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ORIGINAL RESEARCH ARTICLE

Volatile composition of light red wines aged in Canary pine barrels from La Palma (Canary Islands, Spain)

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ABSTRACT

Multivarietal wines aged in barrels made from the resinous heartwood of the Canary Pine (*Vinos de Tea*) in La Palma (Canary Islands, Spain) were analysed, together with a control sample and a Greek Retsina wine. The concentrations of various families of varietal and fermentative volatile compounds were determined by gas chromatography and mass spectrometry. Results showed the significant presence of the terpene family, especially terpinen-4-ol and α-terpineol (probably derived from contact with the resinous wood of the barrels), regardless of grape variety. Samples taken from commercial wineries presented significantly lower concentrations of α-terpineol than samples from traditional artisan producers. The principal component analysis clearly differentiated both from the Retsina. It also revealed a correlation between the length of time that wine aged in Canary pine barrels and a sharp increase in α-terpineol, which can be considered a marker of the typicity of these unique traditional wines on the verge of disappearance.

KEYWORDS: pine barrels, vino de Tea, volatile composition, Canary pine wood, wine, wine aroma

INTRODUCTION

In the last decade, the variety of winemaking containers used by cellars has increased worldwide. This includes the use of cement tanks, egg-shaped fermenters and clay vessels. American and French oak barrels, the most common woods used for winemaking, now compete with a variety of barrels made of local types of oak, chestnut, acacia, alder, beech, mulberry, ash and cherry. These woods have different properties to French and American oak and provide wines with different organoleptic and physicochemical qualities (De Rosso *et al*., 2009). Nonetheless, the International Organization of Vine and Wine has only approved oak and chestnut for wine aging (Carpena *et al*., 2020). The influence of pine barrels on the characteristics and qualities of wine has not yet been explored in the literature. This study analyses the volatile compounds of wines aged in pine barrels, specifically the *Vino(s) de Tea* (VT) from La Palma (Canary Islands, Spain), making it a unique contribution to the advancement of knowledge on this hitherto disregarded topic. It is a continuation of previous work aimed at exploring the cultural and heritage aspects of VT (Alonso González and Parga-Dans, 2020).

The Canary Islands, a subtropical Spanish archipelago located near the Atlantic North African coast, boast a diverse range of local cultivars, soils and weather conditions. Vines were the dominant commercial crop for centuries until the expansion of banana plantations during the 20th century. Today, viticulture is the second most important agricultural product in terms of both surface area and production in the islands. The northwestern area of La Palma, comprising the municipalities of Tijarafe, Puntagorda and Garafía, is an isolated region dominated by pine woodlands of the local species *Pinus canariensis*. A blend of red and white *Vitis vinifera* varieties has been used there for centuries, including Negramoll, Listán Negro, Listán Blanco, Listán Prieto, Almuñeco, Vijariego Negro and Albillo. The wine is aged in barrels made from the heartwood of Canary pine, called *Tea*. According to local wine tasters, this wood provides these wines with herbaceous, mentholated and fruity aromas with a hint of resin, evoking the Greek wine Retsina (Díaz *et al*., 2000). However, while *Vinos de Tea* (VT) are traditionally aged in pine barrels with no added resin, Retsinas are typically aged in clay vessels with pitch (resin) from Aleppo pine (*Pinus halepensis*) added in amounts of less than 1% during fermentation (Lazarakis, 2018). Most Retsinas are produced from the Rhoditis (pink-skinned) and Savatiano (white) cultivars. The pitch provides the wines with their distinctive taste, colour and volatile profile, with higher levels of phenolic compounds and esters derived from benzoic, salicylic and cinnamic acids (Proestos *et al*., 2005).

In the past, the production of pine barrels was a necessity in northwestern La Palma, where Canary pine was the only material available for centuries. The resinous heartwood of pine, the so-called *Tea,* which confers its name to the wines under study, was highly valued for construction purposes because of its solidity, durability and resistance to rotting (García Esteban *et al*., 2005). Canary pine is an endemic variety whose characteristics include a greater number of resin canals and higher extractive components than any other pine (Climent *et al*., 2002). Its characteristics greatly differ from those of *P. halepensis*, whose resin is used in Retsina winemaking (Lazarakis, 2018). For decades, Canary pine has been a protected species; therefore, new barrels cannot be produced. Most barrels range from 80 to 200 years in age and have been subjected to recurrent repairs and stave replacements. They do not have uniform capacities, because pine barrels were made on demand according to the winemakers' needs and availability of large pines nearby. Consequently, barrel capacities can range from 80 to 400 litres. Moreover, they are subject to annual scraping and sanding for cleaning and maintenance purposes. This determines the profile of the following year's wine, as scraping the barrels exposes fresher pine resin and extractives on the barrels' inner surface, facilitating an increased transfer of compounds from barrel to wine. These activities can continue thanks to traditional knowledge passed from generation to generation. Consequently, both human and legal factors prevent the industrialisation of VT from relying on the standardised production processes applicable elsewhere. As is the case with many other traditional foods for which replicability is not an option, the study of VT needs to be dynamic and based on a mixed-method approach.

The sensory determination of VT volatile compounds is also necessary, given the status of VT as a traditional food on the verge of disappearance. Compared to 9450 litres produced in 2007, only 1350 litres were produced in 2018, posing a risk to its very survival (Alonso González and Parga-Dans, 2020) Given the current protection and production status of VT, the specification of its characteristics is relevant and timely, as described by Cayot (2007). These include, firstly, its protection by the Designation of Origin Vinos de La Palma as a differential quality product. This makes it necessary to prove the difference between certified and non-certified products, that is, their typicality and unique sensorial characteristics beyond panels of experts. This is even more compelling given the divergences within the expert tasting panel of the Designation of Origin, regarding the qualification of VT. Various wines have been disqualified in recent years by expert panels on the grounds of having "too much" or "too little" character, referring to the typical aroma or taste of VT. In other words, there is a lack of agreement about what constitutes authentic VT. Second, the production of VT wines is transitioning from small-scale homemade and artisanal to commercial and quasi-industrial and, consequently, to the eventual reformulation and adaptation of the wines to standard winemaking criteria.

Wine aroma depends on the correlation between human perception thresholds and the complex balance between several volatile compounds (Sáenz-Navajas *et al*., 2017). Normally, one of the main contributors to wine aroma are varietal compounds, which are derived from the grapes and can be found in both bound and volatile forms (Ayestarán *et al*., 2019). In the case of VT, however, they

are secondary to the unifying influence of the pine barrels. This is because both traditionally and currently, winemakers use a mixture of white, pink-skinned and red grapes, whose volatile and phenolic characteristics have yet to be studied. The amount of each variety used for VT varies yearly among producers depending on the ripening and weather conditions. Therefore, it is fundamental to analyse the common factor in VTs: the use of Canary pine barrels for wine aging. The main goal of this study was to understand the modifications of the volatile composition of VT resulting from Tea aging. The starting hypothesis was that fermenting and aging in pine barrels results in wines with different characteristics to those fermented and aged in barrels of other kinds of wood as reported in the literature (Fernández de Simón *et al*., 2014). The significance of the study is that it opens up novel avenues for research in winemaking techniques with potential benefits and impacts within the wine sector. To test our hypothesis, all known VT currently produced in La Palma, both commercially and homemade, were studied by Gas Chromatography or Mass Spectrometry (GC/MS).

