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Polyphenols Extraction from Different Grape Pomaces Using Natural Deep Eutectic Solvents

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Abstract: Exploiting by-products from the oenological industry to extract antioxidant chemicals is a shared goal that combines the need to reduce the wine sector's environmental impact with the need to improve the availability of these biomolecules, according to a circular economy approach. Natural deep eutectic solvents (NaDES) have recently captured researchers' interest as a safer and more environmentally friendly alternative to traditional solvents due to their effectiveness, low toxicity, and stability. In this work, we set out to investigate several NaDES for the extraction of phenolic chemicals from local monovarietal grape pomace resulting from different vinification procedures (including both red and rosé vinification of Negroamaro and Primitivo grapes; rosé vinification of Susumaniello grapes and white vinification of Chardonnay, Fiano and Malvasia bianca grapes), with the additional goal of generalizing the use of NaDES to extract chemicals of interest from organisms selected from the wide plant biodiversity. Three binary choline chloride-based NaDES (DES-Lac, DES-Tar, and DES-Gly, with lactic acid, tartaric acid, and glycerol as hydrogen bond donors, respectively) were compared to ethanol as a conventional solvent, and the extracts were evaluated using HPLC/MS and colorimetric techniques. The results revealed that each NaDES produces a substantially higher total phenolic yield than ethanol (up to 127.8 mg/g DW from Primitivo rosé grape pomace). DES-Lac and DES-Tar were more effective for anthocyanins extraction; the most abundant compound was malvidin 3-O-glucoside (highest extraction yield with DES-Lac from Susumaniello pomace: 29.4 mg/g DW). Regarding phenolic compounds, DES-Gly was the most effective NaDES producing results comparable to ethanol. Unexpectedly, Chardonnay pomace has the greatest content of astilbin. In most cases, grape pomace extracts obtained by rosé and white vinification provided the maximum yield. As a result, NaDES have emerged as a viable alternative to traditional organic solvent extraction techniques, allowing for higher (or equal) yields while significantly lowering costs, hazards, and environmental impact.

Keywords: anthocyanins; antioxidants; polyphenols; NaDES; green chemistry; waste valorization; circular economy

Citation: Frontini, A.; Luvisi, A.; Negro, C.; Apollonio, M.; Accogli, R.; De Pascali, M.; De Bellis, L. Polyphenols Extraction from Different Grape Pomaces Using Natural Deep Eutectic Solvents. *Separations* **2024**, *11*, 241. https://doi.org/10.3390/separations11080241

Academic Editors: José Manuel Romero-Márquez and Alfonso Varela-López

Received: 17 July 2024
Revised: 30 July 2024
Accepted: 6 August 2024
Published: 8 August 2024

1. Introduction

Grape pomace is considered the most abundant by-product of the winemaking process [1]. Globally, vineyard surface area is gradually declining, despite a relatively stable wine production volume [2], maybe because of rising yield per hectare. As a result, there are still a lot of winery by-products created; it is estimated that 10 to 13 million tons of grape pomace are produced annually worldwide [3]. Minimal amounts of stalk residue are present in this biomass, which is primarily made up of grape seeds and skins [4]. Grape

pomace is currently utilized in part by distilleries to recover ethanol and generate standard spirits, but it is more typically a cost than a resource for winemakers.

Furthermore, the disposal of winery by-products has a negative environmental impact due to their high antioxidant and antibacterial activity, which prohibits other applications [5]. For this reason, the carbon footprint associated with grape pomace in Italy for the 2016 vintage was estimated to be 834,300 tons [6]. On the other hand, this by-product contains various high-value fractions, including lipids, proteins, oligosaccharides, minerals, dietary fibers, pectic chemicals, and, above all, antioxidants [7]. According to Lucarini et al. [8], the most important fractions found in waste biomasses in a biorefinery approach include fine chemicals used in medicine manufacture and compounds used as food and health supplements (including phenolic compounds). This is due to the significant economic potential acquired from the critical role these biomolecules play in human health [9], making grape pomace a plentiful and low-cost source of them. The polyphenolic composition varies according to grape cultivar, growing location, vinification method, and other factors [4]. The principal ingredients are anthocyanins and flavan-3-ols, but flavanols, phenolic acids, and stilbenes are also found in significant proportions [10]. Over the previous two decades, the international wine market has seen a decline in red wine demand while increasing demand for white and rosé wines [11]. Maceration is absent or shorter in white and rosé wine production than in red vinification, resulting in a much-reduced process of solvation of molecules (including polyphenols) from the solid phase to the liquid phase. As a result, red vinification pomace is made up of fermented biomasses, as opposed to those used in rosé and white winemaking, which are partially or not fermented. To date, current methods of extracting these chemicals have serious environmental consequences [12], making the quest for alternatives a critical need. In recent years, there has been a growing interest in deep eutectic solvents as green alternatives to traditional organic solvents. According to Abbott et al. [13], these solvents are classified into five kinds depending on the nature of hydrogen bond acceptors (HBA) and donors (HBD) [14]. Type III DES are the most employed for extracting hydrophilic polar chemicals; they are made up of a quaternary ammonium salt (HBA), usually choline chloride (ChCl), and several classes of molecules (HBDs), primarily organic acids, alcohols, amides, and sugars [14]. Because of the large number of potential starting molecules, these solvents have several appealing properties, including non-toxicity, low cost, affordability, ease of preparation, good stability, and the flexibility to be customized [15]. If derived from bio-based natural metabolites, they are known as NaDES (Natural Deep Eutectic Solvents) [16]. Several NaDES have been investigated for phenolic extraction from various natural biomasses, including grape pomace, but further research is needed to fully understand the behavior and potential of these solvents. Loarce et al. [17] and Iannone et al. [18] extracted phenolics from red grape pomace using NaDES, a mixture of choline chloride, lactic acid, and tartaric acid, although neither used the ultrasound-assisted extraction (UAE) approach. Other authors [19] reported UAE results on red grape skins using a choline chloride and glycerol-based NaDES, but at a different molar ratio. In addition, no works on NaDES extraction from grape pomace arising from three different vinification processes can be found in the literature. The goal of this work is to test different NaDES for their efficiency and effectiveness in extracting specific phenolic compounds from grape pomace, as well as to assess the potential of a green and safe extraction of bioactive molecules for waste biomasses valorisation; the results could represent a further step in the research on this topic, offering a characterization of the phenolic profile of local monovarietal grape pomace produced by different winemaking methods. We compared three NaDES (choline chloride as a hydrogen bond acceptor and lactic acid, tartaric acid, and glycerol as hydrogen bond donors) with 60% ethanol as a traditional solvent for phenolic compounds UAE extracted from several monovarietal grape pomaces. We used pomace from different local cultivars and vinification methods resulting in eight samples: two from red vinification (Negroamaro and Primitivo cultivars), three from rosé vinification (Negroamaro, Primitivo, and Susumaniello cultivars), and three from white vinification (Chardonnay, Fiano, and Malvasia bianca cultivars). Lactic acid,

tartaric acid, and glycerol are approved food additives in the EU [20], (also known as E270, E334, and E422, respectively); choline is an essential component of the human diet [21], and it is frequently added as choline chloride in commercially available formulas, with a daily tolerable upper intake level of approximately 3.5 g for adults [22].

2. Materials and Methods

2.1. Chemicals

Choline chloride (≥98%) was obtained from PanReac Química SLU (Castellar del Vallès, CT, Spain); acetonitrile, hexane (≥97%), DL-lactic acid (≥90%), glycerol (≥99%), L(+)-tartaric acid (≥99.5%), Folin-Ciocalteu reagent, gallic acid malvidin-3-glucoside (oenin chloride), (+)catechin, quercetin-3-β-D glucoside and kaempferol-3-*O*-glucoside were purchased from Sigma-Aldrich (St. Louis, MO, USA); formic acid, ethanol and bi-distilled water were obtained from VWR SAS (Fontenay-sous-Bois, France), sodium carbonate was purchased from Carlo Erba reagent SpA (Rodano, Milano, Italy).

