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Evaluation of Fractions Obtained Through Steam Distillation and Hydroalcoholic Maceration of Wood Chips from *Pinus mugo* for Flavouring Italian Spirit *grappa*

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Abstract: In the Italian Alps, mountain pine (*Pinus mugo*) is traditionally used to flavour the Italian spirit *grappa*. While its shoots and needles are well-studied, little is known about the potential of its wood and bark. This study explores the sequential extraction of *Pinus mugo* wood chips for grappa aromatisation, combining steam distillation and hydroalcoholic maceration to isolate volatile and non-volatile compounds. The wood chips were subjected to steam distillation to extract essential oils, followed by maceration in a 40% ethanol solution for 33 days. Three extracts were produced: essential oil, and hydroalcoholic extracts from fresh and post-distillation wood chips. The daily monitoring of maceration included pH, ORP, and colour analysis using the CIELAB methodology. The essential oil yield was 0.36 ± 0.12 mL per kg of wood chips. Fresh wood chips exhibited faster extraction and colour development compared to spent material. A sensory analysis distinguished *grappas* flavoured with essential oils but found no perceptible differences between those flavoured with fresh versus spent wood chips. This approach promotes the sustainable valorisation of *Pinus mugo* through circular extraction methods, enabling the customisation of *grappa*'s sensory profile and supporting diversification in Non-Wood Forest Products.

Keywords: spirits; essential oils; solid–liquid extraction; alcoholic beverages; sequential extraction; forest by-products

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1. Introduction

The use of conifers as flavouring agents in *grappa* is a traditional practice in the Italian Alps. *Grappa* is a PGI Italian spirit produced by distilling fermented grape marc derived from cultivation and vinification within Italy. The minimum percentage of ethanol permitted is 37.5% v/v; however, *grappas* are typically produced at 40% v/v ethanol content [1,2]. The same legislation defines aromatised *grappa*, which is obtained by the infusion of fruits or aromatic plants, which give a special aroma and colour to the spirit. Therefore, *grappa* is already a symbol of Northern Italy, and it is a widespread opinion that its aromatisation strengthens the link with the territory of origin. In general, a wide range of plant materials has been tested for flavouring spirits and liquors. From a chemical perspective, *grappa* aromatisation is a solid–liquid extraction using a botanical as the source of aroma-active compounds. It has been reported that 57 taxa have been studied for *grappa* aromatisation [3]. Among these, conifer species are the most mentioned; for instance, in the Pinaceae family, *Pinus* spp. is employed both in *grappa* and liquors. The choice of conifers in *grappa* aromatisation is usually limited to specific plant organs, such as cones, buds, leaves, and young shoots, subjected to hydroalcoholic maceration within the spirit [3]. A wide variety of products containing these flavouring agents is available on the market. In these products, traditional maceration is used to confer the peculiar taste requested for aromatisation to the *grappa*. Regarding the compounds responsible for this aroma, different studies analysed the chemical composition of the cones and sprouts of *Pinus mugo* and, consequently, the compounds extracted during distillation and maceration [4–10], while a limited number of works also focused on the composition of wood and bark [7,10]. However, both green parts and wood are responsible for significant changes in the taste and aroma of distilled beverages, since they allow for the simultaneous extraction of both volatile compounds, responsible for the olfactory profile, and non-volatile compounds, related to the tactile characteristics of the final product.

Steam distillation is an extraction technique commonly applied to plant material, often used to separate essential oil and other volatile compounds. Steam distillation is usually performed at atmospheric pressure and implies the passage of water vapour at 100 °C across the plant charge, determining the extraction of volatile compounds. The alternative uses of steam frequently described in the scientific literature are steam blanching and steaming, where steam is typically employed as a pre-treatment to cause damage to the plant tissues and favour further processes such as solid–liquid solvent extraction or drying [11–13].

A substantial amount of *Pinus mugo* is available as a forestry by-product, deriving from efforts to contain the expansion of this species into other land uses (e.g., pastures) [14,15]. In this context, several producers have started distilling the green shoots to extract *Pinus mugo* essential oil, while the wooden parts are usually discarded. However, wood still contains essential oils and other compounds that could be used. In general, the aromatisation of *grappa* with conifers yields results that are well appreciated by consumers.

This study delves into the prospect of obtaining different aroma-active fractions from *Pinus mugo* wood chips. This is carried out by segregating the extraction of volatile and non-volatile compounds from *Pinus mugo* wood chips and dividing the maceration process into two separate unit operations, namely steam distillation and the subsequent hydroalcoholic extraction of the spent material. The resulting extraction fractions are then utilised to aromatise the Italian spirit *grappa*. Our primary hypothesis posits that by decoupling these extraction processes, producers can distinguish and customise their *grappas*.

2. Materials and Methods

2.1. Raw Materials and Treatments

Pinus mugo wood chips were provided by Magnifica Essenza company (Cavalese, Trento, Italy) in November 2023.

The wood chips were extracted by steam distillation and hydroalcoholic maceration. The moisture content of the wood material was determined by oven-drying at 105 °C for 24 h [16]. The samples were kept in the oven for 24 h until they reached a variation <0.2% throughout one hour. The measurement was performed on fresh wood chips and on wood chips previously subjected to distillation in three replicates.

2.2. Steam Distillation

Water and steam distillation was performed through a 20 dm^3 stainless steel extractor (Albrigi Luigi Srl, Verona, Italy) equipped with a tube-in-tube condenser and a cohobation system. The distillation apparatus was set with 1 dm^3 of water below the grid level and filled with wood chips above the grid. In each distillation, 5 kg of *Pinus mugo* wood chips were used. The heat source was represented by an electric plate set to the power of 2 kW for the entire operation. Throughout the distillation process, temperature and yield were monitored. The temperature of the still was monitored from the built-in thermometer; the cooling water temperature was measured periodically through a PT100 temperature probe. The cooling water flow rate was managed to keep the condensate output flow rate constant. The total cooling water was estimated as a product of the flow rate and duration. The distillation step was scheduled to last for 60 min. Each extraction was performed in triplicate.

At the end of the extraction process, essential oil and aromatic water (or hydrolat) were separately collected and stored in refrigerated conditions (4 °C). In relation to the essential oil, yield (%) was calculated as a ratio between the essential oil yield (cm^3) and the wood chips mass (g):

$$\mu\mathrm{EO}\ (\%) = \frac{\text{essential oil}\ (\mathrm{cm}^3)}{\text{wood chips}\ (\mathrm{g})} \times 100 \tag{1}$$

2.3. Hydroalcoholic Maceration

Both the fresh and post-distillation spent wood chips were subjected to maceration in a hydroalcoholic solution. A 40% alcohol solution was used in the experiment to simulate the alcohol content of *grappa* [1]; with a solid–liquid ratio of 1:10, 60 g of wood chips were placed into 600 cm^3 of hydroalcoholic solution for 33 days [5]. Dark glass bottles were used as containers and were stored at room temperature. All the extractions were performed in three replicates for both species. Throughout the maceration process, measurements of the pH and oxygen redox potential (ORP) were performed daily with the multiparameter device XS PC7 Vio (XS Instruments, Modena, Italy). Temperature was also measured using the same instrument. The colour of the solution was monitored through the Smart Analysis device (DNA Phone Srl, Parma, Italy) based on the CIELAB method. Chroma, hue, and ΔE were calculated according to the following equations [17]:

$$\mathrm{Chroma} = \sqrt{\mathrm{a}^2 + \mathrm{b}^2} \tag{2}$$

$$\mathrm{Hue} = \tan^{-1}\left(\frac{\mathrm{b}}{\mathrm{a}}\right) \tag{3}$$

$$\Delta\mathrm{E} = \sqrt{(\mathrm{L}_1 - \mathrm{L}_2)^2 + (\mathrm{a}_1 - \mathrm{a})^2 + (\mathrm{b}_1 - \mathrm{b}_2)^2} \tag{4}$$

