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The Valorization of Spanish Minority Grapevine Varieties—The Volatile Profile of Their Wines as a Characterization Feature

Ángela Díaz-Fernández [1], Sandra Cortés-Diéguez [2], Gregorio Muñoz-Organero [3], Félix Cabello [3], Belén Puertas [4], Anna Puig-Pujol [5], Carme Domingo [5], M. Esperanza Valdés-Sánchez [6], Daniel Moreno Cardona [6], José Félix Cibriain [7], Oier Dañobeitia-Artabe [8], José-Antonio Rubio-Cano [9], Jesús Martínez-Gascueña [10], Adela Mena-Morales [10], Camilo Chirivella [11], Jesús-Juan Usón [12] and Emilia Díaz-Losada [1,*]

[1] Estación de Viticultura e Enoloxía de Galicia-AGACAL, Ponte San Clodio s/n, 32428 Leiro-Ourense, Spain; angela.diaz.fernandez@xunta.gal

[2] Biotecnología Industrial e Ingeniería Ambiental, BiotecnIA, Edificio Campus Auga, Campus Sur, Universidad de Vigo, 32004 Ourense, Spain; smcortes@uvigo.gal

[3] Institute of Rural, Agrarian and Food Research and Development of Madrid (IMIDRA), Finca El Encín, Ctra. A-2 km 38, 28805 Alcalá de Henares, Spain; gregorio.munoz@madrid.org (G.M.-O.); felix.cabello@madrid.org (F.C.)

[4] Instituto de Investigación y Formación Agraria, Pesquera y de la Producción Ecológica, Ctra. Cañada de la Loba (CA-3101) Pk. 3.1, 11471 Jerez de la Frontera, Spain; mariab.puertas@juntadeandalucia.es

[5] Catalan Institute of Vine and Wine—Institute of Agrifood Research and Technology (INCAVI-IRTA), Plaça Àgora 2, 08720 Vilafranca del Penedés, Spain; apuigpujol@gencat.cat (A.P.-P.); carme.domingo@gencat.cat (C.D.)

[6] Center for Scientific and Technological Research of Extremadura (CICYTEX), Food and Agriculture, Technology Institute of Extremadura (INTAEX), Avenue Adolfo Suárez s/n, 06071 Badajoz, Spain; esperanza.valdes@juntaex.es (M.E.V.-S.); daniel.moreno@juntaex.es (D.M.C.)

[7] Estación de Viticultura y Enología de Navarra (EVENA), C. del Valle de Orba, 34, 31390 Olite, Spain; jf.cibriain.sabalza@navarra.es

[8] Diputación Foral de Bizkaya, Avda. Lehendakari Aguirre, 9, 48014 Bilbao, Spain; oier.danobeitia@bizkaia.eus

[9] Instituto Tecnológico Agrario de Castilla y León (ITACYL), Finca Zamadueñas, Ctra. Burgos km. 119, 47071 Valladolid, Spain; rubcanjo@itacyl.es

[10] Instituto Regional de Investigación y Desarrollo Agroalimentario y Forestal de Castilla-La Mancha (IRIAF), Ctra. Toledo-Albacete s/n, 13700 Tomelloso, Spain; jmartinezg@jccm.es (J.M.-G.); amenam@jccm.es (A.M.-M.)

[11] Servicio de Producción Ecológica e Innovación, Instituto Tecnológico de Viticultura y Enología, Av. del General Pereyra, 4, 46340 Requena, Spain; chirivella_cam@gva.es

[12] Centro Transferencia Agroalimentaria de Aragón, Avda. de Movera S/N, 50001 Zaragoza, Spain; jjuson@aragon.es

* Correspondence: emilia.diaz.losada@xunta.gal or cortes.dieguez@gmail.com; Tel.: +34-988788086

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Abstract: Despite the large number of existing varieties of *Vitis vinifera* L., only few occupy a large niche in today's highly globalized wine market. The increasing consumer demand for diversified products, as well as the changing climatic conditions, make establishing a process of varietal diversification essential to achieve both challenges. It is for this reason that the study of minority varieties, which have a higher level of adaptation to each area of origin, is of particular interest. With the main objective of achieving an in-depth knowledge of minority varieties in Spain, the national research project 'Valorization of Minority Grapevine Varieties for their Potential for Wine Diversification and Resilience to Climate Change' (MINORVIN), has been proposed. Within this extensive project, the present study describes the aroma profiles of 60 single-variety wines, corresponding with 44 different varieties, with 12 of these varieties being studied at the same time in several Spanish regions. Volatile compounds were determined through three consecutive vintages using gas chromatography-mass spectrometry (GC-MS) and gas chromatography–flame ionization detector (GC-FID). Compounds were grouped into major compounds, including alcohols, C_6 compounds, esters, acetates, acids, carbonyl compounds, and other type of compounds, and minor compounds, including lactones, terpenes, and C_{13}-norisoprenoids, according to their concentration in the wines being analyzed. Among this last group of compounds, lactones were quantitatively the most abundant, followed by terpenes. This study reflects that minority variety wines show distinctive aromatic profiles, supporting the importance of valuing and promoting the autochthonous minority grapevine varieties for the Spanish winemaking industry.

Keywords: *Vitis vinifera* L.; minority grapevine varieties; distinctive aromatic profiles; oenological quality marker

1. Introduction

Climate change is a serious threat to different economic sectors, with agriculture being one of the most sensitive, especially for perennial crops such as vines, which have a major economic impact within Europe. Not only grape production, but also the wine quality will be highly determined by the weather, the latter being one of the most determinant factors influencing the grapevine [1,2]. Nowadays, climate change is already impacting important social, economic, and political factors [3]. Indirectly, it has also affected landscapes, the use of land, and rural life in different regions worldwide [4].

An increase in the global temperature has triggered a generalized advancement in different phenological stages, and, in consequence, in the berry ripening data [4]. This also results in a desynchronization among technological and phenolic grape maturation stages [5]. Jones et al. [6] projected that, if the climate conditions continue in this direction, the winegrowing areas that produce high quality wines nowadays will overwhelm the margins of their climatic limits, which would necessarily translate into wine style changes.

Despite the great *Vitis vinifera* L. varietal diversity, with more than 13,000 varieties of *V. vinifera* L. subsp. *vinifera* varieties registered in the *Vitis* International Variety Catalogue [7], one third of the world's registered vineyard area, approximately 7.3 million hectares [8] is occupied by only 13 varieties, and more than 50% of this area is exclusively occupied by 33 varieties [9]. The existing *Vitis vinifera* L. varietal diversity is one of the resources to be explored in terms of dealing with climatic change effects and mitigate its consequences [4,10–14]. Several other reasons are gaining increasing interest from some winegrowers and wineries in recovering minority varieties; a rising interest has been demonstrated in other areas which are linked to grape and wine fields, such as viticulture-related media or consumers; and a highly globalized wine market, as well as the homogenization of wine products have both triggered the study of minority varieties gaining more enthusiasm and importance within recent years [15–19]. Some of these unknown or presently forgotten varieties, as a result of being neglected in past decades due to their lower yields or lower alcoholic degrees, may provide more tolerant genetic resources which are more capable of dealing with the warming climates, thus potentially contributing to increasing the varietal diversity available for the production of distinct and differentiated wines [20].

The great implication of aroma in defining the quality of a wine [21–23], as well as the role that the volatile compounds formed in grapes play in varietal identification procedures [24–27], encourage the importance of determining certain features, such as the aromatic potential of these minority varieties, under study for the production of quality wines. In this regard, this study is part of a wider project for the valorization of minority varieties (MINORVIN), for which some results have already been published regarding the susceptibility to downy mildew (*Plasmopara viticola*) and the phenological characteristics displayed by the studied minority varieties [28,29]. In this case, the characterization of the volatile compounds of 60 single-variety wines has been carried out for three consecutive vintages.

The main aims of this research were to (1) identify the aromatic compounds in single-variety wines made from minority grape varieties, (2) evaluate if there are differences in the aromatic composition of wines made from the same grape variety but from different regions, and, finally, (3) value the aromatic potential of these minority varieties for the development of quality wines.

2. Materials and Methods

2.1. Plant Material

Forty-four pre-phylloxeric *Vitis vinifera* L. varieties, collected from twelve different autonomous communities in Spain, were included in the 'Valorization of minority grape varieties for their capacity to diversify viticulture and oenology and to minimize the effects of climate change in wine quality' MINORVIN project. 'Tempranillo' and 'Moscatel de Grano Menudo' ('Muscat à Petit Grains') have been included as the red and white reference varieties, respectively.

This study includes the evaluation of 60 wines, corresponding with 44 different varieties. Some varieties are considered to be from a single unique region, while others, such as 'Albana´, 'Cadrete' (synonym of 'Santa Fé'), 'Castellana Blanca', 'Folgasao' (synonym of 'Cagarrizo'), 'Hebén', 'Jarrosuelto', 'Morate', 'Rufete Serrano' (synonym of 'Verdejo Serrano'), 'Sanguina', 'Terriza', 'Tinto Jeromo', 'Tortozona Tinta', or 'Zurieles', had more than one origin location. The different vinification processes of these varieties were studied in order to compare the influence of each region on the volatile varietal profile. More detailed information is shown in Table 1.

Table 1. Minority grapevine varieties included in the study and their origin.

