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Comparison between Conventional Ageing Process in Barrels and a New Rapid Aging Process Based on RSLDE: Analysis of Bioactive Compounds in Spirit Drinks

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Abstract: "Aging" is a practice that allows alcoholic beverages to mature and gives them particular flavors and colors. In this context, oak or durmast wooden barrels are used in this process, thus providing different types of aging. This conventional process produces a slow enrichment of organic compounds in the spirit inside the barrels. Organic substances present in the internal part of the barrels slowly undergo the phenomenon of extraction by the liquid phase (solid–liquid extraction). In this work, a new procedure based on rapid solid–liquid dynamic extraction (RSLDE) was used to evaluate the potential of obtaining the effects of aging in spirits in shorter times than conventional methods. For this purpose, a comparison between two solid–liquid extraction techniques, RSLDE and conventional maceration, was made. Four water/ethanol 60:40 (*v*/*v*) model solutions were prepared and put in contact with medium-toasted chips using the two extraction procedures (conventional and non-conventional) and determining dry residue and total polyphenol content. Reversed phase high-performance liquid chromatography (RP-HPLC) analyses allowed the identification and quantification of furfural, ellagic acid and phenolic aldehydes (vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde). The aging procedure with medium-toasted chips was tested on a young commercial *grappa* using maceration and RLSDE.

Keywords: bioactive compounds; chips; alcoholic beverages; maceration; RSLDE; grappa; distillates; aged beverages

Citation: Naviglio, D.; Trucillo, P.; Perrone, A.; Montesano, D.; Gallo, M. Comparison between Conventional Ageing Process in Barrels and a New Rapid Aging Process Based on RSLDE: Analysis of Bioactive Compounds in Spirit Drinks. *Processes* **2024**, *12*, 829. https://doi.org/10.3390/pr12040829

Academic Editors: Sheng Du, Li Jin, Xiongbo Wan, Zixin Huang and Dariusz Dziki

Received: 11 March 2024
Revised: 11 April 2024
Accepted: 17 April 2024
Published: 19 April 2024

1. Introduction

Spirits and liqueurs define a category of alcoholic beverages produced by the distillation of grains, fruits or vegetables that have first been fermented through alcoholic fermentation [1]. During the distillation process, the liquid is concentrated to increase its alcohol grade by volume (vol/vol%). Distilled spirits and liqueurs contain much more ethyl alcohol than other alcoholic beverages, such as wine, beer or mixed alcoholic beverages with a grade of around 40% (*v*/*v*). The aromatic characteristics of distillates are obtained mainly from agricultural raw materials, which are processed during various treatment stages, including fermentation, distillation, and barrel aging [2,3].

Generally, a spirit drink is characterized by an alcoholic strength equal to or greater than 15% (*v*/*v*), produced by distillation or maceration, followed by a flavoring step. Freshly distilled spirits have a harsh taste, which can be attributed to the lack of various

chemical reactions. For this reason, liqueurs require time to mature after distillation [4,5]. Aging is indeed a process used in the production of alcoholic beverages, such as wine, whiskey, and some types of beer. During aging, the beverage interacts with the container (such as wooden barrels), which can impart specific flavors, aromas, and colors to the drink, thus contributing unique characteristics to the beverage. However, it is important to note that the aging process and its effects can vary depending on the type of beverage and the specific production methods used. Therefore, many high-quality alcoholic beverages require aging in barrels for long periods of time [6]. Indeed, the objective of the aging process is to impart the aromas of the barrel's wood, such as oak, maple, acacia, chestnut and cherry. During the aging period, numerous chemical reactions occur that significantly change the taste and aroma of the alcoholic beverage [7–9]. However, the procedure for aging alcoholic beverages is characterized by a slow process of solid–liquid extraction that is based on the phenomena of diffusion and osmosis. Compounds contained in the wood of barrels are more slowly extracted because the process occurs at room temperature. To obtain faster aging, smaller barrels can be used, since in this case the amount of liquid in contact with wood is greater than in larger barrels (larger contact surface). However, the procedure is slow, and the overall process is particularly expensive.

In order to overcome the above-described drawbacks, novel and inexpensive techniques have been developed to simplify the aging process while ensuring that wood-bound volatiles are released into drinks and have similar sensory properties to those aged in barrels. These alternatives typically include oak chips or larger oak pieces [10]. The use of chips for the aging of wines is permitted in several countries, such as the United States, Australia and Chile. In Italy, it is only permitted on table wines, but the statement "aged in barrique" nowadays is forbidden on the label. Moreover, to enhance the final taste of aged spirits, the effect of toasting oak chips on the sensory characteristics and chemical composition of the wine was recognized to be greater than the oak type used [11,12]. Toasting oak increases the quantities of compounds deriving from the thermal degradation of lignin (vanillin, eugenol, guaiacol and its derivatives) and from the pyrolysis of cellulose and hemicellulose (furfural and 5-methylfurfural) and decreases the concentration of the two isomers of whiskey lactone. Similarly, during the aging of a distillate in a barrel, a series of chemical and physical interactions occur, involving the surrounding atmosphere and the maturing distillate, transforming the composition and, therefore, the final taste [13]. Recently, a growing interest has emerged in methods of predicting, controlling, and simulating the effects of maturation, given that the aging of distillates is one of the most important and expensive factors influencing their quality and their price. On the other hand, a new winemaking practice to rationalize work and reduce production costs for wine aging involves the use of wood chips that are 100 to 300 times cheaper than traditional barrels. Due to these favorable production conditions, newly emerging wine-producing countries such as New Zealand, California, Argentina, South Africa and Hungary are conquering the mass market with wines produced with this technique that have a good quality/price ratio and greater flexibility with respect to the tastes of the modern consumer. Among cheaper and faster alternatives than the conventional barrel aging method, maceration of oak pieces in wines and spirits is a well-known technique [14–20]. The use of chips, slats or strips immersed in the spirits has the aim of increasing the ratio between wood surface and volume liquid; this procedure promotes a faster solid–liquid extraction of the compounds from the wood. In this way, a larger surface is exposed to the liquid than 40%, as in the case of barrels. The products thus obtained are cheaper than those aged in barrels, but they have similar chemical characteristics and sensory properties. Therefore, even water, which is a highly polar solvent, can extract organic compounds in a heterogeneous phase. In traditional maceration, the effects of diffusion and osmosis are predominant; therefore, substances not chemically linked to the internal structure of the solid matrix tend to dissolve in the liquid. For this reason, a necessary condition for the traditional maceration process is that the substances to be extracted are soluble in the extractant liquid. Furthermore, to increase the extraction efficiency, it is necessary to increase