MATERIALS AND METHODS

1. Samples: vineyards, wines and woods

For our purposes, we analysed all currently produced VT and compared them with a single Retsina wine. As with other traditional food products lacking standard production methods, VT is influenced by many variables that hinder reproducibility and make the results difficult to interpret. These include the different grape varieties, the vintages, the tanks to produce and age the wine, the additives and processing aids used, and the differences between home/artisanal and commercial wineries. Taking into account this complexity, we collected 15 VT samples from the northwestern area of La Palma, which contains the municipalities of Puntagorda, Garafía and Tijarafe (see Table 1). The vineyards are located in high-elevation areas at between 800 and 1450 meters above sea level, with soils originating in basaltic lava flows characteristic of a volcanic island. All the samples, except the red wine DO-14, were light reds produced from different proportions of native red and white varieties dominated by Negramoll, followed in importance by Listán Negro, Listán Blanco, Listán Prieto, Albillo and Tintilla.

Traditionally produced VTs were collected directly from the pine barrels (TEA-TRAD samples), while samples of VT produced by commercial wineries were collected in bottles available on the market (DO samples). This is because commercial VTs are aged in pine barrels for brief periods of between 20 and 30 days. The humidity and temperature conditions of the traditional wines varied significantly. They were mostly kept in cellars made in natural or excavated caves, as well as in 'pajeros', which are tiny traditionally built structures for winemaking built at high elevations near the vineyards, and which generally comprise a winepress made of Canary pine and an area for wine barrels. In contrast, commercial wineries store their wines at a controlled temperature of between 15° and 17 °C in their cellars. Collecting control samples from artisanal or small farm wineries was difficult, because their wines are generally fermented and aged in pine barrels, and therefore the fermenting musts are already in the barrels. Moreover, the barrels are not highly porous and therefore do not strongly oxygenate the wines. It is thus unnecessary to leave wine in other containers, such as demijohns, to refill the barrels. Barrel dimensions vary considerably, ranging from 150 to 400 litres. This is because the pine barrels were made by local craftsmen who used the available raw material on site, rather than based on a fixed predesigned model. Additionally, barrel repair often involves the removal of staves and a reduction in size. Due to their great age, the number of times the barrels have been used and the extent of stave toasting is unknown. Toasting the wood generally affects aroma release in wines.

TABLE 1. Description of the wines analysed, including main grape varieties, wine type, vintage, tanks used for fermentation and aging, and type of producer.

Sample	Variety	Type	Vintage	Fermentation	Ageing	Producer
TEA-TRAD-1	Prieto (90%) and others	Light red	2018	Pine Cask (1 month)	Stainless Steel	Homemade
TEA-TRAD-2	Almuñeco (90%) and others	Light red	2018	Stainless Steel	Pine Cask (1 month)- Stainless Steel	Homemade
TEA-TRAD-3	Negramoll and blend	Light red	2016	Stainless Steel	Pine Cask (3 years)	Homemade
TEA-TRAD-4	Blend	Light red	2016	Pine Cask (3 months)	Stainless Steel	Homemade
TEA-TRAD-5	Blend	Light red	2017	Pine Cask (3 months)	Stainless Steel	Homemade
TEA-TRAD-6	Vijariego, Almuñeco, Albillo criollo	Light red	2018	Pine Cask (1month)	Stainless Steel	Homemade
TEA-TRAD-7	Blend	Light red	2018	Pine Cask (3 months)	Stainless Steel	Homemade
TEA-TRAD-8	Blend	Light red	2016	Pine Cask	Pine Cask (1 year)	Homemade
TEA-TRAD-9	Blend	Light red	2018	Pine Cask (1 month)	Stainless Steel	Homemade
TEA-TRAD-10	Blend	Light red	2018	Pine Cask (1 month)	Stainless Steel	Homemade
CONTROL	Vijariego, Albillo Criollo	Light red	2018	Stainless Steel	Stainless Steel	Professional (control)
DO-12	Blend	Light red	2016	Stainless Steel	Pine Cask (15 days)	Professional
DO-13	Blend	Light red	2017	Stainless Steel	Pine Cask (20 days)	Professional
DO-14	Blend	Red	2017	Stainless Steel	Pine Cask (22 days)	Professional
RETSINA	Rhoditis	White	2017	Amphorae	Amphorae (6 months)	Professional
CONTROL+TEA	Vijariego, Albillo Criollo	Light red	2018	Stainless Steel	Pine Cask (3 months)	Professional (control)

However, given the age of the pine barrels and the high number of vintages for which they are used, it is unlikely that toasting considerably affects wine aroma. Another factor that adds complexity to the sample is the fact that commercial winemakers do not make VT every year, but only when the yearly harvest is abundant and when their previous VT has been sold on the market. Thus, only two control samples could be collected from a commercial winery, one before (CONTROL) and another after brief aging (30 days) in a pine barrel (CONTROL+TEA). This wine had not yet been released to the market. Finally, a traditional Retsina wine fermented in a clay vessel (amphora) with pitch (resin) from Aleppo pine surrounding the Greek vineyards was collected for comparative purposes (RETSINA sample).

2. Extraction and GC-MS conditions

The analysis was partly based on the methodologies developed by Roda et al. (2019) and Sánchez Palomo et al. (2007). Further details on analysis conditions, gas chromatography and mass spectrometry (GC-MS) detection characteristics are described elsewhere (Mislata et al., 2020) The equipment and systems were provided by Agilent Technologies, and sample materials, patterns and utensils by Sigma Aldrich. One hundred mL of wine was centrifuged for 15 min at 6000 rpm. Then, a solution of 2-octanol at 100 µg/L was added as an internal standard to yield a final concentration of 1 µg/L in the samples. The 2-octanol (≥ 96 %) used as the reagent in the aroma analysis was of analytical quality and was purchased from Sigma-Aldrich (Merck Life Science, Barcelona, Spain).The other reagents employed (Sigma Aldrich) were Benzaldehyde ≥ 99 %; 2-hexenal ≥ 95 %; trans-3-hexen-1-ol 97 %; cis-2-hexen-1-ol 95 %; cis-3-hexen-1-ol > 98 %; 1-hexanol ≥ 99 %; 1-octanol , ≥ 99 %; 1-octen-3-ol ≥ 98 %; benzyl alcohol 99.8 %; phenyl ethyl alcohol ≥ 99 %; linalool ≥ 95.0 %; Terpinen-4-ol ≥ 95.0 %; Epoxylinalool (Linalool oxide) ≥ 97.0 %; b-citronellol 95 %; geraniol 98 %; α-terpineol 90 %; Eugenol 99 %; Isoeugenol 98 % (mixture of cis and trans); and methyl salicylate ≥ 99 %. The mixture was passed through an SPE cartridge (Agilent Bond Elut ENV, 500 mg, 6 mL). These cartridges were preconditioned and the compounds eluted with pentane-dichloromethane (50/50) and dried (final volume 200 µL). GC-MS analyses were performed by an Agilent GC 7890A system coupled to an Agilent 5975C inert MSD mass spectrometer (electron impact source triple-axis detector). Separation was performed with an Agilent DB-WAX UI column (60 m × 0.25 mm × 0.25 µm, Agilent). Helium was used as a carrier gas at a constant flow of 2.1 mL/min. Oven temperature was held at 60 °C for 15 min, then increased at a rate of 3 °C/min to 220 °C and held there for 25 min. The MS transfer line temperature was 280 °C. The mass spectrometer was operated at 70 eV, with analysis in scan mode (m/z 10-500 AMU).

