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DOI: https://doi.org/10.1016/j.apsoil.2019.103433

Coldea, T.E., Socaciu, C., Mudura, E., Socaci, S.A., Ranga, F., Pop, C.R., Vriesekoop, F. and Pasqualone, A. 2020. Volatile and phenolic profiles of traditional Romanian apple brandy after rapid ageing with different wood chips. *Food Chemistry*, 320, 126643.

Volatile and Phenolic Profiles of Traditional Romanian Apple Brandy after Rapid Ageing with Different Wood Chips

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Abstract: The aim of this work was to find differences in the volatile and phenolic profiles of the traditional Romanian apple brandy *pălinca* aged with various species of wood chips. Seven types of wood species, two types of oak (*Quercus petraea* and *Quercus robur*), plus sweet chestnut, mulberry, walnut, fir and cherry, were considered. The majority of volatile compounds characterizing the aroma profile of *pălinca* were esters, particularly ethyl esters, with ethyl isobutyrate, ethyl isovalerate, ethyl caproate, ethyl octanoate and ethyl decanoate as the most abundant. The most important source of catechin was cherry wood. Rutin and juglone were solubilised only in walnut wood aged brandy. Vanillin, increased significantly in chestnut aged apple brandy. Given the cost and difficulty in handling wooden barrels, and as an alternative being able to select from a range of specific wooden chips, this work could potentially guide actors in beverage industry to less expensive alternatives.

Keywords: apple brandy; *pălinca*; seasoned wood; polyphenols; volatile compounds.

Highlights:

- *Pălinca* is a traditional double batch-distilled Romanian fruit brandy.
- Rapid ageing of *pălinca* impacts both the volatile and phenolic profiles regardless of the wood types employed.
- Fir and cherry wood contributed the largest quantity of phenolic compounds to *pălinca.*
- The lowest contribution to volatile profile of *pălinca* was given by the mulberry wood.
- The esters of fatty acids contributed the most to the volatile profile of *pălinca.*

1. Introduction

Since ancient times, Romania has a strong tradition of producing fruit brandies, with resurgence in both producing and consumption, especially in areas where fruits are grown and harvested (Salanţă, Tofană, Pop, Pop, Coldea & Mudura, 2017). The use of wood in the ageing of spirits, including fruit brandies, has a great influence on their final taste and aroma (Canas, Caldeira, Anjos, Lino, Soares & Belchior, 2016).

Wood-ageing is one of the costliest factors influencing the quality of distilled beverages. Traditional wood-ageing involves the use of wooden barrels, typically constructed from appropriate oak species, of varying volumes, at lengthy periods of time. Despite the classical method of wood-ageing, several alternative techniques have been tested in order to reduce the ageing period, considering both the economical point of view and the notion of environmental sustainability (Cîrstea, Moldovan-Teselios, Cîrstea, Turcu & Darab, 2018). These alternative techniques include the use of ultrasound to enhance the extraction of wood compounds in wine production (Tao, Zhang & Sun, 2014) and spirit production (Caldeira, Pereira, Clímaco, Belchior & De Sousa, 2004; Delgado-González, Sánchez-Guillén, García-Moreno, Rodríguez-Dodero, García-Barroso & Guillén-Sánchez, 2017), the application of electric fields (Zhang, Zeng, Sun, Yu, Yang & Ma, 2013) and high pressure (Tchabo, Ma, Kwaw, Zhang, Xiao & Tahir, 2017) as efficient, non-thermal and cost-effective alternatives. Since the International Organisation of Vine and Wine (OIV) approved the use of wood staves or sticks (as alternatives to barrels) to hasten the ageing period, different methods have been applied on alcoholic beverages to enhance their sensorial properties, the flavour and phenolic profiles. Recently, greater attention has been given to the use of wooden fragments

and even powders to facilitate a rapid ageing of wines (Cabrita, Barrocas Dias & Costa Freitas, 2011), brandies (Canas, et al., 2016; Rodríguez-Solana, Rodríguez-Freigedo, Salgado, Domínguez & Cortés-Diéguez, 2017), and apple ciders (Fan, Xu & Yu, 2006) in order to achieve a significant reduction in the overall maturation period. The cost and complexities of barrel stock management, together with the reduction in maturation time, has guided the industry to engage with these cost-effective alternatives. While these wood products typically undergo some sort of heat treatment (toasting or charring); the use of untoasted wood is not unprecedented (Sanz et al., 2010a). Traditional handicrafts of wooden fragments represent important components with notable cultural or religious significance in East European countries, dating back many centuries. During the ageing process of some local fruit brandies (called *horinca* or *pălinca*) originated from the Maramureș County in Northern Romania, dried, unheated, wooden handicraft objects, typically made from polar or mulberry, are added as miniatures into the bottles (Dippong, Avram & Mihali, 2019). The ageing period for this wood embedding technique lasts between some days to few months, depending on each product.

The abundant and diverse forests in Eastern Europe facilitate a diverse choice of readily available wood species, makes for easy access to both oak and alternative wood species for the ageing process of alcoholic beverages. Oak (*Quercus* spp.) is the most commonly used wood in tight cooperage with a great beneficial influence on the volatile and phenolic composition (Alañón, Castro-Vázquez, Díaz-Maroto, Hermosín-Gutiérrez, Gordon & Pérez-Coello, 2011). *Quercus robur* (aka pedunculate oak) and *Quercus petraea* (aka sessile oak) are the most commonly used European oak species in tight cooperage (Alañón et al., 2011).

89 The availability and extractability of ellagitanins, phenolic- and volatile compounds, together
90 with the water tightness of the oak tyloses, make some oak species the preferred wood for
91 cooperage for the wine and distilled industry. However, producers will also consider wood
92 alternatives such as chestnut (*Castanea sativa*), cherry (*Prunus avium*), walnut (*Juglans*
93 *regia*), acacia (*Robinia pseudacacia*), mulberry (*Morus alba* and *Morus nigra*), ash
94 (*Fraxinus excelsior* and *Fraxinus Americana*), beech (*Fagus sylvatica*), alder (*Alnus*
95 *glutinosa*), lime (*Tilia cordata*) and fir (*Abies alba*) for beverage cooperage (Alañón et al.,
96 2011; De Rosso, Cancian, Panighel, Vedova, & Flamini, 2009; Martínez-Gil, del Alamo-
97 Sanza, Sánchez-Gómez & Nevares, 2018). While oak is used in the vast majority of wooden
98 barrels for alcohol maturation; chestnut is a very distant second commonly used wood. It has
99 a suitable porosity, which facilitates the micro oxygenation of the spirit and the abundant
100 release of polyphenols into the distillate (Canas et al., 2016). Cherry wood has a high porosity
101 and is highly oxidative, which has been successfully utilised for short ageing periods
102 (Chinnici, Natali, Bellachioma, Versari & Riponi, 2015; Magalhães et al., 2011). Mulberry
103 wood is tender and elastic, having medium porosity and a low release of compounds during
104 ageing (De Rosso et al., 2009). European walnut tree is one of the darkest wood species (Liu,
105 Timar, Varodi & Sawyer, 2017) and is recognized for its high and distinct antioxidant activity
106 (Diouf, Merlin, & Perrin, 2006).

107 Wood for the maturation of spirits is exposed to a heat treatment associated with the
108 typical manufacture of wooden barrels when the staves are being bent into the quintessential
109 convex and bulging shape of a barrel, which represents the firing process (Schahinger &
110 Rankine, 2005). A simple extension of the firing process converts into the toasting process

111 or the heat treatment can be further extended into a charring process (Singleton, 1995). As a
112 result of the heat treatment, the toasted wood might release a greater amount of polyphenols
113 which maybe due to the protective role of Maillard reaction compounds, such as melanoidins,
114 formed during toasting process (Magalhães et al., 2011; Zhang, Cai, Duan, Reeves & He,
115 2015). Polyphenols have antioxidant activity (Alañón et al., 2011). Furthermore, Maillard
116 reaction compounds (such as pyrazines and other furanic compounds) are partially
117 responsible for the brandy colour, as well as cacao and caramel aromas (Canas et al., 2016;
118 Rodríguez Madrera, Gomis & Mangas Alonso, 2003). However, some Maillard reaction
119 compounds, including furfural, present a carcinogenic risk (Parisi & Luo, 2018). Some of
120 these products are also formed during the distillation process especially when classical
121 method by direct heating of the mash is applied (Coldea, Socaciu, Pârv & Vodnar, 2011) and
122 during the toasting process of cooperage (Marques Bortoletto, Casagrande Silvello
123 & Alcarde, 2018). The more intensive the toasting process, the greater the amount of these
124 compounds are formed, potentially affecting the safety of the spirit. However, no risks
125 associated with the consumption of spirits has been reported for average drinkers
126 (Monakhova & Lachenmeier, 2012).