the temperature, on which diffusion and osmosis depend, according to Fick's Law. However, a possible drawback consists in the degradation of thermolabile compounds extracted or in favoring undesirable reactions [21–25].

Starting from these premises, the aim of this work was to evaluate a new method for obtaining the aging of spirits as an alternative method to the traditional one. This procedure is based on rapid solid–liquid dynamic extraction (RSLDE). The RSLDE occurs through the generation of a negative pressure gradient from the inside to the outside of the solid matrix. Therefore, it can be conducted at room or even sub-room temperature, avoiding the alteration of temperature-sensitive compounds, but also with other advantages. In fact, extraction requires much shorter times than maceration (2 h vs. 20 days) and allows the recovery and reuse of solvents with less environmental impact, according to the principle of the circular economy [26].

On the other hand, as reported in the literature, the areas of application of RSLDE are numerous and include the pharmaceutical, cosmetic, herbal, food and beverage sectors [27,28]. RSLDE can even be used for the extraction of bioactive compounds from agricultural and food waste, guaranteeing their possible reuse and reintroduction in the market as industrial by-products, according to the current eco-sustainable model of the circular economy [29].

To evaluate the efficiency of the alternative aging procedures, model water/ethanol solutions (60:40, *v*/*v*), with the addition of medium-toasted chips, were subjected to maceration and RLSDE techniques. Subsequently, the extracts obtained were subjected to various determinations, such as the dry residue, total polyphenols and the content of phenolic acids, furfuran derivatives and phenolic aldehydes deriving from wood, and identified as influencing the aroma and taste of aged spirits and drinks. Finally, a comparison between the two methods was carried out on a young commercial Italian spirit (named as *grappa*) subjected to aging using toasted chips.

2. Materials and Methods

2.1. Chemicals, Reagents, and Instrumentation

All solvents and reagents were of analytical grade and were purchased from Merck (Darmstadt, Germany), Carlo Erba (Milan, Italy), and Sigma-Aldrich Co. (Buchs, Switzerland); Folin Ciocalteau, anhydrous sodium carbonate, reagent and 2,4,6-tri(2-pyridyl-s-triazine) (TPTZ) were purchased from Sigma (Milan, Italy); Furfural, ellagic acid, vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde standards used to identify the antioxidant compounds of the extracts were obtained from Sigma (Milan, Italy). All the reactives and reagents were used without previous alterations or pre-treatments.

2.2. Materials and Preparation of Samples

The chips used belonged to the Nobile® line, Laffort Italia S.R.L. (Tortona Alessandria, Italy), a company specializing in oenological products. Both Nobile® Fresh and Nobile® Sweet chips used in this work were qualified as suitable for the development of products for direct human consumption according to Regulation (CE) 606/2009. Nobile® Fresh and Nobile® Sweet are oak fragments of 7 to 20 mm in diameter that derive from the hardwood of French oak Quercus Petraea dried in air at room temperature. The Nobile® Fresh were unroasted, while the Nobile® Sweet underwent a medium roasting in the oven (Figure 1).

Figure 1. Nobile® Sweet chips (**left**) and Nobile® Fresh chips (**right**).

To determine the effectiveness of the extraction process and the stability of the extracted compounds, solid–liquid chip extraction was carried out in a water/ethanol solution of 60:40 (*v*/*v*) with Millipore water and 96% (*v*/*v*) Ethyl alcohol from Carlo Erba.

2.3. Maceration vs. RSLDE Techniques

Maceration was carried out for 15 days, as suggested in the technical data sheet of the commercial chips (Laffort Italia S.R.L., Tortona Alessandria, Italy). Vice versa, the duration of the extraction tests carried out with RSLDE was 3 h and 16 min (49 extraction cycles) and 17 h and 52 min (268 extraction cycles), respectively. Each extractive cycle consisted of a 2 min static phase and a dynamic phase of 2 min for a total cycle time of 4 min. The duration determined with these RSLDE experiments was optimized in order to obtain a comparable quality of maceration, which lasted for 15 days. The maximum cycle number defined for RSLDE was 1000, corresponding to approximately 3 days of extraction.

The extraction tests were carried out on a young commercial *grappa* using 10 g of Nobile® Sweet chips in 600 mL of *grappa* for 3 days. The same amount of chips and *grappa* were used for maceration for 15 days.

Preliminarily, the solid–liquid extraction was carried out in model solutions of water/ethanol (60:40, *v*/*v*), using unroasted and medium-toasted chips. In order to follow the extraction, solutions were stored in bottles (under reducing conditions) and sampled over time to reveal and compare only the extraction process from the wood and the stability of the extracted compounds.

