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A chemometric and sensory study of Spanish Red Wines labelled *"Tempranillo Crianza 2010"* with Protected Designation of Origin

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A B S T R A C T

A chemometric and sensory study was conducted of ten Spanish red wines, all described as *"Tempranillo Crianza 2010"*, with Protected Designation of Origin (PDO). The analysis considered the following physicochemical parameters: alcohol content, SO_2 level, acidity, tannin, antioxidant capacity and colour. In the chemometric study, Principal Component Analysis of the colour, Cluster Analysis, Analysis Of Variance (ANOVA) and the Kruskal-Wallis test showed that the samples corresponding to PDOs #8, #9 and #10 presented the highest number of differences from the rest. In the sensory analysis, Samples #9 and #10 were identified as the most different. From both types of study, we conclude that Samples #8, #9 and #10 present the greatest differences, while the remaining samples were very similar in their chemometric and sensory characteristics.

1. Introduction

In Spain and throughout the European Union, the classification of wine quality includes the concepts of Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI), under the provisions of European Union (EU) Regulation 1308/2013 reflecting qualities that are intrinsically linked to the diversity of native grapes and the unique conditions of each wine region. Furthermore, the EU has issued detailed regulations covering everything from cultivation practices to winemaking and labelling, to assure the authenticity and quality of European wines (European Union, 2013).

The conditions to label a wine as PGI are more flexible than those indicated for a wine with PDO. However, in some instances PGI wines may exhibit characteristics very similar to those of PDO wines. This situation is understandable, given the flexibility of the standards for PGI wines. In addition, and more surprisingly, similarities can also be found among wines from different PDOs, although they are produced under much stricter conditions. This unexpected coincidence is due to the shared presence of natural factors and to the specific winemaking techniques that may be applied in similar ways in different regions. The expertise and knowledge of winemakers, coupled with their aim to maximise the quality of their terroir, can result in wines having nearly identical profiles, despite coming from geographically distant locations. This diversity within coherence reflects the richness and complexity of the world of wine.

In Spain, according to data for 2022, there are 101 registered PDOs for wine, each described in detail in the corresponding *"pliego de condiciones"* (specifications documents) setting out the conditions the wine producer must meet to qualify for the PDO description (Government of Spain, 2015).

This document is drafted and approved by the corresponding Regulatory Councils, the governing bodies of each PDO. The specifications that are issued must be consistent with European, national and regional regulations, and cover aspects such as the production area, processing and aging methods, authorised grape varieties, maximum yields per hectare, and physicochemical characterisation. In other words, the specifications documents determine the typicity of the wine, including its technical and sensory characteristics, the grape variety and the nature of the terroir (Cadot et al., 2010).

Accordingly, wines with the same PDO present similar qualities, due to their mandatory compliance with the specification document and their geographical proximity. However, these characteristics should be clearly distinguished from other wines with PDOs for different geographical areas.

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In practice, however, there are noticeable similarities in the specifications of some PDOs, for instance, regarding winemaking practices. One of the most recurrent aspects among these PDOs is the list of permitted grape varieties, revealing a systematic repetition of grapevines that does not contribute to the authenticity sought in PDO wines. Such is the case of the "*Tempranillo*" variety, which is included in the majority of PDOs in Spain.

In addition to similarities in winemaking techniques and in the grape varieties that are authorised, all PDO wines must use the same terms to describe their aging, with expressions such as "*Crianza*", "*Reserva*" and "*Gran Reserva*". These designations refer to the minimum time that a red wine must be stored in the barrel in contact with wood and then in the bottle before it is commercialised. With respect to the above terms, these minimum periods are 24, 36 and 60 months, respectively.

In sum, these circumstances explain why we may encounter wines with different PDOs that exhibit very similar overall characteristics, making them difficult to distinguish for a non-specialist wine taster.

In view of these considerations, the aim of the present study is to determine certain characteristics of a given set of Spanish red wines, specifically "*Tempranillo Crianza 2010*" corresponding to different PDOs, by means of a chemometric and sensory analysis, seeking to objectively identify their differences and similarities. This study is a continuation of a previous investigation conducted in 2018 and published as "*Use of ISO 5495:2009 to Determine Sensory Preferences of Consumers of Spanish Red Wines with Designation of Origin*" (Quesada-Granados et al., 2018). With this research work, we want to highlight the existence of what we believe is a problem of globalization in the world of wine, and more specifically in the wine panorama in Spain. The study is approached from a perspective not previously studied by other authors, hence how novel it may be, and which may be very interesting for red wine consumers in Spain considering the great offer and diversity of existing purchasing options and very different prices. The usefulness of this research work is to show that there may be options at lower prices that have similar characteristics to others at a higher price but maintain the quality of red wine. Undoubtedly, the current climate change panorama and the normalization of climatic conditions, not only in Spain but throughout the world, can make red wines become more and more similar regardless of where they are made and increase this situation of globalization. If something positive can be extracted from this situation, it would be that consumers will have more competitiveness and choice options at more affordable prices while maintaining a similar quality in all these options. This research work simply wants to highlight this situation that already fully affects us, even if only in a specific way, using a certain type of Spanish red wine as an example of the situation.

2. Materials and methods

2.1. Materials

As this is a follow-up to a previous research study (Quesada-Granados et al., 2018), the red wine samples used are the same as those described in the above-mentioned article. In short, we analysed ten Spanish wines from different regions, all with PDO status and labelled as "*Crianza 2010*; Government of Spain, 2003), made exclusively from 100% Tempranillo grapes. These wines are readily available in retail stores and are priced at an intermediate range compared to wines with similar attributes, excluding both the most expensive and the cheapest options available in the market (Table 1). The 2010 vintage was selected due to its availability as the only harvest with a substantial number of samples, which enabled us to ensure the comprehensive nature of this study. Thus, three lots of six bottles (750 mL bottles) for each sample were acquired to complete both the physicochemical analyses and the sensory test comparisons. To store so many bottles, samples were acquired as the time for analysis arrived.