127 The ageing process is an important step not only for improving the sensory profile of
128 alcoholic beverages but also for gaining other characteristics of interest such as the increase
129 of antioxidant activity and the content in phenolic compounds (Alañón et al., 2011;
130 Rodríguez Madrera, Suárez Valles, Diñeiro García, Del Valle Argüelles & Picinelli Lobo,
131 2010) and, as a consequence, become of interest also from the technological point of view

because improves the beverage complexity, limpidity, colour stability and the intensity of flavour and aroma (Chinnici et al., 2015; De Rosso et al., 2009; Tao et al., 2014).

The main contributors to brandies' sensorial characteristics derived from wood have been found to include volatile terpenoids, phenols, benzoic and cinnamic aldehydes (Canas et al., 2016; De Rosso et al., 2009). Many compounds extracted from the wood originate from the degradation of macromolecules by heating during cask fabrication. Phenolic compounds such as vanillin and other aromatic aldehydes, influence the sensorial properties of beverages, such as aroma; while furan compounds influence colour, astringency and bitterness. The quality of distilled beverages is often influenced by the level of wood exposure during the maturation process, which is strongly related to beverage matrix, origin and species of wood used in cooperage, length of the maturation period, the wood surface area to beverage-volume ratio and in the case of toasted wood, the degree of toasting (Canas et al., 2016; De Rosso et al., 2009). Over time, during maturation, a physical alignment of the ethanol and water molecules occurs and the distillate becomes smoother and less pungent (Rodríguez Madrera, Suárez Valles & Picinelli Lobo, 2011). A number of chemical modifications in the composition of beverage take place during the process of wood maturation such as evaporation, degradation of some compounds and/or reactions between distillate and wood compounds, extraction of different wood compounds into distillate, and the absorption and adsorption of other compounds from the spirit into the wood.

The current study presents an extensive research on the impact of seven different types of wood chips, as an alternative way to shorten the ageing period of fruit brandies and to produce differentiated, high quality products in a cost-efficient manner.

2. Materials and Methods

2.1. Materials

Two apple varieties (Jonathan and Sinap Orlovsky in a 1:2 ratio, 2018 harvest) were used for the production of the brandy used in this study. The apple brandy was obtained locally from Ocolișel (Cluj County Transylvania region, Central part of Romania) as a fresh distillate resulting from the traditional, local method (double distillation in a copper alembic) as previously described (Coldea et al., 2014), with an ethanol content of 46.25% ABV.

For the rapid ageing process we used wood fragments (5 x 5 x 20 mm) obtained from the heartwood of pedunculate oak (*Quercus robur)*, sessile oak (*Quercus petraea*), mulberry (*Morus alba*), fir (*Abies alba*), walnut (*Juglans regia*), chestnut (*Castanea sativa)* and cherry (*Prunus avium*), all sourced locally in Romania. The wood fragments were naturally seasoned in open air, shielded from light, for three months without applying any thermal (toasting) treatment as practised locally (Dippong et al., 2019). Thirty g of naturally seasoned wood fragments were placed in 1 L of apple brandy and kept for 60 days, away from light at room temperature. The samples were shaken daily for 5 min during the ageing period. At the completion of the maturation period (60 days), all samples were filtered to remove all traces of wood. A control apple brandy without any wood exposure was used as a reference for comparison to the wood aged brandies. All experimental variables and control were set up in triplicate. All the samples were kept at -20 °C until being analyzed.

All used chemicals (ethanol, methanol, acetaldehyde, ethyl acetate, 1-propanol, 2-butanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1-butanol, 3-methyl-1-

176 butanol, furfural, 3-pentanol, acetonitrile) had purity over 99% (Merck, Darmstadt,
177 Germany). Gallic acid and acetic acid (≥ 99% purity) were purchased from Sigma-Aldrich
178 (Steinheim, Germany).
179

180 *2.2. GC-FID Analysis*

181 Analysis of major volatile compounds in apple brandies was carried as previously
182 reported (Coldea et al., 2011) with some modifications. Samples were filtered through 0.45
183 μm nylon Whatman filters (Schleicher & Schuell, England). An Agilent (Agilent
184 Technologies, CA, USA) gas chromatograph 6850A, fitted with an FID was employed. One
185 microliter from each sample was introduced on ZB-WAX plus (Zebrom™) capillary column
186 (60m x 0.25mm x 0.25μm). The injector temperature was 240°C the carrier gas was helium
187 (flow rate 1 ml/min) and the detector (FID) temperature was 250°C. The initial oven
188 temperature was set at 35°C and then programmed as follows: 35-58°C (at the rate of
189 12°C/min), 58-85°C (at the rate of 3°C/min), 85-155°C (at the rate of 30°C/min), 155-230°C
190 (at the rate of 200°C/min). The main components (methanol, acetaldehyde, ethyl acetate, 1-
191 propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-
192 butanol, furfural), were identified by comparing their retention times to appropriate
193 standards. For the quantitative evaluation we employed 3-pentanol as an internal standard by
194 adding 0.1 ml 3-pentanol to 10 ml of sample. Each analyse was carried out in triplicate.
195

196 *2.3. Extraction of volatile compounds for GC–MS analysis*

197 The extraction of volatile compounds was performed using the in-tube extraction
198 technique (ITEX). Using a CombiPAL AOC-5000 auto sampler, 1.5 mL sample with 6.5 mL
199 distilled water were placed in a 20 ml headspace vial, sealed and incubated for 30 minutes at
200 40ºC, under continuous agitation. After incubation, the volatile compounds from the gaseous
201 phase from the vial were adsorbed repeatedly (30 strokes) into a porous polymer fibre
202 microtrap (ITEX-2-Trap-TXTA, Tenax TA 80/100 mesh) and then were thermally desorbed
203 directly into the GC-MS injector as described elsewhere (Socaci et al., 2014). All samples
204 were analysed in triplicate.
205
206 *2.4. GC–MS analysis*
207 The separation of volatile compounds was carried out on a GC-MS QP-2010 model
208 (Shimadzu Scientific Instruments, Kyoto, Japan) (Socaci et al., 2014), employing a Zebron
209 ZB-5 ms capillary column of 30 m × 0.25 mm i.d. and 0.25 μm film thickness (Phenomenex,
210 USA). The carrier gas was helium 1 mL/min and the split ratio 1:50. The initial oven
211 temperature was set at 40ºC (hold for 10 min), then 40-120°C (at the rate of 12°C/min), 120-
212 240ºC (at the rate of 10ºC/min), and finally held for 5 minutes at 240ºC. The injector, ion-
213 source and interface temperatures were set at 250°C. The MS detection used for the
214 qualitative analysis was performed on a quadrupole mass spectrometer operating in full scan
215 electron impact (EI) at ionization energy of 70 eV. The method was optimized in respect to
216 the extraction temperature which decreased from 60ºC to 40ºC and the sample volume was
217 increased from 1 mL to 1.5 mL compared to Socaci et al. (2014).
218 The identification of volatile compounds was performed by comparing their mass spectra

with those in the NIST27 and NIST147 mass spectra libraries from the US National Institute of Technology and Standards (NIST) and by retention indices drawn from www.flavornet.org (for columns with a similar stationary phase to ZB-5 ms). The relative contribution (peak area percentage) of each compound was calculated as a fraction of its integrated ion area from total ion chromatograms (TIC) area (100%).

