the methodology presented in a previous work (Rodrigues et al. 2013). Briefly, a reversed-phase C18 column (250 mm × 4.6 mm, particle size 4 µm), model Synergi Hydro-RP 80A from Phenomenex (USA), thermostated at 29 °C, was employed. Run time was 70 min and the flow rate was 0.7 mL min⁻¹. The mobile phase consisted of solvent A (water/formic acid, 99.5:0.5, V/V) and solvent B (acetonitrile/formic acid, 99.5:0.5, V/V). During 50 min, a linear gradient from 99:1 (V/V) A/B to 50:50 (V/V) A/B was adopted. After that, a gradient from 50:50 (V/V) A/B to 1:99 (V/V) A/B was employed over 5 min, and maintained for 5 more minutes. After 2 min, the initial condition 99:1 (V/V) A/B was restored and maintained for an additional 8 min. The UV–Vis spectra were acquired from 200 to 600 nm, such that the chromatograms were accomplished at 280, 320, 360 and 520 nm for the

Fig. 1 HPLC–DAD chromatograms of phenolic compounds in wine lees from the 1st and 2nd rackings monitored at: **a** 280 nm, **b** 320 nm, and **c** 360 nm. Peak numbers correspond to those indicated in Table 1

detection of flavan-3-ols, hydroxycinnamic acids, flavonols, and anthocyanins, respectively.

The column eluate was partitioned to permit only about 0.35 mL min^{-1} to enter the ESI interface. A scan range between 100 and 800 m/z was used to acquire the mass spectra. For anthocyanins, the MS operating conditions were: ESI source in positive ionization mode; capillary voltage, 2500 V; skimmer, 40 V; dry gas (N_2) temperature, 325°C ; flow rate, 11 L min^{-1} ; nebulizer gas, 30 psi; and fragmentation energy of 1.6 V. For the other phenolic compounds, the MS operation conditions were: ESI source in negative mode; capillary voltage, -3000 V ; skimmer, -72 V ; flow rate, 8 L min^{-1} ; nebulizer gas, 30 psi; dry gas (N_2) temperature, 310°C ; and fragmentation energy of 1.6 V.

The identification of phenolic compounds was based on: (1) retention time and elution order in the chromatographic column; (2) UV–Vis and MS spectra, compared to analytical standards analyzed under the same conditions; (3) data from the literature. The quantification was performed by HPLC–DAD, using ten-point analytical curves (linear, $r^2 \geq 0.996$) of their respective standards, with

concentrations ranging from 0.1 to 10 mg L^{-1} for anthocyanins and from 0.5 to 100 mg L^{-1} for the other phenolic compounds. The total contents of anthocyanins (TA) and of phenolic compounds (TPC) were calculated from the total sum of the chromatographic areas corresponding to all the identified peaks for anthocyanins and for other phenolic compounds, respectively. All analyzes were conducted in three replicates.

Results and discussion

Phenolic compounds

In Fig. 1 is shown the chromatographic profile of the lyophilized wine lees generated in the 1st and 2nd rackings of Merlot red wine production, showing no qualitative difference in terms of phenolic compounds. In both samples, eight majoritarian phenolic compounds were separated by HPLC, being six of them identified or tentatively identified grounded on the methodology presented at Sect. 2.4, including data from the literature (Bimpilas et al. 2015;

Table 1 Identification of the phenolic compounds present in first and second racking wine lees ($n = 3$)

Peak n.	t_R (min)	λ_{max} (nm)	MS^- (m/z)	MS^{2-} (m/z)	Identity
1	11.4	270	169	125	Gallic acid ^a
2	21.1	279	447	285	Kaempferol-3- <i>O</i> -galactoside ^b
3	23.2	276	491	329/302/221	n.i.
4	25.4	277	479	317	Myricetin-3- <i>O</i> -glucoside ^b
5	28.7	278	477	301	Quercetin-3- <i>O</i> -glucuronide ^b
6	32.5	201	—	—	n.i.
7	34.2	372	317	179/151	Myricetin ^a
8	40.1	371	301	151/179	Quercetin ^a

n.i. not identified

Identity based on: ^acommercial standards; ^bliterature data (e.g. mass spectra and elution order)

Simirgiotis et al. 2009; Vallverdú-Queralt et al. 2015; You et al. 2012). Data from 13 analytical standards of phenolic compounds (retention time, elution order, UV–Vis, and mass spectra) were also utilized to endorse their presence or absence.