The harvests under consideration were officially rated as Excellent and Very good (CECRV, 2014), with the exception of a single PDO for which no data could be found on the quality of its harvest in 2010. These ratings are based on a comprehensive assessment of climate data, including rainfall and temperature, together with analytical and sensory data from the wines obtained during the specific vintage studied (Borges et al., 2012; Jones & Storchmann, 2001; Salinger et al., 2015). The assessment of the vintage quality is determined by impartial institutions that compile all relevant information on harvest quality into comparative tables (CERV, 2014). Hence, the quality of the harvest can be accurately understood as a consequence of applying scientific data, serving as a credible indicator of wine quality. Consequently, in this research, the quality of the vintage was utilised as a benchmark, notwithstanding the potential limitations associated with this factor.

Table 1
Characteristics of the wine samples.

Sample PDO	PDO location territory (2010 harvest)	Price (€)	Harvest quality (CECRV, 2014)
S#1	North	5.42	Excellent
S#2	North-West	5.22	Excellent
S#3	North-Centre	6.90	Excellent
S#4	North	5.84	Excellent
S#5	North-West	9.30	Excellent
S#6	South-Centre	3.65	Excellent
S#7	South-Centre	4.60	Very Good
S#8	North-East	7.05	Very Good
S#9	North-East	8.00	Excellent
S#10	South-East	8.55	–

" – "indicates the non-existence of data for the quality of the harvest in 2010.

All the samples were obtained from retail outlets in Granada or from online sources, immediately before the sampling process. The bottles were stored under optimal conditions, featuring low light, no noise, 80% relative humidity and at temperatures of 7–10 °C, ideal for preserving wine. These storage conditions were maintained by utilising wine cabinets until 24 h before the analysis.

All bottles were opened 15 min before the analysis began. At that point, a sufficient sample was taken for the corresponding physicochemical analyses. All wines were purchased in 750 mL bottles.

2.2. Methodology

2.2.1. Chemometric study

The analytical techniques used are described in the *Compendium Of International Analysis Of Methods* (OIV, 2015) and are commonly employed in wineries, focusing on components of the wine that may affect its overall characteristics. Alcohol content was determined by hydrometry, according to Method OIV-MA-AS312-01B (OIV, 2015) by distillation of wine made alkaline by a suspension of calcium hydroxide and measurement of the alcoholic strength of the distillate; Reducing sugars, according to Method OIV-MA-AS311-01[a] (OIV, 2015), reducing substances comprise all the sugars exhibiting ketonic and aldehydic functions and are determined by their reducing action on an alkaline solution of a copper salt; Total acidity, according to Method OIV--MA-AS313-01(OIV, 2015) by potentiometric titration or titration with bromothymol blue as indicator and comparison with an end-point color standard; Volatile acidity, according to Method OIV-MA-AS313-02 (OIV, 2015) where volatile acids are separated from the wine by steam distillation and titrated using standard sodium hydroxide; Total malic acid, according to Method OIV-MA-AS313-10 (OIV, 2015) where malic acid, separated by means of an anion exchange column, is determined colorimetrically in the eluent by measuring the yellow coloration it forms with chromotropic acid in the presence of concentrated sulfuric acid; Folin-Ciocalteu Index (TPI), according to Method OIV-MA-AS2-10 (OIV, 2015) where all phenolic compounds contained in wine are oxidized by Folin-Ciocalteu reagent and the blue coloration produced has a maximum absorption in the region of 750 nm, and is proportional to the total quantity of phenolic compounds originally present; Content of free and total sulfur dioxide, according to Method OIV-MA-AS323-04B (OIV, 2015) where free sulfur dioxide is determined by direct titration with iodine. The combined sulfur dioxide is subsequently determined by iodometric titration after alkaline hydrolysis. When added to the free sulfur dioxide, it gives the total sulfur dioxide; CIELAB chromatic characteristics, according to Method OIV-MA-AS2-11 (OIV, 2015). The purpose of this spectrophotometric method is to define the process of measuring and calculating the chromatic characteristics of wines and other beverages derived from trichromatic components: X, Y, Z, L^*, C^*_{ab}, h^*_{ab}, a^* and b^* by attempting to imitate real observers with regard to their sensations of colour (CIE, 1986; Piñeiro et al., 2024; Shuyue et al., 2023). In addition to the CIELAB space, the Intensity (INT) and Tone (TON) of the color of the wines were determined by using the MSCV® software that uses the sum of the absorbances at 420 nm, 520 nm and 620 nm to calculate the intensity of the color of the wine, and the quotient between the absorbance at 420 nm and absorbance at 520 nm, (A^{420}/A^{520}), to calculate the color tone of the wine (Uysal et al., 2023); Tannins, as described by Maietti et al. (2012) where the determination of total condensed tannins was obtained using a colorimetric method with vanillin, HCl and methanol as reagents and the absorption was measured at 500 nm; and Flavonoids, as described by Dewanto et al. (2002) using a colorimetric method where the absorbance was measured immediately against the blank at 510 nm.

In addition to the aforementioned analytical techniques, the physicochemical characterisation of the wines was complemented by determining the Total Antioxidant Capacity of each sample, by methods including modified [2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate)] Assay (ABTS) and (2,2-diphenyl-1-picrylhydrazyl radical) assay (DPPH) performed in our laboratory (Samaniego-Sanchez et al., 2007, 2011) and the Photochem method (Popov & Lewin, 1999), that uses photoinduced chemiluminescence to measure total antioxidant capacity.

The chemometric analysis was conducted using Statgraphics Centurion v16 software (Statistical Graphics Corp., 1999) applying Analysis Of Variance (ANOVA)/Kruskal-Wallis tests, Fisher's Least Significant Difference Procedure (Fisher's LSD), Principal Components Analysis (PCA), Cluster Analysis (HCA) and Discriminant Analysis. The chromatic characteristics were determined using CIELAB MSCV® 2012 software developed by the colour group at the University of La Rioja and the University of Zaragoza. Statistical significance levels of $p \leq 0.05$ were considered significant.

2.2.2. Sensory study

The sensory characteristics of the samples were analysed by means of a triangular difference test, with 18 tasters, an assumed significance level (α) of 0.05 and forced choice. To achieve the required confidence level, each taster evaluated three triads, as allowed by International Organization for Standardization (ISO), resulting in significance levels $\alpha = 0.10$, $\beta = 0.05$, and $\rho d = 30\%$. Considering the risk characteristics of the test, we calculated that a minimum of 25 correct responses would be required to establish both perceptible and statistical differences. Therefore, with fewer than 25 correct responses we cannot reject the hypothesis that the samples are equal (Aenor, 2008, 2021).