Whiteness index (WI) (Equation (5)) and Yellowness index (YI) (Equation (6)) were computed as reported by [18]:

$$\mathrm{WI} = 100 - \sqrt{(100 - \mathrm{L})^2 + \mathrm{a}^2 + \mathrm{b}^2} \tag{5}$$

$$\mathrm{YI} = 142.86 \times \frac{\mathrm{b}}{\mathrm{L}} \tag{6}$$

At the end of the maceration period, the solutions were filtered using 67 g/m^2 filter paper (Vetrotecnica, Padova, Italy). The final product was bottled and stored for sensory evaluation. For each replication, one subsample was collected and stored at 4 °C for chemical analysis.

2.4. Grappa Flavouring

Based on the flavouring material, three types of *grappa* were produced: *grappa* flavoured with *Pinus mugo* essential oil, and two *grappas* flavoured through hydroalcoholic maceration of fresh wood chips (as a reference for the traditional maceration productive process) and post-distillation spent wood chips from both plant species. The EO-based *grappa* was flavoured with 0.5 cm^3 of essential oil in 600 cm^3 of 40% alcohol solution.

This dilution was established through preliminary sensory trials aimed at detecting the recognition threshold.

2.5. Chemical Analysis

All three types of flavoured *grappa* were analysed by GC-MS. Volatiles were extracted by means of liquid–liquid extraction with pure dichloromethane (Sigma-Aldrich, Merk SPA, Milan, Italy). To 20 cm^3 of grappa, 0.1 mm^3 of 1-Heptanol (1 mg/cm^3) was added as an internal standard and extraction was performed in a separation funnel (3×20 cm^3). The combined organic phases were washed with a saturated NaCl solution and then concentrated under a flow of nitrogen to 1 cm^3. The samples were filtered with a syringe filter (0.22 μm) and subjected to analysis. The analysis was performed on an Agilent Technologies 7890A gas chromatograph coupled with a selective 5977 mass detector, injecting 1 mm^3 of the extracts. The components were separated on a silica capillary column, HP-5MS (5% diphenyl- and 95% dimethyl-polysiloxane, 30 m × 0.25 mm, 0.25 μm film thickness; Agilent Technologies, Santa Clara, CA, USA). Helium was used as the carrier gas at a flow rate of 1 cm^3/min. The GC oven temperature was held for 2 min at 40 °C, increased to 160 °C at the rate of 3 °C/min, then at 10 °C/min to 250 °C and finally held at 250 °C for 5 min. The separated components were further analysed by a mass spectrometer. The temperatures of the MSD transfer line, ion source, and quadruple mass analyser were set at 280 °C, 230 °C, and 150 °C, respectively. The ionisation voltage was 70 eV, and mass detection was performed in scan mode, with a m/z range of 30 to 500. Data processing was operated by Mass Hunter in combination with the NIST library software, with matching $> 85\%$ (Agilent Technologies, Santa Clara, CA, USA). Compounds with matching $> 85\%$ were included and recognised based on comparison with the standard MegaMix #1 (Restek, Milano, Italy), the NIST library and Kovats indices. Safety assessment for the presence of heavy metals was performed by ICP-MS [19].

2.6. Sensory Evaluation

The sensory profiles of the three types of finished products were tested through discriminant tests and descriptive evaluation. In particular, two types of sensory tests were performed at the TESAF Department, University of Padova (Legnaro, Italy). A discrimination test, specifically a triangle test, was chosen to establish whether there are perceivable differences between the samples.

The triangle tests were administered using a simplified version of the standard procedure. This test was chosen to test for perceptible differences due to different flavouring additions to a homogeneous base spirit [20,21]. A total of 24 panellists carried out the triangle tests. The samples were displayed simultaneously in three series. In each series, three samples were presented, with one sample being different from the others, i.e., the odd sample. The samples (a, grappa flavoured with fresh wood chips; b, grappa flavoured with post-distillation spent wood chips; and c, grappa flavoured with *Pinus mugo* essential oil) were arranged in three combinations and randomly assigned to each panellist. The volume of each sample was 2 cm^3, presented into black 29 cm^3 plastic glasses, labelled with a three-digit random code. The assessors were instructed to smell and taste each grappa to identify any difference in odour, taste, and aroma and were asked to recognise the odd sample.

Data were collected anonymously through digital forms. At the beginning of each test, the panellists were asked to provide personal information to classify all the participants into mutually exclusive categories based on gender, age class, smoker/non-smoker, grappa appreciation, and tasting experience. Ethical approval was assigned by the Ethical Committee for the Research at the Department of Land, Environment, Agriculture and

Forestry based on the Regulation of the Ethical Committee for the Research (2 October 2024). The answers were subsequently gathered in Excel (Version 16.66.1) and subjected to statistical analysis.

2.7. Statistical Analysis

Statistical analysis was performed through the software Rstudio (Version 2023.09.1+494). For hydroalcoholic maceration, the effects of time and raw material condition (i.e., fresh and spent woodchips) on pH, ORP, and CIELAB colour parameters (L^*, a^*, b^*, Chroma, hue, and ΔE) were evaluated using a two-way ANOVA. When time was found to be statistically significant, a kinetic model for the corresponding dependent variable was developed. If a mechanistic model was available in the literature, it was applied; otherwise, a linear model was used. The model coefficients were then tested using a t-test to assess differences attributed to raw material conditions. Furthermore, the Shannon–Weaver index was applied to the chemical composition of each sample in order to compare the chemical diversity of the different *grappas* based on the number of compounds and the relative abundance of each compound [22].

Data obtained from the GC-MS analyses and Shannon–Weaver indices were analysed by means of a One-Way ANOVA and Tukey HSD test with "condition" (grappa flavoured with essential oil, fresh wood chips, and post-distillation spent wood chips) as the dependent variable.

Finally, the significance of the triangle tests was assessed following the procedure established by ISO 4120/2021 [21] based on the Chi-square test between the measured and expected distributions.

3. Results

3.1. Steam Distillation and Hydroalcoholic Extraction

The fresh woodchips used had a moisture content of 40.66 ± 0.82%. The moisture content differed significantly between fresh and spent materials. Distillation had a significant effect on the wood chips' moisture (p = 0.001). Post-distillation, the spent wood chips exhibited a higher moisture content (52.79 ± 0.93%) compared to the fresh wood chips (40.66 ± 0.82%) (Table 1). This difference should be related to the water steam that goes through the charge during distillation and dampens the material to allow the extraction of the essential oil.

Table 1. Operating parameters of the distillation process and yield.

Heating time (min)	28.00 ± 5.29
Condensation time (min)	65.16 ± 2.70
Total operating time (min)	93.16 ± 7.94
Water flow rate (dm^3/min)	1.81 ± 0.12
Total water use (dm^3)	117.44 ± 3.17
Initial temperature (°C)	13.67 ± 2.08
Essential oil yield (cm^3/kg)	0.36 ± 0.12

In terms of essential oil, *Pinus mugo* yielded 0.36 ± 0.12 cm^3 for each kg of fresh wood chips introduced into the distiller. The distillation process was performed according to the operating parameters reported in Table 1.