The volatile compounds were identified by their retention times and the mass fragments were compared with those of the pure standard compounds when available. The quantification of compounds lacking standards

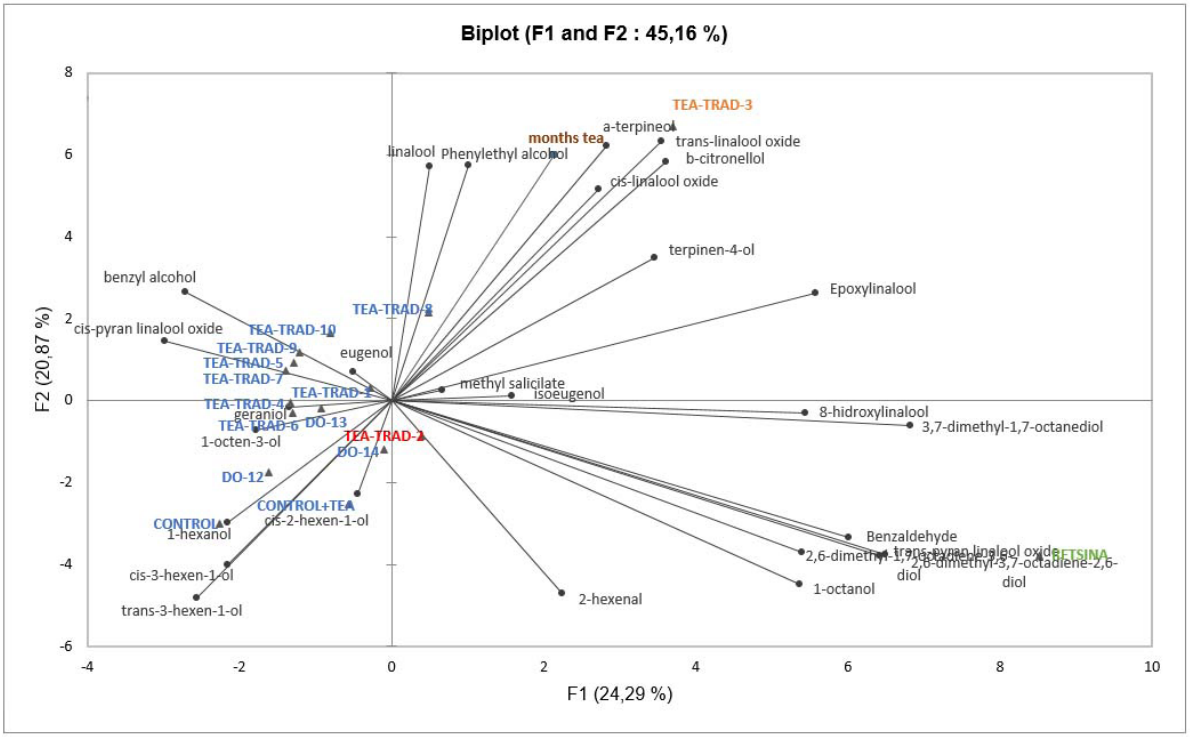


FIGURE 1. Biplot of the PCA carried out on the average concentrations of the quantified volatile compounds for each sample. The variable "months tea" has been added as a supplementary variable representing the number of months of aging in *tea*. The colours indicate the composition of the clusters produced by the HCA: samples with the same colour belong to the same cluster.

was carried out using the internal standard (IS) method. The results of the volatile compounds assay are expressed as semi-quantitative data in µg/L of 2-octanol equivalents, giving their relative abundance rather than their actual concentration. The relative areas of the compounds were transformed into µg/L of 2-octanol by reading off their calibration line, thus establishing a correlation between concentration and peak area; then a slope and y-intercept were derived. The concentration of 2-octanol was correlated with the relative area of each compound using the ratio of peak area to internal 2-octanol standard. All extractions and extract analyses were carried out in duplicate.

The selection of volatile compounds to be analysed was based on a literature review, with the aim of exploring those related to pine, turpentine and resin. These included aldehydes (benzaldehyde, 2-hexenal), C6 compounds (*trans*-3-hexen-1-ol, *cis*-2-hexen-1-ol, *cis*-3-hexen-1-ol and 1-hexanol), alcohols (1-octanol, 1-octen-3-ol, benzyl alcohol and phenyl ethyl alcohol), monoterpenes (linalool, terpinen-4-ol, epoxy linalool, b-citronellol, geraniol and α-terpineol), polyoxygenated terpenes (*cis*-linalool oxide, *trans*-linalool oxide, *cis*-pyran linalool oxide, *trans*-pyran linalool oxide, 2,6-dimethyl-3,7-octadien-2,6-diol, 2,6-dimethyl-1,7-octadien-3,6-diol, 3,7-dimethyl-1,7-octanediol and 8-hydroxylinalool) and volatile phenols (eugenol, isoeugenol, methyl salicylate and ethyl salicylate).

3. Statistical analysis

All data are expressed as µg/L of 2-octanol equivalents, means and standard deviation. All the samples were compared to find the differences between the compounds using two sets of multivariate analyses: one aimed at discerning potential differences between VT and Retsina and the other at elucidating the distinctive chemical compounds of VT. In both cases, a one-way analysis of variance (ANOVA) was performed on each compound with "sample" as the only variable factor. Duncan's post hoc mean was used to compare the variables showing a significant sample effect. A principal component analysis (PCA) was carried out (including and excluding Retsina) by adding "months aging in pine barrel" as an illustrative variable acting on the average concentration. The coordinates of the wines in the interpreted principal components were submitted to subsequent hierarchical cluster analysis (HCA), using the Ward minimum variance method to identify groups of wines with similar compositions. The significance level was set at $\alpha = 5$ %. The XLSTAT (2014.1.10) software was used for all statistical analyses.