2.2. Grape Pomace

Monovarietal grape pomaces obtained from different *Vitis vinifera* L. cultivars and vinification methods in the 2023 vintage were supplied by a local winery (Apollonio Casa Vinicola, Monteroni di Lecce, Lecce, Italy): two grape pomaces from red vinification process (five days maceration, from cultivars Negroamaro and Primitivo), three from rosé vinification process (two hours maceration, from cultivars Negroamaro, Primitivo and Susumaniello) and three from white vinification process (no maceration, from cultivars Chardonnay, Fiano and Malvasia bianca) were collected between 23 August 2023 and 29 September 2023 and immediately stored at −80 °C. Then, a representative sample from each monovarietal pomace was used to determine the dry weight, by leaving the sample in oven at 105 °C until constant weight; the dry weight was calculated as follows:

$$DW\ (\%) = (W1 \times 100)/W2 \quad (1)$$

where, W1 is the dry weight of the sample after exposure to 105 °C, and W2 is the fresh weight of the same sample before exposure to 105 °C.

At the same time, the various monovarietal pomaces were freeze-dried (Alpha 2-4 LSCplus, Christ, Osterode am Harz, Germany), finely ground in a mill (G3 Ferrari, Rimini, Italy), and soaked in hexane (10 mL of hexane per gram of dry weight) for 15 min under magnetic stirring to extract and separate the lipophilic phase contained in grape seeds, thereby avoiding interference during analyses. The mixture was filtered through a Miracloth filter (pore size 22–25 μm, Sigma-Aldrich, St. Louis, MO, USA) to remove the lipophilic phase. The solid phase, made up of pomace, was collected and dried.

2.3. DES Preparation

The eutectic solvents were obtained as previously reported [23]; briefly, the two components of each DES were mixed at the reported molar ratio (Table 1) in a flask. Then, each mixture was heated at 80 °C under constant magnetic stirring until a homogenous, colorless and odorless solution was obtained (approximately 60 min). Then, enough water was added to each DES up to 50% of the final volume (*v*/*v*). The pH was measured with a digital pH meter (Accumet AB200, Fisher Scientific, Hampton, NH, USA).

Table 1. List of different NaDES solvents employed and their composition.

Solvent	HBA	HBD	Molar Ratio	Final Water Content (*v*/*v*)	pH
DES-Lac	Choline chloride	Lactic acid	1:1	50%	1.47
DES-Tar	Choline chloride	Tartaric acid	1:1	50%	0.56
DES-Gly	Choline chloride	Glycerol	1:1	50%	2.76

2.4. Solid-Liquid Extraction

The extractions were performed in an ultrasonic bath (180 W, DU-45S, ArgoLab, Arezzo, Italy) set at 28 kHz for thirty minutes at 45 °C, with a dry weight: solvent ratio of 1:20 (w/w). The solvents employed were DES-Lac, DES-Tar, DES-Gly (Table 1) and an ethanol-water solution acidified with formic acid (EtOH: H_2O: HCOOH 60:39.9:0.1 $v/v/v$). After the extraction, the samples were centrifuged at 3200× g for 10 min with an Eppendorf centrifuge 5810 R (Hamburg, Germany), and the extraction repeated on the pellet as indicated above. The two supernatants were mixed and filtered with a 0.22 µm syringe filter. Each extraction was performed in triplicate.

2.5. Total Phenolic Content

Total phenolic content was determined by the colorimetric Folin-Ciocalteu method, as previously reported [24]; the extracts were diluted up to 50-fold with bi-distilled water and mixed with the Folin-Ciocalteu reagent; subsequently, the pH of the solution was adjusted with 1M sodium carbonate (Na_2CO_3) and the absorbance at 765 nm of the solution was registered against blank after 1 h, with a JASCO V-550 UV/VIS spectrophotometer (Cremella, Lecco, Italy). The results are expressed as gallic acid equivalents (GAE), calculated with standard solutions of gallic acid at different dilutions.

2.6. HPLC/DAD/TOF

The extracts were characterized by an Agilent 1200 Liquid Chromatography system (Agilent Technologies, Palo Alto, CA, USA) equipped with a standard autosampler. The HPLC column was an Agilent Zorbax Extended C18 (1.8 µm, 2.1 × 50 mm). Separation was carried out at 40 °C with a gradient elution program at a flow rate of 0.5 mL/min. The mobile phases consisted of water plus 0.1% formic acid (A) and acetonitrile (B). The following multistep linear gradient was applied: 0 min, 5% B; 13 min, 25% B; 19 min, 40% B. The injection volume in the HPLC system was 5 µL. The HPLC system was coupled to a DAD (Agilent Technologies, Palo Alto, CA, USA) set at 280 nm and an Agilent 6320 TOF mass spectrometer equipped with a dual electrospray ionization (ESI) interface (Agilent Technologies, Palo Alto, CA, USA) operating in negative ion mode. Detection was carried out within a mass range of 50–1700 m/z. Accurate measurements of the mass corresponding to each total ionic current (TIC) peak were obtained with a pump (Agilent G1310B) introducing a low flow (20 µL/min) of a calibration solution containing internal reference masses at m/z 112.9856, 301.9981, 601.9790, 1033.9881, and using a dual nebulizer ESI source in negative ion mode [25]. The anthocyanins were identified with the same chromatography system. Phase A was water plus 2% formic acid, and phase B was acetonitrile: water: formic acid (53:45:2). The HPLC column was an Agilent Zorbax Extended C18 (1.8 µm, 2.1 × 50 mm). Separation was carried out at 40 °C with a gradient elution program at a 0.5 mL/min flow rate. The following multistep linear gradient was applied: 0 min, 5% B; 12 min, 15% B; 20 min, 30% B; 35 min. 45% B. The injection volume in the HPLC system was 5 µL. TOF operated with positive ionization, using the internal reference masses at m/z 121.0508, 149.0233, 322.0481 and 922.0097. Finally, wavelength DAD detection was 520 nm. For both phenolic and anthocyanins, characterization mass spectrometer conditions were as follows: capillary voltage 3.0 kV in negative mode and 3.5 kV in positive mode; nitrogen was used as the nebulizer and desolvation gas; drying gas temperature: 300 °C; drying gas flow: 12 L/min, nebulizing gas pressure: 40 psig; finally, the source temperature was 120 °C. Mass Hunter software (B.07.00; Agilent Technologies, Palo Alto, CA, USA) was used to process the mass data of the molecular ions. The compounds were quantified using calibration curves of authentic standards (gallic acid, catechin, quercetin 3-β-D-glucoside, kaempferol 3-*O*-glucoside, resveratrol, malvidin 3-*O*-glucoside).

2.7. Statistics

Statistical tests were conducted on both total phenolic content and on HPLC/MS quantitative analysis results; a one-way ANOVA was performed to assess differences among the solvents used (within each monovarietal pomace sample), followed by a post hoc Tukey's test for honestly significant differences (HSD). In the case of quantitative analysis results, different tests were conducted separately for each compound. All data were reported as mean ± standard deviation. The analyses were performed using the R software (version 4.0.3, R Core Team [26]).

3. Results

3.1. Pomace Dry Weight

Table 2 displays the dry weight data (as percentages of fresh weight) for each sample. Pomaces from white and rosé vinification have lower values than those from red vinification because in red vinification, the pomace is pressed to recover as much must as possible, whereas in white and rosé vinification, the must is drained rather than pressed, to avoid excessive solvation of pigmented substances.

Table 2. Dry weight (%) of each sample of pomace.

Vinification Method	Sample	Dry Weight (%)
Red	Negroamaro	49.4 ± 0.4
	Primitivo	49.5 ± 0.8
Rosé	Negroamaro	39.7 ± 1.4
	Primitivo	39.6 ± 1.8
	Susumaniello	42.6 ± 1.7
White	Chardonnay	35.2 ± 1.3
	Fiano	38.6 ± 1.1
	Malvasia bianca	29.1 ± 2.1

Values are the mean ± standard deviation (n = 3).