Variety-Origin	Variety	Wine Elaboration	Geographical Origin	Research Centre
'Albana-A'	'Albana'	W	Aragón	CTA
'Albana-C'	'Albana'	W	Cataluña	INCAVI
	'Albillo del Pozo'	W	Castilla-La Mancha	IRIAF
	'Albilla do Avia'	W	Galicia	EVEGA
	'Bastardo Blanco'	W	Extremadura	CICYTEX-INTAEX
	'Benedicto'	R	Castilla-La Mancha	IRIAF
'Cadrete-N'	'Cadrete' (syn. 'Santafé')	R	Navarra	EVENA
'Santa Fé-A'	'Santa Fé' (syn. 'Cadrete')	R	Aragón	CTA
	'Callet'	R	Islas Baleares	UIB
'Castellana Blanca-CM'	'Castellana Blanca'	W	Castilla-La Mancha	IRIAF
'Castellana Blanca-M'	'Castellana Blanca'	W	Madrid	IMIDRA
'Castellana Blanca-N'	'Castellana Blanca'	W	Navarra	EVENA
	'Cayetana'	W	Extremadura	CICYTEX-INTAEX
	'Cenicienta'	R	Castilla y León	ITACYL
	'Corchera'	R	Andalucía	IFAPA
	'Diega 1'	R	Navarra	EVENA
	'Diega 2'	W	Navarra	EVENA
	'Estaladiña'	R	Castilla y León	ITACYL
	'Evena 1'	W	Navarra	EVENA
	'Folgasao' (syn. 'Cagarrizo')	W	Extremadura	CICYTEX-INTAEX
	'Garró'	R	Navarra	EVENA
	'Gorgollosa'	R	Islas Baleares	UIB
	'Greta'	W	Aragón	CTA
'Hebén-E'	'Hebén'	W	Extremadura	CICYTEX-INTAEX
'Hebén-M'	'Hebén'	W	Madrid	IMIDRA
	'Hondarribi Beltza' (HB)	R	País Vasco	DV
	'Indiana'	W	Andalucía	IFAPA
'Jarrosuelto-A'	'Jarrosuelto'	W	Aragón	CTA
'Jarrosuelto-CM'	'Jarrosuelto'	W	Castilla-La Mancha	IRIAF
'Jarrosuelto-N'	'Jarrosuelto'	W	Navarra	EVENA
	'Mandregue'	R	Aragón	CTA
	'Maquías'	W	Castilla-La Mancha	IRIAF
	'Marco 1 (MC1)—Albariño Tinto'	W	Galicia	EVEGA
	'Marco 2 (MC2)—Albarín Tinto'	R	Galicia	EVEGA

Table 1. *Cont.*

Variety-Origin	Variety	Wine Elaboration	Origin	Research Centre
	‘Melonera’	R	Andalucía	IFAPA
	‘Montonera del Casar’	W	Castilla-La Mancha	IRIAF
‘Morate-M’	‘Morate’	R	Madrid	IMIDRA
‘Morate-N’	‘Morate’	R	Navarra	EVENA
	‘Ratiño’	W	Galicia	EVEGA
	‘Rayada Melonera’	R	Madrid	IMIDRA
	‘Riera 2’	R	Cataluña	INCAVI
	‘Riera 43’	R	Cataluña	INCAVI
	‘Riera 46’	W	Cataluña	INCAVI
‘Rufete Serran-CL’	‘Rufete Serrano’ (syn. ‘Verdejo Serrano’)	W	Castilla y León	ITACYL
‘Verdejo Serrano-E’	‘Verdejo Serrano’ (syn. ‘Rufete Serrano’)	W	Extremadura	CICYTEX-INTAEX
‘Sanguina-C’	‘Sanguina’	R	Cataluña	INCAVI
‘Sanguina-CM’	‘Sanguina’	R	Castilla-La Mancha	IRIAF
‘Terriza-CM’	‘Terriza’	R	Castilla-La Mancha	IRIAF
‘Terriza-M’	‘Terriza’	R	Madrid	IMIDRA
‘Tinto Jeromo-CL’	‘Tinto Jeromo’	R	Castilla y León	ITACYL
‘Tinto Jeromo-CM’	‘Tinto Jeromo’	R	Castilla-La Mancha	IRIAF
‘Tortozona Tinta-A’	‘Tortozona Tinta’	R	Aragón	CTA
‘Tortozona Tinta-CM’	‘Tortozona Tinta’	R	Castilla-La Mancha	IRIAF
‘Tortozona Tinta-M’	‘Tortozona Tinta’	R	Madrid	IMIDRA
‘Tortozona Tinta-N’	‘Tortozona Tinta’	R	Navarra	EVENA
	‘Trobat’	R	Cataluña	INCAVI
	‘Xafardán (Tinta Oubiña)’	R	Galicia	EVEGA
	‘Zamarrica’	R	Galicia	EVEGA
‘Zurieles-CM’	‘Zurieles’	W	Castilla-La Mancha	IRIAF
‘Zurieles-E’	‘Zurieles’	W	Extremadura	CICYTEX-INTAEX

CICYTEX-INTAEX (Centro de Investigaciones Científicas y Tecnológicas de Extremadura-Instituto Tecnológico Agroalimentario de Extremadura), CTA (Centro de Transferencia Agroalimentaria), DV (Diputación de Vizcaya), EVEGA (Estación de Viticultura e Enoloxía de Galicia), EVENA (Estación de Viticultura y Enología de Navarra), UPNA (Universidad Pública de Navarra), IFAPA (Instituto de Investigación y Formación Agraria, Pesquera), IMIDRA (Instituto Madrileño de Investigación y Desarrollo Rural, Agrario y Alimentario), INCAVI (Institut Català de la Vinya i el Vi), IRIAF (Instituto Regional de Investigación y Desarrollo Agroalimentario y Forestal de Castilla-La Mancha), ITACYL (Instituto Tecnológico Agrario de Castilla y León), UIB (Universidad de les Illes Balears). A—Aragón, C—Cataluña, CL—Castilla y León, CM—Castilla-La Mancha, E—Extremadura, M—Madrid, N—Navarra. W—white wine elaboration, R—red wine elaboration.

2.2. *Wine Samples*

Grapes were harvested in the different research centers (Table 1) for three consecutive vintages, namely 2019, 2020, and 2021. Each variety was collected in different datasets according to their grape ripening stage and health status. Different potential alcoholic strengths were obtained depending on the variety study potential, resulting in single-variety wines that, on average, were among between 12 and 13.5% v/v in red varieties and between 11 and 12.5% v/v in white varieties. Microvinifications were all carried out in steel tanks using the same neutral commercial yeast and without forcing the malolactic fermentation in red varieties, with all wines being developed as young ones. Wine samples were received on different days from EVEGA, and, until all samples from the same harvest were received for their analysis, we maintained them in the meantime under the same light and temperature conditions.

2.3. *Volatile Composition*

2.3.1. Chemicals

The internal standards, all of them purchased from Merk (Madrid, Spain), used in the chromatographic determinations were as follows: 4-methyl-2-pentanol, for major volatile compounds (higher alcohols, methanol, acetaldehyde, ethyl acetate, acetoine, ethyl lactate, 2-phenyl-ethanol, and 2,3-butanediol); 4-decanol, for C_6 alcohols and terpenes; and 1-

heptanol for volatile fatty acids, ethyl esters, and acetates of higher alcohols. *n*-pentane, anhydrous sodium sulfate, dichloromethane, and methanol were purchased from Scharlau (Sentmenat, Spain). The standards for volatile compounds were purchased from the following commercial suppliers: Merck (Madrid, Spain), Fluka (Seelze, Germany), Aldrich (Madrid, Spain), Alfa Aesar (Barcelona, Spain), and Sigma (Madrid, Spain).

Furthermore, the 1 g Isolute ENV+ cartridges used were purchased from Biotage (Hengoed, UK).

2.3.2. Determination of Volatile Compounds

- Major Volatile Compounds

Methanol, higher alcohols, ethyl acetate, acetaldehyde, acetoine, 1-hexanol, and 2-phenylethanol were determined according to the methodology described by Bouzas et al. [30]. Additionally, 50 µL of 4-methyl-2-pentanol (50 mg·L^{-1}) was added as an internal standard to 5 mL of the wine sample. Then, 2 µL of this mixture was injected in an Agilent 7890A gas chromatograph (Palo Alto, CA, USA), equipped with a split injector, an electronic flow control, and a flame ionization detector (FID). Ethyl esters, acetates, acids, and C_6 compounds were previously extracted using solid phase extraction (SPE) processes, following the methodology from López-Vázquez et al. [31], with slight modifications. SPE was carried out in cartridges of Isolute ENV + SPE (1 g), previously conditioned with 15 mL of methanol, followed by 20 mL of distilled water. The samples used were based on 50 mL of wine diluted 1:1 with distilled water. Furthermore, 100 µL of 4-decanol (0.144 mg·L^{-1}) was added as an internal standard for C_6 compounds, and 1 mL of 1-heptanol (0.213 g·L^{-1}) was added for acetates, ethyl esters, and acids. Aromatic fraction was released with 30 mL of dichloromethane. Additionally, 60 mL of *n*-pentane and a tip of anhydrous sodium sulfate were added to the sample for water elimination. Afterwards, samples were concentrated to 1.5 mL in a 40 °C bath with a Vigreux column with refrigeration, and finally, the obtained extract was injected in an Agilent 6890 (Palo Alto, CA, USA) gas chromatograph coupled to a mass spectrometer (GC-MS).

The determined major volatile compounds are shown in Table 2.

Table 2. Major wine volatile compounds identified.

Major Volatile Compounds (mg·L^{-1})	
Alcohols	methanol 1-butanol 2-methyl-1-butanol 3-methyl-1-butanol 2-methyl-1-propanol propanol 2-phenylethanol benzyl alcohol
C_6 compounds	hexanol trans 3-hexen-1-ol cis-3-hexen-1-ol
Ethyl Esters	ethyl hexanoate ethyl octanoate ethyl decanoate ethyl lactate diethyl succinate
Acetates	ethyl acetate isoamyl acetate hexyl acetate 2-phenylethyl acetate

Table 2. *Cont.*

Major Volatile Compounds ($mg \cdot L^{-1}$)	
Volatile Acids	acetic acid butyric acid isobutyric acid isopentanoic acid hexanoic acid octanoic acid decanoic acid
Carbonyl compounds	acetaldehyde acetoin
Other compounds	glycerol acetol 2-3-butanediol levo 2-3-butanediol meso

- Minor Volatile Compounds

The determination of lactones was carried out via direct injection, as proposed by Peinado et al. [32], adding 50 µL of 4-methyl-2-pentanol (50 $mg \cdot L^{-1}$) as an internal standard into 5 mL of the wine sample, directly injecting 2 µL of this mixture in an Agilent 7890A gas chromatograph (Palo Alto, CA, USA), equipped with a split injector, an electronic flow control, and a flame ionization detector (FID).