Monitoring the extraction process set the basis for implementing steam distillation and hydroalcoholic maceration to extract volatile and non-volatile compounds from *Pinus mugo* wood chips.

Regarding the solid–liquid extraction, measurements of pH and ORP were performed throughout the maceration period. These parameters remained stable over time (i.e., no significant difference was found according to time). The pine-flavoured *grappa*s showed significant differences (p = 0.01) between the fresh and spent material, which were characterised, respectively, by a pH of 6.02 ± 0.16 and 5.51 ± 0.04 (Table 2). In line with the results related to the pH values, the ORP was found to be significantly different (p = 0.01) between the *grappa*s flavoured with pine fresh and post-distillation spent wood chips. Indeed, these samples reached the ORP values of 72.67 ± 2.52 mV and 44.67 ± 8.96 mV, respectively (Table 2).

Table 2. Values of pH and ORP (mV) by condition of the starting material: fresh and post-distillation spent wood chips.

	Fresh	**Spent**	
pH	5.51 ± 0.04	6.02 ± 0.16	p = 0.01
ORP (mV)	72.67 ± 2.52	44.67 ± 8.96	p = 0.01

This observation may be attributed to the different treatments the wood material underwent prior to hydroalcoholic maceration. The fresh wood chip samples exhibited higher ORP values, whereas the spent wood chip samples showed lower ORP values, suggesting a slightly enhanced antioxidant capacity in the solution made with spent woodchips. This result could be linked to the application of steam, which likely damaged the plant tissues, thereby facilitating the extraction of antioxidant compounds from the wood chips [11–13].

Extraction Kinetics

Since no variation in pH and ORP in time was noticed throughout the maceration process, these parameters were considered to describe the final *grappa*s subjected to further chemical and sensory analyses. A One-Way Analysis of Variance (ANOVA) and Tukey HSD test were computed on the values of pH and ORP as the dependent variables, differentiated in relation to the independent variable "condition" (fresh and post-distillation spent wood chips).

Variation in colour parameters in the $L^*a^*b^*$ colour space was analysed as a function of time. Extraction kinetics was modelled by applying linear and exponential functions. Peleg's equation was applied, as reported in the literature for the solid–liquid extraction of plant materials [23] and ANOVA was executed on the values of the slope (m) and asymptote (q). The extraction of wood compounds in alcoholic beverages has been previously described by Peleg's pseudo-second-order kinetics. This model has been fitted to extraction mechanisms which involve two processes: an instant washing of compounds from the wood surface, and a slow diffusion of compounds through the wood pores [23–25]. Additionally, linear models were tested. In accordance with the principle of model parsimony, the simpler linear model was preferred whenever Peleg's model did not significantly improve the explained variance, and ANOVA was performed on the values of the angular coefficient (m) and intercept (q). Coefficients of determinations (R^2) and p-values have been estimated to evaluate the fitted models (Table 3). In the linear models, m refers to the angular coefficient, which corresponds to the extraction rate, and q refers to the intercept, which represents the difference at the beginning of the maceration (time equal to 0). Since we used a model solution, no differences at time 0 exist. Thus, the significance of the model intercept relies on a fast change that occurred between the 0 and the first sampling point (i.e., 24 h). In the exponential models, q identifies the asymptote, which describes the extraction capacity, and m identifies the slope of the line, corresponding to the compound solubilisation rate. On these parameters, the analysis of variance highlighted significant differences in relation to the fresh or post-distillation spent plant material.

Table 3. Values of angular coefficient (m), intercept (q), and coefficients of determinations (R^2) of the fitted models for the colour parameters of hydroalcoholic extracts obtained from the fresh and post-distillation spent wood chips [1].

	Fresh Wood Chips			**Spent Wood Chips**		
	m	**q**	**R^2**	**m**	**q**	**R^2**
b*	$-6.53 \pm 3.06 \times 10^{-4}$	$9.64 \pm 1.31 \times 10^{0}$	$7.49 \pm 2.45 \times 10^{-2}$	$-6.11 \pm 4.05 \times 10^{-4}$	$1.36 \pm 0.58 \times 10^{1}$	$7.58 \pm 1.46 \times 10^{-2}$
Chroma	$-6.51 \pm 3.10 \times 10^{-4}$	$9.65 \pm 1.31 \times 10^{0}$	$7.49 \pm 2.48 \times 10^{-2}$	$-6.10 \pm 4.04 \times 10^{-4}$	$1.36 \pm 0.58 \times 10^{1}$	$7.58 \pm 1.43 \times 10^{-2}$
ΔE	$-1.11 \pm 3.51 \times 10^{-3}$	$4.14 \pm 2.63 \times 10^{0}$	$8.07 \pm 6.18 \times 10^{-2}$	$-1.22 \pm 5.73 \times 10^{-3}$	$5.14 \pm 0.64 \times 10^{0}$	$8.10 \pm 9.26 \times 10^{-3}$
YI	$-7.09 \pm 2.58 \times 10^{-4}$	$1.46 \pm 2.14 \times 10^{1}$	$0.84 \pm 3.82 \times 10^{-2}$	$-6.85 \pm 3.94 \times 10^{-4}$	$2.11 \pm 1.04 \times 10^{1}$	$7.97 \pm 1.64 \times 10^{-2}$
WI	$1.19 \pm 0.16 \times 10^{-4}$	$8.95 \pm 1.74 \times 10^{1}$	$8.71 \pm 5.70 \times 10^{-2}$	$1.68 \pm 0.04 \times 10^{-4}$	$8.50 \pm 0.87 \times 10^{1}$	$8.64 \pm 1.52 \times 10^{-2}$

[1] all models and coefficients were significant for $p < 0.05$.

Extraction kinetics showed significant results for the maceration time in relation to the CIELAB colour parameters. In particular, the L^* parameter followed a linear model (Figure 1a). The significance of the linear model was not increased by applying Peleg's exponential model. Chroma, b^*, and ΔE followed an exponential model based on Peleg's equation (Figure 1b–d). Finally, hue and a^* did not show statistically significant changes over time. These results allowed for modelling the extraction kinetics, highlighting that *grappas* obtained from the fresh and spent *Pinus mugo* wood chips showed significant differences in relation to the extraction rate and extraction capacity.