3.2. Total Phenolic Content

The total phenolic content results shown in Figure 1 indicate that NaDES allowed for higher yields of total phenols compared to ethanol; in fact, for each of the eight samples, ethanol yielded significantly less than each NaDES (except for the extractions from Negroamaro red and rosé and Susumaniello rosé, where DES-Gly and ethanol showed no statistically significant difference). The highest value was obtained from Primitivo rosé grape pomace with DES-Tar (127.8 GAE mg/g DW), while the lowest was obtained from an ethanol extract of Negroamaro red pomace (35.8 GAE mg/g DW). Regardless of the solvent utilized, the highest results were achieved from rosé vinification pomaces, although even white grape pomaces provided distinguishable values, presumably higher than those from red grape pomace, despite the absence of anthocyanins.

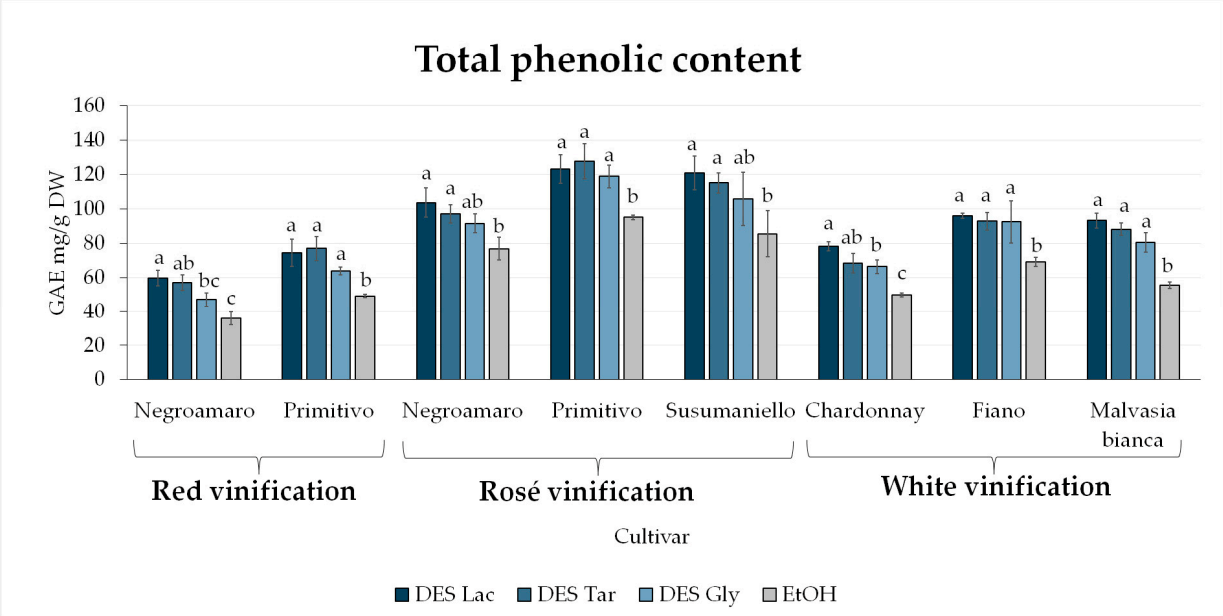

Figure 1. Total phenolic content, expressed as mg of gallic acid equivalent (GAE) per gram (dry weight) of pomace. For each sample, a one-way ANOVA test was performed to assess the statistically significant difference among different solvents tested, followed by Tukey post hoc test (HSD); for each pomace sample, bars with different letters differ at $p < 0.05$.

3.3. HPLC/DAD/TOF

3.3.1. Anthocyanins

The main anthocyanins identified by HPLC/MS are reported in Table 3.

Figure 2 illustrates the chromatograms for the 13 compounds detected by HPLC/DAD/TOF (labeled with letters from A to M as indicated in Table 3), while Table 4 reports the quantification of the principal anthocyanins found in each pomace sample. Malvidin-3-O-glucoside (also known as oenin chloride) is the most abundant, as illustrated in Figure 2 and Table 4. The highest yield is obtained with DES-Lac from Susumaniello rosé grape pomace (29.4 mg/g DW), which is significantly greater than that obtained with DES-Gly and ethanol from the same sample. When the solvent efficiencies for each sample and metabolite were compared, 33 out of 45 cases (9 compounds and 5 pomace cultivars, Table 4) contained at least one NaDES that extracted significantly more than ethanol. Interestingly, ethanol extracts more efficiently from pomace from red wine production, particularly Negroamaro pomace. The extractions from rosé grape pomaces gave the highest results (for each compound quantified, each rosé grape pomace shows a content at least twice as high as each red pomace, except for malvidin 3-(6′acetyl)-glucoside and malvidin 3-O-glucoside 4 vinylguaiacol).

Primitivo has lower levels of delphinidin 3-O-glucoside, cyanidin 3-O-glucoside, and petunidin 3-O-glucoside (both in red and rosé vinification), but higher levels of malvidin 3-O-glucoside 4 vinylphenol and malvidin 3-O-glucoside 4 vinylguaiacol. Susumaniello rosé had a higher amount of peonidin 3-O-glucoside (up to 12.2 mg/g DW when extracted with DES-Tar) compared to other pomaces, regardless of the solvent used.

Table 3. Main putative anthocyanins identified by HPLC/DAD/TOF.

ID	RT	Name	Formula [M-H]$^-$	MW exp [M-H]$^-$	MW calc [M-H]$^-$	Δ ppm	Ref.
A	11.313	Delphinidin 3-O-glucoside	$C_{21}H_{21}O_{12}$	465.1034	465.1028	−1.34	[25,27]
B	13.020	Cyanidin 3-O-glucoside	$C_{21}H_{21}O_{11}$	449.1081	449.1078	−0.66	[25,27]
C	14.393	Petunidin 3-*O*-glucoside	$C_{22}H_{23}O_{12}$	479.1184	479.1187	−0.57	[25,27]
D	16.093	Peonidin 3-*O*-glucoside	$C_{22}H_{23}O_{11}$	463.1248	463.1235	−2.8	[25,27]
E	17.140	Malvidin 3-*O*-glucoside [1]	$C_{23}H_{25}O_{12}$	493.1359	493.1341	−3.84	[25,27]
F	20.673	Petunidin 3-(6′acetyl)glucoside	$C_{24}H_{25}O_{13}$	521.1314	521.129	−4.58	[25,27]
G	22.140	Peonidin 3-(6′acetyl)-glucoside	$C_{24}H_{25}O_{12}$	505.1365	505.1341	−4.83	[25,27]
H	22.973	Malvidin 3-(6′acetyl)-glucoside	$C_{25}H_{27}O_{13}$	535.1461	535.1446	−2.84	[25,27]
I	23.805	Malvidin 3-(6′caffeoil)-glucoside	$C_{32}H_{31}O_{15}$	655.1669	655.1657	−1.79	[25,27]
J	24.186	Petunidin 3-(6′coumaroyl)-glucoside	$C_{31}H_{29}O_{14}$	625.1558	625.1552	−0.93	[25,27]
K	24.747	Malvidin 3-(6′coumaroyl)-glucoside	$C_{32}H_{31}O_{14}$	639.1725	639.1708	−2.6	[25,27]
L	25.579	Malvidin 3-*O*-glucoside 4 vinylphenol	$C_{31}H_{29}O_{13}$	609.1619	609.1603	−2.6	[25]
M	25.845	Malvidin 3-*O*-glucoside 4 vinylguaiacol	$C_{32}H_{31}O_{14}$	639.1733	639.1708	−3.8	[25]

[1] Confirmed by standard compound.