Terpenes and C_{13}-norisoprenoids were previously separated using SPE, following methodology from López-Vázquez et al. [31], as was previously detailed for ethyl esters, acetates, acids, and C_6 compounds, adding 100 µL of 4-decanol (0.144 $mg \cdot L^{-1}$) as an internal standard as for C_6 compounds. Afterwards, the extracts were injected in an Agilent 6890 (Palo Alto, CA, USA) gas chromatograph coupled to a mass spectrometer (GC-MS). The evaluated minor volatile compounds are shown in Table 3.

Table 3. Minor wine volatile compounds identified.

Volatile Compounds ($\mu g \cdot L^{-1}$)	
Lactones	γ butyrolactone
Terpenes	linalool trans linalool oxide (furan) cis linalool oxide (furan) trans linalool oxide (pyran) cis linalool oxide (pyran) ho-trienol α terpineol citronelol nerol geraniol hodiol 1 (trans-3,7-dimethyl-1,5-octadiene-3,7-diol) endiol (3,7-dimethyl-1-octen-3,7 diol)
C_{13} norisoprenoids	α damascone β damascone β ionone γ ionone

The volatile compounds were identified by comparing their retention times (RT) with their pure standards and their mass spectra with the NIST Mass Spectral library.

The compounds were semi-quantified as internal standard equivalents, and the corresponding answer factor of each compound was utilized to assess the concentration in each wine sample.

2.3.3. Data Analysis

Chemical data were analyzed using Xlstat Basic+ 2023.3.0 (Addinsoft, France, Paris). Significant differences among different varieties, and within the same varieties but with different origins, were revealed using one-way analysis of variance (ANOVA).

Principal component analyses (PCA) were carried out to achieve separation among the varieties, as well as those within the same variety but with different origins, according to their volatile composition.

3. Results and Discussion

3.1. Volatile Composition of Wines

The fifty aromatic compounds determined were classified into ten chemical families, seven major compounds, namely alcohols, C_6 compounds, esters, acetates, acids, carbonyls, and other compounds (Table 2), and three minor compounds, namely lactones, terpenes, and C_{13}-norisoprenoids (Table 3).

The sum of the concentrations of the major and minor volatile compounds identified grouped by chemical families are detailed in Tables S1 and S2 for white varieties, and Tables S3 and S4 for red varieties.

3.1.1. Major Volatile Compounds

Among the major compounds, methanol must be distinguished because it is located in the solid part of the berry, such as in seeds pectin, meaning it is not considered a fermentative compound. The average methanol values were around 30 mg·L^{-1} in the white varieties, with 'Folgasao' displaying the lowest value of 19.58 mg·L^{-1}, while 'Montonera del Casar' stands out as having the highest concentration (59.34 mg·L^{-1}). Among the red varieties, the average value was 168.38 mg·L^{-1}, with 'Tortozona Tinta-CM' exhibiting the lowest value (64.85 mg·L^{-1}), and 'Cenicienta' displaying the highest one (272.03 mg·L^{-1}). When evaluating the methanol values among the different varieties studied, significant differences were found (Table 4).

Regarding the fermentative compounds, different factors will have different influences, such as the sanitary degree of the grape, the maturity level, the cleanliness level of the must and the possible clarification techniques employed, the fermentation temperature, the type of yeast, nutrients, the oxygen level, as well as possible pre-fermentative and fermentative deviations [33–39]. Some of these factors are highly dependent on the liters of vinification, with it sometimes being quite difficult to control small volumes or microvinifications, which is the main type of vinification in this study.

- Alcohols

Alcohols are the main group at the quantitative level, as other studies have also shown [40]. Values around 300 mg·L^{-1} contribute to the wine complexity, while values above 400 mg·L^{-1} imply a negative effect on the wine quality [40]. Among the identified alcohols, 3-methyl-1-butanol was the most abundant one in every white and red variety, being even higher in the latter ones, associated with malty descriptors in the literature [41], but also reported for contributing to the green character of wine by Sáenz-Navajas et al. [42]. More than half of the white varieties showed values above the average. High values could be related to a high turbidity of must [34,43], which, in this case, could be the result of a poor clearing process. The 'Folgasao' variety showed 414.13 mg·L^{-1}, which could be 'a priori' negative; however, it should be noted that it shows a great 2-phenylethanol content of 43.98 mg·L^{-1}, a value much higher than those for the rest of the white varieties studied, and one which could provide a rose aroma to the wines [44], as well as a higher benzyl alcohol content, often associated with sweet and fruity descriptors [45], with 5.03 mg·L^{-1}, only surpassed by 'Greta', 'Jarrosuelto-A', and 'Verdejo Serrano-E'. These last two alcoholic compounds are potentially positive for the aroma and, therefore, are important for wines' aromatic profile description. Benzyl alcohol has a varietal origin and can appear in grapes in free and/or bound forms. This is the reason why studied wines from 'Folgasao', 'Greta', 'Verdejo Serrano-E', and 'Jarrosuelto-A' could undergo a release of these compounds, thus increasing their aromaticity. Contrary to this, 'Albana-A' is the variety that showed the lowest content of 2-phenylethanol, followed by 'Indiana' and 'Evena 1'. Regarding the benzyl alcohol, it was 'Ratiño' which exhibited the lowest value (1.74 mg·L^{-1}). Among the red varieties, 'Tinta Jeromo-CL' displayed the lowest 2-phenylethanol value (12.81 mg·L^{-1}), while 'Riera 2' showed the highest (49.76 mg·L^{-1}). Regarding the benzyl alcohol, 'Zamarrica' showed the lowest value (2.86 mg·L^{-1}), while 'Tinta Jeromo-CL', unlike the previous compound, in this case, showed the highest value, with 9.82 mg·L^{-1}.

Regarding the ANOVA results set out in Table 4, every compound determined showed significant differences among varieties, with propanol showing the lowest significance among them.

- C_6 compounds

Among the C_6 compounds, 1-hexanol and cis- and trans-3-hexenol were identified. They could be considered varietal indicators as their origin comes as a result of the enzymatic lysis of linoleic and linolenic acids, mainly during the pre-fermentation stages [46,47], them being concentration-dependent in terms of the amount of these acids in each type of grape [47,48]. However, they are responsible for the green and sour aromas in wine, which could hide other varietal aromas. As in the case of alcohols, higher contents of this group of compounds are also related with musts that show high levels of turbidity during alcoholic fermentation [34]. White varieties showed a high average content of 62.50 mg·L^{-1}, with 'Castellana Blanca-M' having the highest content (194.80 mg·L^{-1}), in contrast to 'Hebén-E', 'Montonera del Casar', 'Albillo del Pozo', and 'Jarrosuelto-A', which had the lowest contents, being below 10 mg·L^{-1}. Red varieties showed a much higher average content, around 120 mg·L^{-1}. 'Xafardán (Tinta Oubiña)' showed the highest average value (361.16 mg·L^{-1}), followed by 'Tortozona Tinta-M' (289.45 mg·L^{-1}). In both reds and whites, trans-3-hexenol was the major compound.

With regard to the ANOVA results (Table 4), all of the compounds analyzed showed high significant differences among the varieties considered.

- Esters and acetates

These are mainly fermentative compounds and are principally responsible for the fruity notes [46,49] in wines. They are qualitatively the most abundant, together with acids. White varieties showed ester and acetate average values of 32.30 and 60.43 mg·L^{-1}, respectively, with ethyl lactate being the main compound in the esters group, followed by ethyl octanoate. Within acetates, ethyl acetate is the main compound, then followed by 2-phenylacetate. In terms of its potential aromatic importance, 2-phenylacetate, which showed the highest concentration in 'Folgasao' (30.89 mg·L^{-1}) and 'Ratiño' (29.13 mg·L^{-1}), could provide a great aromaticity to their wines, associated with honey-like aromas in wines [50]. In contrast, 'Greta', 'Indiana', and 'Albana-A' were the varieties that showed the lowest values. Red varieties showed average values which were not far away from those shown by whites, with values of 70 and 77 mg·L^{-1}, respectively; they also showed higher acetate average values than esters, with ethyl lactate once again being the highest contribution compound among the esters family, and ethyl acetate being the highest among the acetates. In red varieties, high ethyl lactate values were found, exhibiting fruity and buttery descriptors [51], generally as a result of having undergone malolactic fermentation. 'Estaladiña', 'Tinto Jeromo-CL', 'Xafardán (Tinta Oubiña)', and 'Zamarrica' were the varieties with the highest ethyl lactate content, with 'Estaladiña' being the one with the highest ester content, while 'Santa Fé-A' and 'Benedicto' showed the lowest ester content, together with 'Melonera', 'Mandregue', and both 'Tortozona Tinta-CM' and 'Tortozona Tinta-A'.

Table 4. The determined major volatile compounds and the significance of the factor 'variety' according to one-way ANOVA.