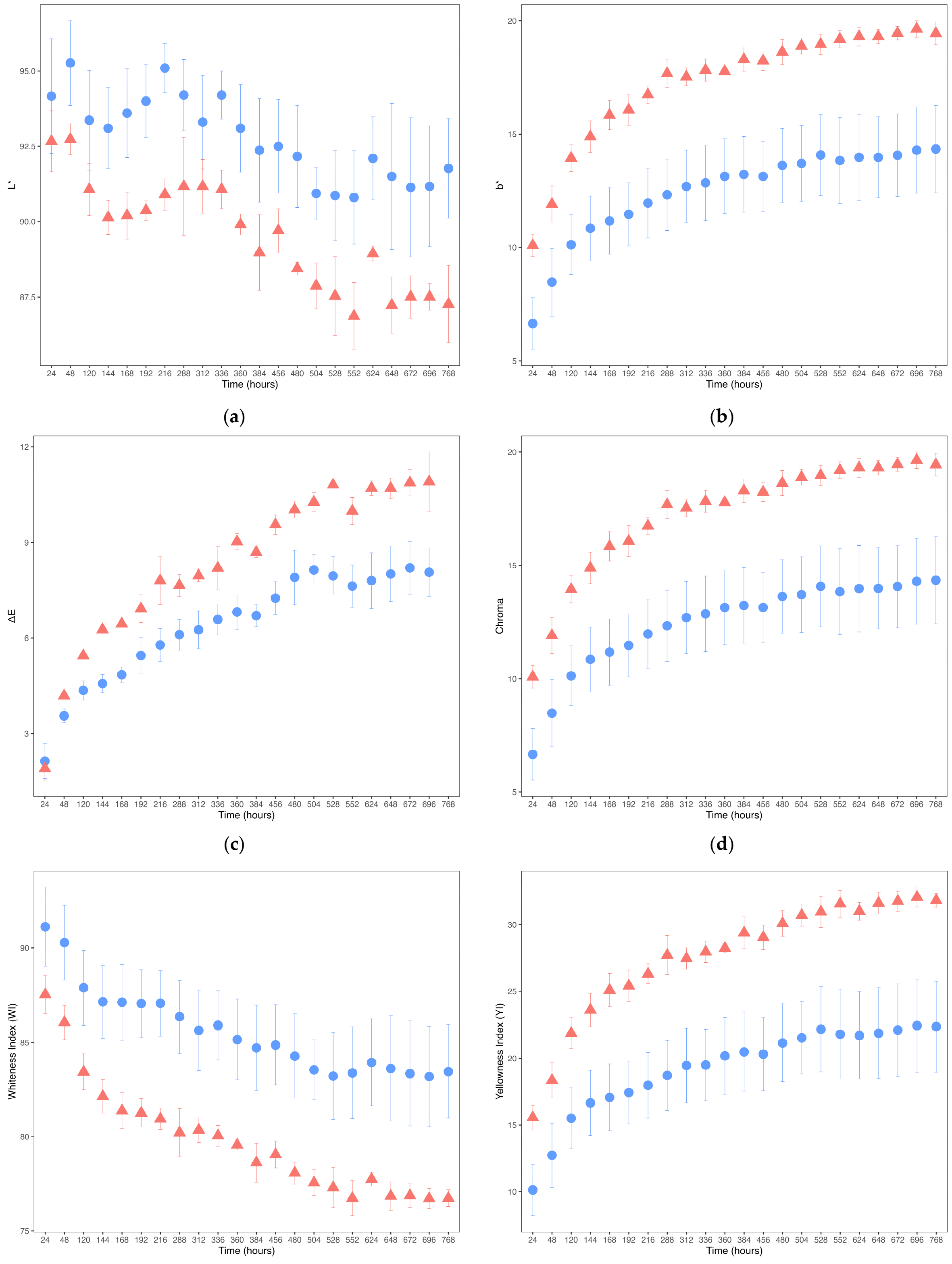
The absence of statistically significant results for hue as a function of time also suggested that most of the extraction occurred at first contact between the wood material and the solvent. Therefore, we assumed an immediate extraction that resulted in a fast change in colour. Values of hue around 90 proved the samples' yellow colour [26,27]. The a^* values showed similar results.

The Chroma and b^* exponential models were highly significant for the slope. The calculation of Chroma gave results similar to the b^* value. Since the values of a^* were generally close to zero, and given Equation (2), the a^* values did not contribute to significant variations in the Chroma results. Within the first 200 h of maceration, the fresh wood chips showed a faster extraction rate as compared to the spent material, with a faster increase in saturation (Chroma) and a faster shift towards yellower colour ($+b^*$).

The values of L^* (Figure 1a) decreased throughout maceration, with a variation following a linear model. The spent wood chips were characterised by a higher lightness than the fresh wood chips. Despite after a few hours of extraction, the difference between the spent and fresh materials could already be noticed (intercept $p = 0.047$), the L^* differences became more appreciable throughout the extraction period, as demonstrated by the slope ($p = 0.008$).

Computation of the Yellowness index (YI) and Whiteness index (WI) gave further evidence of the colour variation over time. Both indices were modelled through Peleg's exponential model. The YI showed high significance for the slope ($p = 0.009$); while the WI resulted significantly both for the slope ($p = 0.016$) and for the asymptote ($p = 0.007$). As represented in Figure 1e–f, the *grappas* obtained from the fresh wood chips showed a higher YI and a faster decrease in the WI over time; on the contrary, the samples obtained from the spent wood chips showed a lower YI and a slower decrease in the WI during extraction. These results summarise the variation in the L^* and b^* parameters in time.

Additionally, to outline the colour change during maceration, variation in ΔE as a function of time also showed exponential growth, with differences related to the condition of the starting material. The fresh chips showed a significantly higher extraction rate ($p = 0.003$) than the spent material. The probability associated with the zero hypothesis for the asymptotic value was, instead, $p = 0.05$. As represented in Figure 1c, the ΔE variation increased faster during the first 200 h, up to a plateau, representing the extraction capacity defined by the asymptote.



(**a**) (**b**)

(**c**) (**d**)

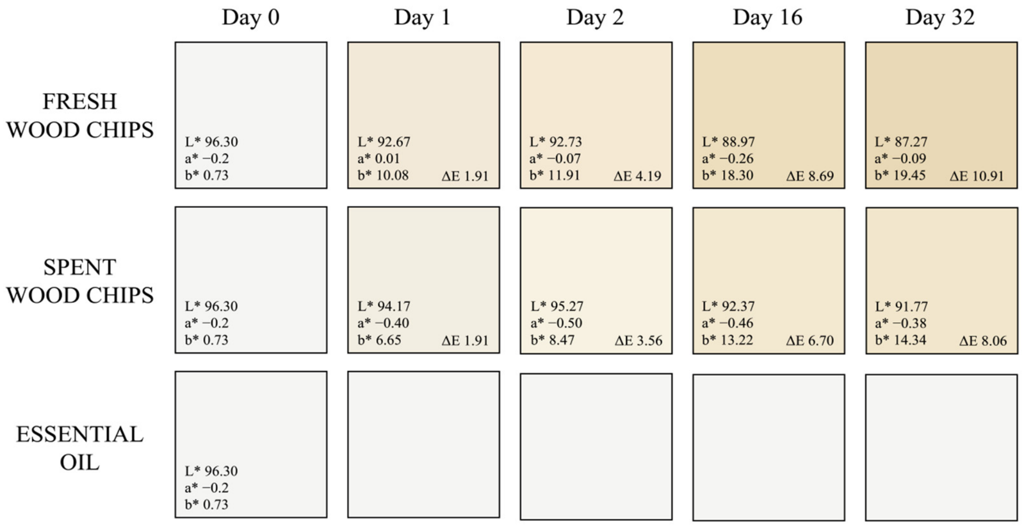
(**e**) (**f**)

Figure 1. Variation in colour parameters and indices during hydroalcoholic extraction of fresh (red triangles) and post-distillation spent (blue circles) wood chips. (**a**) L—lightness; (**b**) b*—blue to yellow; (**c**) ΔE; (**d**) Chroma; (**e**) Whiteness index (WI); (**f**) Yellowness index (YI).