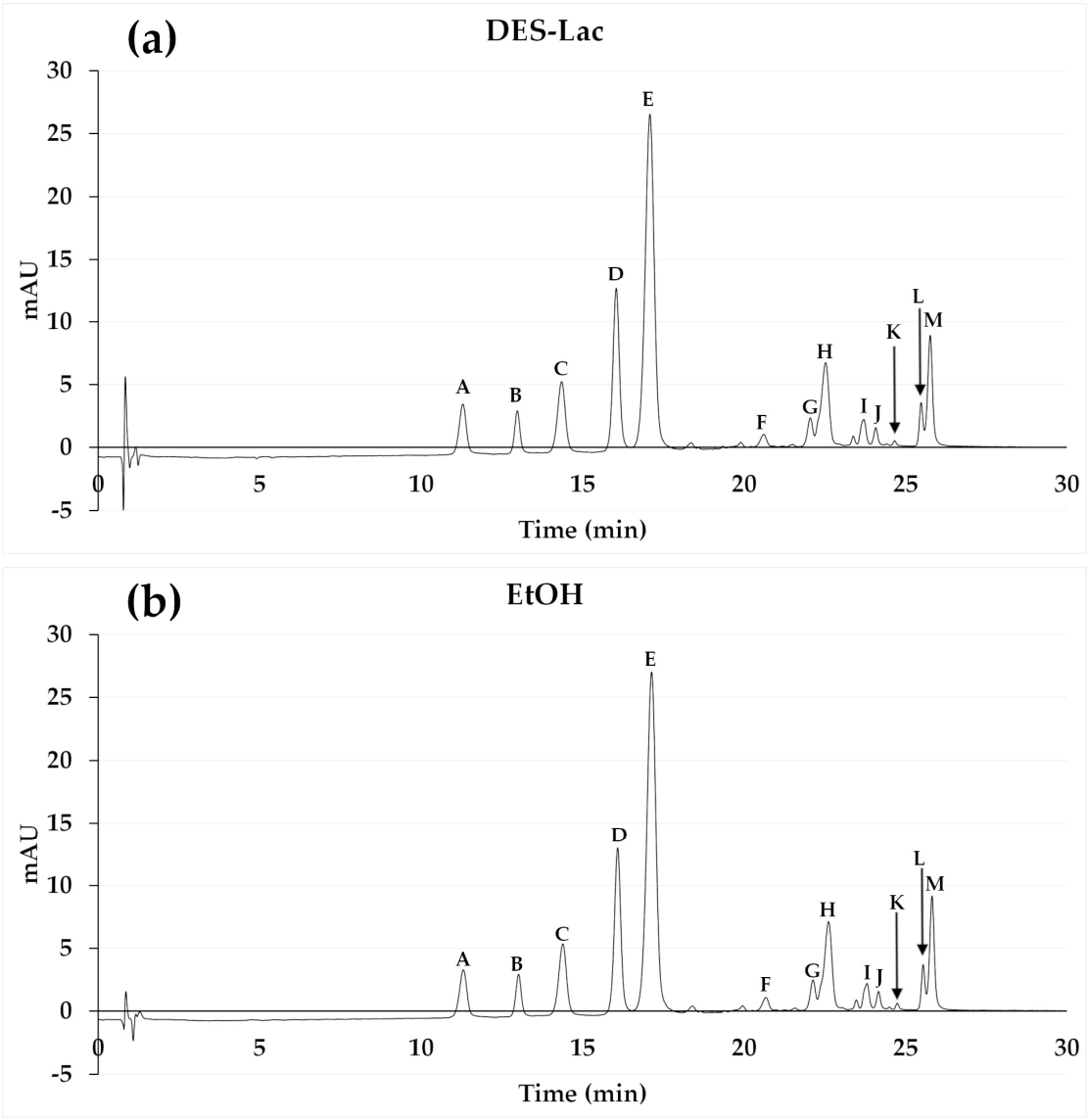

Figure 2. Representative HPLC/DAD chromatograms at λ = 520 nm. (**a**) Anthocyanins extracted with DES-Lac from Susumaniello rosé grape pomace; (**b**) anthocyanins extracted with ethanol from Susumaniello rosé grape pomace. The capital letters above each peak indicate the chemical compound as shown in Table 3.

Table 4. HPLC/MS quantification of the main putative anthocyanins in the extracts.

	Red Vinification		Rosé Vinification		
	Negroamaro	**Primitivo**	**Negroamaro**	**Primitivo**	**Susumaniello**
	Delphinidin 3-*O*-glucoside [1] (μg/g DW)				
DES-Lac	237 ± 55 [a]	84 ± 9 [a]	2169 ± 266 [a]	365 ± 18 [a]	2572 ± 105 [a]
DES-Tar	214 ± 12 [a]	106 ± 20 [a]	2033 ± 167 [a]	365 ± 9 [a]	2487 ± 158 [a]
DES-Gly	38 ± 6 [b]	15 ± 3 [b]	867 ± 288 [b]	151 ± 26 [c]	1581 ± 367 [b]
EtOH	191 ± 34 [a]	89 ± 7 [a]	1721 ± 154 [a]	225 ± 42 [b]	1815 ± 200 [b]
	Cyanidin 3-*O*-glucoside [1] (μg/g DW)				
DES-Lac	120 ± 9 [a]	59 ± 4 [a]	2218 ± 358 [a]	240 ± 8 [a]	1914 ± 175 [ab]
DES-Tar	110 ± 11 [ab]	61 ± 9 [a]	2283 ± 170 [a]	241 ± 6 [a]	2047 ± 156 [ab]
DES-Gly	88 ± 11 [b]	47 ± 4 [a]	2014 ± 183 [a]	207 ± 14 [a]	1689 ± 88 [b]
EtOH	123 ± 5 [a]	55 ± 7 [a]	2130 ± 306 [a]	168 ± 22 [b]	1695 ± 108 [ab]
	Petunidin 3-*O*-glucoside [1] (μg/g DW)				
DES-Lac	479 ± 43 [ab]	208 ± 9 [b]	4315 ± 561 [ab]	994 ± 57 [b]	4076 ± 189 [b]
DES-Tar	554 ± 28 [a]	323 ± 41 [a]	5548 ± 474 [a]	1411 ± 65 [a]	5431 ± 369 [a]
DES-Gly	329 ± 45 [b]	174 ± 12 [b]	4180 ± 659 [b]	1094 ± 124 [b]	4165 ± 390 [b]
EtOH	573 ± 15 [a]	300 ± 43 [a]	5115 ± 642 [ab]	985 ± 143 [b]	4377 ± 342 [b]
	Peonidin 3-*O*-glucoside [1] (μg/g DW)				
DES-Lac	371 ± 63 [a]	495 ± 37 [a]	4351 ± 558 [a]	3425 ± 210 [ab]	11892 ± 650 [ab]
DES-Tar	347 ± 24 [a]	573 ± 83 [a]	4334 ± 187 [a]	3658 ± 184 [a]	12249 ± 808 [a]
DES-Gly	325 ± 41 [a]	502 ± 53 [a]	4083 ± 143 [a]	3305 ± 173 [ab]	10648 ± 333 [b]
EtOH	429 ± 29 [a]	552 ± 89 [a]	4234 ± 642 [a]	2800 ± 356 [b]	10763 ± 547 [ab]
	Malvidin-3-*O*-glucoside (mg/g DW)				
DES-Lac	3.5 ± 0.1 [a]	4.5 ± 0.9 [a]	21.5 ± 2.1 [a]	20.9 ± 0.9 [a]	29.4 ± 1.3 [a]
DES-Tar	3.2 ± 0.2 [a]	4.3 ± 0.5 [a]	20.4 ± 1.4 [a]	21.9 ± 0.9 [a]	28.9 ± 1.6 [ab]
DES-Gly	3.0 ± 0.4 [a]	4.1 ± 0.3 [a]	18.9 ± 1.2 [a]	20.1 ± 0.8 [ab]	26.3 ± 0.8 [b]
EtOH	3.3 ± 0.7 [a]	4.2 ± 0.7 [a]	19.9 ± 2.5 [a]	18.7 ± 2.0 [b]	26.6 ± 1.3 [b]
	Malvidin 3-(6′caffeoil)-glucoside [1] (μg/g DW)				
DES-Lac	230 ± 24 [b]	458 ± 68 [ab]	1415 ± 187 [ab]	2530 ± 143 [ab]	7475 ± 239 [ab]
DES-Tar	195 ± 27 [b]	388 ± 61 [b]	1124 ± 81 [b]	2384 ± 364 [b]	6684 ± 716 [b]
DES-Gly	259 ± 33 [ab]	513 ± 42 [ab]	1639 ± 71 [a]	3068 ± 135 [a]	8211 ± 255 [a]
EtOH	331 ± 55 [a]	585 ± 103 [a]	1713 ± 228 [a]	2567 ± 316 [ab]	8315 ± 510 [a]
	Malvidin 3-(6′acetyl)-glucoside [1] (μg/g DW)				
DES-Lac	281 ± 17 [ab]	1041 ± 153 [a]	1054 ± 125 [a]	2678 ± 60 [a]	2186 ± 71 [ab]
DES-Tar	242 ± 31 [b]	924 ± 97 [a]	1046 ± 75 [a]	2798 ± 125 [a]	2210 ± 151 [a]
DES-Gly	275 ± 25 [ab]	911 ± 97 [a]	962 ± 37 [a]	2513 ± 155 [a]	1873 ± 84 [b]
EtOH	336 ± 54 [a]	1102 ± 156 [a]	940 ± 77 [a]	2140 ± 186 [b]	1915 ± 153 [ab]
	Malvidin 3-*O*-glucoside 4 vinylphenol [1] (μg/g DW) [1]				
DES-Lac	254 ± 44 [a]	217 ± 25 [a]	910 ± 134 [a]	2480 ± 118 [a]	1082 ± 42 [a]
DES-Tar	98 ± 3 [b]	201 ± 22 [a]	844 ± 37 [a]	2609 ± 107 [a]	1086 ± 18 [a]
DES-Gly	95 ± 2 [b]	197 ± 3 [a]	831 ± 48 [a]	2527 ± 175 [a]	995 ± 43 [b]
EtOH	108 ± 3 [b]	221 ± 6 [a]	860 ± 6 [a]	2003 ± 213 [b]	917 ± 35 [c]
	Malvidin 3-*O*-glucoside 4 vinylguaiacol [1] (mg/g DW)				
DES-Lac	3.3 ± 0.2 [a]	7.9 ± 0.7 [a]	7.5 ± 0.7 [a]	17.9 ± 0.5 [a]	6.8 ± 0.2 [a]
DES-Tar	3.0 ± 0.3 [a]	7.3 ± 0.6 [a]	7.4 ± 0.3 [a]	18.7 ± 0.8 [a]	6.8 ± 0.4 [a]
DES-Gly	2.8 ± 0.4 [a]	7.2 ± 0.7 [a]	7.1 ± 0.3 [a]	17.1 ± 1.0 [a]	5.8 ± 0.2 [b]
EtOH	3.6 ± 0.6 [a]	8.2 ± 1.3 [a]	7.0 ± 0.6 [a]	14.7 ± 1.3 [b]	5.9 ± 0.5 [ab]