	Alcohols								C_6 Compounds		
Compound	methanol	1 butanol	2 metil, 1 butanol	3 metil, 1 butanol	isobutanol	propanol	2-phenyl ethanol	benzyl alcohol	hexanol	trans 3-hexen-1-ol	cis 3-hexen-1-ol
Pr > F (Model)	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.050	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Significance	***	***	***	***	***	*	***	***	***	***	***
	Esters					**Acetates**				**Carbonyls**	
Compound	ethyl hexanoate	ethyl octanoate	ethyl decanoate	ethyl lactate	diethyl succinate	isoamyl acetate	hexyl acetate	2-phenyl ethyl acetate	ethyl acetate	acetaldehyde	acetoin
Pr > F (Model)	0.154	0.013	0.088	<0.0001	<0.0001	0.053	0.836	1.000	<0.0001	<0.0001	<0.0001
Significance	*ns*	*	*ns*	***	***	*ns*	*ns*	*ns*	***	***	***
	Acids							**Others**			
Compound	acetic acid	butyric acid	isobutyric acid	isopentanoic acid	hexanoic acid	octanoic acid	decanoic acid	glycerol	acetol	2-3-butanediol levo	2-3-butanediol meso
Pr > F (Model)	<0.0001	0.784	0.352	0.624	0.313	0.082	0.516	<0.0001	0.001	<0.0001	0.001
Significance	***	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	***	***	***	***

Notation *, *** indicate significance at $p < 0.05$, $p < 0.001$, respectively. *ns* indicates non-significant difference.

When considering the ANOVA results (Table 4), ethyl hexanoate and ethyl decanoate did not show significant differences between different varieties, and low significant differences were shown for ethyl octanoate, while high significant differences were observed for the other evaluated compounds. Regarding acetates, no significant differences were observed among varieties, except for ethyl acetate, a compound that is largely determined by the type of processing.

- Volatile acids

This is the most abundant group after alcohols. They enhance the freshness of wines, and they trigger the equilibrating of their fruity notes [52]. White varieties have showed an average concentration of 182.95 mg·L^{-1}, ranging from 72.46 mg·L^{-1} in 'Cayetana' to 377.74 mg·L^{-1} in 'Marco 1 (MC1)-Albariño Tinto'. Excluding acetic acid, which displays the highest concentration but is also highly dependent on the winemaking process rather than on the variety, both hexanoic and octanoic acid were the most abundant. Hexanoic acid was also observed by Díaz-Fernández et al. [53] to be the major acid present in grapes of several traditional cultivated white varieties from the northwest of the Iberian Peninsula. In this case, 'Zurieles-CM' was the variety that showed the highest hexanoic acid value, followed by 'Jarrosuelto-CM'. Contrary to this, 'Jarrosuelto-N' and 'Albana-C' showed the lowest values. With respect to the red varieties, they showed higher volatile acids concentrations, also including higher acetic acid values. As it happened with white varieties, apart from the acetic acid, hexanoic and octanoic were the major acids found, with the latter being described as emitting buttery, cheesy, and sweat-like odors [52]. These were also revealed to be the major acids in the grapes of several red varieties studied by Díaz-Fernández et al. [54]. In red varieties, isobutyric acid was also among the major acids. 'Marco 2 (MC2)-Albarín Tinto' showed the highest concentration, while 'Garró' showed the lowest.

In terms of the ANOVA results (Table 4), no significant differences were appreciated between the varieties for the different acids analyzed, except for acetic acid, which, as was detailed above for ethyl acetate, is strongly influenced by the winemaking process and not by the variety.

- Carbonyl compounds

Acetoin and acetaldehyde were included in this group, deriving one compound from the other, and are therefore in direct relation to each other. Acetaldehyde, as it happened with other compounds previously mentioned, such as acetic acid and ethyl acetate, could increase due to the type of vinification, with microvinification being especially susceptible in this respect. In the white varieties, acetaldehyde levels were around 42 mg·L^{-1}, with 'Hebén-E' standing out with 156.79 mg·L^{-1}. However, this value could be a result of the high oxygen contact with the sample and, as a result, the corresponding ethanol oxidation process, which does not imply a varietal property, as it can be seen that the same variety from a different origin, 'Hebén-M', displayed 29 mg·L^{-1}. We consider this compound and provide their values, as their content may be associated with certain side effects, such as affecting the values of other volatile compounds, either fermentative or varietal. 'Albana-C' and 'Riera 46' were the samples with the lowest contents, being 13.47 and 14.52 mg·L^{-1}, respectively.

The average acetoin values were around 23 mg·L^{-1} in the white varieties, with this value being significantly exceeded by 'Jarrosuelto-N', while 'Albillo del Pozo' showed the lowest value.

Average acetaldehyde values were lower in the red varieties than in the white ones, with around 28 mg·L^{-1}, with 'Gorgollosa', with 112.54 mg·L^{-1}, and 'Santa Fé-A', with 112 mg·L^{-1}, standing out. However, the role of the winemaking process in these values not properly constituting a varietal characteristic should be emphasized. Acetoin values in red varieties were slightly higher than those in the white ones, but without any major differences among the varieties, with an average value of around 36 mg·L^{-1}, with 'Tortozona Tinta–CM' and 'Riera 2' standing out, and the lowest values being exhibited by 'Estaladiña' and 'Zamarrica'.

Regarding the ANOVA results (Table 4), the carbonyl compounds analyzed showed highly significant differences among varieties. However, as was previously detailed for acetic acid and ethyl acetate, these compounds will be strongly influenced by the winemaking process and are not characteristic of each variety.

- Other compounds

From the four additional determined compounds that are included in this group (Table 2), levo-2,3-butanodiol was the major one, with a ratio close to 4 between the levo and meso-2,3-butanodiol isomers in the red varieties and 2.5 among the white ones, with the meso form being understood as a consequence of alcoholic fermentation [55], and the relation among the two forms potentially being positively correlated, in accordance with Son et al. [56], to the sugar levels of the grapes. The levo-2,3-butanodiol isomer stood out notably in some white varieties, namely 'Albana-C', 'Ratiño', 'Marco 1 (MC1)-Albariño Tinto', and 'Rufete Serrano–CL'. 'Riera 2' stood out among red varieties.

Significant differences between varieties were observed for the four compounds included in this group when the ANOVA analysis was performed (Table 4).

- Glycerol

As it is a compound that influences the taste more than the olfactory sensation, not causing any changes in the aroma of the wine [57], this group is discussed in a separate paragraph. Red varieties have a higher average concentration than white varieties, with an average value of 7817.84 mg·L^{-1} compared to 6071.12 mg·L^{-1}, respectively. Among the red varieties, 'Riera 2' stands out, with a value of 12,156 mg·L^{-1}. Among the white varieties, the highest amounts of glycerol correspond with 'Albana-C', 'Verdejo Serrano–E', and 'Marco 1 (MC1)-Albariño Tinto'. It is assumed that all of these varieties present a greater volume and fullness in the mouth, data which must be corroborated through sensory analysis. Contrary to this, the white varieties 'Cayetana' and 'Indiana' and the red varieties 'Tortozona Tinta' and 'Garró' showed the lowest glycerol content, therefore resulting in wines with less body on the palate.

3.1.2. Minor Volatile Compounds

Seventeen varietal compounds were identified and grouped into lactones, terpenes, and C_{13}-norisoprenoids (Table 3), groups that could have an important role in terms of the grape and wine aromas [58–60]. These compounds have a varietal origin, which makes them the most important ones in terms of their theoretical capacity to establish differences between the studied varieties. However, compounds like terpenes or C_{13}-norisoprenoids, together with some fermentative-derived compounds, could also be affected by the grape origin [61].

Quantitatively, the lactone group was the most important, as it was identified in mg·L^{-1}. In contrast, the terpenes group was the most important from a qualitative point of view, being the chemical group that 'a priori' would have the most important role in the aromatic wine profiles, triggering a greater final aromatic complexity.

Because of the type of vinification carried out, which were mostly microvinifications due to the small quantities of grapes available, it is very likely that the wines obtained do not reflect the full aromatic potential of the varieties studied. However, they do allow us to establish differences between them.

- Lactones

γ butyrolactone was the compound determined in this group, being one of the better-known lactones, and often associated with fatty and creamy descriptors [62]. White varieties showed an average value of 8000 µg·L^{-1}. 'Ratiño' showed the highest lactone concentration (21,400 µg·L^{-1}), followed by 'Folgasao' and 'Albana-C', while 'Zurieles-CM' showed the lowest content (4370 µg·L^{-1}). Regarding the red varieties, they generally showed higher lactone values than white varieties, with an average concentration around 13,000 µg·L^{-1}, with 'Tinta Jeromo-CL' and 'Marco 2 (MC2)-Albarín Tinto' standing out with more than 20,000 $\mu g \cdot L^{-1}$.

Regarding ANOVA results, shown in Table 5, γ butyrolactone showed highly significant differences among the evaluated varieties.

- Terpenes

Regarding terpenes, which are considered very important grape-derived compounds that are principally responsible for the characteristic aroma of muscat varieties, as well as of other non-muscat varieties [63], their high concentration among the white varieties should be noted, with 'Albilla do Avia' and 'Marco 1 (MC1)-Albariño Tinto', both from Galicia, showing values of 168.83 $\mu g \cdot L^{-1}$ and 112.41 $\mu g \cdot L^{-1}$, respectively, followed by 'Folgasao' and 'Verdejo Serrano–E', both from Extremadura. Their wines will be, 'a priori', more aromatic than those produced with the rest of varieties. However, a decisive aspect in determining the aromaticity of each variety will be the aroma threshold of each compound identified and their proportion, with terpenes such as linalool or geraniol showing much lower thresholds than monoterpenes with a certain degree of oxidation, such as the determined linalool oxides [64]. Varieties showing lower concentrations of terpenes were 'Jarrosuelto-N', 'Diega 2', 'Evena 1', and 'Albillo del Pozo'. Within this group of compounds, hodiol and endiol were, in general, those showing the greatest impact on the varietal profile of the varieties studied. Their content should be highlighted in 'Albilla do Avia' and 'Folgasao'. 'Albilla do Avia' also stands out for its high cis linalool oxide (furanoid) and α terpineol contents, with the last compound being associated with an anise descriptor [65], together with linalool, associated with lavender, floral, and citrus odors [58], with this last compound also being quite high in 'Jarrosuelto-A'. 'Marco 1 (MC1)-Albariño Tinto' showed the highest values of hotrienol, citronellol, and geraniol, with the latter compound potentially contributing to the fruity and floral notes [66]. 'Riera 46' showed the highest mean value of linalool pyranoid isomers. 'Jarrosuelto-CM' and 'Castellana Blanca-CM' were the varieties with the highest mean concentration of cis linalool oxide (furanoid), while 'Marco 1 (MC1)-Albariño Tinto' and 'Folgasao' stood out for their high concentration of citronellol, associated with a citrus descriptor. Regarding the red varieties, the average terpene concentration was slightly higher (11%) than that of the white varieties. This indicates a higher number of red varieties with higher terpene contents in the study than in the white varieties. This amount of terpene compounds among the red varieties is almost certainly due to the release of compounds present in the grape skins during alcoholic fermentation, as the compounds involved in varietal aroma are mainly found in grape skins [67], involving the production of the red wines a maceration phase with these skins. This could underpin the growing interest that exists today regarding the potential contribution of terpenes to the aroma of red wines [68]. However, the evaluation of a treatment with skins in the development of white varieties could be considered an option to increase the presence of aromatic compounds in the wines produced, as has already been tested in some studies [69].