It has been highlighted that variations in the colour parameters can be associated with differences in chemical composition [28–30]. Indeed, some studies have demonstrated that the extraction of tannins and phenolic compounds contributes to the colour and aroma of wood-aged spirits, in association with oxidation reactions. Distilled beverages are usually subjected to an ageing period in wooden barrels. In this procedure, several reactions occur, influencing the physicochemical and sensory characteristics of the spirits. As commonly observed in the solid–liquid extraction processes, it has been reported that the colour difference in spirits aged in wood casks increased faster in the first weeks, up to an equilibrium [23]. The CIELAB coordinates of those spirits at the end of the ageing period were similar to those obtained in the present study. This phenomenon was also visible in the study by [24]; the extraction of wood chips in wine model solutions for 20 days followed a second-order kinetics, with a faster increase in the first 10 days.

Therefore, the maceration of wood chips in alcoholic beverages could result in an increase in colour difference within the first 10 days. In accordance with previous research, this change in colour might be associated with the extraction of polyphenols and tannins, which influence the phytochemical composition of the spirit and consequently the sensory properties of the spirit.

In the present work, measurements of the colour parameters over time gave useful insights for monitoring the extraction kinetics of the *grappas* subjected to maceration. An immediate extraction has been noticed in the first 24–48 h, as suggested by the colour hue. Additionally, this fast change was detectable by the human eye, as supported by the high ΔE after 48 h. On the contrary, the *grappas* flavoured with essential oils did not acquire any colour. In this case, essential oils could be added to the grappa samples right after steam distillation, thus reducing the time needed for aromatisation (Figure 2).



	Day 0	Day 1	Day 2	Day 16	Day 32
FRESH WOOD CHIPS	L* 96.30 a* −0.2 b* 0.73	L* 92.67 a* 0.01 b* 10.08 ΔE 1.91	L* 92.73 a* −0.07 b* 11.91 ΔE 4.19	L* 88.97 a* −0.26 b* 18.30 ΔE 8.69	L* 87.27 a* −0.09 b* 19.45 ΔE 10.91
SPENT WOOD CHIPS	L* 96.30 a* −0.2 b* 0.73	L* 94.17 a* −0.40 b* 6.65 ΔE 1.91	L* 95.27 a* −0.50 b* 8.47 ΔE 3.56	L* 92.37 a* −0.46 b* 13.22 ΔE 6.70	L* 91.77 a* −0.38 b* 14.34 ΔE 8.06
ESSENTIAL OIL	L* 96.30 a* −0.2 b* 0.73				

Figure 2. Colour variation in grappa samples over maceration of fresh and post-distillation spent wood chips in comparison with colour of *grappa* samples flavoured with essential oil.

3.2. Analysis of Grappa Flavouring

Grappa flavouring was tested by analysing the volatile fraction by GC-MS and using sensory evaluation to test the consumer perception of different aromatisation methods.

3.2.1. Chemical Composition

The analysis of the samples' chemical composition by GC-MS provided a characterisation of the products obtained from *Pinus mugo* wood chips, giving evidence of the aromatic profile of the different flavoured *grappa*. The results of the GC-MS analyses are presented in Table 4. As highlighted by the Shannon–Weaver index, the samples were characterised by different numbers of compounds and relative abundance of the predominant compounds. Based on the GC-MS analyses, it was possible to explore which compounds were the most prominent in the *grappa* samples.

Table 4. Results of the GC-MS analyses of the *grappa* samples. The results of the GC-MS analyses of the *grappas* obtained from different flavouring agents: essential oil, fresh wood chips, and post-distillation spent wood chips. Concentration is expressed as a percentage of volatile compounds. For each compound, the average of the three extraction replicates was reported with standard deviations [1].

Compound	**Concentration (%)**			
	Essential Oil	**Fresh**	**Spent**	
2-Butenal, 3-methyl-	0.01 ± 0.02	<LOD	<LOD	n.s.
Hexanal	1.05 ± 0.25 ^{a}	1.04 ± 0.07 ^{b}	0.21 ± 0.04 ^{b}	**
Furfural	<LOD	<LOD	<LOD	n.s.
1-Hexanol	0.12 ± 0.03 ^{a}	1.01 ± 0.21 ^{a}	0.03 ± 0.00 ^{b}	***
Cyclopentane, 1,2,3,4,5-pentamethyl-	2.21 ± 1.12	11.09 ± 3.99	10.95 ± 2.67	n.s.
Methyl hexanoate	0.12 ± 0.09	<LOD	<LOD	***
α-Pinene	14.53 ± 2.27	<LOD	<LOD	*
Ethanone, 1-(1-methylcyclohexyl)-	0.94 ± 0.47	5.32 ± 1.05	4.89 ± 1.07	n.s.
Octane, 3-methyl-6-methylene-	0.11 ± 0.06	1.1 ± 0.43	0.81 ± 0.18	n.s.
Benzaldehyde	0.1 ± 0.05 ^{b}	1.17 ± 0.19 ^{a}	0.45 ± 0.05 ^{b}	***
β-Cymene	2.02 ± 0.39	<LOD	<LOD	**
β-Pinene	5.06 ± 0.54 ^{a}	0.24 ± 0.05 ^{b}	0.22 ± 0.06 ^{b}	*
β-Myrcene	1.89 ± 0.33	<LOD	<LOD	*
Ethyl hexanoate	<LOD ^{b}	0.54 ± 0.13 ^{a}	0.03 ± 0.01 ^{b}	***
3-Carene	24.74 ± 1.47 ^{a}	2.24 ± 0.44 ^{b}	1.57 ± 0.28 ^{b}	**
o-Cymene	4.71 ± 0.42 ^{a}	0.96 ± 0.18 ^{b}	0.43 ± 0.07 ^{b}	**
D-Limonene	17.13 ± 1.86	<LOD	<LOD	*
m-Mentha-6,8-diene, (R)-(+)-	<LOD	0.85 ± 0.2	0.83 ± 0.18	**
Benzeneacetaldehyde	7.36 ± 1.48 ^{a}	0.06 ± 0.01 ^{b}	0.03 ± 0.01 ^{b}	*
Eucalyptol	0.01 ± 0.00	<LOD	<LOD	***
p-Cresol	0.02 ± 0.02	0.06 ± 0.01	0.09 ± 0.02	n.s.
p-Cymene	0.25 ± 0.06	<LOD	<LOD	***
Isoterpinolene	<LOD	0.02 ± 0.00 ^{b}	0.05 ± 0.01 ^{a}	**
Camphene hydrate	0.18 ± 0.06	<LOD	<LOD	***
4-Carene	1.19 ± 0.27	<LOD	<LOD	**
Benzene, (2-methyl-1-propenyl)-	0.70 ± 0.17 ^{a}	0.23 ± 0.03 ^{b}	0.16 ± 0.06 ^{b}	***
α-Pinene oxide	<LOD	0.01 ± 0.00 ^{b}	0.06 ± 0.01 ^{a}	***
Ethanone, 1-(2-methylphenyl)-	0.01 ± 0.01	<LOD	<LOD	**
Phenol, 2-methoxy-	<LOD	<LOD	<LOD	*
Nonanal	0.08 ± 0.01	<LOD	<LOD	*
4,5-Dimethylnonane	0.01 ± 0	<LOD	<LOD	***
Camphene hydrate	0.07 ± 0.03	<LOD	<LOD	***
trans-p-Menth-2-en-1-ol	0.05 ± 0.02	<LOD	<LOD	***
cis-β-Terpineol	<LOD	<LOD	<LOD	**