Peaks 1, 7, and 8 were assigned as gallic acid, myricetin, and quercetin, respectively, based on their retention time, elution order, UV–Vis, MS spectra and MS^2 fragmentation patterns (Fig. 1 and Table 1), which are the same that the one achieved with analytical standards, as well as the data previously informed in the literature (Vallverdú-Queralt et al. 2015; You et al. 2012). Based on Barcia et al. (2014) and grounded in its mass spectra data, peak 2 was tentatively identified as kaempferol-3-*O*-galactoside. Once in the negative ionization mode, the MS presented the deprotonated molecule $[M - H]^-$ at m/z 447, while the MS^2 spectrum displayed a peak at m/z 285 $[M - H - 162]^-$ that corresponds to the elimination of a dehydrated hexose.

Peak 4 was tentatively assigned as myricetin-3-*O*-glucoside, showing a $[M - H]^-$ ion at m/z 479 and a MS^2 spectrum with a peak at m/z 317 $[M - H - 162]^-$ that, similarly to the peak 2, is related to the loss of a dehydrated hexose. Besides, its retention time and mass spectra match the data reported by Bimpilas et al. (2015).

The MS of peak 5, in the negative ionization mode, displayed the deprotonated molecule $[M - H]^-$ at m/z 477 and a MS^2 spectrum with a peak at m/z 301 $[M - H - 176]^-$, which results from the cleavage of a dehydrated glucuronic acid. Considering that at m/z 301 units the ion is consistent with the structure of the aglycone quercetin, peak 5 was tentatively identified as quercetin-3-*O*-glucuronide, being the mass spectra data in line with the one previously described in the literature (Vallverdú-Queralt et al. 2015).

As it can be seen in Fig. 2, except for kaempferol-3-*O*-galactoside and quercetin, that are analogous in both 1st and 2nd racking wine lees, the wine lees from the 2nd racking displayed the concentration of phenolic

Fig. 2 Phenolic compounds present in first and second racking wine lees. The numbers are correspondent to the phenolic compounds reported on Table 1 and TPC is the total phenolic compounds. The data are expressed as mean $\pm$ SD ($n = 3$)

compounds from 2.4 to 4.8 times higher than the ones from the 1st racking. Quercetin- and myricetin-derivatives, as expected, were found in larger amounts than other phenolic compounds, since these ones are reported as the main flavonols naturally found in grapes and wines from Merlot cultivar (Castillo-Muñoz et al. 2007). Furthermore, the high proportion of free flavonol aglycones (ca. 60% and 75% at 1st and 2nd racking, respectively), can be related to their very low solubility, which results in their precipitation concurrent with sedimentation of lees (Barcia et al. 2014).

Anthocyanins

As it was already shown for phenolic compounds, both the wine lees generated in the 1st and 2nd rackings of Merlot red wine production displayed no qualitative difference regarding anthocyanins. In this sense, fifteen anthocyanins from freeze-dried 1st and 2nd racking wine lees were separated by HPLC (Fig. 3), being 12 tentatively identified based on the combined information obtained from chromatographic elution on a C_{18} column and from

Fig. 3 HPLC–DAD chromatograms of anthocyanins in wine lees: **a** Wine lees from the 1st racking, and **b** Wine lees from the 2nd racking, monitored at 520 nm. Peak numbers correspond to those indicated in Table 2

characteristics of UV–Vis and mass spectra data (Table 2), comparing all these results with the data reported in the literature (Acevedo De la Cruz et al. 2012; Ginjom et al. 2011; Lopes-Lutz et al. 2010; Núñez et al. 2004; Papoušková et al. 2011; Pomar et al. 2005; Ruiz et al. 2013; Stefova and Ivanova 2011). All the identified anthocyanins are derivatives of 6 anthocyanidins (delphinidin, cyanidin,

petunidin, peonidin, pelargonidin and malvidin) and classified into three groups, according to their acylation: anthocyanidin-3-hexosides, 3-(6-acetyl)-hexosides, and 3-(6-coumaroyl)-hexosides.