The high concentrations of terpene compounds found in 'Diega 1', followed by 'Morate-M', 'Tortozona Tinta-A', and 'Mandregue', should be highlighted. Contrary to this, 'Benedicto' and 'Garró' showed lower concentrations of terpenes, and, therefore, likely present a lower varietal aromatic complexity. As in the case of the white varieties studied, hodiol and endiol were among the terpenes that showed a higher average concentration, especially in 'Estaladiña' and 'Diega 1', respectively. Regarding the other terpenes identified, linalool stood out in 'Terriza-M', while its lowest concentration was exhibited by 'Cadrete-N'. 'Tortozona Tinta-A' and 'Zamarrica' showed the highest levels of linalool oxide compounds, with both cis and trans isomers being higher in the former, then followed by 'Zamarrica'. These data are of utmost importance for the varietal differentiation process. 'Tortozona Tinta-A' also showed the highest citronellol content, as well as one of the highest hotrienol values, together with 'Hondarribi Beltza' and 'Santa Fé–A'. Nerol stood out in 'Mandregue'. Finally, geraniol showed its highest contents in 'Riera 2'.

Table 5. Minor volatile compounds determined and the significance of the 'variety' factor, according to one-way ANOVA.

	Lactone	**Terpenes**							
Compound	γ butyrolactone	linalool	trans linalool oxide (furan)	cis linalool oxide (furan)	trans linalool oxide (pyran)	cis linalool oxide (pyran)	oh-trienol	α terpineol	citronellol
Pr > F (Model) ***Significance***	<0.0001 ***	0.001 ***	<0.0001 ***	<0.0001 ***	<0.0001 ***	<0.0001 ***	<0.0001 ***	<0.0001 ***	0.224 *ns*
	Terpenes				**C_{13} Norisoprenoids**				
Compound	nerol	geraniol	hodiol 1	endiol	α ionone	β ionone	α damascone	β damascone	
Pr > F (Model) ***Significance***	<0.0001 ***	<0.0001 ***	0.025 *	<0.0001 ***	<0.0001 ***	<0.0001 ***	<0.0001 ***	<0.0001 ***	

Notation *, *** indicate significance at $p < 0.05$, $p < 0.001$, respectively. *ns* indicates non-significant difference.

When considering the ANOVA results shown in Table 5, significant differences were found among varieties for every terpene compound analyzed, except for citronellol. Hodiol 1 was the compound that showed the lowest significance, while the rest showed highly significant differences.

- C_{13}-norisoprenoids

Four C_{13}-norisoprenoids, shown in Table 3, were identified. The influence of these compounds is of great interest due to their general low perception thresholds, which makes them present a significant potential impact on the aroma of wines [70]. The mean value of C_{13}-norisoprenoids in the white varieties was 0.64 $\mu g \cdot L^{-1}$, with 'Hebén-M' and 'Hebén–E', 'Maquías', and 'Verdejo Serrano-E' showing the highest concentrations, at more than 1 $\mu g \cdot L^{-1}$. Contrary to this, 'Jarrosuelto–CM', together with 'Albilla do Avia', 'Ratiño', and 'Evena 1', showed the lowest concentrations.

Damascones were the compounds with the highest average contribution in this chemical group of white varieties, with both α and β damascone showing their highest average contribution in 'Hebén–M', and their lowest average concentration values being found in 'Castellana Blanca–M'.

α ionone showed its highest concentration in 'Verdejo Serrano', while 'Jarrosuelto-CM' showed the lowest. β ionone, associated with floral, red, or dark berry aromas [71], as well as violet descriptors in red wine, and which plays an important role in terms of aroma [70], showed the highest value in the 'Zurieles-CM' white variety, with 0.42 $\mu g \cdot L^{-1}$, while the same variety from a different region, 'Zurieles–E', showed the lowest value (0.03 $\mu g \cdot L^{-1}$). This highlights the different behaviors displayed by the same variety when grown in different regions. The presence of both compounds together have been associated with floral notes [66].

C_{13}-norisoprenoids values were, in general, much higher in red than in white varieties, with an average value of 1.30 $\mu g \cdot L^{-1}$. 'Tortozona Tinta-CM', 'Riera 43', 'Sanguina-C', and 'Santa Fé-A' showed the highest values, all being over 2 $\mu g \cdot L^{-1}$.

α ionone predominates in 'Riera 2', followed by 'Sanguina–C' and 'Santa Fé-A'. The contribution of α ionone was significantly lower in 'Garró' and 'Gorgollosa' varieties.

The concentration of β ionone stands out in 'Diega 1', followed by 'Riera 43' and 'Santa Fé-A'. The red variety 'Rayada Melonera' showed the lowest concentration of this norisoprenoid.

α damascone showed its highest concentrations in 'Trobat', followed by 'Tortozona Tinta–A', while β damascone showed its highest concentrations in 'Riera 43' and 'Tortozona Tinta-CM'. On the opposite side, 'Cenicienta' and 'Riera 2' and 'Benedicto' and 'Terriza–M' showed their lowest concentrations, respectively.

Regarding the ANOVA results shown in Table 5, it can be seen that every C_{13}-norisoprenoid analyzed showed significant differences among the studied varieties.

3.1.3. Volatile Relationships between Varieties

For a better interpretation of the results, and in order to understand if there is any relationship between the volatile compounds and the varieties or between the volatile compounds and the territory, a series of principal component analyses (PCA) were performed with some of the determined major and minor volatile compounds chemical groups, whereby the different identified compounds were grouped and evaluated.

In this case, and differently from the ANOVA analysis, in which every compound was included, a number of compounds were decided to be excluded from the PCA analysis, either due to their excessive concentration when compared to others, as is the case of methanol compared to other alcohols, or due to the influence of the winemaking process on their concentration in wines, as is the case of ethyl acetate and acetic acid, as these factors could affect or bias the obtained results, since what we really want to determine with the PCAs was whether there is some kind of relationship between the varieties based on their volatile composition, or rather whether the territory in which they were established can influence their volatile composition.

The first PCA analysis is based on alcohol compounds (Figure 1), and this achieves a good differentiation among the white and red varieties, with most of the red samples being on the positive side of F1 and most of the white samples being on the negative side.