The sensory sessions were conducted in the tasting room of the Seminar for Gastronomic and Oenological Studies, located at the School of Pharmacy of the University of Granada, during the academic years 2012–2013, 2013–2014 and 2014–2015. This extended period was necessary due to the significant number of sessions and tasters required. In any case, the number of tasters participating in the tests was determined by the available operability conditions and the seating capacity of the tasting room. The participants in the various sessions consisted of 40% men and 60% women, all of whom were regular red wine consumers but not professionals in wine tasting. The ages of the tasters ranged from 23 to 55 years.

Two clearly-differentiated groups of tasters participated in the study: 1. Long-term tasters, recruited from the staff at the School of Pharmacy of the University of Granada ($n = 15$); 2. Occasional tasters, recruited in each academic year, and consisting of undergraduate and postgraduate students from the University of Granada ($n = 15$).

In each tasting session, there were consistently ten tasters from the long-term group and eight from the occasional group. If any absence occurred, the missing taster was replaced by another from the same group, to ensure that the 18 tasters required for each tasting session were always present. The tasting sheets used were designed following the guidelines of the corresponding ISO standards in the Spanish language, although for the present manuscript, they have been translated into English (Fig. S1). The wine-tasting glasses used for the triangular test were in accordance with those described in the ISO and Aenor standard UNE 87022 (Aenor, 1992; ISO, 1977).

3. Results and discussion

3.1. Chemometric study of physicochemical characteristics

The CIELAB chromatic characteristics, the Intensity (INT) and Tone (TON) of the samples are listed in Table 2. In order to conduct a valid comparison of the chromatic characteristics and due to the complexity of the CIELAB chromatic study (Hernández et al., 2011; Shuyue et al., 2023), the samples were also subjected to a Principal Component Analysis (PCA). The purpose of this analysis was to obtain a small number of linear combinations of the ten chromatic variables which account for most of the variability in the data. In this case, a single component was extracted, since only one had an eigenvalue ≥1.0. This component accounted for nearly 88% of the variability in the original data. The values found for principal component No. 1 of the CIELAB chromatic space, INT and TON are shown in Table 3.

The physicochemical and chromatic characteristics of the samples are summarised in Table 4. After verifying the parametric or non-parametric distribution of the analytical data, ANOVA/Fisher's LSD test or the Kruskall-Wallis test was used, as appropriate, to identify statistical differences among them. For the physicochemical criteria considered, these tests revealed significant statistical differences among the samples ($p \leq 0.05$, $p \leq 0.01$, and $p \leq 0.001$), with the sole exception of the malic acid criterion ($p > 0.05$). All samples underwent malolactic fermentation, such that levels of malic acid fell to a similar level in every case. In this respect, differences were observed between Sample #10 and the others, but were not statistically significant.

The statistical differences found in almost all of the analytical parameters considered may be due, primarily, to the influence exerted by Sample #10. This wine is produced in a more south-easterly region of the Iberian Peninsula than any of the other samples, where the climatic influence on grape maturation might be the cause of these differences in composition. Other criteria, such as free and total SO_2, although not directly related to climatology, may be associated with the need for more intensive use of this substance due to the varying climatic influence on the other wine components. Similarly, the higher malic acid values found in Sample #10 may be due to partial malolactic fermentation influenced by climatic conditions during the fermentation process (Dantas et al., 2023; Robles et al., 2019; Van Leeuwen & Darriet, 2016).

To complete this study, Fig. 1 provides information on the total number of statistically significant differences and similarities found in the various analytical parameters, among all the samples considered. It has been constructed by counting the times that each PDO (S#1 … S#10) presented similarities or differences with another PDO for a certain physicochemical parameter described in Table 4. Once this count is done, the median and average of the times that there were similarities or differences have been calculated. Therefore, this table extends the data introduced in Table 4.

As expected, the highest number of total similarities found corresponds to the malic acid content, followed by the tannin content. As mentioned earlier, all samples underwent malolactic fermentation, and so it was to be expected that the malic acid contents would be largely similar. In the case of tannins, the number of similarities found could be

Table 2
Study of the color space, color intensity and color tone for each sample analysed from MSCV® software.

PDO	X	Y	Z	CIELAB L^*	CIELAB C^*_{ab}	CIELAB h^*_{ab}	CIELAB a^*	CIELAB b^*	INT [a]	TON [b]
S#1	1.738	0.737	0.006	6.7	36.07	18.4	34.22	11.38	10.47	0.913
S#2	2.361	1.017	0.01	9.1	40.81	22.47	37.71	15.6	9.849	0.951
S#3	3.8	1.678	0.013	13.7	49.09	28.51	43.14	23.43	9.343	1.045
S#4	2.56	1.111	0.008	9.9	42.03	23.75	38.47	16.93	10.02	0.961
S#5	2.145	0.915	0.005	8.3	39.47	21.06	36.84	14.19	10.6	0.931
S#6	1.41	0.615	0.007	5.6	31.51	17.51	30.05	9.48	10.38	0.887
S#7	1.174	0.519	0.009	4.7	27.71	16.66	26.54	7.95	10.1	0.931
S#8	1.419	0.614	0.005	5.5	31.82	17.36	30.37	9.49	10.67	0.908
S#9	1.964	0.838	0.006	7.6	38.01	19.95	35.73	12.97	10.35	0.972
S#10	2.346	1.013	0.008	9.1	40.63	22.56	37.52	15.59	10.03	0.995

[a] : INT is wine color intensity.
[b] : TON is wine color tone.

Table 3
Principal Component Analysis for color space, INT and TON from MSCV® software.

Component Number	Eigenvalue x 10/Percentage variance	Cumulative percentage
1	87.778	87.778
2	9.710	97.488
3	1.921	99.409
4	0.448	99.856
5	0.120	99.977
6	0.022	99.999
7	0.001	100.000
8	0.000	100.000
9	0.000	100.000
10	0.000	100.000

PDO	Component 1 coefficient	Component 1 Value
S#1	0.334839	32.7125626
S#2	0.334979	39.40641342
S#3	0.251358	50.84062203
S#4	0.334887	41.23236923
S#5	0.322762	37.16227153
S#6	0.33516	28.50004822
S#7	0.312986	25.05868955
S#8	0.334756	28.54619125
S#9	−0.283609	35.32605688
S#10	0.30558	39.27091284

Component 1 Color = 0.334839*X+0.334979*Y+0.251358*Z+0.334887 *CIELAB L^*+0.322762*CIELAB C^*_{ab}+0.33516*CIELAB h^*_{ab}+0.312986* CIELAB a^*+0.334756*CIELAB b^*-0.283609*INT+0.30558*TON.

understood as a consequence of the grape variety (Tempranillo), the harvest quality (Excellent), and the predominantly northern location of most of these PDOs.