2.4. Analysis of the Extracted Samples

2.4.1. Determination of Dry Residue

For the determination of the dry residue, 10 mL of the extracted sample was dried in the oven. The oven temperature was first set at 75 °C for the removal of the alcohol, and when the volume of the liquid became negligible, the temperature was raised to 105 °C to aid the evaporation of traces of water. The dry extract was recovered from the oven and, having cooled to room temperature, was weighed with an analytical balance with a sensibility of 0.1 mg. This operation was repeated until reaching a constant weight. Each determination was repeated 3 times, and the mean result was reported.

2.4.2. Determination of Total Polyphenols Using the Folin–Ciocalteu Method

Total phenol concentrations in plant extracts were determined spectrophotometrically by the Folin–Ciocalteu assay using gallic acid as a standard (mg GAE/g) [30]. A 125 µL intake of the methanolic extract was mixed with 500 µL of distilled water and 125 µL of the reagent of Folin–Ciocalteu were added. After vigorous stirring of the mixture followed by standing for 3 min, an aliquot of 1250 µL of 7% Na_2CO_3 was added. The solution was placed for 90 min at room temperature in a dark place. Lastly, absorbance was

measured at 760 nm using a spectrophotometer UV-Vis (SmartSpec 3000, Bio-Rad Laboratories, Inc., Hercules, CA, USA). A calibration curve of gallic acid was prepared, and the results, determined from the regression equation of the calibration curve, were expressed as the mass of equivalent gallic acid over the mass of the sample. The same procedure was followed for the samples. From the sample absorbance values at 760 nm, the total polyphenols expressed as mg gallic acid equivalent per gram were determined.

2.5. HPLC Analysis

The chromatographic measurements were carried out with a Waters 1525 binary HPLC and a Waters 2996 photo diode array (PDA) detector; this analysis was used to support the determination of the UV spectra (230–400 nm) of the samples. The analytical column was a reverse phase C18 (250 mm × 4.6 mm; 5 µm) (Phoenomenex, Torrance, CA, USA); The mobile phase was eluent A water/formic acid (98:2, *v*/*v*) and eluent B methanol-water-formic acid (70:28:2, *v*/*v*/*v*). All the HPLC eluents used were purchased from Sigma Aldrich, Milan, Italy. The flow rate was set at 1 mL/min, with an injected volume of 20 µL. Before injections, the samples were filtered with nylon syringe filters of 0.45 µm with an external diameter of 25 mm from Millipore, Merck (Milan, Italy). The Limit Of Detection (LOD) determined for all compounds was in the range of 1 to 5 ppm. The elution program is described in Table 1.

Table 1. High performance liquid chromatography method for analysis of phenolic acids.

Time, min	Reservoir of Water-Formic Acid (98:2, *v*/*v*)	Reservoir of Methanol-Water-Formic Acid (70:28:2 *v*/*v*)
0	90%	10%
3	90%	10%
25	40%	60%
43	40%	60%
55	0%	100%
65	0%	100%

2.6. Analysis of a Young Commercial Grappa

A total of 10 g of Nobile® Sweet chips was put in contact with 600 mL of young commercial *grappa*. The sample was subjected to two extraction methods: maceration for 15 days and RSLDE at a different number of cycles.

2.7. Statistical Analyses

Results are the mean values ± SD (standard deviation) of 3 replicates. The significance level was set at $p = 0.05$.

3. Results and Discussion

In the present work, the potential of an alternative procedure to traditional aging in alcoholic beverage barrels was evaluated. Initially, solid–liquid extraction was conducted in water/ethanol 60:40 (*v*/*v*) model solutions using toasted and unroasted chips. Following the extraction, the solutions were stored in bottles (reductive environment) and sampled over time with the aim of revealing and comparing only the extraction process from the wood and the stability of the extracted compounds. Dry residue, total polyphenol content and RP-HPLC analysis were determined on the different solutions obtained, which allowed the identification and quantification of furfural, ellagic acid and phenolic aldehydes (vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde). The RP-HPLC analysis shows that unroasted chips (Nobile® Fresh) have a lower content of bioactive compounds than medium-roasted chips (Nobile® Sweet). On the other hand, furfural and phenolic aldehydes are essentially formed following roasting from the degradation of hemicelluloses and lignin, respectively. While ellagic acid is also present in the solutions in which

the unroasted chips have been extracted, it can derive both from the degradation of the ellagitannins during the roasting treatment and from the hydrolysis of the ellagitannins during the aging process. This is probably linked to the fact that ellagitannins, from which ellagic acid can derive, are present in greater quantities in unroasted chips, as they degrade with roasting [31]. This greater quantity of ellagitannins is probably also responsible for the higher values of total polyphenols and dry residue for the solutions obtained by extraction of the unroasted chips. This may seem to contradict the lesser variation in color that occurred during the extraction of the Nobile® Fresh chips compared to the Nobile® Sweet ones, as the partially oxidized and polymerized ellagitannins are considered responsible for a large part of the color of the heartwood [32].

On the other hand, a study by Canas et al., 2013 reported that other compounds, not quantified by the total amount of polyphenols or the dry extract, can determine the color of brandy [33]. During the roasting process, various substances are produced following the interaction between sugars and amino acids, known as the Maillard reaction. Therefore, the color is influenced by melanoidins and probably other colored compounds that form during this reaction [34].

Based on this hypothesis, higher roasting intensities can favor the formation and accumulation of these compounds; such concentrations do not significantly influence the dry extract but contribute to the evolution of color [35]. Once the number of cycles necessary to equalize the extraction yield of the maceration had been estimated, an unaged (young) commercial *grappa* was subjected to extraction with Nobile® Sweet chips using the two methods to verify the effects of the interaction of the compounds extracted with the drink compounds. The data obtained show that the extraction yield is greater for maceration, as reported in Table 2.