2.5. HPLC-DAD-ESI(+) MS Analysis

There were introduced 10 µl of previously filtered sample for injecting in HPLC system. For separation of phenolic compounds was used an Agilent 1200 HPLC system equipped with Diode Array Detector (DAD), coupled with mass detector (MS) single quadruple Agilent 6110 (Agilent Technologies, CA, USA) according to the method by (Mudura et al., 2018). The HPLC was fitted with an Eclipse XDB C18 column (150 x 4.6 mm x 5 µm from Agilent Technologies, CA, USA). The column temperature was kept at 25°C. The compounds were separated by using a gradient mobile phase which consisted of [water: 0.1% acetic acid in acetonitrile (99:1)] (solvent A) and [0.1% acetic acid in acetonitrile] (solvent B). The gradient applied was as follows: A:B @ 95:5% (v/v) (min 0-2), from 95:5% to 60:40% (v/v) (min 2-18), from 60:40% to 10:90% (v/v) (min 18-20), then isocratic for 4 min at 10:90% (v/v) before decreasing from 10:90% to 95:5% (v/v) (min 24-25), at a flow rate of 0.5 ml/min. For the semiquantitative analysis the compounds were monitored at 280 nm, based on gallic acid calibration curve (R^2=0.999) the phenolic compounds were calculated and expressed as mg gallic acid equivalents (GAE)/L. Qualitative identification was carried out using MS fragmentation employing an ESI (+)

ionization model under the following conditions: 3000 V capillary voltage, at 300ºC, and nitrogen flow 8L/min, *m/z*:100-1000, full-scan. Two levels of energy were used to obtain 50 or 100 fragments in the range *m/z*: 100-1000 Da.

2.6. Statistical Analysis

Data are reported as means ± standard deviation (SD) for triplicate determinations. The ANOVA analysis of variance was used to compare the mean values, using SPSS 19.0 statistical analysis (IBM, New York, USA) and Tukey's Honestly Significant Differences (HSD) test with a confidence interval of 95% or 99%. A *p*-value below 0.05 was considered statistically significant.

3. Results and Discussion

3.1. Major volatile compounds in wood-aged apple brandy

The most abundant major volatile in the apple brandy was methanol (at ~ 1000 mg per 100 mL alcohol), followed by ethyl-acetate (at ~400 mg per 100 mL ethanol) and 3-methyl-1-butanol (at ~ 180 mg per 100 mL ethanol) (Table 1). Methanol is a typical volatile compound present in many fruit brandies. The interest for this compound is focusing not only the negative health related aspects (Levy, Hexdall, Gordon, Boeriu, Heller & Nelson, 2003), but also its contribution to fruit brandy authenticity (Coldea, Mudura & Socaciu, 2017). The presence of methanol in brandies can indicate the origin of raw material used (Coldea et al., 2011). Apples are important sources of pectin ranging between 11.6-32.6 g/kg fresh mass (Rop, Jurikova, Sochor, Mlcek & Kramarova, 2011), as such, among the fruit brandies, apple

263 brandies can contain elevated levels of methanol due to the degradation of methoxylated
264 pectin when compared to other fruit brandies (Coldea et al., 2011), a fact also reinforced by
265 the (EC) No. 110/2008 Regulation of the European Parliament and of the Council. The
266 highest methanol content was recorded in fir wood aged brandy. In our experiments, while
267 there were statistically significant differences between the various samples with regards to
268 methanol, the variation within all wood-exposed samples was within +1.5% of the control
269 which represents a negligible influence.

270 Higher alcohols, such as propanol, butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-
271 1-butanol and 3-methyl-1-butanol are formed as by-products of ethanolic fermentation, being
272 related to the yeast quality and to sugar and amino acids availability via Ehrlich pathway. In
273 specific proportions, they positively influence the aroma of distillates (Rodríguez-Solana,
274 Galego, Pérez-Santín & Romano, 2018), however, when present in excess of 350 mg/100 mL
275 AA higher alcohols are often indicative of poor quality distillates. Higher alcohols represent
276 a substantial part of the fusel oils, and their separation during distillation is strictly monitored,
277 even though fusel oils are not completely eliminated from the final spirit. Among the
278 identified higher alcohols, 3-methyl-1-butanol registered the highest content (Table 1), in
279 agreement with previous findings (Zhao, Xu, Li, Fan & Jiang, 2009). Similar negligible
280 variations as seen with regards to methanol (±1.5% between the control and any of the wood-
281 exposed samples) were also observed for 1-propanol, 1-butanol, 2-methyl-1-propanol, 2-
282 methyl-1-butanol and 3-methyl-1-butanol. However, 2-butanol was present at markedly
283 higher levels (compared to the control) in all (but the pedunculate oak) samples (Table 1),
284 with a >25% average increase. Cherry and mulberry wood caused a small, but significant,

285 reduction in ethyl-acetate (2.5 and 3.5% respectively); whereas mulberry and walnut wood
286 caused a small, but significant, reduction in acetaldehyde (3 and 2.5% respectively).
287 However, cherry wood caused a significant increase in acetaldehyde (+37%). Most wood
288 types (except sessile) caused a >5% decrease in furfural; while cherry wood caused ~15%
289 decrease.

290 Ethyl-acetate is the most common ester in all alcoholic beverages (Cortés, Rodríguez,
291 Salgado & Domínguez, 2011). Our control brandy (non-wood) contained 409 mg/100mL
292 AA) ethyl-acetate, which was higher when compared to our previous study (Coldea et al.,
293 2011) under similar conditions. The exposure to wood caused minor variations in the level
294 of ethyl-acetate, with the greatest variations being sessile oak which caused a 2.3% increase,
295 while mulberry wood caused a 3.5% decrease.

296 Acetaldehyde is a common fermentation product in yeast fermentations (Coldea et al.,
297 2011; Vriesekoop, Barber & Pamment, 2007). In a similar fashion to methanol and ethyl-
298 acetate, acetaldehyde is an extremely volatile compound that occurs in the head fraction of
299 the distillation, its content in the final distillate is strongly dependent of the separation applied
300 during distillation (Mangas, Rodríguez, Moreno & Blanco, 1996a). In this study we found
301 higher values for acetaldehyde in comparison to our previous study on apple brandy (Coldea
302 et al., 2011) and almost double when compared to earlier studies (Winterová, Mikulíková,
303 Mazáč, & Havelec, 2008). The ratio of acetaldehyde, ethyl acetate and amyl alcohols
304 contribute greatly to the final flavour and quality of distillates (Apostolopoulou, Flouros,
305 Demertzis & Akrida-Demertzi, 2005). Compared to the non-wood control brandy (at 40.69
306 mg/100mL AA), the acetaldehyde content did not alter significantly following exposure to

any of the woods, except for exposure to cherry wood which caused an increase by about 35% (Table 1). This marked increase in acetaldehyde is most likely due to the oxidative nature of cherry wood (Chinnici et al., 2015), which could have facilitated to oxidation of ethanol to acetaldehyde.

3.2. Minor volatile compounds in wood-aged apple brandy

The quality of fruit distillates is influenced by a multitude of factors, of which the main are the specie and the quality of raw material, the geographical origin, varietal source, processing procedure and the ageing method applied (Coldea et al., 2011; Coldea, Socaciu, Moldovan & Mudura, 2014; Śliwińska, Wiśniewska, Dymerski, Wardencki, & Namieśnik, 2015). The comparison of the minor volatile compounds of the wood-aged apple brandy in this study indicates a significant effect of the wood type used in the process (Table 2). All the minor volatile compounds identified in our study have in the past also been found in apple related products (Dimick, Hoskin & Acree, 1983; Reis, Rocha, Barros, Delgadillo & Coimbra, 2009).

Focussing on the non-wood-aged apple brandy, the minor volatiles were made up of terpenes, higher alcohols, esters, ketones and aldehydes, with the esters being the most abundant, representing more than 70% of all minor volatiles. As in previous studies, the esters of fatty acids had the highest contribution in the profile of brandies (Coldea et al., 2014; Rodríguez-Solana et al., 2018). We noted the absence of volatile organic acids in our apple brandy, which could be due to the efficiency of the reflux during distillation process. Volatile organic acids, known to make only a small contribution to brandy flavour (Coldea et al., 2014), remain in distillation residue, and only a small fraction passes through to the distillate,

where in the presence of ethanol, much of the volatile organic acids are converted into esters (Bajer, Bajerová, Surmová, Kremr, Ventura & Eisner, 2017).