However, other parameters usually associated with polyphenolic content (such as TPI, Flavonoids, Photochem results, ABTS and DPPH) show minimal similarities. This diversity might be explained by the fact that all these wines are classified as "*Crianza*" and meet the legal requirements for this aging category. However, the regulations do not specify the exact number of months the wine should remain in the wood or bottle, but only a minimum period. Hence, there is considerable variability in the aging periods applied, which directly influences parameters closely related to polyphenolic content, given the profound changes in polyphenolic content that occur during aging (Del Barrio Galán et al., 2022).

The highest number of total differences among the samples were found in the colour (Component 1 color), followed by the total SO_2 content. All the samples were derived from the same grape variety (Tempranillo) and corresponded to harvests classed as Excellent or Very good (Table 1). Therefore, and due to a similar synthesis of colouring compounds during grape veraison, one might expect them all to present a very similar colour. However, the final colour in a wine does not depend solely on the colouring content of the grape during veraison, but also on other factors inherent to the winemaking process (Pérez-Gil et al., 2022; Uysal et al., 2023).

In our study, the colour differences found are probably due to differences in skin maceration times during the winemaking process. Moreover, as mentioned above, the known influence of the aging period on the colour of the wine and the impossibility of ascertaining the actual time the samples remained in the wood/bottle, beyond the minimum periods established for the "*Crianza*" designation, could also account for the different colours observed in these wines. In short, the combination of these two factors (maceration and aging) would underlie the differences found in this parameter (Pérez-Gil et al., 2022; Uysal et al., 2023).

By contrast, differences are to be expected in the total SO_2 contents of the samples considered, in view of the wide range of application of this additive, which each producer can employ according to their specific needs, as long as the legally established maximum content for total SO_2 is respected (Zagrodzki et al., 2023).

Fig. 2 shows the number of statistically significant differences (and similarities) expressed as the medians, obtained from Fig. 1, found among the various PDOs. We observe that Sample #9 presents the highest number of differences, followed by Samples #8 and #10. Sample #9 is produced in the north-east of the study zone, and corresponds to Excellent harvest quality. Accordingly, Sample #9 can be considered the most distinctive of the PDOs analysed. Sample #8 is also produced in the north-east and has a similar number of statistically significant differences (Fig. 2), but is considered of lower harvest quality than Sample #9. Hence, this sample, too, is notably different from the other PDOs analysed. For the remaining PDOs, most of the harvests involved are classed as Excellent, but Sample #8 has the lower Very Good harvest quality, and perhaps for that reason, the number of differences found is higher.

Samples #8 and #9 are both produced in Eastern Spain, which may have influenced their unique properties. In previous research, Quesada-Granados et al. (2018) confirmed that Sample #8 was different from the other samples and was preferred by consumers. Sample #10 also presented a large number of statistically significant differences from the other samples. The harvest quality of this PDO is unknown, but like Samples #8 and #9, it is produced in eastern Spain. The Mediterranean influence may contribute to the uniqueness of Samples #8 and Sample #10, while for Sample #9, both the location and the harvest quality may play a significant role (Van Leeuwen & Darriet, 2016). It is noteworthy that Sample #10 is a recent PDO. In this case, we hypothesise that the producers may have employed production and winemaking strategies specifically aimed at differentiating their wine from that of more traditional competitors.

The highest number of statistically significant similarities were found for Samples #3 and #4 (Fig. 2). Both these PDOs are produced in northern Spain, while Sample #3 is more centrally situated in the peninsula. Both of the northern PDOs have a longstanding winemaking tradition, and in both cases the 2010 harvest quality was rated as Excellent. Five of the ten PDOs considered are produced in northern

Table 4
Chemometric study of the physicochemical characteristics of the PDO wines analysed, after applying the ANOVA, Fisher LSD and Kruskal-Wallis tests.