Table 4. *Cont.*

Compound	Concentration (%)			
	Essential Oil	**Fresh**	**Spent**	
α-Campholenal	0.25 ± 0.06	<LOD	<LOD	**
allo-Ocimene	0.13 ± 0.03	<LOD	<LOD	*
Pinocarveol	0.16 ± 0.09 ^{b}	0.28 ± 0.05 ^{a}	0.07 ± 0.01 ^{a}	***
Cyclohexanol, 4-(1-methylethyl)-	0.30 ± 0.13 ^{b}	0.74 ± 0.12 ^{a}	0.45 ± 0.26 ^{a}	**
4-Isopropylcyclohexanone	0.03 ± 0.01 ^{c}	0.03 ± 0.01 ^{b}	0.05 ± 0.01 ^{a}	***
Phenol, 4-ethyl-	0.04 ± 0.04	<LOD	<LOD	*
Ethyl benzoate	0.01 ± 0.00 ^{b}	0.50 ± 0.07 ^{a}	0.03 ± 0.01 ^{b}	***
Borneol	0.33 ± 0.17 ^{b}	1.23 ± 0.35 ^{a}	0.34 ± 0.16 ^{a}	**
p-Mentha-1,5-dien-8-ol	0.10 ± 0.05 ^{b}	0.16 ± 0.03 ^{a}	0.17 ± 0.04 ^{a}	**
trans-Pinocamphone	0.10 ± 0.04	1.12 ± 0.11	0.90 ± 0.38	n.s.
(-)-4-Terpineol	0.70 ± 0.31	<LOD	<LOD	***
Octanoic Acid	0.04 ± 0.02	0.32 ± 0.03	0.2 ± 0.1	n.s.
p-Cymen-8-ol	0.65 ± 0.27	4.86 ± 0.52	2.33 ± 1.09	n.s.
α-Terpineol	1.30 ± 0.95	<LOD	<LOD	*
Myrtenol	0.30 ± 0.17 ^{b}	0.57 ± 0.11 ^{a}	0.16 ± 0.06 ^{a}	***
Ethyl octanoate	0.01 ± 0.00 ^{b}	0.18 ± 0.01 ^{a}	0.07 ± 0.04 ^{ab}	*
Verbenone	0.29 ± 0.14 ^{b}	0.80 ± 0.09 ^{a}	0.42 ± 0.17 ^{a}	***
cis-Carveol	0.05 ± 0.02	<LOD	<LOD	***
Caron	0.12 ± 0.05	<LOD	<LOD	***
Benzenemethanol, α-(1-methylethyl)-, (R)-	0.06 ± 0.01	<LOD	<LOD	**
(R)-citronellol	0.10 ± 0.05 ^{b}	0.34 ± 0.09 ^{ab}	0.06 ± 0.02 ^{a}	**
Thymol methyl ether	<LOD	1.12 ± 0.12	0.53 ± 0.18	**
3-Isopropylbenzaldehyde	0.12 ± 0.05 ^{a}	0.09 ± 0.00 ^{b}	0.03 ± 0.01 ^{b}	***
Carvotanacetone	0.13 ± 0.06	<LOD	<LOD	***
3-Carvomenthenone	0.15 ± 0.07 ^{b}	0.33 ± 0.02 ^{a}	0.16 ± 0.11 ^{a}	**
Phellandral	0.1 ± 0.05	<LOD	<LOD	***
cis-Anethol	0.38 ± 0.17 ^{a}	0.03 ± 0.00 ^{c}	0.14 ± 0.01 ^{b}	***
Thymol	0.06 ± 0.02	<LOD	<LOD	n.s.
Thymoquinon	<LOD ^{c}	0.33 ± 0.05 ^{a}	0.10 ± 0.00 ^{b}	***
Limonene-1,2-diol	<LOD ^{b}	0.46 ± 0.02 ^{a}	0.36 ± 0.10 ^{a}	**
α-Terpinyl acetate	0.24 ± 0.01	0.73 ± 0.17	0.55 ± 0.16	n.s.
Triacetin	0.01 ± 0.01 ^{c}	0.95 ± 0.35 ^{b}	2.9 ± 0.76 ^{a}	***
Copaene	0.09 ± 0.03	<LOD	<LOD	.
β-Elemene	0.17 ± 0.07	<LOD	<LOD	.
Ethyl decanoate	0.04 ± 0.02	<LOD	<LOD	***
Vanillin	<LOD ^{b}	3.88 ± 0.52 ^{a}	2.22 ± 0.4 ^{a}	**
Carvone hydrate	<LOD ^{b}	0.13 ± 0.02 ^{a}	0.06 ± 0.01 ^{a}	**
Carvenone oxide	0.05 ± 0.00 ^{b}	0.19 ± 0.03 ^{ab}	0.05 ± 0.00 ^{a}	*
Isoeugenol	<LOD	0.22 ± 0.05 ^{b}	0.26 ± 0.06 ^{a}	***
2′,4′-Dihydroxypropiophenone	0.03 ± 0.01	<LOD	<LOD	.

Table 4. *Cont.*

Compound	Concentration (%)			
	Essential Oil	Fresh	Spent	
Ethyl cinnamate	0.01 ± 0.00 ^{b}	0.18 ± 0.04 ^{a}	0.02 ± 0.01 ^{b}	**
γ-Cadinene	1.05 ± 0.38	<LOD	<LOD	.
Acetoisovanillone	<LOD ^{b}	0.17 ± 0.02 ^{ab}	0.18 ± 0.05 ^{a}	**
β-Selinene	0.06 ± 0.02	<LOD	<LOD	.
Isoeugenol methyl ether	0.05 ± 0.02	0.13 ± 0.05	0.31 ± 0.23	n.s.
α-Muurolene	5.86 ± 1.87	<LOD	<LOD	*
Butylated Hydroxytoluene	0.02 ± 0.01	0.79 ± 0.39	0.62 ± 0.35	n.s.
Guaiacylacetone	0.04 ± 0.01	0.19 ± 0.07	0.24 ± 0.08	n.s.
α-Cadinene	0.07 ± 0.03	<LOD	<LOD	.
α-Calacorene	0.17 ± 0.02	<LOD	<LOD	*
Spathulenol	0.13 ± 0.04 ^{b}	0.26 ± 0.05 ^{a}	0.12 ± 0.03 ^{a}	**
Caryophyllene oxide	0.23 ± 0.03 ^{b}	0.34 ± 0.04 ^{a}	0.09 ± 0.02 ^{a}	**
Humulane-1,6-dien-3-ol	0.17 ± 0.01 ^{b}	0.32 ± 0.07 ^{a}	0.17 ± 0.07 ^{a}	*
Cubenol	0.03 ± 0.00 ^{b}	0.04 ± 0.01 ^{a}	0.03 ± 0.01 ^{a}	**
epi-α-Cadinol (τ-Cadinol)	0.26 ± 0.03 ^{b}	0.41 ± 0.10 ^{a}	0.27 ± 0.09 ^{a}	**
epi-α-Muurolol	0.12 ± 0.02 ^{b}	0.21 ± 0.04 ^{a}	0.13 ± 0.04 ^{a}	**
α-Cadinol	0.19 ± 0.06 ^{b}	0.46 ± 0.10 ^{a}	0.31 ± 0.12 ^{a}	**
Homovanillic acid	<LOD ^{b}	0.49 ± 0.03 ^{ab}	2.59 ± 1.39 ^{a}	*
7-Acetyl-2-hydroxy-2-methyl-5-isopropylbicyclo[4.3.0]nonane	<LOD ^{b}	1.52 ± 0.28 ^{a}	0.75 ± 0.32 ^{a}	**
Benzyl Benzoate	0.01 ± 0.00	0.05 ± 0.03	0.09 ± 0.04	n.s.
β-Hydroxypropiovanillone	<LOD ^{b}	0.89 ± 0.22 ^{a}	0.95 ± 0.28 ^{a}	*
p-Coumaric acid ethyl ester	<LOD	<LOD	<LOD	**
Alloaromadendrene oxide-(1)	0.01 ± 0.01	<LOD	<LOD	**
Sclarene	0.02 ± 0.01	<LOD	<LOD	*
Rimuene	0.04 ± 0.01	<LOD	<LOD	*
Ethyl hexadecanoate	0.03 ± 0.02	0.21 ± 0.07	0.24 ± 0.07	n.s.
Isoparvifuran	0.01 ± 0.00	<LOD	<LOD	*
Thunbergol	<LOD	<LOD	<LOD	*
Linoleic acid ethyl ester	0.01 ± 0.00 ^{b}	0.48 ± 0.09 ^{b}	1.08 ± 0.32 ^{a}	**
Ethyl oleate	<LOD ^{b}	0.08 ± 0.02 ^{b}	0.17 ± 0.02 ^{a}	**
1,2,3,4-tetrahydro-5,8-dimethyl-Acridin-9-amine	<LOD ^{b}	42.35 ± 4.91 ^{a}	53.11 ± 6.65 ^{a}	**
Levopimaric acid methyl ester	0.04 ± 0.01	0.87 ± 0.29	0.54 ± 0.08	n.s.
Dehydroabeityl alcohol	<LOD ^{b}	0.35 ± 0.07 ^{a}	0.19 ± 0.03 ^{a}	**
Pinocembrin	<LOD ^{b}	3.58 ± 0.71 ^{a}	4.33 ± 1.42 ^{a}	*
Methyl levopimarate	<LOD	0.11 ± 0.05	0.04 ± 0.02	n.s.
Total number of compounds identified	85	65	65	