In agreement with previous studies (Bajer et al., 2017; Coldea et al., 2014), ethyl esters represent the majority of aroma profile of apple brandy. The main ethyl esters contributors in our study were ethyl-acetate, ethyl isobutyrate, ethyl isovalerate, ethyl caproate, ethyl octanoate and ethyl decanoate, many of which are responsible for the fruity floral flavour (Zhao, Xu, Li, Fan, & Jiang, 2009). These ethyl ester arise from the raw material (Dimick et al., 1983), through a range of metabolic activities during the fermentation process (the fatty acid esters of caproic, caprilic, capric and lauric acids), as a consequence of specific yeast strains, and through the yeast autolysis generated during the distillation process (Coldea et al., 2017; Rodríguez-Solana et al., 2018). Elevated temperatures (25+^{o}C) during the fermentation contribute to losses of esters due to volatilisation whereas low fermentation temperatures (the traditional fermentation process of fruit pomace usually takes place in the open air, within a wide range of temperatures (5-25^{o}C) promote the formation of short chain esters (Zhao et al., 2009).

Isobutyl-acetate, hexanal, ethyl-butyrate, ethyl-2-methyl-butyrate, ethyl-isovalerate, 1-hexanol, 2-methylbutyal-isovalerate, hexyl-acetate, ethyl-caproate, hexyl-2-methylbutanoate, and ethyl-nonanoate are known to be responsible for apple flavours (Dimick et al., 1983, Śliwińska et al., 2015). 1-Hexanol is also responsible for a grassy, herbaceous and fruity aroma to distillates (Rodríguez Solana et al., 2018; Śliwińska et al., 2015) and its abundance in fruit spirit depends on the freshness of raw material (Rodríguez Madrera & Suárez Valles, 2007). Hexyl-2-methylbutanoate, is known for its green aroma in

apple brandy (Śliwińska et al., 2015), and 2-methylbutyl-isovalerate a slightly green, but heavy apple skin aroma, with hexyl acetate and ethyl caproate having found to significantly contribute to the specific aroma of apple brandy (Śliwińska et al., 2015). Among the compounds responsible apple flavour, the exposure to wood increased the concentration of isobutyl-acetate, hexyl-2-methylbutanoate, and ethyl-nonaoate in all wood types with the greatest increase in cherry wood for isobutyl-acetate and chestnut wood for both hexyl-2-methylbutanoate, and ethyl-nonaoate. 1-hexanol, hexyl-acetate, and 2-methylbutyl-isovalerate increased in all wood types (Table 2), except for 1-hexanol in cherry wood, 2-methylbutyl-isovalerate in mulberry wood and hexyl-acetate in fir, cherry and walnut wood. This data suggest that some apple-flavour associated compounds are being accentuated by wood-ageing. However, ethyl-butyrate, ethyl-2-methylbutyrate, and ethyl-isovalerate were substantially reduced in their relative concentrations in all wood types. Ethyl-caproate was also reduced in most wood types, but only to a minor extend and a minor increase in cherry wood. This data suggests that from additive effects with regards to wood exposure and spirit ageing; wood also plays a subtractive role with regards to apple flavours in apple brandy.

Isoamyl-acetate, isobutyl-acetate, ethyl-caproate, 2-methylbutyl-acetate, ethyl-octanoate, hexyl-2-methyl-butanoate, and ethyl-nonanoate all contribute to ripe banana flavour (Dimick et al., 1983; Coldea et al., 2017); while 2-heptanone contributes a more ketonic, unripe banana aroma. Among the minor volatile compounds, ethyl octanoate was the major ester detected in our samples (Table 2), which contributes to sweet, floral, fruity, banana, and apple/pear brandy aromas (Peinado, Moreno, Bueno, Moreno & Mauricio, 2004). Almost all compounds that contribute to a banana flavour increase in relative

373 concentration when exposed to any of the woods used in this study (Table 2). The only
374 banana-related compound that decreased was ethyl-caproate in all wood-aged *pălinca*
375 samples, except for cherry wood which caused an increase in ethyl-caproate.

376 The longer fatty acid esters such as: methyl-laurate, ethyl-laurate, and ethyl-
377 tetradeconoate have all been associated with apple and contribute waxy and soapy sensations
378 (Dimick et al., 1983; Coldea et al., 2017); while slightly shorter fatty acid esters such as ethyl
379 octanoate and ethyl decanoate contribute less intense, oily flavours (Coldea et al., 2017). Of
380 the longer fatty acid esters, only ethyl-laurate was present at a notable relative concentration
381 (Table 2), which increased following the wood ageing period in all woods except for the
382 mulberry wood where there was a minor decrease in ethyl-laurate.

383 We detected three terpenes in the control apple brandy sample (limonene, α-farnescene,
384 and α-bergamotene), which have all previously been associated with apples (Reis et al.,
385 2009), with α-farnesene being specifically associated with apple skin (Huelin & Murray,
386 1966), and with fruit brandies (Bajer et al., 2017). Terpenes are often, even at low olfactory
387 thresholds, involved in the sensorial differentiation of beverages (Zhao et al., 2009).
388 Limonene contributes to citrus and herbal aroma notes (Rodríguez-Solana et al., 2018;
389 Śliwińska et al., 2015). The terpene with the greatest relative abundance was α-farnescene,
390 which entirely disappeared when exposed to both oaks, fir, and chestnut, and substantially
391 disappeared in the remining woods. Limonene and α-bergamotene were present in the control
392 sample at a very low relative presence, of which α-bergamotene entirely disappeared in all
393 woods except for cherry wood. Limonene on the other hand did not substantially change

394 when the brandy was exposed to wood except for sessile oak and mulberry where there were
395 substantial increases.

396 Acetaldehyde, benzaldehyde and nonanal were the main aldehydes found in the non-
397 wood-aged brandies (Tables 1 and 2). Nonanal is known for its floral, fruity, green and woody
398 aroma (Śliwińska et al., 2015). While benzaldehyde is a common natural constituent of stone
399 fruit spirits (Bajer et al., 2017), it is also formed by the enzymatic hydrolysis of amygdalin
400 found in the pips and was previously reported in apple brandy (Bajer et al., 2017).
401 Benzaldehyde was substantially reduced following ageing on pendula oak, cherry, chestnut
402 and fir oak wood, but increased somewhat when the brandy was aged in sessile oak, walnut
403 and cherry wood. The increase in benzaldehyde during wood-ageing in cherry wood is in
404 agreement with findings from De Rosso and coworkers (2009). Only minor, but statistically
405 significant, changes were found in the apple brandy when aged in any of the wood types
406 (Table 2). Interestingly, hexanal was not detected in the non-wood-aged spirit, however, both
407 oak woods, fir, mulberry and walnut woods contained low levels of hexanal; while chestnut
408 and cherry wood did not yield hexanal in the wood-aged brandy. This phenomenon, where
409 minor volatile compounds were present in some wood-aged samples but not in the control
410 samples includes: ethyl-pentanoate in cherry aged samples, isobutyl-caprylate in chestnut
411 aged samples, ethyl(z)-4-decenoate, methyl-15-methylhexadecanoate and hexyl benzoate in
412 fir aged samples (Table 2). This means that fir wood contributed four unique volatile
413 compounds to the fir-aged brandies.

414

415 *3.3. Phenolic compounds in wood-aged apple brandy*

The control (non-wood-aged) apple brandy contained a small number of phenolic compounds of which chlorogenic acid was the most abundant (Table 3). Chlorogenic acid is a common contributor to the phenolic profile of in apple wine (Herrera Alvarez, Ferreira Zielinski, Alberti, & Nogueira, 2017; Tošović, Marković, Dimitrić Marković, Mojović & Milenković, 2017). Gallic acid and protocatechuic acid were present in the non-wood-aged apple brandy at intermediate levels, while vanillic acid and syringic acid were present at trace levels only. All wood types absorbed the traces of vanillic acid and syringic acid following the ageing period, with the exception of chestnut wood where there was 56-fold increase in syringic acid. There were minor changes in the protocatechuic acid content, a distinctive compound for apple brandies (Rusu Coldea, Socaciu, Fetea, Ranga & Pârlog, 2011), in both oak woods and chestnut wood, while the protochatechuic acid disappeared from all other wood types following ageing (Table 3). Protocatechuic acid had the highest amount in chestnut-aged samples (3.32 mg/L GAE) which was significantly higher compared with values reported elsewhere (Zhang et al., 2013).