	S#1	S#2	S#3	S#4	S#5	S#6	S#7	S#8	S#9	S#10
Alcohol content ($p \leq 0.001$)	14.10 ± 0.40 (e)	13.45 ± 0.10 (b)	14.30 ± 0.15 (f,a,c)	13.95 ± 0.05 (d,a,c)	14.45 ± 0.15 (g,a,c)	13.75 ± 0.15 (c,a,b,d)	14.50 ± 0.30 (i,c,e)	14.45 ± 0.25 (h,c,e,g)	15.20 ± 0.20 (k)	12.75 ± 0.15 (a)
Reducing Sugars ($p \leq 0.001$)	1.20 ± 0.10 (a)	1.40 ± 0.15 (b,a)	2.10 ± 0.15 (i)	1.50 ± 0.10 (c,a,k)	1.60 ± 0.05 (e,a,c,k)	1.70 ± 0.20 (f,c,e,k)	1.50 ± 0.18 (d,a,c,e,f,k)	2.30 ± 0.18 (k,i)	1.90 ± 0.14 (h,i,f,k)	1.70 ± 0.06 (g)
Volatile acidity ($p \leq 0.01$)	0.71 ± 0.07 (k,i)	0.45 ± 0.12 (b)	0.54 ± 0.04 (e,b)	0.55 ± 0.06 (f,b,e)	0.53 ± 0.05 (d,b,e,f)	0.40 ± 0.07 (a,b,d)	0.60 ± 0.08 (g,k,e,f,d,i)	0.51 ± 0.08 (c,b,e,f,d,a,g)	0.60 ± 0.11 (h,k,e,f,d,g,c,i)	0.70 ± 0.06 (i)
Total acidity ($p \leq 0.001$)	5.70 ± 0.30 (i)	5.30 ± 0.20 (e)	4.60 ± 0.30 (a)	5.30 ± 0.20 (f,i,e)	5.30 ± 0.40 (g,i,e,f)	4.70 ± 0.30 (b,a)	5.30 ± 0.10 (h,i,e,f,g)	5.10 ± 0.30 (c,e,f,g,b,h)	5.10 ± 0.40 (d,e,f,g,b,h,c)	6.20 ± 0.30 (k)
Malic acid ($p > 0.05$)	0.09 ± 0.03 (a)	0.09 ± 0.02 (b,a)	0.09 ± 0.03 (c,a,b)	0.09 ± 0.04 (d,a,b,c)	0.09 ± 0.01 (e,a,b,c,d)	0.09 ± 0.02 (f,a,b,c,d,e)	0.09 ± 0.01 (g,a,b,c,d,e,f)	0.09 ± 0.03 (h,a,b,c,d,e,f,g)	0.09 ± 0.02 (i,a,b,c,d,e,f,g,h)	1.22 ± 0.07 (k)
Free sulfur dioxide ($p \leq 0.001$)	12.00 ± 3.00 (b)	9.00 ± 1.00 (a,b)	24.00 ± 4.00 (i,h)	22.00 ± 1.00 (f,i,h)	24.00 ± 2.00 (k,i,f,h)	19.00 ± 1.00 (c,f)	20.00 ± 3.00 (d,f,c,h)	21.00 ± 1.00 (e,i,f,k,c,d,h)	22.00 ± 1.00 (g,i,f,k,c,d,e,h)	23.00 ± 2.00 (h)
Total sulfur dioxide ($p \leq 0.001$)	47.00 ± 3.00 (b)	46.00 ± 1.00 (a,b)	70.00 ± 6.00 (e)	84.00 ± 4.00 (h)	82.00 ± 5.00 (g,h)	58.00 ± 3.00 (c)	65.00 ± 3.00 (d,e)	80.00 ± 3.00 (f,h,g)	95.00 ± 3.00 (i)	125.00 ± 6.00 (k)
TPI (folin) ($p \leq 0.001$)	2990.00 ± 75.00 (k)	2882.00 ± 97.00 (i,k)	2715.00 ± 65.00 (e)	2695.00 ± 85.00 (d,e)	2590.00 ± 50.00 (c,d)	2795.00 ± 59.00 (g,i,e,d)	2806.00 ± 42.00 (h,i,e,d,g)	2750.00 ± 50.00 (f,e,d,g,h)	2483.00 ± 67.00 (b,c)	2315.00 ± 47.00 (a)
Tannins ($p \leq 0.05$)	795.00 ± 49.00 (a)	815.00 ± 25.00 (b,a,g)	850.00 ± 34.00 (d,a,g,b)	862.00 ± 32.00 (f,g,b,d)	880.00 ± 34.00 (i,g,d,f)	852.00 ± 43.00 (e,a,g,b,d,f,i)	876.00 ± 34.00 (h,g,d,f,i,e)	815.00 ± 33.00 (c,a,g,b,d,f,e)	895.00 ± 29.00 (k,g,d,f,i,e,h)	875.00 ± 36.00 (g)
Flavins ($p \leq 0.001$)	1700.00 ± 48.00 (k)	1692.00 ± 34.00 (i,h)	1650.00 ± 34.00 (h,k)	1632.00 ± 20.00 (g,i,h)	1459.00 ± 42.00 (c,b)	1548.00 ± 44.00 (d)	1568.00 ± 43.00 (f,d)	1551.00 ± 18.00 (e,d,f)	1432.00 ± 28.00 (b,a)	1396.00 ± 34.00 (a)
Photochem ($p \leq 0.001$)	1.50 ± 0.06 (k)	1.45 ± 0.07 (i,k)	1.05 ± 0.04 (d)	1.10 ± 0.06 (f,d)	1.00 ± 0.05 (c,d,f)	1.36 ± 0.06 (h,i)	1.10 ± 0.08 (g,d,f,c)	1.05 ± 0.05 (e,d,f,c,g)	0.98 ± 0.04 (b,d,c,e)	0.84 ± 0.08 (a)
ABTS ($p \leq 0.001$)	26.84 ± 0.31 (k)	25.32 ± 0.47 (i)	23.89 ± 0.36 (f)	23.56 ± 0.41 (e,f)	23.15 ± 0.30 (c,e,d)	24.55 ± 0.37 (h,g)	24.03 ± 0.25 (g,f,e)	23.35 ± 0.21 (d,f,e)	22.95 ± 0.25 (b,c,d)	22.05 ± 0.31 (a)
DPPH ($p \leq 0.001$)	4.10 ± 0.19 (e)	5.10 ± 0.26 (g)	5.50 ± 0.38 (k,g)	5.30 ± 0.25 (i,g,k)	4.90 ± 0.40 (f,g,i,h)	5.20 ± 0.38 (h,g,k,i)	3.30 ± 0.19 (b,a)	3.80 ± 0.38 (d,e,b)	3.50 ± 0.18 (c,a,b,d)	3.10 ± 0.32 (a)
Component 1 color ($p \leq 0.001$)	32.71 ± 0.19 (d)	39.41 ± 0.26 (h,g)	50.84 ± 0.42 (k)	41.23 ± 0.09 (i)	37.16 ± 0.25 (f)	28.50 ± 0.03 (b)	25.06 ± 0.48 (a)	28.55 ± 0.27 (c,b)	35.33 ± 0.12 (e)	39.27 ± 0.09 (g)

Letters (x) are read per line and for each parameter, thus, the same letter indicates $p > 0.05$; Alcohol content % V/V; Reducing sugars g/L; Volatile acidity g/L Acetic acid; Total acidity g/L Tartaric acid; Malic acid g/L; Free SO_2 mg/L; Total SO_2 mg/L; TPI (folin) μg/L Gallic acid; Tannins μg/mL; Flavins μg/mL; Photochem mM ascorbic equivalent; ABTS mM trolox equivalent; DPPH mM trolox equivalent.

regions, and in each of these cases the harvest quality is considered Excellent. This circumstance, combined with the traditional methods employed in the production of Samples #3 and #4, may account for the higher number of similarities observed. Moreover, the acknowledged winemaking tradition of these PDOs could have served as an inspiration for other wine-producing regions, leading them to mimic aspects of their winemaking production. Hence, the number of similarities found among these PDOs, which although not excessive (3.5 and 3 out of a possible 9), distinguishes them from the other PDOs considered.