Values are mean ± standard deviation ($n = 3$); for each individual compound, the means in a column with different superscript letters differ at $p < 0.05$, while means with the same letter did not show any statistical difference ($p > 0.05$; the statistical tests conducted were: one-way ANOVA followed by Tukey post hoc test, HSD); [1] quantified as malvidin-3-glucoside equivalent.

3.3.2. Other Phenolic Compounds

Table 5 lists the 31 phenolic compounds discovered using HPLC/MS. Five compounds are classified as phenolic acids, eight as flavan-3-ols, eleven as flavanols, and four as stilbenes. The only identified flavanone is tetrahydroxy-Dimethoxyflavanone-Hexoside, while an anthocyanin (Malvidin 3-(6′caffeoil)-glucoside) is visible at λ = 280 nm and corresponds to the higher peak in the chromatograms (peak 29, Figure 3). The flavanols are all glycosylated, except for quercetin and kaempferol, which are also found as aglycones.

Table 5. Main putative phenolic compounds identified by HPLC/DAD/TOF.

ID	RT	Name	Formula $[M-H]^-$	MW exp $[M-H]^-$	MW calc $[M-H]^-$	Δ ppm	Ref.
1	1.714	Gallic acid Hexoside	$C_{13}H_{15}O_{10}$	331.0659	331.0671	3.6	[25]
2	2.827	Caffeic acid	$C_9H_7O_4$	179.0348	179.035	1.27	[25]
3	2.847	Caffeic acid glucuronide	$C_{15}H_{15}O_{10}$	355.0661	355.0671	2.68	[28]
4	3.680	(Epi)Catechin-(4,8″)-(Epi)Catechin	$C_{30}H_{25}O_{12}$	577.1342	577.1351	1.58	[25]
5	4.027	(Epi)Catechin-(4,8″)-(Epi)Catechin	$C_{30}H_{25}O_{12}$	577.1349	577.1351	0.48	[25]
6	4.327	Catechin [1]	$C_{15}H_{13}O_6$	289.0718	289.0718	−0.14	[25]
7	5.167	Coumaroyl Hexoside Is. 1	$C_{15}H_{17}O_8$	325.0937	325.0929	−2.4	[25]
8	5.663	(Epi)Catechin-(4,8″)-(Epi)Catechin	$C_{30}H_{25}O_{12}$	577.1343	577.1351	1.54	[25]
9	5.927	Coumaroyl Hexoside Is. 2	$C_{15}H_{17}O_8$	325.0925	325.0929	1.24	[25]
10	6.296	Epicatechin	$C_{15}H_{13}O_6$	289.0714	289.0718	1.28	[25]
11	6.603	Tetrahydroxy-Dimethoxy-Flavanone-Hexoside	$C_{23}H_{25}O_{13}$	509.1293	509.1301	1.54	[25]
12	7.430	3-*O*-Galloyl (Epi)Catechin-(4,8″)-(Epi)Catechin	$C_{37}H_{29}O_{16}$	729.1455	729.1461	0.8	[25]
13	7.916	3-*O*-Galloyl (Epi)Catechin-(4,8″)-(Epi)Catechin	$C_{37}H_{29}O_{16}$	729.1464	729.1461	−0.35	[25]
14	8.368	Myricetin 3 Hexoxide	$C_{21}H_{19}O_{13}$	479.0842	479.0831	−2.35	[25,27]
15	8.736	Tetrahydroxy-Dimethoxy-Flavanone-Hexoside	$C_{23}H_{25}O_{13}$	509.1294	509.1301	1.38	[25]
16	9.776	Epicatechin gallate	$C_{22}H_{17}O_{10}$	441.0829	441.0827	−0.43	[28,29]
17	10.116	Quercetin 3-*O*-Hexuronide	$C_{21}H_{17}O_{13}$	477.0671	477.0675	0.74	[25,27]
18	10.144	Quercetin	$C_{15}H_9O_7$	301.0347	301.0354	2.1	[27]
19	10.243	Quercetin 3-β-D-glucoside [1]	$C_{14}H_{23}O_{17}$	463.0914	463.0941	5.69	[25,27]
20	10.450	Piceatannol	$C_{14}H_{11}O_4$	243.0671	243.0663	−3.39	[27]
21	10.463	Dihydroquercetin 3-*O*-Rhamnoside (Astilbin)	$C_{21}H_{21}O_{11}$	449.1103	449.1089	−2.98	[25,27]
22	10.552	Larycitrin 3-*O*-Hexoside	$C_{22}H_{21}O_{13}$	493.0988	493.0988	−0.08	[25,27]
23	11.194	Quercetin 3-*O*-Rhamnoside	$C_{21}H_{19}O_{11}$	447.0941	447.0933	−1.92	[25]
24	11.643	Kaempferol 7-*O*-Hexuronide	$C_{21}H_{17}O_{12}$	461.0704	461.0725	4.59	[25,27]
25	11.803	Kaempferol 3-*O*-glucoside [1]	$C_{21}H_{19}O_{11}$	447.0932	447.0933	0.29	[25,27]
26	12.450	Syringetin 3-*O*-Hexoside	$C_{23}H_{23}O_{13}$	507.1149	507.1144	−0.88	[25,27]
27	12.788	Piceid	$C_{20}H_{20}O_8$	389.1261	389.1242	−4.9	[27]
28	12.987	Viniferin	$C_{28}H_{21}O_6$	453.1348	453.1344	−0.86	[27]
29	13.290	Malvidin 3-(6′caffeoil)-glucoside	$C_{32}H_{31}O_{15}$	655.1660	655.1668	1.28	[30]
30	13.481	Resveratrol [1]	$C_{14}H_{11}O_3$	227.0717	227.0714	−1.63	[25,27]
31	16.184	Kaempferol	$C_{15}H_9O_6$	285.0417	285.0405	−4.26	[25]

[1] Confirmed by standard compound.