Gallic acid is a compound considered as an oak wood ageing marker (Marques Bortoletto & Alcarde, 2015), is strongly related to the contact period in brandy (Spaho et al., 2019) and the ageing technique applied (Rodríguez-Solana, Salgado, Domínguez & Cortés-Diéguez, 2014). In this study, gallic acid substantially increased in both oak woods, cherry and chestnut wood, but disappeared from all other wood types. The substantial presence of chlorogenic acid in the control increased by about 80% after aging in mulberry wood, but was not detectable in any of the other wood types. The two oak woods contributed roughly the same phenolics, in similar concentrations, during the wood-ageing period. This study found gallic

438 acid, ellagic acid, ferulic acid and protocatechuic acid in both oak woods, which is in
439 agreement with previous studies using oak wood for spirit maturation (Alañón et al., 2011;
440 Rodríguez-Solana et al., 2014; Zhang et al., 2015). In this study, ferulic acid was present at
441 higher concentrations compared to previously published results (Rodríguez-Solana et al.,
442 2014). The higher occurrence of ferulic acid in our samples can be explained by its
443 sensitiveness to high toasting temperatures which were applied in Rodríguez-Solana and
444 coworkers' study (2014). The only main point of differentiation between the two oak woods
445 was that the sessile contributed protocatechuic aldehyde, which was not detected in the
446 pedunculate aged samples. Overall, sessile oak, pedunculate oak, fir, chestnut, cherry,
447 mulberry, and walnut woods contributed 11, 12, 7, 14, 9, 8, and 5 phenolic compounds
448 respectively, with a total quantity of 53, 53, 163, 103, 213, 141, and 55 mg/L GAE
449 respectively. Among the phenolic identified in our study, there was not a single phenolic
450 compound that was present in all wood types. However, almost all wood types contributed
451 p-hydroxybenzoic acid and vanillin, except for walnut wood and cherry wood which did not
452 contribute one of these compounds (Table 3). Vanillin, responsible for taste, aroma and
453 flavour of brandies aged in oak wood, is a marker of wood ageing (Rodríguez-Solana et al.,
454 2017). For a greater vanillin yield it is recommended to use a greater wood surface area
455 exposure (Rodríguez-Solana et al., 2014). Both benzoic aldehydes (vanillin and
456 syringaldehyde) were present in most wood aged samples, which is in agreement with
457 previous studies (Table 4) in barrel aged distillates (Rodríguez-Solana et al., 2014).
458 Syringaldehyde was not detected in untoasted cherry wood, but has been shown to be
459 associated with toasting of wood (Cabrita et al., 2011; Sanz et al., 2010a; Sanz et al., 2010b).

460 Similar to our findings, substantial amounts of syringaldehyde were reported previously in
461 untoasted oak and chestnut exposed samples (De Rosso et al., 2009). It has been argued that
462 vanillin is only formed in cherry wood following a heat treatment (Sanz et al., 2010a), which
463 supports our data in that we did not detect any vanillin in our cherry wood exposed samples.
464 In our samples, vanillin was present at considerable levels in chestnut, walnut and fir exposed
465 apple brandies, which is almost twice the amount compared to the oak-exposed brandies
466 (Table 3). Protocatechuic aldehyde has previously been reported in unseasoned cherry and
467 chestnut woods (Sanz et al., 2010a; Sanz et al., 2010b), and not detected in oak barrel aged
468 distillates (Rodríguez-Solana et al., 2014). In this study, protocatechuic aldehyde was
469 detected in sessile, cherry and chestnut wood aged samples, with significantly higher
470 quantities in cherry wood aged samples (32.27 mg/L GAE). Furthermore, apart from both
471 oak woods, all other woods contributed catechin. Catechin was present most abundantly in
472 cherry wood exposed brandy at almost 19 mg/L GAE, more than twice the next highest level
473 of catechin detected (in chestnut matured samples). An association between high catechin
474 levels and cherry wood has previously been reported elsewhere (Sanz et al., 2010a), which
475 might indicate that catechin at elevated levels can be anticipated when spirits are matured in
476 cherry wood.

477 In the fir-aged samples we detected homovanilic acid, secoisolariciresinol, taxiresinol,
478 and at very substantial quantities, which we did not detect in any other wood type. The latter
479 three compounds however, are typical biomarkers for fir wood, and possess antioxidant,
480 antimicrobial and anti-inflammatory activities (Willför et al., 2003) and would impart a very
481 resiny flavour. However, despite the limited presence of homovanillic acid in our samples, it

has previously been recorded in beverages matured in untoasted chestnut, oak and cherry wood in trace amounts (De Rosso et al., 2009). Walnut wood also yielded a number of phenolic compounds we did not detect in any other wood types, these were *p*-coumaric acid, rutin, and juglone. Juglone is well recognized for its antioxidant and antimicrobial activities and is considered a biomarker for walnut wood (Cosmulescu, Trandafir, Nour, Ionica, & Tutulescu, 2014; Wianowska, Garbaczewska, Cieniecka-Roslonkiewicz, Dawidowicz & Jankowska, 2016; Willför et al., 2003). Scopoletin is a compound commonly associated with oak aged spirits, and its relative presence has been shown to reflect the period of wood maturation (Otsuka & Zenibayashi, 1974), as such scopoletin has previously been reported in oak and chestnut aged spirits (Alañón et al., 2011). In our samples, scopoletin was also found in both oak woods and chestnut with no significant differences between the oak and chestnut wood aged samples regarding scopoletin (Table 3). However, our data shows that scopoletin is also released from cherry wood, but not from mulberry, fir or walnut wood. Cherry wood was the most abundant source of scopoletin (13.03 mg/L GAE).

Mulberry wood contributed dicaffeoylquinic acid as a unique phenolic compound at very high levels (94.68±2.19 mg/L GAE). Cherry wood was the greatest contributor of phenolic compounds with most of the phenolic compounds making a substantial contribution each (10-58 mg/L GAE) to the wood-aged samples. Coniferaldehyde and protocatechuic aldehyde were previously found in considerable amounts in cherry wood extracts (Alañón et al., 2011), which agrees with our findings. The phenolic compounds quantified in this research might not represent high-doses, however, these compounds are of technological interest by

503 potentially acting as authenticity markers for the type of wood used in the ageing of spirits
504 (Alañón et al., 2011; Rusu Coldea et al., 2011; Coldea et al., 2017).

505 Chestnut wood is a rich source of gallic acid and ellagitannins and is often chosen for
506 beverage ageing especially due to its sensorial impact which includes a degree of bitterness
507 and astringency (Puech, Prida & Isz, 2007; Alañón et al., 2011; Zhang et al., 2015).

508 Hydroxybenzaldehyde, which is not dependent on the ageing period (Mangas,
509 Rodríguez, Moreno, Suárez, & Blanco, 1996b), was absent in the control brandy and
510 remained absent in fir, cherry and walnut exposed brandies (Table 3). However,
511 hydroxybenzaldehyde was found in high levels in chestnut wood exposed brandy at
512 approximately twice the quantity compared to both oak types.

513 Sinapaldehyde was detected in both oaks, cherry and chestnut exposed brandies only,
514 but absent in the control and mulberry, fir and walnut wood exposed brandies (Table 3).
515 Similarly, coniferaldehyde was detected in both oaks, cherry, mulberry and chestnut exposed
516 brandies only, but absent in the control and fir and walnut wood exposed brandies. Both
517 coniferaldehyde and sinapaldehyde have been reported previously, at similar levels in oak
518 matured apple brandies (Rodríguez-Solana et al., 2014). Cherry wood exposed apple
519 brandies yielded the highest levels of both coniferaldehyde and sinapaldehyde in cherry wood
520 exposed brandies, with 58.26 mg/l GAE, 45.76 mg/l GAE, respectively, representing
521 between 4 and 10-fold higher levels compared to any of the other woods that yielded these
522 compounds. Both coniferaldehyde and sinapaldehyde were reported in seasoned and toasted
523 chestnut and oak woods with a considerable increase following toasting (Cabrita et al., 2011;
524 Sanz et al., 2010b).