The retail prices of the samples varied significantly ($p \leq 0.001$) according to the location of the PDO (Table 1), but no such differences were observed according to harvest quality ($p > 0.05$). When neither of these factors was taken into account, the prices continued to vary significantly ($p \leq 0.001$), although this might simply be attributed to the commercial and competitive criteria of the producers.

To complete the chemometric study, we performed a multivariate analysis of all the analytical criteria considered, in order to identify global differences among the samples, and hence among the different PDOs.

In this process, we first conducted a cluster analysis to reveal the similarities and differences among the samples, according to the physicochemical parameters considered. This was done using the Nearest Neighbour classification method, as this was the only one that respected the initial distribution of the samples by origin. The agglomeration criterion used was Squared Euclidean (Gutierrez & Gonzalez, 1991; Álvarez, 1995; Santos & Pérez, 1996). Fig. 3a shows the dendrogram obtained in the cluster analysis. To more clearly visualize the relationships observed in the cluster analysis, Fig. 3b has been created based on a Principal Components Analysis (Alonso González et al., 2024).

The samples identified in the earliest stage of agglomeration, and thus the most similar, are Samples #4 and #5. Both PDOs correspond to an Excellent harvest, are produced in northern regions and enjoy similar soil and climatic conditions. However, their average selling prices differ considerably (Table 1), in contrast to what might be expected from their physicochemical similarity (Table 4).

The second level of agglomeration is formed by the cluster of Samples #4, #5 and #9. Sample #9 also originates from a northern region of the peninsula, and shares soil characteristics with the other PDOs at this level of agglomeration. Its market price is similar to that of Sample #5 (Table 1).

The third level of agglomeration contains only Samples #1 and #2, both with an Excellent vintage rating. Although the production zones of these samples are both in the north of the peninsula, there is some distance between them, with Sample #1 being located the further to the north of the two. Due to proximity alone, Sample #2 might be expected to form part of the same cluster as Samples #1, #4 and #5. Indeed, these wines are all very similarly priced (Table 1).

From this point onward, the initial cluster of Samples #4 and #5 is successively joined, in the following order, by Samples #3, #7, #6 and #8. This successive agglomeration initially follows a logical sequence in terms of the respective geographical locations, progressing southwards through the peninsula. However, this logic is disrupted with the

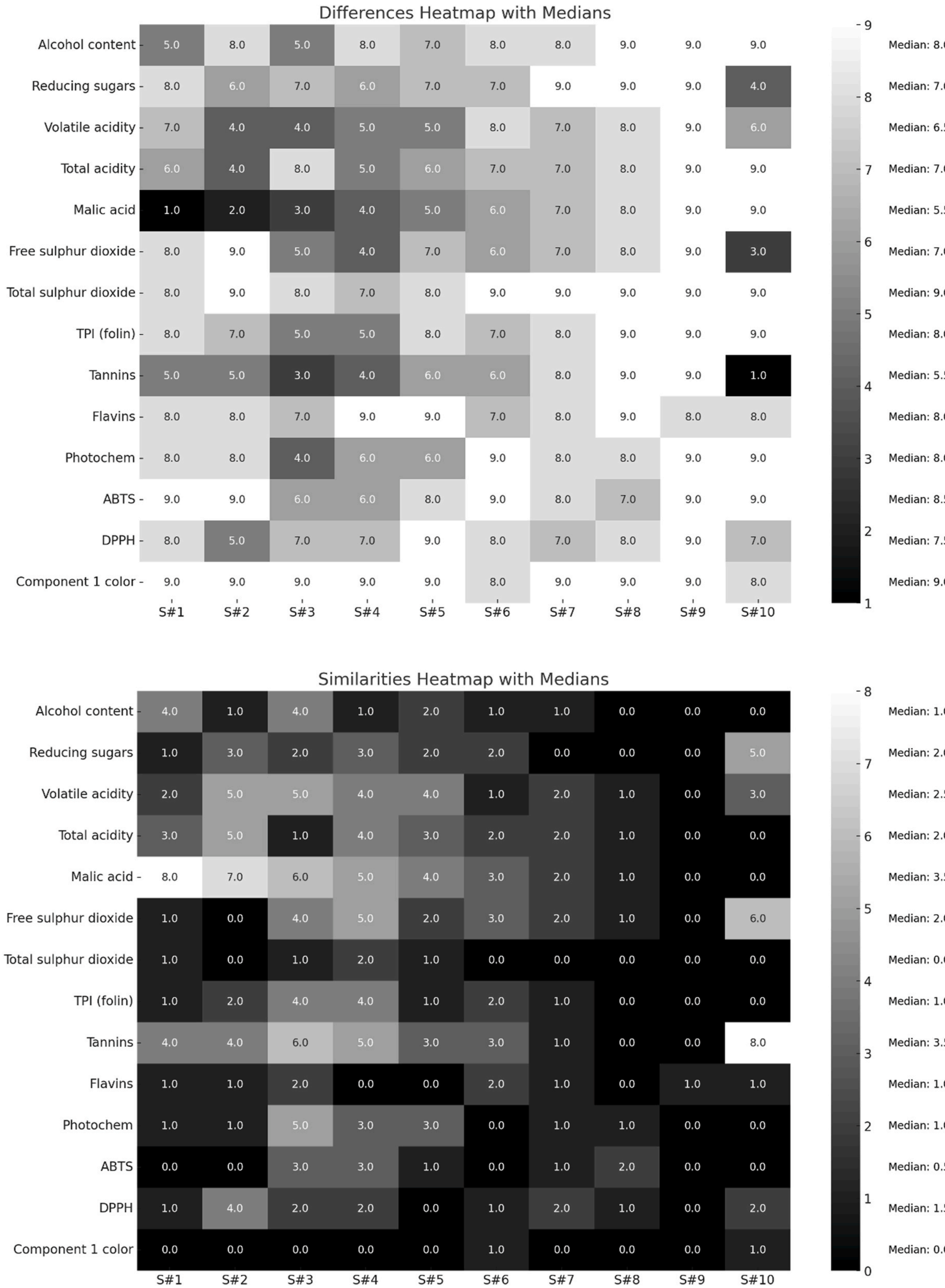

Fig. 1. Overall statistically significant similarities and differences between the different physicochemical determinations.