The HPLC/DAD analyses at λ = 280 nm on extracts with both DES-Gly and ethanol demonstrate that the primary peaks are attributed to catechin, epicatechin, and its dimers (peaks 4, 6, 10, 13, Figure 3a,b). Another noticeable peak is number 17, which corresponds to quercetin 3-O-hexuronide. Eight phenolic compounds were quantified by HPLC/MS (Table 6); for the comparison among solvents, there is some difference based on the nature of the molecule extracted and quantified, but in this case, NaDES proved to be less effective in the extractions of these molecules compared to anthocyanins; however, when the values obtained for the eight compounds were compared between grape cultivars (for a total of 64 comparisons), in 40 cases at least one NaDES extracted as much as ethanol (no significant difference), whereas in the case of the quercetin 3-hexuronide from Primitivo rosé, DES-Gly gave a significantly higher extraction yield than ethanol, while for resveratrol extraction from Fiano DES-Lac extracted significantly more than each other. In general, DES-Gly proved to be the most successful NaDES for the extraction of phenolic compounds; in fact, in ten instances, it extracted a significantly higher quantity of a chemical than both other NaDES, whereas another NaDES extract significantly more in only two cases. In the instance of catechin, ethanol performed better than all other NaDES.

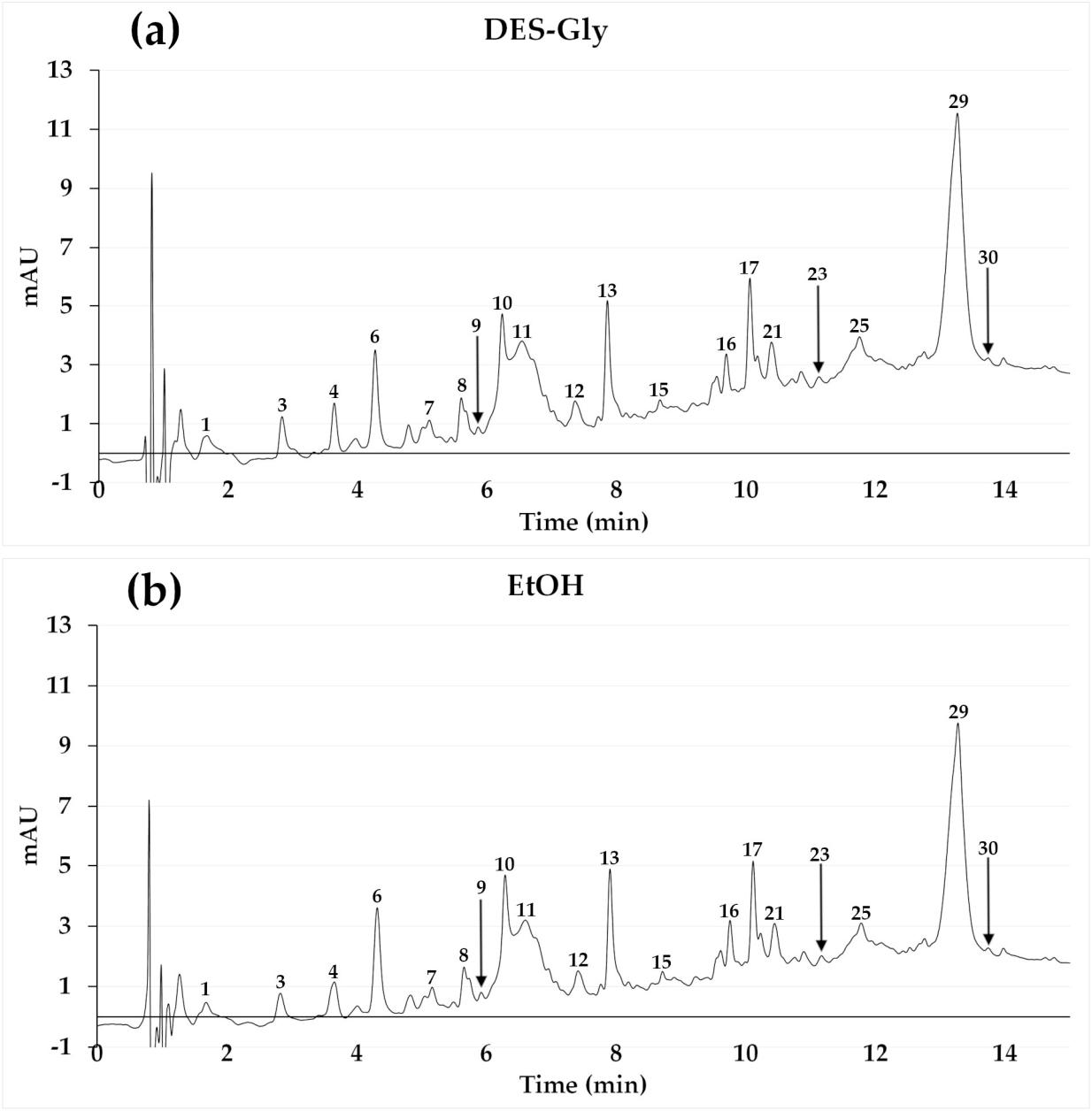

Figure 3. HPLC/DAD chromatograms at λ = 280 nm. (**a**) Phenolic compounds extracted with DES-Gly from Primitivo rosé grape pomace; (**b**) Phenolic compounds extracted with ethanol from Primitivo rosé grape pomace. The numbers above each peak indicate the chemical compound as shown in Table 5.

When comparing the samples, it is worth noting that the trend observed for anthocyanins concerning the lower content in pomaces from red vinification is only partially confirmed (Table 6). This is certainly true for quercetin and kaempferol glycosides, but not for resveratrol or, more importantly, astilbin. Another feature that stands out is the significantly larger concentration of kaempferol 3-O-glucoside and astilbin in Chardonnay pomace. Instead, Susumaniello pomace contains significantly less epicatechin and catechin.

Table 6. HPLC/MS quantification of the main phenolic compounds in the extracts. Letters in heading correspond to abbreviation of the cultivar from which the pomace is derived (Negra.: Negroamaro; Primi.: Primitivo; Susum.: Susumaniello; Chard.: Chardonnay; Fiano; MalBia: Malvasia bianca).