Table 2. Dry residue of model solutions with Nobile® Fresh chips extracted using the two methods.

Time, Days	Maceration		RSLDE 49 Cycles (196 min)		RSLDE 268 Cycles (1072 min)		RSLDE 360 Cycles (1440 min)	
	Dry residue (g/L)	Non-volatile amount extracted (%)	Dry residue (g/L)	Non-volatile amount extracted (%)	Dry residue (g/L)	Non-volatile amount extracted (%)	Dry residue (g/L)	Non-volatile amount extracted (%)
0.005	---	---	0.62 ± 0.03	3.5	---	---	---	---
0.734	---	---	---	---	0.75 ± 0.02	4.5	---	---
1	---	---	---	---	---	---	1.51 ±0.06	8.6
6	0.63 ± 0.07	---	---	---	0.85 ± 0.03	5.5	1.75 ± 0.05	10.5
15	1.37 ± 0.02	8.2	0.61 ± 0.02	3.7	0.83 ± 0.02	5	1.77 ± 0.03	11.1
80	1.45 ± 0.02	8.7	0.56 ± 0.04	3.4	0.98 ± 0.03	5.9	1.81 ± 0.04	12.5
210	1.71 ± 0.03	10.3	0.68 ± 0.5	4.2	---	---	---	---

3.1. Extraction of Model Solutions

Furthermore, the comparison with an aged commercial *grappa* of the same brand, which was aged in barrels for 12 months, showed a significantly higher content of total polyphenols and phenolic and furan compounds deriving from wood compared to the two alternative aging techniques.

3.1.1. Extraction of Nobile® Fresh Chips

The dry residue and the total polyphenol content of the extractions obtained by maceration and by RSLDE containing Nobile® Fresh chips are shown in Tables 2 and 3.

The maceration process has been performed for 210 days, during which the contact between chips and solvent was constant under discontinuous stirring. Different was the process of RLSDE. In RLSDE 50 cycles extraction, the total extraction time is 200 min, corresponding to 0.005 days; instead, in RLSDE 286 cycles extraction, the extraction time is 1072 min, corresponding to 0.744 days. After RLSD extraction, the liquid extract was

withdrawn, separated from chips and stocked at room temperature in the dark. Then, measurements were performed on these samples at 6, 15, 80 and 210 days, respectively.

Table 3. Total polyphenols (GAE/L) of the model solutions with Nobile® Fresh chips extracted with the two methods (GAE: mg of gallic acid equivalent).

Time, Days	Maceration	RSLDE 49 Cycles (196 min)	RSLDE 268 Cycles (1072 min)	RSLDE 360 Cycles (1440 min)
0.005	---	170 ± 5	---	---
0.734	---	---	368 ± 5	---
1	---	---	---	440 ± 6
6	257 ± 9	---	380 ± 6	480 ± 2
15	510 ± 12	176 ± 7	402 ± 3	510 ± 9
80	426 ± 8	168 ± 6	446 ± 2	553 ± 4
210	593 ± 8	187 ± 2	---	---

The solutions obtained through maceration yielded higher values for both dry residue and total polyphenols, indicating an increased extraction yield after 6 and 15 days of observation. Nevertheless, in the solutions resulting from RSDLE, the values of dry residue and total polyphenols have the ability to increase by increasing the number of cycles. This suggests that it might be sufficient to increase the number of extraction cycles to achieve extraction yields comparable to those of a 15-day maceration. Furthermore, the greater yield of maceration was confirmed by the evolution of the color of the solutions and the decrease in pH. In fact, as can be seen in Figure 2, the solution obtained from the maceration of the chips developed a more intense color than that resulting from 268 extraction cycles, which is in turn more intense than that obtained from 49 extraction cycles.

Data reported in Tables 2 and 3 show that, over time, the values of the dry residue and polyphenols tend to increase, suggesting an evolution of the extracted compounds.

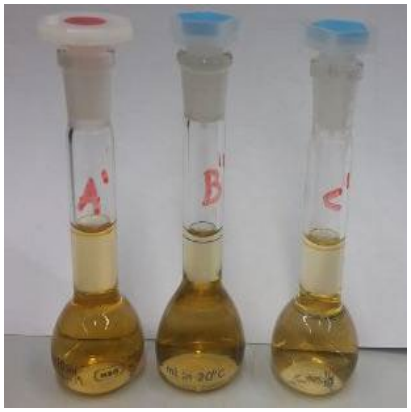

Figure 2. Model solutions with Nobile® Fresh chips obtained from: A′: Maceration; B′: RSLDE 268 cycles; C′: RSLDE 49 cycles.

Additionally, the decrease in pH, characteristic of the aging process [36] and indicative of the extraction of phenolic compounds and/or other acidic compounds, was larger in the case of maceration (Table 4).

Table 4. Measurement of the pH of the solutions extracted with the two methods using Nobile® Fresh chips.

Solutions	pH
Hydroalcoholic solution	6.39
Maceration after 210 days	3.66
RSLDE 49 cycles after 210 days	4.44
RSLDE 268 cycles after 80 days	4.22

3.1.2. Extraction of Nobile® Sweet Chips

Similarly, in Tables 5 and 6, the dry residue and total polyphenol content of the model solutions containing Nobile® Sweet chips by maceration and RSLDE are reported.

Table 5. Dry residue of model solutions with Nobile® Sweet chips extracted using the two methods.