inclusion of Sample #8, which is situated in the northeast. Sample #7 is rated as a Very good vintage, while the others are considered Excellent. However, the proximity between Samples #6 and #7 may explain their successive agglomeration. This is not the case for Sample #8, which joins the cluster at level seven. Given its geographical location, one might expect it to join the main cluster at earlier levels of agglomeration. The unique position of Sample #8 could be explained by its vintage quality (Very good), which, combined with its geographical location, distinguishes it from the other samples. The retail prices of these samples vary considerably, with Samples #3 and #8 costing almost twice as much as Samples #6 and #7. Samples #1 and #2 are only incorporated into the main cluster in the penultimate level, suggesting there are

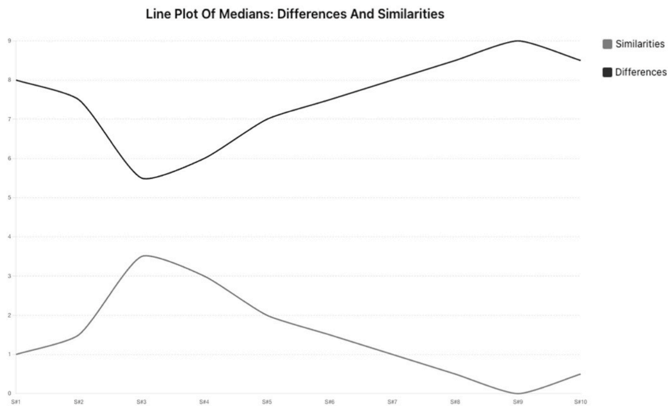

Fig. 2. Overall statistically significant similarities and differences between the different PDOs.

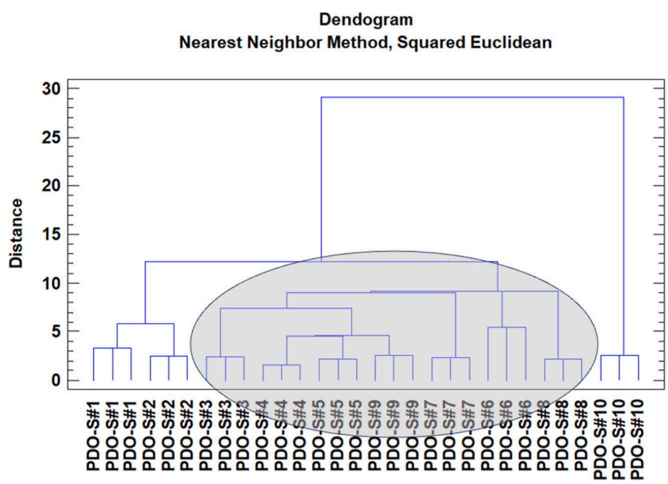

Fig. 3a. Dendrogram obtained after applying Cluster Analysis for physicochemical determinations data.

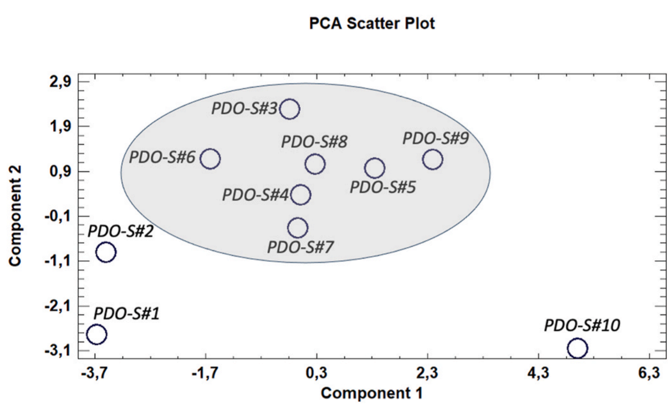

Fig. 3b. Scatter Plot obtained after applying Principal Component Analysis for physicochemical determinations data.

significant differences between the components of these two clusters. As expected, Sample #10, the southernmost of those analysed, joins the cluster at the last level, confirming the differences between this PDO and the rest, undoubtedly due to its geographical location and characteristic climatic conditions. Although the vintage quality is unknown, the price of this wine is among the highest, together with Samples #5 and #9, which may be indicative of Excellent quality. In summary, our principal components analysis distinguishes three main groups based on similarities: one with Samples #3, #4, #5, #6, #7, #8 and #9, a second group with Samples #1 and #2 and the third group with Sample #10 alone.

3.2. Sensory study

The sensory similarities and differences identified in the triangular test are detailed in Table 5. In total, 45 tasting sessions were conducted, following the methodology described above, comparing all the PDOs included in the analysis. Statistically significant sensory differences were found in only 29% of these cases. In the remaining comparisons, the tasters detected no significant differences between the wines. All of the statistically significant differences revealed by the triangular test involved Samples #9 and #10. However, these two PDOs also recorded the highest number of differences among all the PDOs according to the chemometric study. In the case of Sample #9, only in the comparisons with Samples #3, #6 and #8 were the differences not statistically significant. In other words, the tasters perceived similarities between Samples #3, #6, #8 and #9. The remaining comparisons with Sample #9 were statistically significant, with more than 25 correct responses (25 is the minimum number of correct responses needed to infer the existence of statistically significant differences). It is important to note that Samples #3, #8 and #9 are all located in the north of the peninsula, while Sample #6 is situated in the south-central region. For the tasters, the highest number of comparisons with significant differences involved Sample #10. Only in the comparisons with Samples #6 and #7 were no differences found. The remaining comparisons produced statistically different results, although in three cases, they exactly met the minimum number of correct responses (25) required. By region of production, Sample #10 was the southernmost of the PDOs considered. Finally, the tasters found differences between Samples #1 and #7, albeit with the minimum number of correct responses. This difference is readily explicable, as the PDOs in question are located far apart within the Iberian peninsula and were obtained from harvests with different qualities, namely Excellent for Sample #1 compared to Very good for Sample #7. Other than the comparisons mentioned above, the tasters did not find statistically significant differences. In all these comparisons, the median number of correct responses was 18, well below the 25 required to infer the existence of statistically significant differences.