RESULTS & DISCUSSION

The average concentrations of the 28 variables along with the results of Duncan tests are shown in Table 2. All the ANOVAs except the one on ethyl salicylate were significant. To obtain an overall overview of the results, a PCA of the average concentrations is shown in Figure 1. The three principal components accounted for 24.3 %, 20.9 and 14 % of the variance. The subsequent HCA produced a four-cluster partition of three groups containing one wine each (Retsina, TEA-TRAD-2 and TEA-TRAD-3), plus a fourth group of the remaining wines (Figure 2). The PCA and cluster analyses

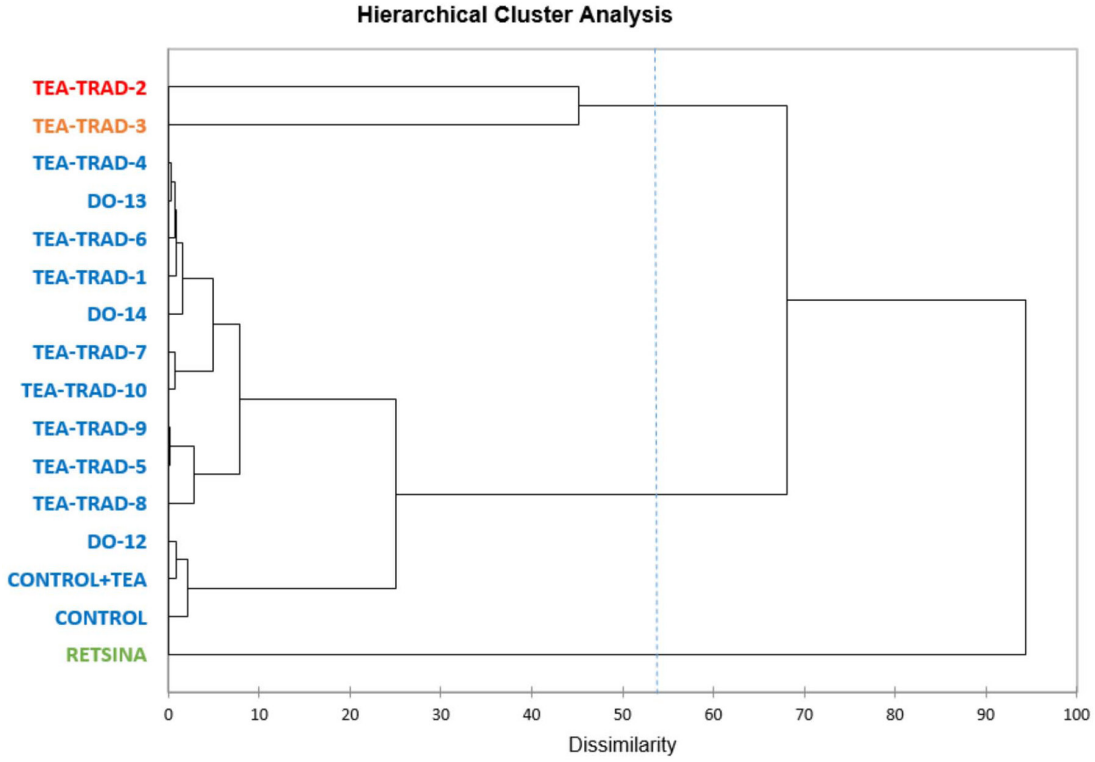


FIGURE 2. Dendrogram resulting from the hierarchical cluster analysis performed on the PCA loadings for the wines. The dotted line and the colours of the sample codes indicate a four-cluster partition.

TABLE 2. Average semiquantitative concentrations of the 28 aroma compounds, the SD (±) in µg/L, and the results of the Duncan test. The letters next to each value indicate significant differences among samples based on a Duncan post hoc test. Averages were calculated for three wine samples analysed in duplicate. Samples with letters in common within a row are not significantly different at p = 0.05.

Part 1/2

Compound	RETSINA	TEA-TRAD-6	TEA-TRAD-3	TEA-TRAD-1	TEA-TRAD-2	TEA-TRAD-10	TEA-TRAD-8	CONTROL+TEA	TEA-TRAD-5	DO-13	TEA-TRAD-9	CONTROL	TEA-TRAD-4	DO-12	DO-14	TEA-TRAD-7
benzaldehyde	157.5 ± 1.8 a	13.5 ± 0.7 cd	0.0 i	15.0 ± 0.05 c	0.0 i	0.0 i	4.0 ± 0.5 gh	12.4 ± 0.1 d	47.5 ± 3.5 b	6.5 ± 0.6 ef	5.0 ± 0.6 fg	3.0 ± 0.3 gh	8.5 ± 0.6 e	2.0 ± 0.2 hi	0.0 i	0.0 i
2-hexenal	1306.5 ± 9.1 b	638.5 ± 63.2 e	0.0 l	185.0 ± 6.1 i	1985.5 ± 78.3 a	214.5 ± 0.6 i	27.0 ± 1.5 kl	752.2 ± 4.4 d	298.5 ± 0.8 gh	50.0 ± 4.2 jkl	89.0 ± 4.1 j	536.0 ± 13.5 f	79.0 ± 1.3 jk	1069.0 ± 20.1 c	341.5 ± 5.8 g	277.0 ± 8.2 h
trans-3-hexen-1-ol	57.0 ± 1.7 fg	131.5 ± 4.9 c	0.0 j	58.5 ± 10.7 f	167.0 ± 19.5 b	0.0 j	29.5 ± 2.0 hi	122.930 ± 0.9 cd	91.0 ± 14.0 e	33.0 ± 2.3 hi	16.5 ± 1.0 ij	215.5 ± 15.3 a	89.0 ± 2.8 e	112.0 ± 11.1 d	39.5 ± 0.9 gh	123.0 ± 5.9 cd
cis-2-hexen-1-ol	0.0 b	0.0 b	0.0 b	0.0 b	0.0 b	0.0 b	0.0 b	3.2 ± 0.1 a	0.0 b	0.0 b	0.0 b	0.0 b	0.0 b	0.0 b	0.0 b	0.0 b
cis-3-hexen-1-ol	0.0 d	0.0 d	0.0 d	0.0 d	0.0 d	0.0 d	0.0 d	4.4 ± 0.1 b	0.0 d	0.0 d	0.0 d	7.5 ± 0.9 a	0.0 d	3.0 ± 0.5 c	0.0 d	0.0 d
1-hexanol	123.0 ± 5.0 ef	299.0 ± 21.2 b	160.5 ± 16.8 e	94.5 ± 7.8 fg	320.0 ± 1.4 b	74.0 ± 3.1 gh	66.0 ± 4.3 gh	288.5 ± 18.0 b	244.5 ± 19.0 cd	63.0 ± 5.8 gh	34.0 ± 1.9 h	470.5 ± 31.9 a	211.0 ± 28.2 d	243.0 ± 33.8 cd	59.0 ± 2.4 gh	276.5 ± 36.1 bc
1-octanol	30.0 0.2 a	6.0 ± 0.1 d	0.0 g	7.0 ± 0.5 c	0.0 g	0.0 g	0.0 g	4.6 ± 0.1 f	0.0 g	9.5 ± 0.6 b	0.0 g	4.5 ± 0.6 f	5.0 ± 0.4 ef	5.5 ± 0.6 de	0.0 g	0.0 g
1-octen-3-ol	9.0 ± 0.2 ef	30.0 3.7 c	0.0 g	31.0 ± 1.2 c	0.0 g	69.0 ± 0.1 a	0.0 g	11.1 ± 0.1 e	0.0 g	42.0 ± 2.3 b	0.0 g	32.5 ± 2.6 c	25.5 ± 3.5 d	6.0 ± 0.1 f	0.0 g	0.0 g
benzyl alcohol	103.0 ± 3.0 hi	276.5 ± 18.2 ef	165.5 ± 10.9 gh	273.5 ± 14.5 ef	114.5 ± 6.4 hi	452.5 ± 17.7 c	501.5 ± 54.1 c	257.3 ± 7.6 ef	707.0 ± 56.8 b	314.0 ± 18.8 de	815.0 ± 49.5 a	180.0 ± 28.5 g	369.5 ± 24.7 d	229.0 ± 34.1 fg	73.0 ± 5.7 i	226.5 ± 10.6 fg
phenyl ethyl alcohol	25069.0 ± 1107.4 e	26962.0 ± 1430.0 e	159853.0 ± 17254.6 a	59091.0 ± 1674.5 d	65395.5 ± 1990.8 d	121563.5 ± 4772.2 b	11451.5 ± 118.2 f	7385.8 ± 493.6 f	108388.0 ± 5651.2 c	26277.5 ± 2049.9 e	12395.0 ± 1398.8 f	6143.5 ± 198.4 f	34698.0 ± 3696.5 e	5312.5 ± 13.1 f	9045.5 ± 245.1 f	121885.5 ± 10888.8 b
linalool	46.0 ± 1.2 gh	34.5 ± 1.0 hi	112.5 ± 20.3 bc	44.0 ± 4.1 ghi	84.0 ± 8.2 e	120.5 ± 6.9 b	160.5 ± 5.1 a	29.5 ± 0.7 i	55.5 ± 4.7 fg	66.5 ± 5.1 f	103.5 ± 3.5 cd	10.0 ± 0.1 j	92.5 ± 5.3 de	65.5 ± 2.0 f	33.0 ± 0.8 hi	92.5 ± 2.0 de
terpinen-4-ol	253.0 ± 4.0 c	121.0 ± 10.0 efg	328.5 ± 44.6 b	108.0 ± 5.6 fg	130.0 ± 10.0 ef	40.5 ± 4.6 j	637.5 ± 12.2 a	94.5 ± 0.5 gh	175.5 ± 3.7 d	46.5 ± 3.5 ij	137.5 ± 3.2 e	5.5 ± 0.1 k	40.0 ± 4.7 j	8.5 ± 0.8 k	190.5 ± 0.5 d	69.5 ± 3.7 hi
epoxylinalool	69.5 ± 1.8 b	13.5 ± 1.8 fgh	113.0 ± 18.4 a	17.0 ± 0.2 efg	12.5 ± 0.7 fgh	26.0 ± 4.2 de	9.0 ± 0.1ghij	39.1 ± 0.1 c	0.0 ij	25.5 ± 3.4 de	10.0 ± 0.5 ghij	22.5 ± 0.5 ef	11.5 ± 0.7 fghi	4.0 ± 0.2 hij	34.0 ± 3.1 cd	0.0 j