Peak 1 was tentatively assigned as delphinidin-3-hexoside, showing a $[M]^+$ ion at m/z 465 and a MS^2 spectrum with a peak at m/z 303 $[M - 162]^+$ that corresponds to the elimination of a dehydrated hexose (162 Da), as also proposed by other authors (Ginjom et al. 2011; Núñez et al. 2004; Papoušková et al. 2011; Pomar et al. 2005). With a $[M]^+$ ion at m/z 449 and a MS^2 spectrum with a peak at m/z 287, that also corresponds to the elimination of a dehydrated hexose, peak 2 was tentatively identified as cyanidin-3-hexoside, matching with data previously published (Ginjom et al. 2011; Núñez et al. 2004; Pomar et al. 2005).

Peaks 3, 6 and 10 were assigned as petunidin-derivatives, being these petunidin-3-hexoside, petunidin-3-(6-acetyl)-hexoside and petunidin-3-(6-coumaroyl)-hexoside, respectively, with $[M]^+$ ions at m/z 479, 521 and 625. All these compounds presented the fragment corresponding to the anthocyanidin, m/z 317, as well as UV–Vis spectral features in accordance with the literature (Acevedo De la Cruz et al. 2012; Ginjom et al. 2011; Lopes-Lutz et al.

Table 2 Identification of the anthocyanins present in first and second racking wine lees ($n = 3$)

Peak n.	t_R (min)	λ_{max}	MS^+ (m/z)	MS^{2+} (m/z)	Identity ^a
1	19.2	282/328/523	465	303	Delphinidin-3-hexoside
2	20.8	278/517	449	287	Cyanidin-3-hexoside
3	21.3	277/527	479	317	Petunidin-3-hexoside
4	23.2	278/527/621	463/432/493	463 → 301, 432 → 133, 493 → 331	Peonidin-3-hexoside/pelargonidin-3-hexoside/malvidin-3-hexoside ^b
5	24.7	275/515	561	399	Malvidin-3-hexoside-pyruvate
6	26.3	283/527	521	317	Petunidin-3-(6-acetyl)-hexoside
7	28.4	278/523	535	331	Malvidin-3-(6-acetyl)-hexoside
8	29.1	252/366/530	611	303	Delphinidin-3-(6-coumaroyl)-hexoside
9	30.1	281/523	595	287	Cyanidin-3-(6-coumaroyl)-hexoside
10	30.6	280/530	625	317	Petunidin-3-(6-coumaroyl)-hexoside
11	30.8	271/523	639	331	Malvidin-3-(6-coumaroyl)-hexoside
12	32.6	281/523/657	609	463/301	Peonidin-3-(6-coumaroyl)-hexoside
13	33.3	275/504	609	447	n.i.
14	35.5	278/504	651	447	n.i.
15	37.3	283/505	755/725	755 → 447 725 → 417	n.i.

n.i. not identified

^aIdentity based on mass spectra and elution order from literature data (Ginjom et al. 2011; Núñez et al. 2004; Papoušková et al. 2011; Pomar et al. 2005; Ruiz et al. 2013)

^bMix of three anthocyanins

2010; Núñez et al. 2004; Papoušková et al. 2011; Pomar et al. 2005).

A mixture of three compounds resulted in peak 4: peonidin-3-hexoside, pelargonidin-3-hexoside, and malvidin-3-hexoside. These ones showed $[M]^+$ ions at 463, 432 and 493 and MS^2 spectrum with fragments that correspond to their anthocyanidins, well marked by the loss of the hexose moiety (Núñez et al. 2004; Papoušková et al. 2011).

Peaks 5, 7 and 11 are malvidin-derivatives, which correspond to malvidin-3-hexoside-pyruvate, malvidin-3-(6-acetyl)-hexoside, and malvidin-3-(6-coumaroyl)-hexoside, respectively, with $[M]^+$ ions at m/z 561, 535 and 639 and MS^2 spectra with peaks at m/z 399 (peak 5) and 311 (peaks 7 and 11). These MS^2 data, respectively, correspond to the loss of a dehydrated hexose (162 Da), a dehydrated hexose plus an acetyl radical (204 Da) and a dehydrated hexose plus a coumaroyl radical (308 Da), being in line with the ones reported in the literature (Núñez et al. 2004; Papoušková et al. 2011; Stefova and Ivanova 2011).