[1] significance levels resulting from the ANOVA were included ("***" $p = 0.001$; "**" $p = 0.01$; "*" $p = 0.05$). Different letters indicate significant differences according to Tukey HSD ($p < 0.05$).

In the previous literature, the volatile chemical composition of wooden parts of *Pinus mugo* was only examined by [7], while most works have analysed extracts obtained from green shoots and needles [4–10].

Pinus mugo essential oil: Samples obtained from pine essential oil were rich in 3-carene (24.74 ± 1.47%), limonene (17.13 ± 1.86%), and α-pinene (14.53 ± 2.27%), but also α-muurolene (5.86 ± 1.87%) and β-pinene (5.06 ± 0.54%). These compounds were also found in *Pinus mugo* wood and bark essential oils by [7]. Moreover, some predominant compounds in wood essential oil were also detected in the essential oils extracted from branches, green shoots, and needles. From a comparison with the qualitative standard ISO 21093:2003, the chemical characterisation of the samples supplemented with wood essential oils met the requirements for *Pinus mugo* essential oil, as reported in Table 5, except for D-Limonene which was slightly higher than the reference range [31].

Table 5. Main compounds of *Pinus mugo* wood chip essential oil compared with the quality requirements set by ISO 21092:2003.

Compound	Concentration (%)	ISO 21093:2003 (Range %)
α-Pinene	14.53 ± 2.27	10–30
β-Pinene	5.06 ± 0.54	3–14
3-Carene	24.74 ± 1.47	5–25
D-Limonene	17.13 ± 1.86	8–14

Pinus mugo fresh and post-distillation spent wood chips: The chemical composition of the *grappa*s obtained from the *Pinus mugo* fresh and post-distillation spent wood chips showed 1,2,3,4-tetrahydro-5,8-dimethyl-Acridin-9-amine as the most prominent compound (42.35% and 53.11%), but also Cyclopentane, 1,2,3,4,5-pentamethyl- (11.09% and 10.95%), and Ethanone, 1-(1-methylcyclohexyl)- (10.95%).

Distillation vs. *Hydroalcoholic maceration*: From a comparison between the two flavouring methods for *Pinus mugo*, some of the main compounds significantly differentiated the samples as a function of the flavouring material. 3-carene was present at lower concentrations (2.24% and 1.57%) in the samples obtained from maceration as compared to those derived from the use of the essential oil ($p = 0.008$), while α-pinene and limonene were not detected in the macerated samples. However, limonene-1,2-diol ($p = 0.003$) was detected in the samples obtained from pine wood chip maceration. Similarly, other compounds were only present in EO-based *grappa*s, such as α-muurolene, β-cymene, β-myrcene, α-terpineol, 4-carene, γ-cadinene, and (-)-4-terpineol, while β-pinene, o-cymene, and p-cymen-8-ol were present also in *grappa*s resulting from maceration but at lower percentages.

Based on the ANOVA, 1,2,3,4-tetrahydro-5,8-dimethyl-Acridin-9-amine significantly differentiated the samples based on the condition of the starting material ($p = 0.002$). This compound was only detected in the samples extracted through hydroalcoholic maceration. Hassan et al. (2017) identified this compound in high concentration in an ethanol extract from *Pinus roxburghii* [32].

By computing the Shannon–Weaver index, we attempted to estimate the chemical diversity and complexity of the flavoured *grappa*s. The highest chemical complexity was recognised in the samples based on *Pinus mugo* essential oil, with a SW index of 2.60 ± 0.12 (Figure 3). As shown in Table 4, mountain pine essential oil also showed the highest number of compounds but lower relative concentrations of the most prominent compounds. However, pine-based *grappa*s showed similarities between the samples based on essential oil and fresh wood chips (SW = 2.57 ± 0.11) (Figure 3). This might suggest that the maceration of the fresh wood chips resulted in a similar chemical complexity compared to the essential oil, which could be related to a higher extraction of volatile compounds. *Pinus mugo* essential oil was characterised by 85 compounds, but 15 compounds accounted for

90% of the total chemical composition, with 3-carene, limonene, and α-pinene comprising over 50% of the mixture. The *grappa*s obtained from the *Pinus mugo* post-distillation spent wood chips showed the lowest SW index (2.11 ± 0.25), which denoted low chemical complexity (Figure 3).

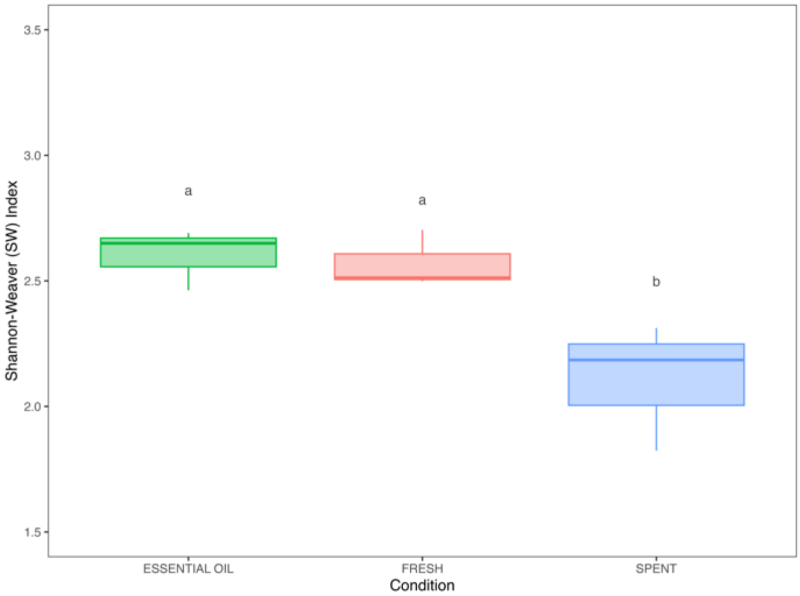


Figure 3. Boxplot of Shannon–Weaver indices for *grappas* obtained from different flavouring agents: essential oil, fresh wood chips, and post-distillation spent wood chips. Letters indicate the significance of the Tukey HSD test.