525 Regarding the sensorial impact of polyphenols, recent literature data is available
526 regarding the olive oil (Pedan, Popp, Rohn, Nyfeler & Bongartz, 2019) but not for distilled
527 beverages. The sensorial impact of phenolic compounds in fruit brandies will be a subject of
528 further studies.
529
530 **4. Conclusions**
531 The results obtained in this study provide the first data on the phenolic and volatile
532 composition of the aged apple brandy (*pălinca*) in the presence of several wood species from
533 the Transylvania region in Romania and contribute to the knowledge about this alcoholic
534 beverage. The wood species considered were: two types of oak (*Quercus petraea* and
535 *Quercus robur*), plus sweet chestnut, mulberry, walnut, fir and cherry wood. Our results show
536 that rapid wood ageing of *pălinca* impacted both the volatile and phenolic profiles regardless
537 of the wood types employed.
538 Most major volatile compounds were not affected when aged in the presence of wood,
539 except for 2-butanol which increased in almost all instances, with the greatest increase (42%)
540 when aged in the presence of mulberry wood. The minor volatiles were represented by
541 terpenes, higher alcohols, esters, ketones and aldehydes, with esters of fatty acids the main
542 contributors to volatile profile of *pălinca,* representing more than 70% of all minor volatiles.
543 The main esters contributors that increased in concentration were ethyl-acetate, isobutyl-
544 acetate, isoamyl-2-methylbutyrate, ethyl-benzoate, ethyl-nonanoate, methyl-deconoate,
545 ethyl-decenoate and ethyl-docecanoate, with mulberry, chestnut and cherry being the major
546 positive affectors. Some apple-flavor associated compounds, such as isobutyl-acetate, hexyl-

2-methylbutanoate and ethyl-nonaoate, were accentuated by wood ageing. On the other hand the main esters that decreased in concentration were ethyl-isobutyrate, ethyl-isovalerate, and iso-butyrate, with fir and walnut being the major negative affectors.

Fir wood contributed the largest number of compounds, not found in the control. These include hexanal, ethyl-4-decenoate, homovanilic acid, secoisolariciresinol, and taxiresinol. The latter three phenolic compounds would impart a very resiny flavour to *pălinca*. The most important source of catechin was cherry wood. Rutin and juglone were solubilised only in walnut wood aged *pălinca*. Vanillin, increased significantly in chestnut aged apple brandy. Gallic acid increased in both oak, cherry and chestnut wood aged apple brandies, and were not found in other wood types.

Given the short ageing period analysed, these results revealed important indicators about the alternative wood types used in wood-ageing of *pălinca*, but more so the inclusion of wood inside bottled apple brandy. Considering the cost and labour insensitivity in handling wooden barrels, the choice of a range wooden chips could potentially guide actors in the beverage industry to viable alternatives.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Acknowledgments

We are grateful for the administrative support received from the University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca, Romania. The authors wish to thank Mrs. Alina Vîlcan (University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca, Romania) for skilful assistance in selection of wood species used in this study.

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

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806 **Table 1.** Major volatile compounds of traditional Romanian apple brandy after rapid ageing with different wood chips (mg/100mL AA). Each
807 analyse was carried out in triplicate.
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	Control	Pedunculate oak	Fir	Chestnut	Cherry	Mulberry	Sessile oak	Walnut
Acetaldehyde	40.69±0.54 ^{b}	40.44±0.71 ^{b}	40.67±1.02 ^{b}	39.77±0.39 ^{b}	55.74±0.09 ^{a}	39.44±0.45 ^{b}	40.91±0.49 ^{b}	39.61±0.34 ^{b}
Ethyl acetate	409.16±0.26 ^{d}	417.25±0.30 ^{b}	416.10±0.15 ^{c}	417.28±0.12 ^{b}	397.45±0.15 ^{f}	394.85±0.65 ^{g}	418.66±0.10 ^{a}	403.25±0.45 ^{e}
Methanol	1050.38±1.93 ^{d}	1062.22±1.23 ^{ab}	1066.59±1.66 ^{a}	1050.90±2.03 ^{d}	1051.22±1.19 ^{d}	1058.66±1.87 ^{bc}	1056.70±1.92 ^{c}	1054.86±1.99 ^{cd}
2-Butanol	0.14±0.01 ^{bc}	0.14±0.02 ^{c}	0.19±0.01 ^{ab}	0.17±0.00 ^{abc}	0.17±0.01 ^{abc}	0.20±0.02 ^{a}	0.17±0.02 ^{abc}	0.16±0.00 ^{abc}
1-Propanol	27.97±0.30 ^{ab}	28.21±0.10 ^{a}	28.25±0.20 ^{a}	27.72±0.03 ^{b}	27.87±0.12 ^{ab}	28.28±0.11 ^{a}	28.09±0.04 ^{ab}	27.94±0.06 ^{ab}
2-Methyl-1-propanol	70.40±0.02 ^{c}	71.00±0.05 ^{a}	71.01±0.00 ^{a}	69.98±0.03 ^{f}	70.09±0.01 ^{e}	70.96±0.00 ^{a}	70.60±0.05 ^{b}	70.24±0.00 ^{d}
1-Butanol	7.37±0.12 ^{ab}	7.42±0.06 ^{ab}	7.40±0.01 ^{ab}	7.29±0.00 ^{b}	7.28±0.02 ^{b}	7.43±0.00 ^{a}	7.34±0.00 ^{ab}	7.32±0.02 ^{ab}
2-Methyl-1-butanol	49.16±0.04 ^{a}	49.19±0.14 ^{a}	49.23±0.19 ^{a}	48.07±0.09 ^{c}	48.56±0.11 ^{b}	49.30±0.04 ^{a}	48.69±0.10 ^{b}	48.58±0.01 ^{b}
3-Methyl-1-butanol	183.20±0.09 ^{c}	184.40±0.01 ^{b}	184.41±0.02 ^{b}	181.89±0.14 ^{f}	182.46±0.10 ^{e}	184.86±0.02 ^{a}	183.25±0.09 ^{c}	182.84±0.04 ^{d}
Furfural	2.91±0.00 ^{ab}	2.76±0.03 ^{c}	2.74±0.09 ^{c}	2.76±0.08 ^{c}	2.52±0.01 ^{d}	2.82±0.00 ^{bc}	2.99±0.00 ^{a}	2.79±0.05 ^{bc}