The peaks 8, 9 and 12, likewise peaks 10 and 11, are classified into the group of *p*-coumaroyl derivatives. Peak 8 was tentatively identified as delphinidin-3-(6-coumaroyl)-hexoside, showing a $[M]^+$ ion at m/z 611 and a MS^2 spectrum with a peak at m/z 303 corresponding to anthocyanidin (Núñez et al. 2004). Similarly to what has been reported by Núñez et al. (2004), peak 9 was tentatively assigned as cyanidin-3-(6-coumaroyl)-hexoside, since it presents a $[M]^+$ ion at m/z 595 and a MS^2 fragment at m/z 287, being the last one consistent with their anthocyanidin moiety, the cyanidin. Peak 12 was tentatively identified as peonidin-3-(6-coumaroyl)-hexoside, with a $[M]^+$ ion at m/z 609 and a MS^2 spectrum with peaks at m/z 301 and 463. According to Núñez et al. (2004), the fragment with m/z 463 corresponds to peonidin-3-hexoside, while the one with m/z 301 matches to the elimination of a dehydrated hexose plus a coumaroyl radical (308 Da).

Figure 4 shows that the lees generated in the 2nd racking present concentration of anthocyanins from 3 to 11 times higher than the ones from the 1st racking, except for peonidin-derivatives that is similar in both the wine lees. A high amount of peonidin and its derivatives in 1st racking wine lees can be grounded on the basis that yeasts correspond to 60–70% of the 1st racking wine lees (Léauté 1990), and their adsorption in yeasts is slightly greater than the other anthocyanins (Morata et al. 2003). Additionally, in the 1st racking wine lees, cyanidin-3-hexoside (peak 2), petunidin-3-(6-acetyl)-hexoside (peak 6), and petunidin-3-(6-coumaroyl)-hexoside (peak 10) were found below the quantification limit.

In fact, we have found that, in terms of phenolic compounds including anthocyanins, in general, the wine lees from the 2nd racking are richer than those from the 1st

Fig. 4 Anthocyanins present in first and second racking wine lees. The numbers are correspondent to the anthocyanins reported on Table 2 and TA is the total anthocyanins. The anthocyanins were quantified as cyanidin-3-glucoside equivalent. The data are expressed as mean $\pm$ SD ($n = 3$)

racking. These outcomes were expected, since wine lees from 1st and 2nd rackings were collected after alcoholic and malolactic fermentations, respectively. Therefore, taking into account their inherent characteristics, the wine lees generated at the alcoholic fermentation present coarser material, i.e., higher total solids content. According to Fornairon-Bonnefond et al. (2001), first racking wine lees present approximately 25% dry matter, which, in turn, consists of 25–35% tartaric salts, 35–45% microorganisms (predominantly yeasts), 30–40% organic residues. On the other hand, the wine lees generated during the malolactic fermentation contain insoluble compounds that precipitate during the stabilization process, like tartrates, polyphenols, polysaccharides, as well as other organics, besides lactic bacteria and yeasts. As a matter of fact, the amount of phenolic compounds that we found in the 2nd racking wine lees is comparable to the one that other authors (Barcia et al. 2014) achieved in grape pomace, thus qualifying these wastes as an outstanding source of phenolic compounds that could be used in pharmaceutical, cosmetic and food industries. In this sense, according to Beres et al. (2017), nowadays there are already commercial food supplements with polyphenols extracted from grape by-products, which highlights the commercial potential of wine lees.

Conclusion

Summing up, the wine lees from both rackings displayed similar chromatographic profiles, showing no qualitative difference in terms of phenolic compounds. Although the wine lees from the 1st racking present a much higher amount of total solids, the ones from the 2nd racking were,

on average, twice richer in phenolic compounds than those from the 1st racking.

Bearing in mind just the quantified compounds, the wine lees from the 2nd racking presented ca. 700 mg anthocyanins and 3300 mg phenolic compounds per kg of dry matter, while the ones from the 1st racking showed ca. 400 mg anthocyanins and 1600 mg phenolic compounds per kg of dry matter.

Indeed, the recovery of phenolic compounds from wine lees brings economic and environmental benefits. However, in cases in which it is not possible to subject all the lees generated in the winemaking process to recover phenolic compounds, the ones from the 2nd racking could be prioritized, since they present higher phenolic contents, similar to what is found in grape pomace—a well-known source employed for this purpose.

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