Part 2/2

Compound	RETSINA	TEA-TRAD-6	TEA-TRAD-3	TEA-TRAD-1	EA-TRAD-2	TEA-TRAD-10	TEA-TRAD-8	CONTROL+TEA	EA-TRAD-5	DO-13	TEA-TRAD-9	CONTROL	TEA-TRAD-4	DO-12	DO-14	TEA-TRAD-7
b-citronellol	207.0 ± 10.0 b	223.0 ± 16.5 b	814.5 ± 140.8 a	222.0 ± 7.1 b	80.0 ± 8.2 cde	65.0 ± 3.2 cde	128.5 ± 3.2 c	66.5 ± 0.5 cde	260.5 ± 0.6 b	21.0 ± 2.9 de	102.0 ± 3.9 cd	31.0 ± 1.6 de	77.5 ± 5.0 cde	30.0 ± 2.7 de	4.0 ± 0.4e	55.5 ± 0.6 cde
geraniol	43.5 ± 0.9 fg	98.5 ± 12.4 e	0.0 j	244.0 ± 15.8 b	163.0 ± 1.2 d	218.5 22.1 ± c	47.0 ± 3.2 fg	54.4 ± 0.4 f	157.5 ± 1.0 d	92.0 ±11.3 e	35.0 ± 2.9 fgh	11.5 ± 1.0 ij	31.5 ± 2.1 ghi	21.5 ± 0.4 hi	289.5 ± 13.2 a	155.0 ± 12.5 d
α-terpineol	3440.0 106.4 de	6464.5 ± 334.0 c	23248.0 ± 3436.8 a	5910.0 ± 100.0 c	1518.0 ± 162.2 ef	1392.5 ± 127.5 f	4751.5 ± 6.2 cd	1197.6 ± 2.2 f	10107.0 ± 154.1 b	632.0 ± 59.6 f	1735.0 ± 42.4 ef	78.5 ± 2.2 f	1803.0 ± 146.9 ef	389.0 ± 10.0 f	109.5 ± 0.6 f	1350.5 ± 61.5 f
cis-linalool oxide	11.0 ± 0.1cd	8.5 ± 0.9 cdef	32.0 ± 5.9 a	10.0 ± 1.1 cde	12.0 ± 0.0 c	18.0 ± 0.8 b	6.5 ± 0.2 efg	5.5 ± 0.0 fg	0.0 h	7.5 ± 1.0 defg	6.0 ± 0.4 fg	7.0 ± 0.2 efg	7.5 ± 0.6 defg	4.0 ± 0.2 g	0.0 h	20.5 ± 0.8 b
trans-linalool oxide	16.0 ± 0.3 c	12.5 ± 0.9 c	95.5 ± 4.6 a	13.0 ± 0.3 c	14.0 ± 0.1 c	5.5 ± 0.3 de	27.0 ± 2.4 b	2.4 ± 0.2 ef	0.0 f	7.0 ± 0.7 d	16.0 ± 1.3 c	2.0 ± 0.1 ef	8.0 ± 0.6 d	3.0 ± 0.3 ef	0.0 f	12.5 ± 1.1 c
cis-pyran linalool oxide	121.0 ± 3.3 g	1007.5 ± 29.0 a	377.5 ± 38.6 d	116.5 ± 5.5 g	188.5 ± 17.5 f	281.5 ± 21.4 e	296.5 ± 21.1 e	33.8 ± 0.3 h	668.5 ± 5.4 b	479.0 ± 38.4 c	640.0 ± 18.6 b	411.5 ± 26.3 d	359.0 ± 1.3 d	684.0 ± 60.4 b	60.0 ± 7.0 h	405.0 ± 9.8 d
trans-pyran linalool oxide	278.0 ± 4.1a	0.0 e	0.0 e	39.0 ± 3.2 b	0.0 e	0.0 e	0.0 e	32.5 ± 0.3 c	0.0 e	0.0 e	0.0 e	3.0 ± 0.1 e	0.0 e	21.5 ± 1.6 d	0.0 e	0.0 e
2,6-dimethyl-3,7-octadien-2,6-diol	50.5 ± 1.0 a	0.0 c	0.0 c	0.0 c	0.0 c	0.0 c	0.0 c	8.4 ± 0.0 b	0.0 c	0.0 c	0.0 c	0.0 c	0.0 c	0.0 c	0.0 c	0.0 c
2,6-dimethyl-1,7-octadien-3,6-diol	2770.0 69.6 a	22.0 ± 1.7 h	0.0 h	105.5 ± 10.3 ef	44.5 ± 0.7 gh	155.5 ± 17.4de	189.5 ± 14.8 d	90.8 ± 1.7 fg	0.0 h	329.0 ± 1.1 c	178.5 ± 6.4 d	168.0 ± 23.9 d	51.5 ± 0.9 fgh	150.5 ± 12.9 de	1939.5 ± 59.0 b	103.5 ± 2.0 ef
3,7-dimethyl-1,7-octanediol	1050.0 1.3 a	65.0 ± 4.3 fg	352.5 ± 18.7 c	54.0 ± 5.7 fg	0.0 h	0.0 h	554.5 ± 87.3 b	182.2 ± 2.3 d	149.5 ± 0.7 de	29.0 ± 1.7 gh	136.0 ± 6.8 de	0.0 h	47.0 ± 1.3 gh	26.0 ± 1.8 gh	101.0 ± 6.7 ef	0.0 h
8-hydroxylinalool	9109.0 ± 368.6 b	281.0 ± 36.7 fg	4899.5 ± 1006.4 c	470.5 ± 27.5 efg	10205.0 ± 182.7 a	4459.0 ± 168.1 c	1032.5 ± 30.3 de	336.6 ± 13.7 fg	0.0 g	751.0 ± 133.3 def	623.5 ± 37.4 efg	535.0 ± 16.8 efg	252.0 ± 6.0 fg	226.0 ± 5.7 fg	1273.5 ± 69.4 d	207.5 ± 11.9 fg
eugenol	9.0 ± 0.4 c	0.0 d	0.0 d	0.0 d	0.0 d	23.5 ± 2.4 b	2.0 ± 0.0 d	0.7 ± d	74.5 ± 10.7 a	5.5 ± 0.8 cd	1.0 ± 0.0 d	1.0 ± 0.1 d	0.0 d	1.0 ± 0.1 d	11.0 ± 0.2 c	0.0 d
isoeugenol	83.0 ± 5.5 c	11.5 ± 1.0 f	108.5 ± 15.0 b	19.0 ± 0.1 f	525.0 ± 36.5 a	70.5 ± 1.0 cd	17.0 ± 0.0 f	9.3 ± 0.0 f	44.0 ± 9.8 e	42.5 ± 4.4 e	43.5 ± 0.6 e	9.5 ± 0.6 f	8.5 ± 0.6 f	11.0 ± 0.1 f	54.0 ± 1.5 de	0.0 f
methyl salicylate	21.0 ± 0.2 de	6.5 ± 0.3 efg	55.5 ± 6.5c	13.0 ± 0.2 efg	460.5 ± 3.7 a	135.0 ± 24.1 b	18.0 ± 0.5 def	4.5 ± 0.1 fg	0.0 g	16.5 ± 3.3 def	20.5 ± 2.1 de	1.0 ± 0.0 g	4.0 ± 0.9 fg	5.0 ± 0.4 fg	29.0 ± 0.1d	0.0 g