809 Different letters per each compound indicate significant differences at $P < 0.05$

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814 **Table 2.** Minor volatile compounds of traditional Romanian apple brandy after rapid ageing with different wood chips. Values are expressed as the
815 relative contribution (peak area percentage) (*n*=3).
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	Control	Pedunculate oak	Fir	Chestnut	Cherry	Mulberry	Sessile oak	Walnut	Significant differences
3-Methyl-1-Butanol	15.14± 1.06	9.39 ±0.81	15.71±1.27	15.17±0.93	17.04±1.20	18.54±0.99	16.74±0.97	16.35±0.63	***
2-Methyl-1-Butanol	5.60± 0.32	4.54± 0.30	5.17±0.20	4.80± 0.48	5.97± 0.38	6.81± 0.45	6.01± 0.26	5.39± 0.51	***
Ethyl Isobutyrate	7.56± 0.71	4.01± 0.55	3.89± 0.12	3.87± 0.38	4.71± 0.19	4.34± 0.31	4.07± 0.27	3.93± 0.32	***
Isobutyl Acetate	0.54± 0.12	0.60± 0.11	0.65± 0.20	0.60± 0.15	0.70± 0.15	0.70± 0.12	0.61± 0.02	0.69± 0.06	NS
Methyl Isovalerate	0.20± 0.05	0.09± 0.03	0.06± 0.01	nd	0.50± 0.10	0.09± 0.02	0.08± 0.00	0.05± 0.02	***
Hexanal	nd	0.17± 0.04	0.59± 0.13	nd	nd	0.29± 0.12	0.14± 0.01	0.13± 0.01	***
Ethyl Butyrate	0.68± 0.12	0.47± 0.01	0.59± 0.05	0.42± 0.05	nd	0.49± 0.13	0.47± 0.04	0.43± 0.08	***
Ethyl 2-Methylbutyrate	4.22± 0.43	3.16± 0.20	3.33± 0.36	3.68± 0.24	3.42± 0.20	3.17± 0.25	2.66± 0.20	3.38± 0.10	***
Ethyl Isovalerate	10.85± 0.50	5.73± 0.28	5.63± 0.30	4.96±0.19	6.36±0.20	5.79±0.39	5.39±0.27	5.44±0.24	***
1-Hexanol	1.80 ± 0.25	2.11±0.31	1.95± 0.20	2.05± 0.30	1.78±0.17	2.22±0.05	2.12±0.20	2.17±0.30	NS
Isoamyl Acetate	3.82 ± 0.20	4.93±0.09	4.88± 0.17	4.80± 0.10	4.87±0.25	4.67±0.21	4.11±0.12	4.87±0.25	***
2-Methylbutyl Acetate	0.48 ± 0.10	0.56±0.12	0.56± 0.09	0.50± 0.09	0.61± 0.10	0.64± 0.00	0.59±0.02	0.54±0.20	NS
2-Heptanone	0.07 ± 0.01	0.10±0.05	0.08± 0.03	0.10± 0.06	0.09±0.03	0.13±0.02	0.10±0.04	0.08±0.01	NS

Ethyl Pentanoate	nd	nd	nd	nd	0.06±0.03	nd	nd	nd	-
Methyl Hexanoate	0.06 ± 0.01	0.09±0.03	nd	nd	nd	0.02±0.01	0.04±0.03	0.14±0.01	NS
Benzaldehyde	0.56 ± 0.03	0.40±0.09	0.21± 0.08	0.29± 0.01	0.43±0.06	0.71±0.11	0.64±0.10	0.70±0.06	***
Ethyl Caproate	8.83 ± 0.37	8.27±0.35	7.94±0.31	8.21± 0.18	9.53±0.11	7.69±0.46	7.63±0.41	7.78±0.28	***
Iso-Butyl-2-Methylbutyrate	0.10±0.01	nd	0.14±0.01	0.18± 0.02	0.06±0.01	0.12±0.03	0.15±0.00	nd	NS
Hexyl Acetate	0.60 ± 0.19	0.66±0.12	0.49± 0.07	0.65± 0.10	0.47±0.16	0.63±0.10	0.65±0.05	0.50±0.05	NS
Limonene	0.06 ± 0.02	0.07±0.01	0.05± 0.01	0.07± 0.02	0.04±0.02	0.11±0.03	0.18±0.02	0.05±0.01	***
2-Methylbutyl Butyrate	0.03 ± 0.01	0.04±0.02	nd	0.04± 0.03	nd	0.02±0.01	nd	nd	NS
2-Nonanone	0.06 ± 0.01	0.08± 0.02	0.04± 0.01	0.09± 0.03	0.04±0.03	0.10±0.02	0.12±0.01	0.04±0.02	***
Ethyl Heptanoate	0.08 ± 0.02	nd	nd	nd	0.13±0.02	nd	0.09±0.03	nd	-
Isoamyl 2-Methylbutyrate	0.44 ± 0.09	0.61±0.10	0.58± 0.04	0.62± 0.10	0.53±0.01	0.51±0.20	0.56±0.09	0.61±0.10	NS
2-Methylbutyl Isovalerate	0.29 ± 0.04	0.42±0.10	0.42± 0.12	0.45± 0.13	0.36±0.09	0.23±0.01	0.38±0.02	0.42±0.12	NS
Nonanal	0.52 ± 0.11	0.64±0.11	0.58± 0.07	0.62± 0.01	0.51±0.08	0.55±0.10	0.69±0.09	0.63±0.01	NS
Isoamyl Isovalerate	0.10 ± 0.00	0.05±0.01	0.06± 0.02	0.06± 0.01	nd	0.04±0.01	nd	nd	NS
Methyl Octanoate	0.39 ± 0.03	0.61±0.10	0.53± 0.01	0.40± 0.06	0.40±0.04	0.37±0.01	0.38±0.04	0.52±0.02	***
Ethyl Benzoate	0.43 ± 0.03	0.67±0.00	0.54± 0.03	0.69± 0.03	0.67±0.04	0.71±0.01	0.78±0.02	0.42±0.03	***
Ethyl Octanoate	19.85± 2.02	26.11±1.14	25.19±0.95	23.30±0.70	22.56±0.59	22.02±0.63	22.27±0.18	22.53±0.40	***

Hexyl 2-Methylbutanoate	4.89 ± 0.20	6.65±0.30	6.20± 0.13	6.79± 0.21	5.15±0.30	5.80±0.16	6.55±0.18	6.21±0.20	***
Isopentyl Hexanoate	0.09 ± 0.02	0.10±0.01	0.12± 0.01	0.13± 0.02	0.07±0.02	0.14±0.01	0.13±0.03	0.14±0.03	*
n.i.	0.14 ± 0.03	0.22±0.02	0.23± 0.02	0.18± 0.01	0.12±0.02	0.28±0.01	0.33±0.02	0.16±0.03	***
Ethyl Nonanoate	0.13 ± 0.02	0.20±0.02	0.20± 0.01	0.22± 0.02	0.16±0.02	0.17±0.03	0.21±0.03	0.21±0.01	***
Methyl Decanoate	0.21 ± 0.03	0.51±0.04	0.33± 0.04	0.43± 0.06	0.29±0.03	0.34±0.05	0.38±0.04	0.49±0.04	***
Isobutyl Caprylate	nd	nd	nd	0.04± 0.01	nd	nd	nd	nd	-
Ethyl 9-Decenoate	0.11 ± 0.03	0.18±0.03	nd	0.19± 0.03	0.09±0.01	0.13±0.02	0.17±0.02	0.16±0.03	***
Ethyl (Z)-4-Decenoate	nd	nd	0.12± 0.03	nd	nd	nd	nd	nd	-
Ethyl Decanoate	8.30 ± 0.29	14.90±0.40	10.83±0.20	12.89±0.18	9.53±0.30	9.61±0.17	11.84±0.13	12.54±0.48	***
Isopentyl Octanoate	0.07 ± 0.01	nd	0.05± 0.02	0.12± 0.02	nd	0.06±0.01	0.11±0.01	0.09±0.02	NS
Alpha-Bergamotene	0.05 ± 0.01	nd	nd	nd	0.04±0.02	nd	nd	nd	-
Alpha-Farnesene	0.71 ± 0.10	nd	nd	nd	0.32±0.04	0.01±0.00	nd	0.04±0.01	NS
Methyl Dodecanoate	0.03 ± 0.01	0.05±0.01	nd	0.05± 0.01	0.04±0.02	nd	0.05±0.02	0.04±0.01	NS
Methyl 15-Methylhexadecanoate	nd	nd	0.03±0.01	nd	nd	nd	nd	nd	-
Hexyl Benzoate	nd	0.02±0.01	0.02±0.01	nd	nd	nd	nd	nd	-
Ethyl Laurate	1.82 ± 0.10	2.57±0.12	1.94± 0.19	2.25± 0.19	2.26±0.21	1.70±0.06	2.52±0.11	1.96±0.11	**
Ethyl Tetradecanoate	0.08 ± 0.02	nd	0.07± 0.01	0.08± 0.02	0.09±0.02	0.05±0.01	0.08±0.02	0.06±0.01	NS

817 *n* – number of replications; nd - not detected; NS - not significant, P>0.05; *significant P≤0.05; **very significant P≤0.01; ***extremely significant P≤0.001

818 **Table 3.** Concentration of phenolic compounds (mg/L GAE) in of different wood aged apple distillates (*n*=3).