Time, Days	Maceration		RSLDE 49 Cycles (196 min)		RSLDE 268 Cycles (1072 min)		RSLDE 360 Cycles (1440 min)	
	Dry residue (g/L)	Non-volatile amount extracted (%)	Dry residue (g/L)	Non-volatile amount extracted (%)	Dry residue (g/L)	Non-volatile amount extracted (%)	Dry residue (g/L)	Non-volatile amount extracted (%)
0.005	---	---	0.30 ± 0.03	1.6	---	---	---	---
0.734	---	---	---	---	0.34 ± 0.02	2	---	---
1	---	---	---	---	---	---	1.2 ± 0.05	6.5
6	---	---	---	---	0.34 ± 0.03	2	1.3 ± 0.07	7.8
15	1.10 ± 0.02	6.6	0.29 ± 0.03	1.7	0.58 ± 0.03	1.7	1.45 ± 0.10	8.5
80	1.31 ± 0.02	7.9	0.40 ± 0.02	2.4	0.75 ± 0.05	4.5	1.51 ± 0.09	8.9
210	1.38 ± 0.02	8.1	1.11 ± 0.07	6.3	---	---	---	---

Table 6. Total polyphenols (GAE/L) of the model solutions with Nobile® Sweet chips extracted with the two methods (GAE: mg of gallic acid equivalent).

Time, Days	Maceration	RSLDE 49 Cycles (196 min)	RSLDE 268 Cycles (1072 min)	RSLDE 360 Cycles (1440 min)
0.005	---	110 ± 5	---	---
0.734	---	---	198 ± 3	---
1	---	---	228 ± 4	403 ± 8
6	---	---	220 ± 5	410 ± 5
15	330 ± 10	116 ± 6	212 ± 4	440 ± 4
80	304 ± 6	132 ± 8	±	445 ± 7
210	379 ± 8	149 ± 3	---	---

Also, in this case, the solutions resulting from the maceration of RSLDE gave higher values of both dry residue and total polyphenols, suggesting a greater extraction yield with values that approached those of the maceration with the increase in the number of cycles. This was confirmed by the evolution of the color of the solutions and by the decrease in pH (Table 7). More intense colors and a lower pH were obtained for the solution obtained by macerating the chips, followed by that resulting from the extraction of RSLDE 268 cycles (Figure 3).

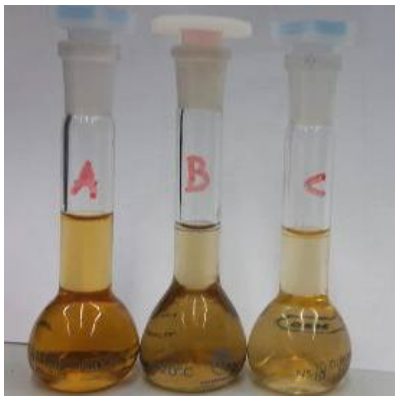

Figure 3. Solutions obtained from: A: Maceration; B: RSLDE 268 cycles; C: RSLDE 49 cycles.

Table 7. Measurement of the pH of the solutions extracted with the two methods using Nobile® Sweet chips.

Solutions	pH
Hydroalcoholic solution	6.39
Maceration after 210 days	3.63
RSLDE 49 cycles after 210 days	4.58
RSLDE 268 cycles after 80 days	4.30

Even in the case of extractions with Nobile® Sweet chips, the same trend was respected for the values of the dry residue and polyphenols reported previously for extractions with Nobile® Fresh chips.

3.2. HPLC Analysis

The available standards were analyzed by chromatographic analysis first individually and then in mixture at wavelengths between 200 and 400 nm (see Table 8). Therefore, each standard was injected into the HPLC-DAD (diode array detector) to define the retention time and absorption peak of each compound. Table 8 shows the identification of the standard compounds, their retention times and the respective absorption maxima of each compound.

Table 8. Identification of chromatographic peaks, retention times and characteristic wavelengths of each compound of standard mixture.

Compounds	Retention Time	Wavelengths	Wavelengths
Furfural	13.40 ± 1.11	233	276
Vanillin	26.14 ± 0.49	238	280–309
Syringaldehyde	28.55 ± 0.45	238	309
Coniferaldehyde	33.69 ± 0.51	243	306–342
Sinapaldehyde	34.89 ± 0.33	246	347
Ellagic acid	42.40 ± 2.48	252	365

Figure 4 shows the HPLC analysis of the same standard mixture with the identification of peaks corresponding to the standards at the two selected wavelengths.