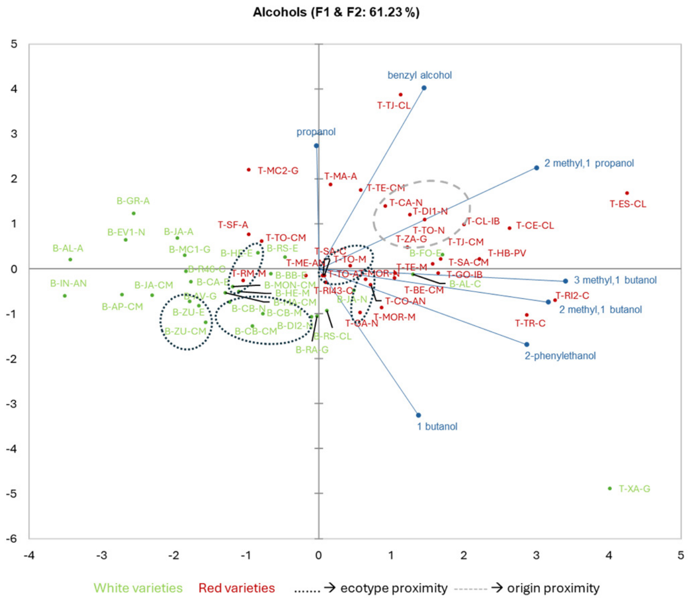

Figure 1. Principal component analysis (PCA) involving alcohol compounds. White varieties (B): B-AL-A: 'Albana-Aragón'; B-AL-C: 'Albana-Cataluña'; B-AP-CM: 'Albillo del Pozo-Castilla la Mancha'; 'B-AV-G: 'Albilla do Avia-Galicia'; B-BB-E: 'Bastardo Blanco-Extremadura'; B-CB-CM: 'Castellana Blanca-Castilla la Mancha'; B-CB-M: 'Castellana Blanca-Madrid'; B-CB-N: 'Castellana Blanca-Navarra'; B-CA-E: 'Cayetana-Extremadura'; B-DI2-N: 'Diega2-Navarra'; B-EV1-N: 'Evena1-Navarra'; B-FO-E: 'Folgasao-Extremadura'; B-GR-A: 'Greta-Aragón'; B-HE-E: 'Hebén-Extremadura'; B-HE-M: 'Hebén-Madrid'; B-IN-AN: 'Indiana-Andalucía'; B-JA-A: 'Jarrosuelto-Aragón'; B-JA-CM: 'Jarrosuelto-Castilla la Mancha'; B-JA-N: 'Jarrosuelto-Navarra'; B-MA-CM: 'Maquías-Castilla la Mancha'; B-MC1-G: 'Marco 1 (MC1)-Galicia'; B-MON-CM: 'Montonera del Casar-Castilla la Mancha'; B-RA-G: 'Ratiño-Galicia'; 'B-R46-C: 'Riera46-Cataluña'; B-RS-CL: 'Rufete Serrano-Castilla y León'; B-RS-E: 'Rufete Serrano-Extremadura'; B-ZU-CM: 'Zurieles-Castilla la Mancha'; B-ZU-E: 'Zurieles-Extremadura'. Red varieties (T): T-BE-CM: 'Benedicto-Castilla la Mancha'; T-CA-N: 'Cadrete-Navarra'; T-SF-A: 'Santa Fé-Aragón'; T-CL-IB: 'Callet-Islas Baleares'; T-CE-CL: 'Cenicienta-Castilla y León'; T-CO-AN: 'Corchera-Andalucía'; T-DI1-N: 'Diega1-Navarra'; T-ES-CL: 'Estaladiña-Castilla y León'; T-GA-N: 'Garró- Navarra'; T-GO-IB: 'Gorgollosa-Islas Baleares'; T-HB-PV: 'Hondarribi Beltza-País Vasco'; T-MA-A: 'Mandregue-Aragón'; T-MC2-G: 'Marco 2(MC2)-Galicia'; T-ME-AN: 'Melonera-Andalucía'; T-MOR-M: 'Morate-Madrid'; T-MOR-N: 'Morate-Navarra'; T-RM-M: 'Rayada Melonera-Madrid'; T-RI2-C: 'Riera2-Cataluña'; T-SA-C: 'Sanguina-Cataluña'; T-SA-CM: 'Sanguina-Castilla la Mancha'; T-TE-CM: 'Terriza-Castilla la Mancha'; T-TE-M: 'Terriza-Madrid'; T-TJ-CL: 'Tinta Jeromo-Castilla y León'; T-TJ-CM: 'Tinta Jeromo-Castilla la Mancha'; T-TO-A: 'Tortozona Tinta-Aragón'; T-TO-CM: 'Tortozona Tinta-Castilla la Mancha'; T-TO-M: 'Tortozona Tinta-Madrid'; T-TO-N: 'Tortozona Tinta-Navarra'; T-TR-C: 'Trobat-Cataluña'; T-RI43-C: 'Riera43-Cataluña'; T-XA-G: 'Xafardán-Galicia'; T-ZA-G: 'Zamarrica-Galicia'.

The first two principal components accounted for 61.23% of the total variance (42.59% and 18.64%). Approximations between the different studied ecotypes for some varieties can be seen in Figure 1, highlighting the following white varieties: B-ZU-E and B-ZU-CM ('Zurieles' from Extremadura and Castilla la Mancha); B-CB-CM, B-CB-M, and B-CB-N ('Castellana Blanca' from Castilla la Mancha, Madrid, and Navarra) in the negative side of F1 and F2 (third quadrant); and B-HE-E and B-HE-M ('Hebén' from Extremadura and Madrid) on the negative side of F1. Concerning the red varieties, the following should be highlighted: T-TO-A and T-TO-M, two ecotypes of 'Tortozona Tinta' from Aragón and Madrid, respectively, located together on the positive side of F1; as well as T-MOR-M and T-MOR-N, 'Morate' from Madrid and Navarra, sited together on the positive side of F1 and on the negative side of F2 (fourth quadrant). Finally, there was a clear approximation among three red varieties from Navarra on the positive side of F1 and F2 (second quadrant).

The second PCA analysis is based on C_6 compounds (Figure 2), completed with the same method as the alcohol compounds, which also achieved a good differentiation among white and red varieties, with a diagonal division of red and white samples between F1 and F2.

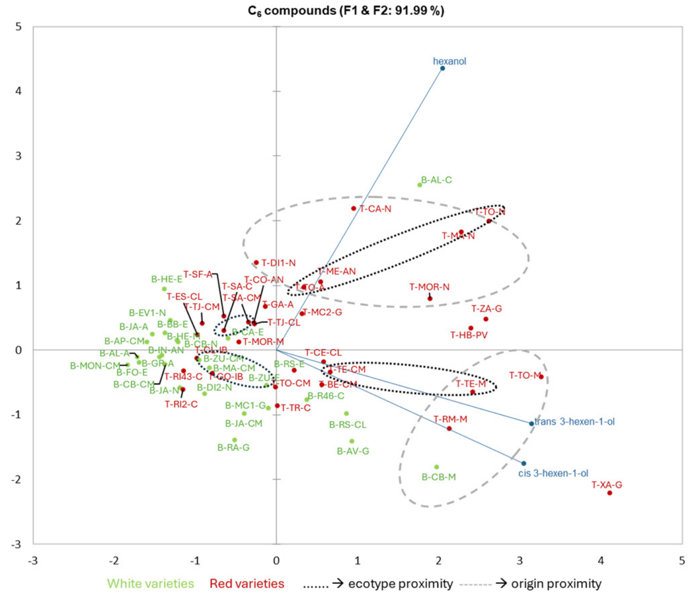

Figure 2. Principal component analysis (PCA) involving C_6 compounds. Abbreviations: see Figure 1.

The first two principal components explain 91.99% of the total variance (65.48% and 26.51%). Approximations between different ecotypes of the same variety can be seen in Figure 2, highlighting the following white varieties: B-ZU-E and B-ZU-CM ('Zurieles' from Extremadura and Castilla la Mancha) on the negative side of F1 and F2 (third quadrant), which are ecotypes already grouped by alcohols in Figure 1. Regarding the red varieties, the following should also be highlighted: two 'Tortozona Tinta' ecotypes were clustered together as with alcohols, but, in this case, they were T-TO-A and T-TO-N from Aragón and Navarra, respectively, placed together on the positive side of F1 and F2 (second quadrant). Both the 'Sanguina' ecotypes studied, T-SA-C and T-SA-CM, were also positioned together on the negative side of F1 and the positive side of F2 (first quadrant). Finally, both 'Terriza' ecotypes, T-TE-CM and T-TE-M, from Castilla la Mancha and Madrid were placed together on the first side of F1 and the negative side of F2 (fourth quadrant). In terms of origin proximity, four of the six varieties studied from Madrid were located close to each other on the same fourth quadrant. Five red varieties studied from Navarra were located near each other on the positive side of F2, and four of them were in the second quadrant.

The third and fourth PCA analyses are based on ester and acetate compounds, respectively (Figures 3 and 4).

The PCA based on esters (Figure 3) achieves a good differentiation among the white and red varieties, with most of the red samples located on the negative side of F1 and the white ones being on the positive side.

The first two principal components accounted for 71.15% of the total variance (43.08% and 28.07%). Approximations between the different ecotypes can be seen in Figure 3, highlighting the following white varieties: B-CB-CM and B-CB-M ('Castellana Blanca' from Castilla la Mancha and Madrid) on the positive side of F1 and the negative side of F2 (fourth quadrant), both ecotypes already grouped by alcohols. Regarding the red varieties, both the 'Sanguina' ecotypes studied, T-SA-C and T-SA-CM, from Cataluña and Castilla la Mancha, and T-MOR-M and T-MOR-N, 'Morate' from Madrid and Navarra, were also located together on the negative side of F1 and F2 (third quadrant). 'Sanguina' ecotypes were already grouped by C_6 compounds, while the 'Morate' ecotypes were grouped by alcohols. In terms of origin proximity, the three red varieties studied from Castilla y León were placed closely on the negative side of F1 and the positive side of F2 (first quadrant), and the red varieties from Galicia were on the positive side of F2.

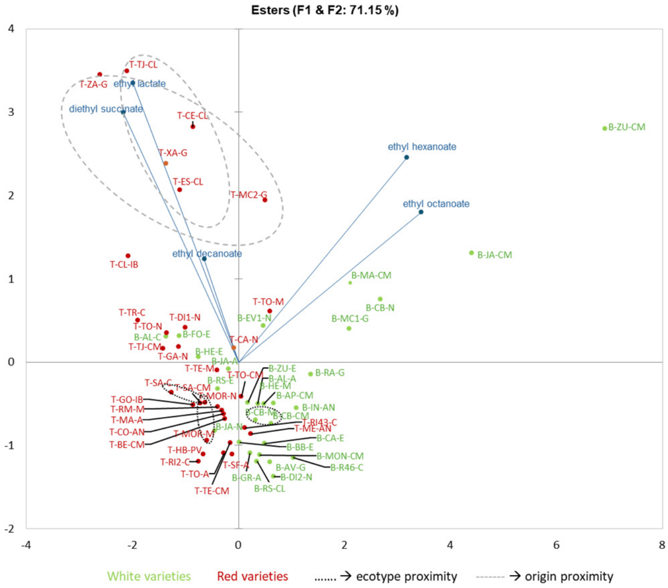

Figure 3. Principal component analysis (PCA) involving esters. Abbreviations: see Figure 1.

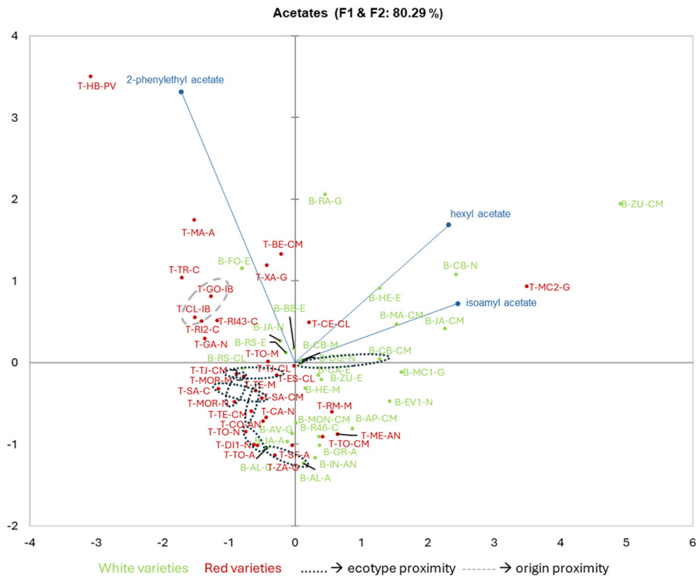

Figure 4. Principal component analysis (PCA) involving acetates. Abbreviations: see Figure 1.