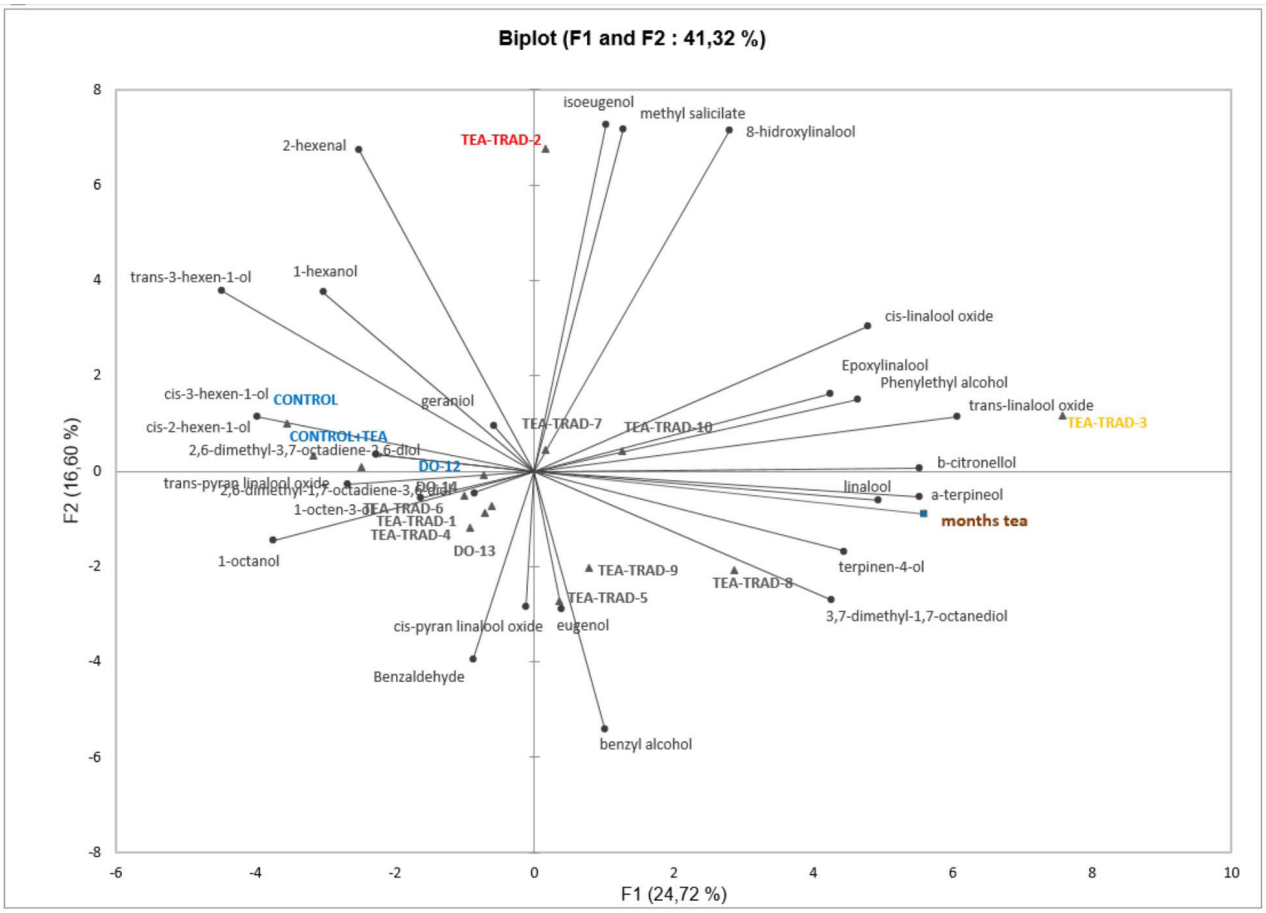


FIGURE 3. Biplot of PCA carried out on average concentrations of quantified volatile compounds for all samples except Retsina. The variable "months tea" has been added as a supplementary variable representing the number of months of aging in *tea*. The colours indicate the composition of the clusters given by the HCA; samples with the same colour belong to the same cluster.

clearly show that the sampled Retsina wine had a different volatile profile to the VT. The PCA, supported by ANOVA (Table 2), shows that Retsina was higher in polyoxygenated terpenes (monoterpenic aromatic precursors), especially *trans*-pyran linalool oxide, 2,6-dimethyl-1,7-octadien-3,6-diol and 3,7-dimethyl-1,7-octanediol. Polyoxygenated terpenes are characteristic of white varieties, such as Muscat, with honey, flower and wax aromas (Sánchez Palomo *et al*., 2006).