	Red Vinification		Rosé Vinification			White Vinification		
	Negra.	Primi.	Negra.	Primi.	Susum.	Chard.	Fiano	MalBia
				Catechin (mg/g DW)				
DES-Lac	0.9 ± 0.1^{b}	1.6 ± 0.1^{b}	3.9 ± 0.4^{bc}	4.9 ± 0.5^{bc}	2.1 ± 0.3^{b}	2.6 ± 0.5^{c}	2.1 ± 0.4^{bc}	3.7 ± 0.4^{b}
DES-Tar	0.8 ± 0.1^{b}	1.5 ± 0.1^{b}	2.4 ± 0.2^{c}	3.2 ± 0.1^{c}	1.4 ± 0.2^{b}	2.1 ± 0.2^{c}	1.6 ± 0.2^{c}	1.9 ± 0.2^{c}
DES-Gly	0.7 ± 0.1^{b}	1.9 ± 0.3^{b}	5.1 ± 0.3^{b}	6.6 ± 0.7^{b}	2.2 ± 0.2^{b}	3.5 ± 0.1^{b}	2.5 ± 0.3^{b}	4.4 ± 0.5^{b}
EtOH	3.0 ± 0.5^{a}	5.2 ± 0.9^{a}	8.8 ± 1.7^{a}	9.1 ± 1.3^{a}	4.1 ± 0.7^{a}	6.1 ± 0.3^{a}	5.0 ± 0.5^{a}	8.7 ± 0.9^{a}
				Epicatechin [1] (mg/g DW)				
DES-Lac	0.4 ± 0.1^{c}	0.6 ± 0.1^{c}	0.9 ± 0.1^{b}	1.3 ± 0.2^{b}	0.8 ± 0.1^{b}	1.4 ± 0.1^{d}	1.3 ± 0.3^{c}	1.2 ± 0.1^{c}
DES-Tar	0.9 ± 0.1^{b}	1.2 ± 0.1^{bc}	1.4 ± 0.1^{b}	1.9 ± 0.2^{b}	1.2 ± 0.1^{b}	1.9 ± 0.1^{c}	1.6 ± 0.1^{c}	1.1 ± 0.3^{c}
DES-Gly	0.8 ± 0.1^{b}	1.9 ± 0.2^{b}	3.7 ± 0.3^{a}	4.7 ± 0.3^{a}	2.3 ± 0.2^{a}	4.8 ± 0.2^{b}	5.7 ± 0.2^{b}	4.0 ± 0.3^{b}
EtOH	2.1 ± 0.2^{a}	3.3 ± 0.6^{a}	4.7 ± 0.8^{a}	5.1 ± 0.7^{a}	2.7 ± 0.4^{a}	5.7 ± 0.4^{a}	6.5 ± 0.5^{a}	5.7 ± 0.6^{a}
				Quercetin 3-*O*-hexuronide [2] (μg/g DW)				
DES-Lac	115 ± 9^{ab}	281 ± 25^{a}	453 ± 20^{a}	1684 ± 205^{ab}	1264 ± 155^{a}	392 ± 52^{a}	884 ± 169^{a}	620 ± 19^{a}
DES-Tar	99 ± 7^{b}	264 ± 15^{a}	476 ± 33^{a}	1696 ± 131^{ab}	1194 ± 76^{a}	374 ± 41^{a}	766 ± 90^{a}	523 ± 57^{a}
DES-Gly	94 ± 15^{b}	286 ± 28^{a}	522 ± 16^{a}	1805 ± 140^{a}	1198 ± 25^{a}	396 ± 8^{a}	941 ± 45^{a}	620 ± 31^{a}
EtOH	141 ± 26^{a}	335 ± 53^{a}	561 ± 99^{a}	1282 ± 210^{b}	1223 ± 140^{a}	445 ± 13^{a}	992 ± 29^{a}	668 ± 97^{a}
				Quercetin-3-β-D-glucoside (μg/g DW)				
DES-Lac	33 ± 7^{b}	43 ± 6^{b}	463 ± 26^{a}	438 ± 75^{a}	565 ± 84^{a}	539 ± 42^{b}	736 ± 99^{bc}	477 ± 21^{ab}
DES-Tar	26 ± 5^{b}	38 ± 5^{b}	413 ± 32^{a}	440 ± 30^{a}	521 ± 39^{a}	519 ± 45^{b}	624 ± 95^{c}	398 ± 33^{b}
DES-Gly	34 ± 4^{ab}	42 ± 6^{b}	476 ± 25^{a}	469 ± 41^{a}	530 ± 15^{a}	478 ± 14^{b}	815 ± 18^{b}	495 ± 28^{ab}
EtOH	49 ± 9^{a}	59 ± 10^{a}	526 ± 95^{a}	433 ± 78^{a}	586 ± 45^{a}	687 ± 29^{a}	993 ± 58^{a}	557 ± 74^{a}
				Astilbin [2] (μg/g DW)				
DES-Lac	18 ± 5^{ab}	64 ± 10^{b}	27 ± 7^{b}	91 ± 8^{a}	21 ± 2^{b}	248 ± 21^{bc}	56 ± 7^{bc}	19 ± 3^{ab}
DES-Tar	12 ± 1^{c}	54 ± 2^{b}	25 ± 1^{ab}	91 ± 4^{a}	22 ± 2^{b}	222 ± 23^{c}	48 ± 7^{c}	15 ± 2^{b}
DES-Gly	15 ± 2^{bc}	64 ± 11^{ab}	31 ± 2^{ab}	106 ± 8^{a}	28 ± 2^{a}	293 ± 16^{ab}	70 ± 3^{ab}	20 ± 1^{ab}
EtOH	23 ± 3^{a}	85 ± 13^{a}	35 ± 7^{a}	101 ± 7^{a}	28 ± 2^{a}	323 ± 18^{a}	84 ± 11^{a}	22 ± 3^{a}
				Kaempferol-3-*O*-glucoside (μg/g DW)				
DES-Lac	4 ± 1^{b}	8 ± 1^{b}	37 ± 4^{b}	72 ± 10^{a}	71 ± 10^{ab}	212 ± 25^{b}	82 ± 15^{b}	66 ± 3^{c}
DES-Tar	4 ± 1^{b}	9 ± 1^{b}	41 ± 5^{b}	81 ± 8^{a}	75 ± 8^{ab}	251 ± 30^{b}	81 ± 15^{b}	69 ± 6^{bc}
DES-Gly	4 ± 1^{b}	9 ± 1^{b}	45 ± 2^{ab}	90 ± 8^{a}	81 ± 2^{ab}	220 ± 9^{b}	110 ± 6^{a}	87 ± 6^{b}
EtOH	6 ± 1^{a}	13 ± 1^{a}	52 ± 6^{a}	89 ± 14^{a}	93 ± 9^{a}	363 ± 11^{a}	132 ± 3^{a}	108 ± 12^{a}
				Malvidin 3-(6′caffeoil)-glucoside [3] (μg/g DW)				
DES-Lac	210 ± 22^{b}	371 ± 61^{ab}	1231 ± 168^{ab}	1897 ± 129^{ab}	5905 ± 215^{ab}	<LoD	<LoD	<LoD
DES-Tar	175 ± 25^{b}	341 ± 55^{b}	933 ± 73^{b}	2074 ± 327^{b}	5147 ± 644^{b}	<LoD	<LoD	<LoD
DES-Gly	207 ± 30^{ab}	436 ± 37^{ab}	1328 ± 64^{a}	2731 ± 121^{a}	7554 ± 229^{a}	<LoD	<LoD	<LoD
EtOH	291 ± 49^{a}	462 ± 53^{a}	1525 ± 205^{a}	1951 ± 285^{ab}	6985 ± 459^{a}	<LoD	<LoD	<LoD
				Resveratrol (μg/g DW)				
DES-Lac	19 ± 3^{b}	25 ± 1^{b}	49 ± 1^{ab}	22 ± 5^{a}	45 ± 4^{ab}	<LoQ	21 ± 5^{a}	<LoD
DES-Tar	9 ± 1^{b}	14 ± 2^{b}	25 ± 1^{b}	10 ± 2^{c}	33 ± 2^{c}	<LoQ	12 ± 2^{b}	<LoQ
DES-Gly	22 ± 3^{b}	25 ± 1^{b}	42 ± 3^{ab}	13 ± 2^{bc}	40 ± 7^{bc}	<LoQ	12 ± 1^{b}	<LoQ
EtOH	53 ± 9^{a}	49 ± 8^{a}	54 ± 10^{a}	20 ± 2^{ab}	52 ± 7^{a}	<LoD	12 ± 3^{b}	<LoD

Values are mean ± standard deviation ($n = 3$); for each individual compound, the means in a column with different superscript letters differ at $p < 0.05$, while means with the same letter did not show any statistical difference (the statistical tests conducted were: one-way ANOVA followed by Tukey post hoc test, HSD); [1] quantified as catechin equivalent; [2] quantified as quercetin-3-β-D-glucoside equivalent; [3] quantified as malvidin-3-glucoside equivalent; <LoQ: below the limit of quantification; <LoD: below the limit of detection.