The PCA analysis based on acetate compounds (Figure 4) also achieves a good differentiation among the white and red varieties, although it is not as clear as with previous chemical families.

Most of the white samples are on the positive side of F1 and most of the red samples are on the negative side. The first two principal components accounted for 80.29% of the total variance (51.23% and 29.06%). Figure 4 shows several approximations among the different ecotypes, especially among the red varieties. Among the white varieties, B-CB-CM and B-CB-M ('Castellana Blanca' from Castilla la Mancha and Madrid) were placed together, as by esters, on the positive side of F1 and F2, with the third ecotype of 'Castellana Blanca', from Navarra, being not far behind. The ecotypes B-AL-A and B-AL-C, 'Albana' from Aragón and Cataluña, were near one another on the negative side of F2. With respect to the red varieties, both of the ecotypes of 'Tinta Jeromo' (T-TJ-CL and T-TJ-CM) from Castilla y León and Castilla la Mancha, of 'Morate' (T-MOR-M and T-MOR-N) from Madrid and Navarra, of 'Sanguina' (T-SA-C and T-SA-CM) from Cataluña and Castilla la Mancha, of 'Terriza' (T-TE-CM and T-TE-M) from Castilla la Mancha and Madrid, and finally, two ecotypes of the four 'Tortozona Tinta' (T-TO-A and T-TO-N) varieties from Aragón and Navarra were placed together on the negative side of F1 and F2 (third quadrant). The ecotypes of most of these varieties were already grouped by previous chemical families. With respect to the origin proximity, both varieties with origin in the Balearic Islands, T-GO-IB ('Gorgollosa') and T-CL-IB ('Callet'), were placed together on the negative side of F1 and on the positive side of F2 (first quadrant).

The next PCA analysis is based on acid compounds (Figure 5). In this case, such a good differentiation was not achieved among the white and red varieties.

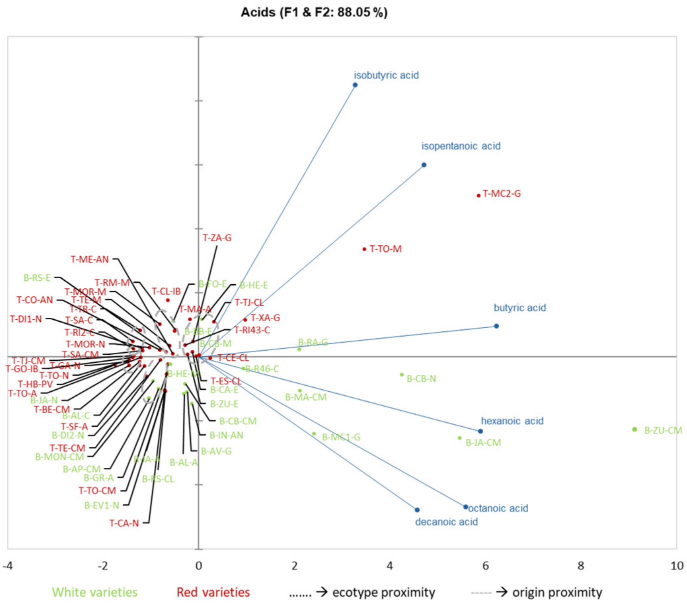

Figure 5. Principal component analysis (PCA) involving acids. Abbreviations: see Figure 1.

The first two principal components account for 88.05% of the total variance (65.4% and 23.00%). Acids do not show a clear proximity among ecotypes of the same variety; contrary to this, several varieties of the same origin placed close to each other, with all of them being red varieties, as follows: 'Morate', 'Terriza', and 'Rayada Melonera' from Madrid (T-MOR-M, T-TE-M, T-RM-M); 'Trobat', 'Sanguina', and 'Riera2' from Cataluña (T-TR-C, T-SA-C, T-RI2-C) in the first quadrant; 'Morate', 'Garró', 'Tortozona Tinta', and 'Diega1' from Navarra (T-MOR-N, T-GA-N, T-TO-N, T-DI1-N) and 'Sanguina', 'Tinta Jeromo', 'Benedicto', 'Terriza', and 'Tortozona Tinta' from Castilla la Mancha (T-SA-CM, T-TJ-CM, T-BE-CM, T-TE-CM, T-TO-CM) being on the negative side of F1.

- Minor compounds

The first PCA analysis of this group of compounds is based on terpene compounds (Figure 6). This analysis did not achieve a good differentiation among the white and red varieties.

The first two principal components accounted for 48.09% of the total variance (28.32% and 19.77%). There are some approximations among the different ecotypes. Among the white varieties, B-CB-CM and B-CB-M ('Castellana Blanca' from Castilla la Mancha and Madrid) were placed together, as were esters and acetates on the negative side of F2, neither being very far from the third studied ecotype of 'Castellana Blanca' from Navarra. Regarding the red varieties, 'Terriza' ecotypes (T-TE-CM and T-TE-M) from Castilla la Mancha and Madrid were placed together, as well as two ecotypes of the four studied 'Tortozona Tinta' (T-TO-CM and T-TO-M) varieties from Castilla la Mancha and Madrid, both of which were located on the positive side of F2. With respect to the origin proximity, three of the four white varieties from Navarra (B-JA-N, B-DI2, and B-EV1) were placed together on the negative side of F1 and F2 (third quadrant). Four of the six white varieties studied from Castilla la Mancha, namely 'Castellana Blanca', 'Zurieles', 'Jarrosuelto', and 'Montonera del Casar' (B-CB-CM, B-ZU-CM, B-JA-CM, and B-MON-CM), were relatively close together on the negative side of F2. The three red varieties from Galicia, 'Marco 2 (MC2)-Albarín Tinto', 'Xafardán (Tinta Oubiña)', and 'Zamarrica', were located close together on the positive side of F1. Four varieties from Extremadura were close to each other, namely 'Zurieles', 'Rufete Serrano', 'Folgasao', and 'Hebén' (B-ZU-E, B-RS-E, B-FO-E, and B-HE-E). The three white varieties studied from Galicia, 'Albilla do Avia', 'Marco 1 (MC1)-Albariño Tinto', and 'Ratiño', were on the positive side of F2 in the upper locations. Finally, the two varieties studied from the Balearic Islands, 'Callet' and 'Gorgollosa' (T-CL-IB and T-GO-IB), were located together on the negative side of F1 and the positive side of F2 (first quadrant).

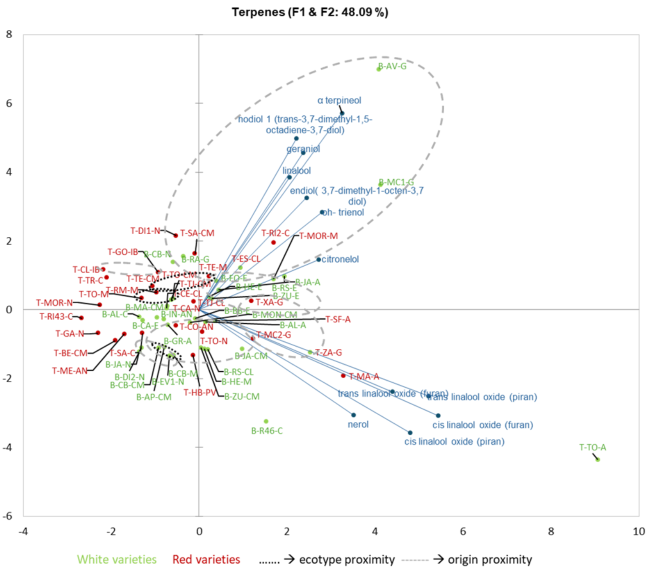

Figure 6. Principal component analysis (PCA) involving terpenes. Abbreviations: see Figure 1.

The last PCA is based on C_{13}-norisoprenoid compounds (Figure 7), which did not achieve a good differentiation among the white and red varieties.

The first two principal components analyses accounted for 77.13% of the total variance (54.48% and 22.65%). There are some approximations between the different ecotypes. Among the white varieties, B-CB-CM, B-CB-M, and B-CB-N, ('Castellana Blanca' from Castilla la Mancha, Madrid, and Navarra) and B-ZU-E together with B-ZU-CM ('Zurieles' from Extremadura and Castilla la Mancha) were placed close together on the negative side of F1 and F2 (third quadrant). Regarding the red varieties, the two ecotypes of 'Morate' from Madrid and Navarra (T-MOR-M and T-MOR-N) were located near one another on the negative side of F2. Finally, the four ecotypes of 'Tortozona Tinta' were located close to each other as pairs, with T-TO-A and T-TO-M, from Aragón and Madrid, being near one another, and T-TO-CM and T-TO-N from Castilla la Mancha and Navarra constituting the other pair. With respect to the origin proximity, five of the studied varieties from Castilla la Mancha were placed close to each other on the positive side of F1, namely B-MA-CM, T-BE-CM, T-TE-CM, T-TO-CM, and T-SA-CM (the white variety 'Maquías' and the red varieties 'Benedicto', 'Terriza', 'Tortozona', and 'Sanguina'), with medium–high norisoprenoid values.

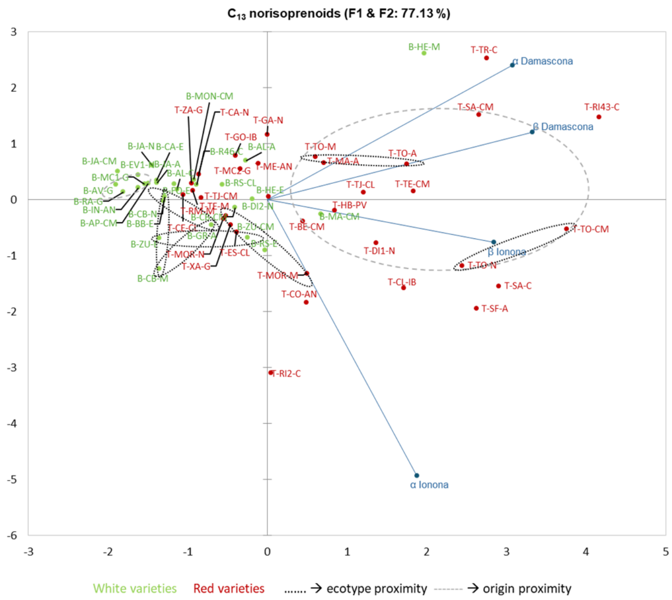

Figure 7. Principal component analysis (PCA) involving C_{13}-norisoprenoids. Abbreviations: see Figure 1.