Other volatile compounds that were found in higher amounts in Retsina were aldehydes, especially benzaldehyde, which is responsible for the bitter almond taste of wines. It is common to find benzaldehyde at high concentrations in white wines (between 20 and 313 µg/L) (Escudero *et al*., 2002), and at much lower concentrations in red wines (Gómez García-Carpintero *et al*., 2012). These aromas may derive from the native Greek Rhoditis grape that is used to produce this Retsina, but currently no relevant data from scientific sources are available (Nanou *et al*., 2020). In turn, Retsina shares with VT a characteristically high level of α-terpineol, which is very likely derived from the addition of *Pinus halepensis* resin during winemaking in amphorae (Lazarakis, 2018). The 3440 µg/L α-terpineol present in the Retsina sample is somewhat higher than the concentrations found in other Retsinas explored in the literature (Kapaklis, 2014). This is probably due to traditional artisanal resin addition practices during its fermentation, which are often replaced by other modern techniques in more industrial Retsinas. Retsina differs from VT in it high amounts of polyoxygenated terpenes (*trans*-pyran linalool oxide, 2,6-dimethyl-3,7-octadien-2,6-diol; 3,7-dimethyl-1,7-octanediol; 8-hydroxylinalool), the alcohol 1-octanol and benzaldehyde.

A second PCA without the Retsina sample (Figure 3) aimed to shed light on the influence of pine barrels on VT and to test whether those made by commercial wineries and modern oenological techniques (coded DO, CONTROL and CONTROL+TEA) differed from homemade/traditional VT (coded TEA-TRAD). Additionally, the second PCA aimed to test the extent to which the duration of aging in pine barrels influenced the wine aroma, if at all. The three principal components accounted for 24.7%, 16.6% and 13.5% of the variance. The HCA shown in Figure 4 yielded a reasonable partition into 4 clusters which comprised two separate groups of TEA-TRAD-2 and TEA-TRAD-3 again, a third group containing three commercially-made wines (the two controls and DO-12) and a fourth with the remaining samples.

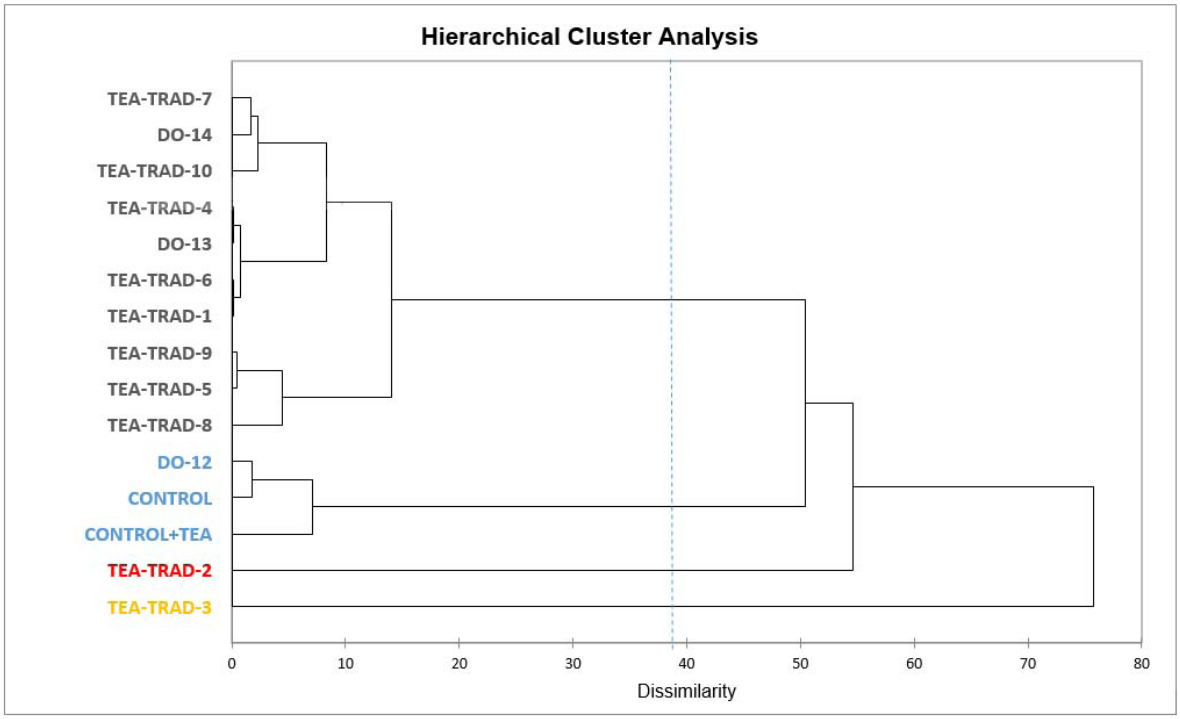


FIGURE 4. Dendrogram resulting from the hierarchical cluster analysis performed on the PCA loadings for the wines in Figure 3. The dotted line and colours of the sample codes indicate a four cluster partition.

The analysis did not establish a clear difference between the commercially-produced wines and those made traditionally mainly for self-consumption. This can be explained by the spread of modern techniques to small-scale or "home" winemaking, including the use of stainless steel tanks, destemmers and presses, commercial yeasts and other oenological products from tannins to tartaric acid that are now widely available in La Palma. Instead, the clearest correlation was between the duration of wine aging in the Canary pine barrels and the concentrations of several of the volatile compounds. None of the negative correlations were significant at 5 %, suggesting that aging in *Tea* adds chemical complexity, without significantly lowering concentrations of the wines' inherent volatile compounds.

Other families of compounds may decrease with longer contact time between wine and barrels, in particular the alcohols with six carbon atoms (C6 alcohols), such as *trans*-3-hexenol. These products provide wines with fresh grass and herbaceous aromas, which can constitute a defect, depending on their concentrations. They are derived from varietal precursors and can help determine wine origin, and they decrease with grape ripening and aging duration (Pedneault *et al*., 2013). The most important C6 alcohols are *trans*-3-hexen-1-ol and *cis*-3-hexenol, because their ratio can serve as an indicator of origin (Gómez García-Carpintero *et al*., 2012). However, only one wine (DO-12) in the sample contained *cis*-3-hexen-1-ol, which can be converted to *trans*-3-hexen-1-ol by isomerisation. This could be the reason for finding such a low level of *cis*-3-hexen-1-ol in VT. The polyoxygenated terpenes show various trends: t*rans*-linalool oxide and especially 3,7-dimethyl- 1-7-octanediol increased with aging time, while *cis*-linalool oxide and 2,6-dimethyl-1-7-octadien-3,6-diol decreased. The compound 1-octen-3-ol, related to fungal contamination via powdery mildew and mould odours, also tended to be less common in the wines aged in the Canary pine barrels.