4. Discussion

The results presented indicate that the efficiency of NaDES is highly dependent on the chemical characteristics of the molecule extracted. In summary, the organic acid-based NaDES was most efficient for the extraction of anthocyanins, while DES-Gly was the most powerful for the recovery of the other phenols. Furthermore, according to the solvents used in this study, NaDES appears to be more efficient than a traditional solvent for extracting anthocyanins and comparable (or slightly less effective) to ethanol for other phenolic compounds. Comparable findings were reported by Lazović et al. [31], who found that a malic acid- and choline chloride-based NaDES was more effective in extracting

anthocyanins from various berries, while a choline chloride-glycerol-based NaDES was the best in extracting other flavonoids and phenolic acids. Cvjetko Bubalo et al. [19] measured anthocyanins, catechin, and quercetin 3-O-glucosides in red grape skin extracts using varied NaDES and methanol. The NaDES based on organic acids removed each anthocyanin more efficiently than those based on glycerol and sugars; however, the differences for quercetin 3-O-glucosides were less pronounced when compared to the control solvent. Huang et al. [32] reported that total anthocyanins extracted using various choline chloride-based eutectic mixtures were higher when organic acids were used as hydrogen bond donors (HBD) compared to glycerol. According to the authors, the greater selectivity of organic acid-based NaDES towards anthocyanins is owing to their physicochemical features, which show an inverse connection with pH and a positive association with polarity. This is consistent with the pH data reported here (Table 1), but it differs from the polarity of the solvent, which is higher in ChCl-glycerol NaDES than in ChCl-lactic acid NaDES [33,34]. In our case, the pH difference may have outweighed the polarity difference (it is well-known that solvent acidity enhances anthocyanin extraction and stability [35]), or other factors might have influenced the results, as various physicochemical properties can affect extraction efficiency. For instance, viscosity is inversely proportional to both electrical conductivity and extraction yield [36]. However, in our investigation, the maximum amount of water (50% of total volume) was added to NaDES to preserve hydrogen bond integrity [37] while drastically reducing viscosity. Moreover, increasing water content in DES means lower solvent costs and less environmental impact. Comparing NaDES with ethanol demonstrates that eutectic mixtures can be a valid alternative to standard organic solvents, providing similar or even greater extraction performances. In fact, Panić et al. [38] tested NaDES for anthocyanin extraction from grape pomace and found that two NaDES produced total anthocyanin yields comparable to ethanol, with no significant statistical difference. Ozkan [39] measured several phenolic compounds from artichoke leaves and discovered that methanol was the most effective solvent for extracting ferulic and sinapic acids, while a ChCl-lactic acid-based NaDES produced the maximum quantities of quercetin and chlorogenic acid. Ma et al. [23] reported that various NaDES are capable of extracting more quercetin and kaempferol from *Camellia oleifera* than methanol, although with almost identical yields for their glycosylated forms. This provides support to the concept that solvent selectivity is decisive and that NaDES can be adapted to the extraction of various metabolites and/or from different biomasses. Focusing on the varietal characterization of the extracts, distinct fingerprints were observed regardless of the solvent used. For instance, while malvidin 3-O-glucoside was the most abundant anthocyanin in each of the five samples from red berries, as widely reported in the literature [40], Primitivo pomace contained much less delphinidin 3-O-glucoside, cyanidin 3-O-glucoside, and petunidin 3-O-glucoside than Negroamaro and Susumaniello (Table 4). Similar trends were seen in the phenolic analysis of fresh grape berries [25,41,42]. In contrast, Primitivo pomace has larger quantities of malvidin 3-O-glucoside derivatives, such as malvidin 3-O-glucoside 4-vinylphenol and malvidin 3-O-glucoside 4-vinylguaiacol. This is interesting because these molecules tend to grow in wine with aging [43] and are involved in wine color changes [44]. Additionally, malvidin 3-O-glucoside 4 vinylphenol was identified in fresh grape berry skin of *Vitis amurensis* [45]. This is consistent with the rapid color change and evolution characteristic in Primitivo wine [46]. Susumaniello pomace, in comparison to other samples, exhibited lower levels of catechin and epicatechin but clearly higher levels of peonidin 3-O-glucoside, reaching 12.2 mg/g DW with DES-Tar extraction. Chardonnay pomace has extremely high quantities of kaempferol 3-O-glucoside and astilbin, which encourages further research. Astilbin, a dihydroflavonol rhamnoside found in numerous organs of *Vitis vinifera*, is known for its sweetening properties, which contribute to wine flavor and smell composition [47]. It has received attention for its potent antioxidative activity and ability to prevent and treat a variety of ailments and diseases, as well as its immunosuppressive properties with little adverse effects [48]. Furthermore, astilbin is a precursor to the highly attractive taxifolin [49]. Landrault et al. [50] discovered a higher

astilbin level in Chardonnay wine produced using the red vinification method compared to other wines, but no further studies are available. Table 5 shows the existence of many stilbenes, including piceatannol, piceid, viniferin, and resveratrol. Interestingly, the best solvents for resveratrol were ethanol, DES-Gly, and DES-Lac. Resveratrol was the only component found at higher amounts in red grape pomaces. This is unsurprising given that resveratrol can be detected in fresh grape berries and formed during fermentation via piceid hydrolysis [51]. This process may have been incomplete in rosé and white pomace. Overall, our observations demonstrate that the production processes for rosé and white wines produce pomaces rich in bioactive components. As a counterproof, Ragusa et al. [52] tested the phenolic content in red, rosé and white wines, reporting a higher concentration in red wines and a similar content between rosé and white wines. Our results are consistent with Tapia et al. [53], who compared grape pomaces resulted from red and white vinification and observed a higher quantity of epicatechin and kaempferol 3-*O*-glucoside in white pomace, as well as other compounds not quantified in our study; in contrast, they reported a higher content of total phenols and catechin in red grape pomace. However, it should be noted that the pomaces are most likely processed differently in that work, as the water content of red and white pomaces is similar (between 65% and 70%), so we can expect that the red grape pomace did not go through the pressing stage, making the results only partially comparable with those presented here. In conclusion, the most abundant compounds contained in pomaces from red grapes are malvidin 3-*O*-glucoside (as well as its form bound to guaiacol) and other anthocyanins, such as peonidin 3-*O*-glucoside; for every pomace, catechin and epicatechin were present in noticeable quantities. However, due to their applications, astilbin, resveratrol and kaempferol are the most demanded and economically valuable chemicals. Anthocyanins are as well in high request, however their prices are typically reduced because they are available as mixed anthocyanin extracts rather than single molecules.

5. Conclusions

This study advances the research into NaDES as antioxidant extractants. Three binary eutectic mixtures were tested for polyphenol extraction from grape pomace, yielding promising results: organic acid-based NaDES were the most effective for anthocyanin extraction, with yields significantly higher than ethanol, while a glycerol-based NaDES performed at least as well. The findings indicate that NaDES are a suitable alternative to traditional organic solvents for extracting active chemicals and antioxidants from plant biomasses, in accordance with green chemistry principles. Therefore, this method enables the valorization of grape pomaces, which has significant environmental implications. However, the recovery of the chemicals of interest from NaDES and the efficient re-use of NaDES require further research. Nevertheless, the analyses of several local grape pomaces from different winemaking processes revealed surprising results: Susumaniello and Primitivo rosé pomace contained the highest levels of anthocyanins and phenolic compounds. Furthermore, the concentration of astilbin in Chardonnay pomace was very high. Pomaces from rosé and white vinification, which are becoming increasingly abundant due to expanding demand for these wine types, constitute a significant reservoir of bioactive chemicals with a wide range of applications in medicines, cosmetics, and nutraceuticals. This could provide a minor source of profits for winemakers while also improving the sustainability of the oenological industry and extraction operations.

Author Contributions: Conceptualization, A.F., M.A. and L.D.B.; Data curation, A.F., C.N. and R.A.; Funding acquisition, L.D.B.; Investigation, A.F., R.A. and M.D.P.; Methodology, A.F. and C.N.; Supervision, A.L., M.A. and L.D.B.; Writing—original draft, A.F. and M.D.P.; Writing—review and editing, A.L., R.A. and L.D.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.4—Call for tender No. 3138 of 16 December 2021, rectified by Decree n.3175 of 18 December 2021 of Italian Ministry of University and Research funded by the European Union—Next Generation EU; Project code CN_00000033, Concession Decree No. 1034 of 17 June 2022 adopted by the Italian Ministry of University and Research, CUP F87G22000290001, Project title "National Biodiversity Future Center—NBFC". In addition, A.F. was funded by the European Social Fund Plus (FSE REACT-EU, PON R&I 2014–2020, Action IV.5—Doctorates on Green topics).

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Acknowledgments: The authors would like to acknowledge Valeriia Novikova for collaboration in English translation and revision.

Conflicts of Interest: The authors declare no conflicts of interest.

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