4. Conclusions

First of all, and potentially the most important aspect reflected in the study, the detailed and complex varietal characterization carried out by the MINORVIN project, within which this volatile study is framed, reflects a great varietal diversity, highlighting, in this particular case, the wide diversity of aromatic profiles shown by the different varieties under study. This reinforces the importance of expanding the study of these minority varieties.

Among the different compounds identified, high significant differences were found for alcohols, C_6, carbonyl, and other determined compounds, while esters, acetates, and acids did not show or showed few significant differences between varieties. Within the minor compounds identified, terpenes, lactones, and C_{13}-norisoprenoids, high significant differences were found for the majority of the volatile compounds identified in each group. These results seem to confirm that terpenes, lactones, and C_{13}-norisoprenoids, as well as C_6 compounds among the major ones, which are considered to be varietal compounds, would fulfil their assumed predisposition to have a better theoretical ability to differentiate between the varieties.

It could be shown as well from the results obtained in PCAs that the determination of a wide range of volatile compounds could help to differentiate between the varieties, as PCAs carried out with C_6 compounds, esters, acetates, acids, and C_{13}-norisoprenoids explained more than 70% of the variability, and alcohols explained more than 60% of the variability found between varieties.

Alcohols, C_6 compounds, and esters showed a clear differentiation among white and red varieties, and showed a clear approximation among the different ecotypes of the same variety but from different origins. Acetates also seem to differentiate between red and white varieties, despite not being as evident as the other chemical groups, showing approximation among different ecotypes from the same variety for several red varieties. Contrary to this, acids, terpenes, and C_{13}-norisoprenoids did not exhibit a clear differentiation among white and red varieties, and neither exhibited approximation among different ecotypes of the same variety.

From a more detailed point of view, among the white varieties, the following should be highlighted: 'Folgasao', from Extremadura, for having greater 2-phenyletanol and benzyl alcohol contents, higher 2 phenylacetate levels, a high γ butyrolactone content, and also a high terpene concentration, especially of citronellol, in comparison with the rest of white varieties studied. Among the alcohols, the following stood out: 'Greta', 'Jarrosuelto', and 'Verdejo Serrano' for their high benzyl alcohol quantities, and 'Ratiño' together with 'Folgasao' for its higher 2-phenylacetate content. Regarding minor compounds, 'Ratiño' together with 'Folgasao' and 'Albana-C' registered the major lactone quantities. With respect to terpenes, 'Albilla do Avia' together with 'Marco 1 (MC1)-Albariño Tinto' and 'Verdejo Serrano' should be highlighted, with high linalool concentrations in the case of 'Albilla do Avia' together with 'Jarrosuelto-A', and of hotrienol, citronellol, and geraniol in case of 'Marco 1 (MC1)-Albariño Tinto'. Finally, if we consider C_{13}-norisoprenoids, 'Hebén-M', 'Hebén-E', 'Maquias', and 'Verdejo Serrano' stood out for their higher contents. Contrary to terpenes, 'Albilla do Avia' would be among the lower C_{13}-norisoprenoids contents identified.

Among the red varieties, regarding alcohols, 'Riera 2' and 'Tinta Jeromo-CL' should be mentioned for their higher 2-phenyletanol and benzyl alcohol contents, respectively. Considering minor compounds, 'Tinta Jeromo-CL' and 'Marco 2 (MC2)-Albarín Tinto' stood out for their higher lactone contents. With respect to terpenes, 'Diega 1', 'Morate-M', and 'Tortozona Tinta-A', the latter having high linalool oxide contents, alongside 'Zamarrica', and high citronellol and hotrienol contents, and 'Mandregue' with its high nerol contents are the red varieties with higher terpene concentrations. 'Terriza-M' should be mentioned for its higher linalool content, as should 'Riera 2' for its geraniol contents, both terpenes among the ones identified with lower perception thresholds. Finally, from a C_{13}-norisoprenoids point of view, 'Tortozona Tinta-CM', 'Riera 43', 'Sanguina-C', and 'Santa Fé-A' were the varieties with higher concentrations.

Significant differences were also found between varieties when the sensorial analyses were performed. The results of the sensory analyses not only showed differences between varieties, but also among regions. These could be the result of the different soil and climatic conditions, as detailed by Puig-Pujol et al. [72] in their study, alluding to the possible relationship between the sandy or loamy textured soils, as well as the acid- and organic-based matter composition of the Galician soils and the sourness and more acidic character of their wines.

The different climatic conditions experienced by the different varieties could be another plausible influencing factor, with Muñoz-Organero et al. [29] having found that the same varieties studied in different locations showed differences in their ripening data. The 'Instituto de la Vid y el Vino de Castilla-La Mancha (IVICAM)', in the same MINORVIN project, has also shown differences in the drought-tolerance capacity of the different varieties (unpublished data), which could also support the different exposures to water stress of the different varieties, depending on their location.

On the other hand, the different agronomic practices used in each field could be another factor to be taken into account in terms of influencing the aromatic composition of the wines studied [73]. All of these factors could also translate in different grape volatile compositions, such as those obtained in this study, since the different aromatic fractions of the grape, such as the varietal, would be significantly influenced by the ripening stage of the berry, the climatic conditions, and soil management [74].

The proximity shown by some of the different studied ecotypes of the same variety, according to the PCA analyses carried out with different chemical families, should be mentioned, as this could be an interesting aspect. It could indicate a greater aromatic similarity between these ecotypes and, therefore, a hypothetic lower differentiation or distancing between them when compared to what occurred in the case of other varieties. Among the white varieties, both ecotypes of 'Zurieles', from Extremadura and Castilla la Mancha, were nearby in alcohols, C_6 compounds, and C_{13}-norisoprenoids PCA analyses. At least two of the ecotypes of 'Castellana Blanca' studied, from Madrid and Castilla la Mancha, were also grouped by alcohols, ester, acetate, terpene, and C_{13}-norisoprenoid PAC analyses. Among the red varieties, the different ecotypes of 'Tortozona Tinta', from Aragón, Madrid, Navarra, and Castilla la Mancha, were partially grouped in a different way by alcohols, $C_{6,}$ acetate, terpene, and C_{13}-norisoprenoid PCA analyses. Also, 'Morate' ecotypes from Madrid and Navarra were grouped by alcohols, ester, acetate, and C_{13}-norisoprenoid

PCA analyses, and, finally, 'Sanguina' ecotypes from Cataluña and Castilla la Mancha were situated in proximity to one another by C_6 compound, ester, and acetate PCA analyses.

Some of these results were corroborated by those obtained by Valdés et al. [75] within the same national project, MINORVIN, when they studied and compared the phenolic composition of different varieties in different locations. Although variety and location factors were significant for all of the polyphenolic families studied, they found that some varieties, regardless of their study location, showed similar phenolic profiles, or stood out for having the highest content of some phenolic families when compared to other varieties studied, as was the case of 'Tortozona Tinta' in the first hypothesis or 'Sanguina' in the second, which suggests a greater similarity between ecotypes in the case of these varieties.

All this previous information analyzed could indicate which varieties could be 'a priori' those with a higher aromatic potential, via the higher concentrations of the compounds known for their potential aromaticity and via which are linked to positive descriptors in grapes and wines.

From an applied point of view, this information provides an initial approach to the production of these varieties and preliminary results, which, despite the fact that they should be considered with caution as most of the wine elaborations consisted of microvinification processes, do provide an indication of the aromatic properties of the wines produced and the experimental data regarding the potential for the development of these minority varieties.

5. Patents

Two *Vitis vinifera* L. varieties have been commercially registered by EVEGA-AGACAL 'Albilla do Avia' and 'Zamarrica', partly because of the results obtained in the present study.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/agronomy14051033/s1, Table S1: Sum of the concentrations of the major volatile compounds identified (mg·L^{-1}) in the white varieties, grouped by chemical family; Table S2: Sum of the concentrations of the minor volatile compounds identified (lactones in mg·L^{-1} and terpenes and C_{13} norisoprenoids in µg·L^{-1}) in the white varieties, grouped by chemical family; Table S3: Sum of the concentrations of the major volatile compounds identified (mg·L^{-1}) in the red varieties, grouped by chemical family; Table S4: Sum of the concentrations of the minor volatile compounds identified (lactones in mg·L^{-1} and terpenes and C_{13} norisoprenoids in µg·L^{-1}) in the red varieties, grouped by chemical family.

Author Contributions: Conceptualization, E.D.-L. and S.C.-D.; methodology, E.D.-L., S.C.-D. and Á.D.-F.; software, E.D.-L. and S.C.-D.; validation, E.D.-L., S.C.-D. and Á.D.-F.; formal analysis, E.D.-L. and S.C.-D.; investigation, E.D.-L., S.C.-D. and Á.D.-F.; wine resources, E.D.-L., G.M.-O., F.C., B.P., A.P.-P., C.D., M.E.V.-S., D.M.C., J.F.C., O.D.-A., J.-A.R.-C., J.M.-G., A.M.-M., C.C. and J.-J.U.; data curation, E.D.-L. and S.C.-D.; writing—original draft preparation, E.D.-L. and S.C.-D.; writing—review and editing, E.D.-L., S.C.-D. and Á.D.-F.; project administration, E.D.-L.; funding acquisition, E.D.-L. All authors have read and agreed to the published version of the manuscript.

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