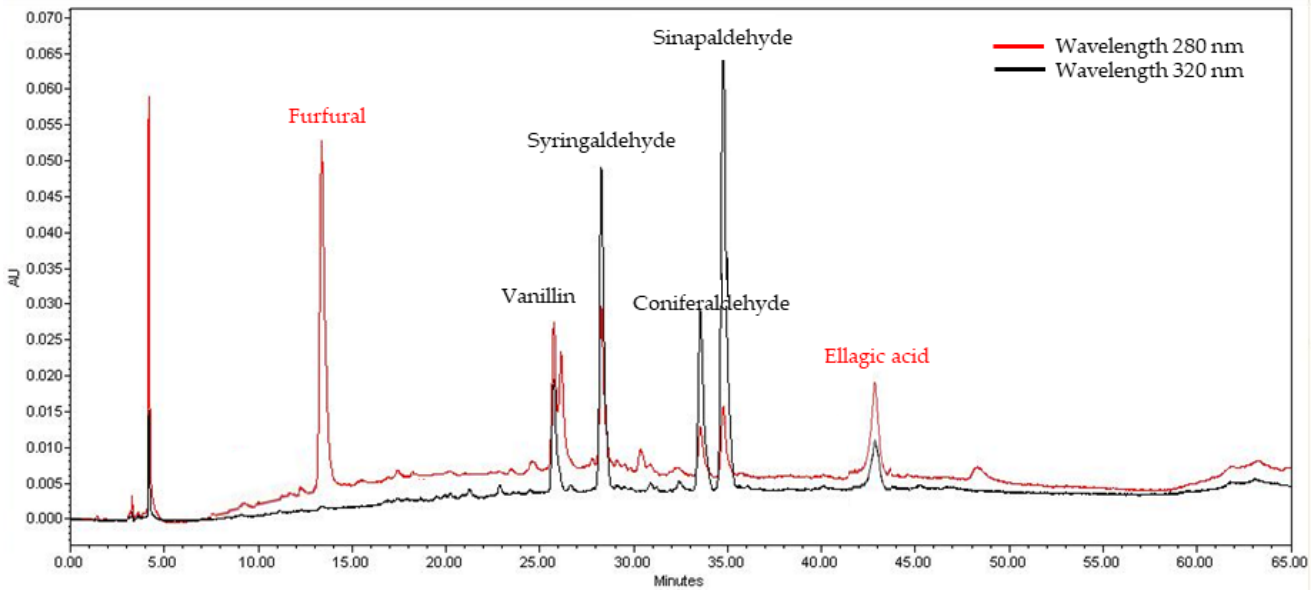

Figure 4. RP-HPLC analysis at 280 nm (red) and 320 nm (black) of the mixture of standard compounds.

Subsequently, under the same chromatographic conditions, HPLC analyses were carried out on the solutions extracted with both methods, which allowed the identification of furfural, ellagic acid and phenolic aldehydes (vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde) based on the standards (Table 8). However, the chromatographic analysis of the solutions obtained by maceration and RSLDE revealed the evident presence of only ellagic acid, while the other compounds were present only in traces (see Figure 4). Therefore, it could be hypothesized that the phenolic and furan compounds present in the samples were not extracted under conditions more suitable for their production. In all cases, the extractions of Nobile® Sweet chips were richer in compounds than those of Nobile® Fresh chips. Furthermore, for all the solutions resulting from the extraction of Nobile® Sweet chips, a higher percentage of cinnamic aldehydes compared to benzoic ones was obtained. This may be due either to the degree of roasting, given that in the degradation of lignin, cinnamic aldehydes are formed, which then evolve to phenolic aldehydes, to a greater ease of extraction of cinnamic aldehydes [37], or to a different response factor of the compounds detected by HPLC.

The comparison of average values of total areas also enabled us to estimate the percentage decrease in extraction yield compared to maceration. This decrease was found to be 64% for 49 cycles of extraction and 48% for 268 cycles of extraction.

From the comparison of the individual peak areas, the extracted quantities of each individually identified analyte were also estimated in terms of percentages compared to maceration (Table 9).

Table 9. Comparison of the percentages of bioactive compounds extracted by RSLDE versus maceration.

Compounds	RSLDE 49 Cycles, %	RSLDE 268 Cycles, %
Furfural	36	48
Vanillin	46	58
Syringaldehyde	36	54
Coniferaldehyde	30	47
Sinapaldehyde	48	81
Ellagic acid	30	36

3.3. Aging Tests on Commercial Grappa

Once the required number of cycles for RSLDE (1030 cycles) to equalize the extraction yield with maceration had been determined, extractions were performed on a young commercial *grappa* using the toasted Nobile® Sweet chips. These chips were found to be richer in compounds compared to the Nobile® Fresh chips. The goal was to examine the effects of the interaction between the extracted compounds and those present in the drink and to assess the proximity of the results to a commercially aged *grappa* in barrels.

Comparing the data in Table 10, it is evident that the dry residue is higher in the aged commercial *grappa*, whereas the total polyphenol content is greater in the young commercial *grappa* subjected to extraction with Nobile® Sweet chips. Additionally, consistent with previous findings, maceration exhibits higher dry residue and polyphenol values than RSLDE. This is further supported by the increased coloration of the *grappa* resulting from maceration (Figure 5).

Table 10. Dry residue and total polyphenols in young commercial *grappa*, young commercial *grappa* with Nobile® Sweet chips, aged commercial *grappa* extracted by maceration and RSLDE 1030 cycles. GAE: mg of gallic acid equivalent.

Sample	Dry Residue g/L	Polyphenols GAE/L
Young commercial *grappa*	1.69 ± 0.02	16 ± 2
RSLDE 1030 cycles with Nobile® Sweet chips	2.84 ± 0.05	483 ± 7
Aged commercial *grappa*	6.99 ± 0.07	32 ± 3

Figure 5. Extracted solutions obtained using the two extraction methods: M: Maceration; NE: RSLDE 1030 cycles.

In the chromatographic conditions used, the HPLC analysis of young commercial *grappa* and that of the same brand aged 12 months did not highlight the presence of peaks of interest, such as phenolic aldehydes, but only the presence of a peak corresponding to furfural (Figure 6a,b).