In conclusion, the chemical analyses suggested that different compounds were extracted through steam distillation and hydroalcoholic maceration, thus resulting in different compositions of the flavoured *grappas*. In particular, the grappa flavoured with steam distillation EO extracts were richer in terpenoids than the *grappas* obtained through maceration alone. The samples flavoured with the fresh wood chips, as compared to those obtained from the post-distillation spent wood chips, showed higher percentages of some more volatile compounds, such as 3-carene, limonene, and α-pinene, which were mainly present in the essential oil. Phenolic compounds such as vanillin and its derivatives were extracted in *grappas* through hydroalcoholic maceration, which might have been favoured by the steam passage during distillation.

3.2.2. Sensory Analysis

The sensory analysis further supported the discrimination of the samples based on the olfactory and tactile features. Since colour might influence consumer preferences and evaluation [33], this parameter was not included in the analysis to focus on smell and taste characteristics.

The discriminant tests significantly differentiated the samples flavoured with wood chips from those flavoured with essential oil ($p < 0.001$). At the same time, no significant difference was detected between the samples based on the fresh and post-distillation spent wood chips.

Since consumers perceived no difference between the fresh and spent material, it would be possible to sequentially combine steam distillation and hydroalcoholic maceration of the spent material to fully valorise raw materials and obtain different flavouring agents at the same time.

3.2.3. Safety Assessment

The *grappa* samples obtained from the hydroalcoholic maceration of pine wood chips were subjected to an ICP analysis to assess the safety of the preparation as food flavouring. Since no reference values for grappa and alcoholic spirits were found, thresholds for contaminants in beverages such as wine and water were considered [34–36]. As reported in Table 6, all the contaminants were lower than these thresholds.

Table 6. Results of the ICP analysis for metal presence in the *grappa* samples.

	mg/L		**mg/L**		**mg/L**
Ag	<0.01	Hf	<0.01	Rh	<0.005
Al	0.14	Hg	<0.01	Ru	<0.001
As	<0.02	Ho	<0.01	S	22.4
Au	<0.01	I	<5	Sb	<0.05
B	<0.10	In	<0.02	Sc	<0.001
Ba	0.01	Ir	<0.01	Se	<0.05
Be	<0.001	K	32.9	Si	2.42
Bi	<0.02	La	<0.01	Sm	<0.05
Br	<5.00	Li	0.00174	Sn	<0.05
Ca	26.50	Lu	<0.001	Sr	0.0487
Cd	<0.001	Mg	15.7	Ta	<0.01
Ce	<0.10	Mn	0.404	Tb	<0.02
Cl	<5	Mo	<0.001	Te	<0.05
Co	<0.001	Na	2.91	Th	<0.05
Cr	<0.001	Nb	<0.005	Ti	0.00271
Cu	0.007056	Nd	<0.01	Tl	<0.05
Dy	<0.01	Ni	<0.001	Tm	<0.005
Er	<0.01	P	3.19	V	0.001184
Eu	<0.01	Pb	<0.02	W	<0.005
Fe	0.0649	Pd	<0.01	Y	<0.001
Ga	<0.01	Pr	<0.05	Yb	<0.001
Gd	<0.01	Pt	<0.01	Zn	0.129
Ge	<1	Re	<0.005	Zr	<0.001

4. Discussion

The application of sequential steam distillation and the hydroalcoholic maceration of the spent material allowed for the extraction of different aroma fractions from the *Pinus mugo* wood chips by segregating the extraction of volatile and non-volatile compounds, which might be associated with olfactory and tactile properties, respectively.

Through steam distillation, the selective extraction of volatile compounds within the essential oil was achieved. Evidence on the extraction and composition of Pinus mugo wood chips EO integrated existing literature [7,10]. In addition, the essential oil was used as a flavouring agent, allowing an immediate aromatisation of the product.

Focusing on the extraction kinetics, the physicochemical analyses demonstrated statistically significant differences among the grappa samples flavoured with the fresh and post-distillation spent wood chips. The colour of all the *grappas* obtained by maceration exhibited an exponential increase in saturation and colour difference over time, with a significant shift toward a yellower hue, as supported by the Yellowness and Whiteness indices [18]. Indeed, colour difference (ΔE) exceeded the perceptual threshold after 48 h, increasing up to a plateau in the first 10 days of maceration. From a comparison between the two flavouring methods, hydroalcoholic extraction produced a distinctive hue, while the use of essential oil did not confer any colour to the *grappa* samples. The possibility to obtain pine-flavoured *grappas* with a different colour could be an important feature for its success on the market [37]. Moreover, it is well known that the colour of food and beverages is one of the main characteristics for ensuring product appeal and differentiation [38,39].

Chemical analyses differentiated the samples primarily based on the extraction method, with greater chemical diversity linked to the use of essential oil and fresh wood chips. For instance, some main compounds, such as 3-carene, which characterised the essential oil, were present in lower concentrations within the samples obtained from the maceration of the post-distillation spent wood chips compared to those flavoured with the fresh wood chips. Examining the chemical composition of the extracts provided valuable insights for the optimisation of steam distillation and hydroalcoholic maceration to enhance the value of forest by-products from *Pinus mugo,* and fostering diversification in the sector of Non-Wood Forest Products. However, when considering the application of extracts as food flavourings, sensory evaluation may be of greater significance, ensuring consumer acceptance and reducing the risk of market failure [20]. Sensory analysis indicated that consumers did not perceive significant differences between the samples flavoured with the fresh and post-distillation spent wood chips, while significant differences were detected based on the flavouring method.

5. Conclusions

The sequential association of two unit operations may enable more efficient utilisation of raw materials, valorising distillation by-products and improving process circularity. Additionally, the combination of different flavouring agents and techniques offers the potential for greater customisation of *grappa*'s sensory profile and more efficient control over its olfactory, tactile, and colour characteristics. This approach provides *grappa* distillers with the possibility to customise their products by using essential oils and extracts sourced from local producers, thereby supporting short supply chains. Moreover, the chosen extraction methods were tested through technologies that can be directly adopted under production conditions, allowing for an assessment in a relevant environment. This makes scaling up to larger quantities, particularly when flavouring with greater amounts of essential oils, more efficient and manageable for producers. At the same time, producers could leverage their expertise in the distillation and extraction processes to apply or further scale up these techniques on an industrial scale, optimising the sensory profile of the final product while also testing additional flavouring agents and raw materials.

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Institutional Review Board Statement: The study was conducted in accordance with the Declaration of Helsinki, and approved by the Ethics Committee of the TESAF department—Università degli Studi di Padova (protocol code 0003293, date 2 October 2024).

Informed Consent Statement: Informed consent was obtained from all the subjects involved in the study.

Data Availability Statement: Dataset available upon request from the authors. The raw data supporting the conclusions of this article will be made available by the authors upon request.

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