The tasting sheet included an optional question related to the attribute(s) that, according to the tasters' criteria, had allowed them to differentiate the sample within each triad, regardless of whether this difference was correctly deduced. Fig. 4 details the attributes noted by the tasters during the comparison sessions. In fact, the majority of tasters (63%) did not answer this question, either because they did not have a clear understanding of the attribute(s) that might contribute to making the sample different, or simply due to negligence or fatigue. The attributes that were noted as enabling them to identify the different sample were: "woody aroma", "acidity", "astringency/dryness", "aftertaste" and "aroma". The woody aroma is the typical aroma of wines that have aged in wood, mainly oak as in our case, and where hints of vanilla, cinnamon, cloves or even coconut can predominate. It is an aroma that is usually predominant on the nose at first smell, although it then gives way to other olfactory notes. The taste sensation of acidity refers to the sensation of freshness when taking a sip of wine and usually produces salivation to help balance the action of tannins. The astringency or dryness produced by a red wine refers to the tactile sensation experienced in the mouth when drinking and is mainly a consequence of the presence of tannins in the wine. Dry mouth appears due to the precipitation of saliva proteins while the salivary channels are blocked. The aftertaste in a red wine refers to the flavors and sensations that remain in the mouth after swallowing the wine and can include fruity, spicy, earthy, mineral flavors, among others, depending on the wine but generally as a pleasant sensation (Issa-Issa et al., 2021). The aftertaste is important because it can reveal a lot about the quality, complexity and structure of the wine, although not all tasters are able to extract all that

Table 5
Similarities and sensory differences according to the triangular test. Indicated as statistical significance level/number of correct responses.

PDO	S#1	S#2	S#3	S#4	S#5	S#6	S#7	S#8	S#9	S#10
S#1		$p > 0.05/19$	$p > 0.05/17$	$p > 0.05/20$	$p > 0.05/16$	$p > 0.05/21$	$p \leq 0.05/25$[a]	$p > 0.05/19$	$p \leq 0.05/26$[a]	$p \leq 0.05/27$[a]
S#2			$p > 0.05/18$	$p > 0.05/19$	$p > 0.05/19$	$p > 0.05/19$	$p > 0.05/17$	$p > 0.05/16$	$p \leq 0.05/27$[a]	$p \leq 0.05/25$[a]
S#3				$p > 0.05/21$	$p > 0.05/15$	$p > 0.05/15$	$p > 0.05/14$	$p > 0.05/20$	$p > 0.05/21$	$p \leq 0.05/26$[a]
S#4					$p > 0.05/17$	$p > 0.05/16$	$p > 0.05/16$	$p > 0.05/18$	$p \leq 0.05/28$[a]	$p \leq 0.05/25$[a]
S#5						$p > 0.05/18$	$p > 0.05/21$	$p > 0.05/16$	$p \leq 0.05/26$[a]	$p \leq 0.05/26$[a]
S#6							$p > 0.05/18$	$p > 0.05/17$	$p > 0.05/17$	$p > 0.05/19$
S#7								$p > 0.05/19$	$p \leq 0.05/27$[a]	$p > 0.05/18$
S#8									$p > 0.05/20$	$p \leq 0.05/26$[a]
S#9										$p \leq 0.05/25$[a]
S#10										

[a] Indicates statistically significant differences.

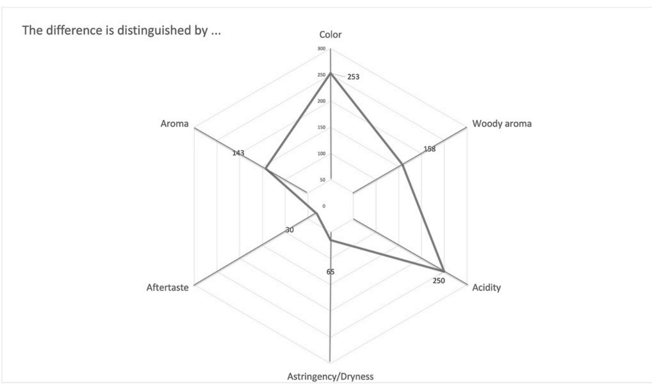

Fig. 4. Attributes detected by tasters during tasting sessions.

information from the aftertaste sensation. The aroma sensation, without specifying anything else, refers to any aromatic and gustatory attribute that the tasters could find in the red wine and that could allow them to differentiate between one wine or another. Fig. 4 illustrates the distribution of the attributes reported by the tasters, among which acidity and colour were the most commonly mentioned, each at 28%. Differences in colour might have been generated in the aging process, as although all samples were "*Crianza*", this term only stipulates a minimum time in the wood/bottle. In consequence, the real aging time may vary greatly from one sample to another, thus influencing its colour. Another attribute that could have differentiated the samples is that of acidity, which the chemometric study showed to vary greatly among the samples. The *woody aroma* attribute was indicated in 18% of the tasters' responses. Again, this could be a consequence of different aging times. The tasters mentioned this attribute *aroma* as the differentiator in a further 16% of cases, but without further description. This attribute may be the result of multiple sensory factors, making it difficult to attribute a more specific origin. The sensations of astringency and dryness of the mouth were referenced as the differentiating attribute in only 7% of the responses. It is curious that this attribute, which is closely related to aging time and acidity but also to the Tempranillo variety (Serrano et al., 2024) for the reasons already mentioned, was not indicated by the majority of tasters.

4. Conclusions

Individually, significant differences were mostly found in the physicochemical and chromatic characteristics of the samples. When the characteristics of the 2010 Tempranillo "*Crianza*" red wines are analysed together, many similarities appear between the Protected Designations of Origin samples, leaving only some of them substantially different from the rest. Similar to what was observed in the chemometric study, the sensory study also demonstrates that most Protected Designations of Origin samples present similarities, with very few being found to be different. Likewise, despite the geographical and soil similarities, the retail prices of red wines from the PDOs varied without any significant influence on these prices because of the quality of the harvest. In conclusion, it can be stated that there are great similarities in most protected designations of origin studied, with only a few being considered sufficiently different. However, despite most similarities, the prices of the "*Tempranillo Crianza 2010*" red wines are very different.

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Declarations of interest.

The authors have no conflict of interest to declare regarding this study.

Ethics approval was not required for this research.

CRediT authorship contribution statement

José Javier Quesada-Granados: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Cristina Samaniego-Sánchez:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Silvia Pastoriza de la Cueva:** Investigation, Formal analysis. **Marina Villalón-Mir:** Investigation, Funding acquisition. **Miguel Navarro-Alarcón:** Writing – review & editing, Investigation, Funding acquisition. **José A. Rufián-Henares:** Writing – review & editing, Resources, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fbio.2024.104561.

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