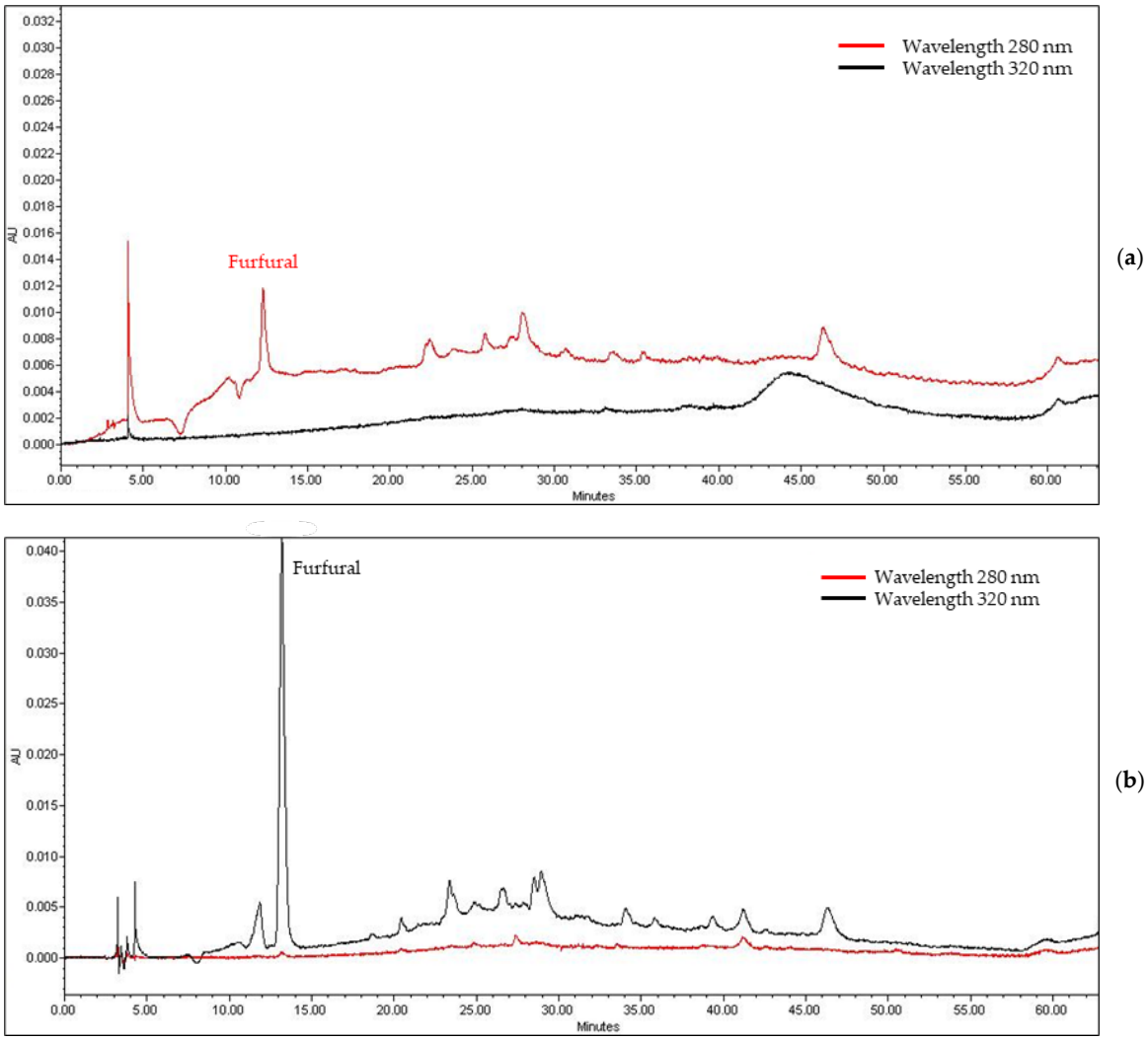

Figure 6. Chromatographic analysis of young commercial *grappa* (**a**) and aged commercial *grappa* (**b**) at 280 and 320 nm wavelengths.

Subsequently, the young commercial *grappa* was subjected to aging with Nobile® Sweet chips and extraction by maceration (15 days) and RSLDE 1030 cycles.

The HPLC analysis of young commercial *grappa* aged with Nobile® Sweet chips and extracted by maceration for 15 days showed a greater extraction yield compared to RSLDE. However, analysis of the sample extracted using RSLDE revealed the presence of a peak that was not present in the analysis of the sample extracted by maceration. The retention time is 18.60 min and could correspond to 4-hydroxybenzaldehyde, based on comparison with the literature [38], but the lack of standards did not allow the compound to be identified with certainty (Figure 7a,b).