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	Control	Sessile oak	Mulberry	Pedunculate oak	Fir	Cherry	Walnut	Chestnut
Hydroxybenzaldehyde	nd	6.56±0.21 [b]	4.56±0.21 [c]	6.27±0.04 [b]	nd	nd	nd	13.45±0.21 [a]
Gallic acid	1.82±0.03 [e]	2.55±0.01 [c]	nd	3.95±0.2 [a]	nd	2.26±0.02 [d]	nd	3.72±0.01 [b]
Vanillic acid	0.01±0.08 [a]	nd	nd	nd	nd	nd	nd	nd
Protocatechuic acid	2.89±0.22 [b]	2.09±0.02 [d]	nd	2.37±0.05 [c]	nd	nd	nd	3.32±0.95 [a]
Syringic acid	0.02±0.01 [b]	nd	nd	nd	nd	nd	nd	1.12±0.07 [a]
Chlorogenic acid	10.27±0.16 [b]	nd	18.83±1.01 [a]	nd	nd	nd	nd	nd
Homovanilic acid	nd	nd	nd	nd	15.93±0.51 [a]	nd	nd	nd
Catechin	nd	nd	4.70±0.09 [d]	nd	5.76±0.22 [c]	18.95±0.42 [a]	2.76±0.11 [e]	7.57±0.11 [b]
p-Hydroxybenzoic acid	nd	6.32±0.61 [c]	3.96±0.13 [d]	7.11±0.95 [c]	4.85±0.65 [d]	10.33±0.89 [b]	nd	14.11±0.05 [a]
Vanilin	nd	2.91±0.21 [e]	3.62±0.05 [d]	3.01±0.06 [e]	5.44±0.02 [c]	nd	5.88±0.10 [b]	7.38±0.02 [a]
p-Coumaric acid	nd	nd	nd	nd	nd	nd	3.69[a]±0.03	nd
Ellagic acid	nd	3.28±0.14 [c]	nd	2.91±0.09 [c]	nd	11.48±0.31 [a]	nd	4.38±0.27 [b]
Rutin	nd	nd	nd	nd	nd	nd	8.90[a]±0.006	nd
Ferulic acid	nd	2.51±0.22 [c]	nd	2.17±0.01 [c]	nd	21.16±0.82 [a]	nd	18.22±0.67 [b]

Secoisolariciresinol	nd	nd	nd	nd	38.95±0.96 [a]	nd	nd	nd
Juglone	nd	nd	nd	nd	nd	nd	4.28±0.21 [a]	nd
Taxiresinol	nd	nd	nd	nd	76.27±1.04 [a]	nd	nd	nd
Dicafeoilquinic acid	nd	nd	94.68±2.19 [a]	nd	nd	nd	nd	nd
Protocatechuic aldehyde	nd	2.32±0.00 [c]	nd	nd	nd	32.27±0.72 [a]	nd	4.53±0.01 [b]
Scopoletin	nd	5.98±0.29 [c]	nd	6.86±0.04 [b]	nd	13.03±0.01 [a]	nd	6.69±0.01 [b]
Lariciresinol	nd	nd	nd	nd	16.54±0.30 [a]	nd	nd	nd
Coniferaldehyde	nd	8.02±0.83 [c]	8.27±0.02 [c]	11.26±0.19 [b]	nd	58.26±1.16 [a]	nd	11.02±0.07 [b]
Syringaldehyde	nd	6.35±0.63 [a]	2.40±0.01 [d]	5.44±0.12 [b]	nd	nd	nd	4.33±0.26 [c]
Sinapaldehyde	nd	2.81±0.02 [b]	nd	3.03±0.01 [b]	nd	45.76±0.66 [a]	nd	3.47±0.01 [b]

820 *n* – number of replications; nd - not detected; *Different letters in superscripts within the same row indicate statistically significant differences ($p<0.05$)

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824 **Table 4.** Literature sources regarding phenolic compounds identified in this study, which have been already detected in brandy and/or wood.

Phenolic compound	Source	Concentration	References
Catechin	Seasoned cherry wood	30150 μg/g	Sanz et al., 2010a
Chlorogenic acid	Apple wine	14-24 mg/L	Herrera Alvarez et al., 2017
	Apple brandy	5.4-14.4 mg/L	Rusu Coldea et al., 2011
Coniferaldehyde	Toasted cherry wood	332.59 μg/g	Alañón et al., 2011
	Seasoned chestnut wood	8.42 μg/g	Sanz et al., 2010b
	Toasted chestnut wood	328.00 μg/g	Sanz et al., 2010b
	Seasoned oak wood	9.3 μg/g	Cabrita et al., 2011
	Toasted oak wood	297.7-953.2 μg/g	Cabrita et al., 2011
	Oak barrel aged brandy	13500 mg/L μg/g	Rodríguez-Solana et al., 2014
Ferulic acid	Oak barrel aged distillates	900 mg/L	Rodríguez-Solana et al., 2014
Gallic acid	Electric field treated oak barrels	0.15-0.56 mg/L	Zhang et al., 2013
	Apple brandy	79.1-176.3 mg/L	Rusu Coldea et al., 2011
Homovanilic acid	Untoasted chestnut and oak wood	1-10 μg/g	De Rosso et al., 2009
	Untoasted cherry wood	0.1-0.9 μg/g	De Rosso et al., 2009
Hydroxybenzaldehyde	Wood aged cider brandy	0.49 mg/L	Mangas et al., 1996
***p*-Coumaric acid**	Heat treated oak wood	53.78 μg/g	Alañón et al., 2011

Phenolic compound	Source	Concentration	References
	Sessile oak wood	26.84 μg/g	Alañón et al., 2011
	Heat treated chestnut wood	116.12 μg/g	Alañón et al., 2011
	Heat treated cherry wood	7.11 μg/g	Alañón et al., 2011
Protocatechuic acid	Oak cooperage wood	239.31 μg/g	Alañón et al., 2011
	Sessile cooperage wood	178.17 μg/g	Alañón et al., 2011
	Apple brandy	1.5-1.7 mg/L	Rusu Coldea et al., 2011
	Electric field treated oak barrels	0.1 mg/L	Zhang et al., 2013
Protocatechuic aldehyde	Unseasoned cherry wood	12.94 μg/g	Sanz et al., 2010a
	Toasted chestnut wood	7.90 μg/g	Sanz et al., 2010b
	Toasted cherry wood	26.92 μg/g	Alañón et al., 2011
Rutin	Walnut extract	74.7 mg GAE/L	Cosmulescu et al., 2014
Scopoletin	Oak medium toasted wood	260.03 μg/g	Alañón et al., 2011
	Chestnut medium toasted wood	285.85 μg/g	Alañón et al., 2011
Sinapaldehyde	Oak barrel aged brandy	7700 mg/L	Rodríguez-Solana et al., 2014
Syringaldehyde	Seasoned cherry wood	1-10 μg/g	De Rosso et al., 2009
	Seasoned chestnut wood	> 10 μg/g	De Rosso et al., 2009
	Seasoned oak wood	> 10 μg/g	De Rosso et al., 2009

Phenolic compound	Source	Concentration	References
	Toasted chestnut wood	374.00 μg/g	Sanz et al., 2010b
	Oak aged brandy	12200 mg/L	Rodríguez-Solana et al., 2014
	Sessile oak aged brandy	8200 mg/L	Rodríguez-Solana et al., 2014
Syringic acid	Seasoned chestnut wood	7.38 μg/g	Sanz et al., 2010b
	Toasted chestnut wood	152.00 μg/g	Sanz et al., 2010b
Vanillic acid	Oak wood	108.81 μg/g	Alañón et al., 2011
	Sessile wood	98.49 μg/g	Alañón et al., 2011
Vanillin	Heat treated oak wood	71.23 μg/g	Alañón et al., 2011
	Heat treated chestnut wood	63.61 μg/g	Alañón et al., 2011
		163.00 μg/g	Sanz et al., 2010b
	Heat treated cherry wood	30.38 μg/g	Alañón et al., 2011
	Seasoned chestnut wood	20.5 μg/g	Sanz et al., 2010b
	Oak wood aged grape marc distillate	4.92 mg/L	Rodríguez-Solana et al., 2017
	Oak aged brandy	2800 mg/L	Rodríguez-Solana et al., 2014
	Sessile oak aged brandy	2400 mg/L	Rodríguez-Solana et al., 2014

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