The correlation matrix of PCA shown in Figure 2 shows significant positive Pearson correlations between the duration of aging in *Tea* and linalool (0.65), terpinen-4-ol (0.87), epoxylinalool (0.53), b-citronellol (0.66), α-terpineol (0.67), *trans*-linalool oxide (0.79) and 3,7-dimethyl-1,7-octanediol (0.89). Terpenes showed significant correlations with aging duration in the pine barrels. Linalool increased slightly with longer durations, ranging from 34 to 160 µg/L, with most samples above 50 µg/L (Ribéreau-Gayon *et al*., 1975).

Geraniol imparts a rose floral bouquet to wines. There was a peak concentration of over 200 µg/L in the wines aged for 20 to 40 days in pine barrels followed by a slight decreasing trend with longer aging duration. A sample aged for three years in pine was found to contain a low concentration of geraniol (47.2 µg/L). In the case of linalool, the decrease was not as significant. This can be explained by the fact that turpentine is a source of linalool that can compensate for its decrease via transformation into α-terpineol (Saeidnia, 2014). Through this process, the fragrant monoterpenes geraniol, linalool and citronellol tend to decrease and be replaced by derivatives such as α-terpineol. Linalool and geraniol can also undergo biotransformation to β-citronellol (King and Richard Dickinson, 2000), which significantly affects wine aroma, making it less fruity, floral and primary (Jackson, 2014). This explains why the samples aged for longer were

high in α-terpineol but low in geraniol (TEA-TRAD-3 and TEA-TRAD-8).

There was a significant correlation between aging duration in pine barrels and the increase in terpinen-4-ol and α-terpineol. The former is a relatively under-researched compound in wine literature, whose aroma has been described as minty, green, earthy and terpenic. Concentrations of terpin-4-ol were within the range of 5.5 µg/L in the control before aging, 328.3 µg/L in the sample aged for 1 year (TEA-TRAD-8) and 637.2 µg/L in the sample aged for three years (TEA-TRAD-3). α-Terpineol is a much better known aromatic compound reminiscent of lilies and resinous pine, with a lemon and lime nuance and musty aromas (Jackson, 2014). It is present in aromatic white wines, such as Albariño, Gewurztraminer or Riesling, generally in small amounts of below 400 µg/L (Welke *et al*., 2013). When obtained from pine resin instead of grapes, α-terpineol is a hydration product of α-pinene, the major component of turpentine (Utami *et al*., 2013). Due to its unique properties, α-pinene is a potential candidate for replacing the addition of sulfites in both red and white wines, with relatively successful results in studies so far (Hou *et al*., 2020). Although this has not been specifically explored in studies on α-terpineol, the antibacterial and antioxidant properties of this compound may explain why most VT producers consider it uneccessary to add preservatives such as sulfites, or they add them in low quantities.

α-terpineol increases in content in most kinds of wine both with the ripening of berries and wine aging (Baron *et al*., 2017). However, its presence in VT is far higher than average, which suggests it is a hydration product whose presence in wine is derived from contact with Canary pine resin. Levels of α-terpineol were notably high in all samples of VT except for two (DO-12 and DO-14), the highest reaching 23248 µg/L in S3. Interestingly, samples from commercial wineries contained the lowest levels of α-terpineol. Traditional VT are well above 1000µg/L (1mg/L) in all cases. This can be explained by sociocultural and marketing factors; commercial producers consider traditional VT aromas to be too harsh for the consumer and they therefore aim to soften them in various ways. In contrast, artisanal producers of VT often argue that commercial wines lack the traditional taste conferred by Canary pine heartwood and consequently consider them unauthentic. In any case, α-terpineol concentration can be considered a characteristic marker of VT. This provides the authorities controlling the Designation of Origin *Vinos de La Palma* with a useful typification tool for measuring their specific attributes.

CONCLUSIONS

As with other traditional food products lacking standard production methods (Cayot, 2007), VT is influenced by many factors that impede the reproducibility of experimental analyses and make their results difficult to interpret. These include different grape varieties, vintages, tanks to ferment and age wine, additives and processing aids, and differences between traditional and commercial wineries. The fact that no two *Tea* casks are the same precludes the possibility of establishing a precise common analytical protocol. Taking into account this complexity, the results of the VT analyses confirm our initial hypothesis: namely that wines produced in pine barrels have characteristically unique volatile profiles. Therefore, these multivarietal wines showed similarities to Greek Retsina wines, as well as clear differences, in terms of their volatile composition. *Vinos de Tea* are distinct and uniquely traditional among the various winemaking cultures in La Palma. They showed high concentrations of various families of compounds that provide them with specific aromatic profiles, which not only differentiate VT wines from other wines but also differentiate the various types of VT. The latter depended on the duration of aging in the Canary pine barrels, since it resulted in significant differences in aromatic profile. The main contributors to the distinctive aromas of VT were terpenes derived from the infusion of pine resin during fermentation and aging in the barrels, especially terpinen-4-ol and α-terpineol, which increased sharply over time to the detriment of geraniol and linalool. The analysis has revealed clear differences between VT produced by commercial wineries employing modern oenological techniques and equipment, and small-scale artisanal or home winemakers. This raises the question of whether the authenticity of traditional wines is currently being respected. The concentration of α-terpineol can help understand what traditional producers see as "authentic", paving the way for clear product typification by the corresponding authorities, in this case the Designation of Origin *Vinos de La Palma*.

To further confirm these findings and to shed more light on the substances that are responsible for the typical aromas of VT, further studies will aim to determine aromatic descriptors through a sensory analysis carried out by a panel of expert wine tasters. The present research has revealed some of the weaknesses associated with a pilot study such as ours; it should be replicated and expanded in the future with a larger sample of wines and more appropriate control samples. First, only one control sample of VT before and after aging in pine barrels was collected. Second, only one Retsina control wine was included in the study. Given the lack of knowledge about Retsina wines in the literature, it would be recommendable to carry out further research on them, including on their varieties and winemaking methods. Third, there is substantial variability among each sample because of the characteristics of VT, for which a blend of white, red and pink-skinned varieties is used, and because it is not produced every year, wines from different harvests. Finally, being a pilot study, a targeted strategy was used to analyse a series of previously defined compounds. It would be recommended to apply untargeted methodology to explore the variability of VT. Notwithstanding, it was the aim of this pilot study to spark debate and raise awareness about this hitherto neglected topic, focusing on a traditional food on the verge of disappearance. Future research should address the aforementioned weaknesses and carry out a fully-fledged study of VT that could pave the way to its modernisation and survival, without losing the differential traits revealed in this study.

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