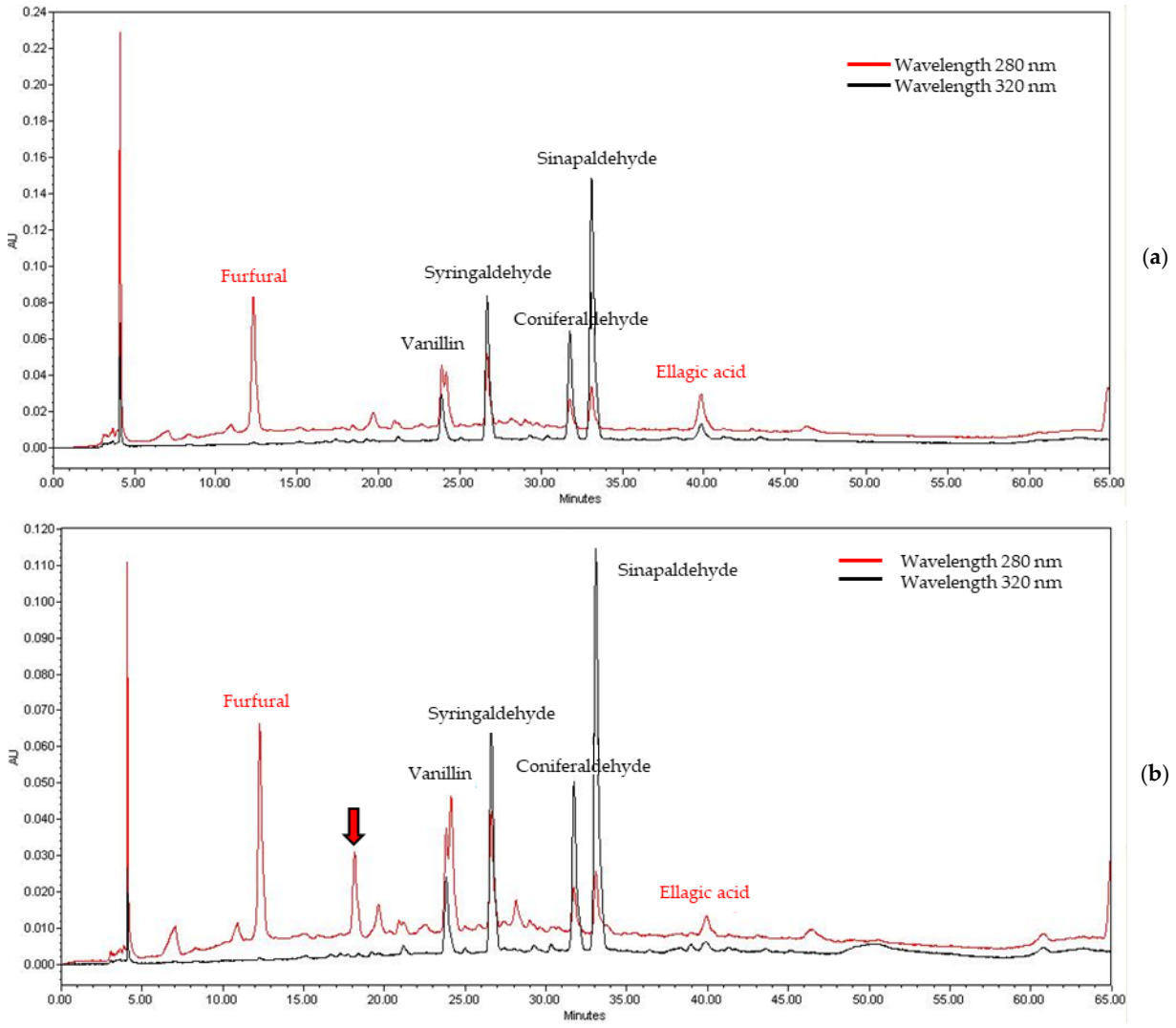

Figure 7. Chromatographic analysis of young commercial *grappa* aged with Nobile® Sweet chips extracted by maceration for 15 days (**a**) and RSLDE 1030 cycles (**b**) at 280 and 320 nm wavelengths. The arrow (**b**) indicates a peak at the retention time of 18.60 min, probably corresponding to 4-hydroxybenzaldehyde.

Also, in this case, a higher percentage of cinnamic aldehydes was observed compared to benzoic ones. The comparison of total areas and individual peaks confirms the greater extraction yield of maceration. Looking at results for *grappa* and for the water/ethanol 60:40% *v*/*v* solution (obtained by extraction with the two methods), results highlight that with the same extraction technique, the total areas appear greater for *grappa* compared to the water/ethanol 60:40% *v*/*v* model solution. This is probably due to the lower pH of *grappa*, which favors the extraction of polyphenolic compounds from the wood [39,40].

Finally, tests were conducted to assess the stability of bioactive compounds over time using the two methods. While these tests are preliminary and only cover the time interval between 0 and 6 days, the compounds demonstrated stability over this period.

4. Conclusions

According to the data obtained by the shown experiments, it is possible to conclude that in all the extracted solutions containing Nobile® Sweet chips, a higher percentage of cinnamic aldehydes was detected compared to benzoic ones. This could be attributed either to the degree of roasting, as the degradation of lignin results in the formation of cinnamic aldehydes that subsequently evolve into phenolic aldehydes. Alternatively, it could be due to a higher ease of extraction of cinnamic aldehydes or a variation in the response factor of the compounds identified during the HPLC analysis.

However, other extraction tests will be necessary to be able to study and reproduce the aging of alcoholic beverages by verifying the effects of all possible process parameters. Future studies will be directed to follow the temporal evolution of *grappa* samples to verify the possibility of interactions between compounds deriving from wood and the drink in a reducing environment. After this, further research will also aim to analyze the volatile extract components. Furthermore, the aging process will be simulated, considering oxygen concentration. In any case, the effectiveness demonstrated by RSLDE in reducing aging times compared to conventional maceration stimulates research interest to encourage the application of this method in the alcoholic beverages sector.

This work was focused on the chemistry of the extraction and on process optimization. However, another issue to be addressed concerns the sensorial analysis, which plays a key role and requires the involvement of a team of tasters (panels). Therefore, based on this, a sensory evaluation requires significant planning and experimentation, which was not the subject of this manuscript but will certainly be carried out in future work.

Author Contributions: Conceptualization, D.N., P.T., D.M. and M.G.; methodology, A.P. and P.T.; software, A.P. and P.T.; validation, D.N., P.T., D.M. and M.G.; formal analysis, A.P. and D.M.; investigation, D.N. and M.G.; resources, D.N. and M.G.; data curation, A.P. and P.T.; writing—original draft preparation, P.T. and M.G.; writing—review and editing, P.T. and D.M.; visualization, D.N., P.T., D.M. and M.G.; supervision, D.N., P.T., D.M. and M.G.; project administration, D.N. and M.G.; funding acquisition, D.N. and M.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest. The research was conducted in the absence of commercial or financial relationships that could be interpreted as a potential conflict of interest with the company Erbagil s.r.l. where the co-author Domenico Montesano works.

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