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Volatile profile of wine Teran PTP

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ABSTRACT

Teran PTP is a protected wine with a recognized traditional denomination produced from a grapevine variety 'Refošk' in winegrowing district Kras in Slovenia (European Union, 2009; Pravilnik, 2008). The aromatic profile of 82 Teran PTP wines produced in years 2011, 2012 and 2013 was monitored. In total the content of 16 volatile compounds was determined. The volatile compounds from wine were extracted following the liquid-liquid extraction and determined with a GC-MS method. The odour activity values and relative odour contributions were calculated for each volatile compound identified. Among sensorial important volatiles the highest odour activity values were determined for ethyl octanoate, ethyl hexanoate, isoamyl acetate and ethyl butyrate. Other research papers also showed, that all red wines investigated except one contained ethyl octanoate, ethyl hexanoate, isoamyl acetate and ethyl butyrate above sensory thresholds.

Key words: Teran PTP, wine, volatile compounds, esters, aroma, GC/MS

IZVLEČEK

AROMATIČNE SPOJINE VINA TERAN PTP

Vino Teran PTP je zaščiteno vino s priznanim tradicionalnim poimenovanjem, ki ga pridelujejo iz grozdja sorte 'Refošk' v vinorodnem okolišu Kras v Sloveniji (European Union, 2009; Pravilnik, 2008). Aromatični profil vina Teran PTP smo spremljali tri leta v 82 vzorcih iz letnikov 2011, 2012 in 2013. Določevali smo vsebnost 16 hlapnih spojin. Za določitev hlapnih spojin smo uporabili ekstrakcijo tekoče-tekoče, kateri je sledila določitev z GC-MS. Za vseh 16 spojin smo izračunali aktivne vonjalne vrednosti in njihove relativne prispevke. Med senzorično pomembnimi hlapnimi spojinami smo največje aktivne vonjalne vrednosti določili za etil oktanoat, etil heksanoat, izoamil acetat in etil butirat. Drugi raziskovalni članki so tudi pokazali, da so vsa preiskovana rdeča vina z izjemo enega vsebovala etil oktanoat, etil heksanoat, isoamil acetat in etil butirat nad pragom zaznave.

Ključne besede: Teran PTP, vino, hlapne spojine, estri, aroma, GC/MS

1 INTRODUCTION

Teran PTP (Recognised Traditional Denomination) is a typical wine from the Kras winegrowing district of the Primorska wine growing region in Slovenia, where it is usually called just »Teran«. The production of this unique red wine has been known since the first century AD (Vodopivec, 1999). Teran PTP is a wine produced from a variety 'Refošk' and known for its deep reddish-violet colour, caused by an abundance of anthocyanins and its medium tannin content (Vanzo et al., 2012). Due to its favorable phenolic compounds (anthocyanins), it is known for having positive health effects and good nutritional value for consumers (Fornasario et al., 2012). Taste of wine teran is both astringent and sour, derived from its high phenolic content and high total acidity. The unique feature of this wine is its fruity odour, reminiscent of raspberries, strawberries and cherries. Fruity odour of Teran PTP is considered most pronounced in the first year after vinification (Vodopivec, 1999).

The volatile fraction of wine determines to a great extent its aroma, which is one of the most

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important characteristics influencing wine quality and consumer preferences (García-Carpintero et al., 2012b). However, the wine volatile fraction is extremely complex, where more than 1000 aromatic compounds have been identified, originating from different chemical groups, mostly higher alcohols, aldehydes, ethyl esters of fatty acids, fatty acids, ketones, monoterpenes and volatile phenols (Andujar-Ortiz et al., 2009). A content of listed aromatic compounds in wines range from a few ng l^{-1} to hundreds of mg l^{-1} (Andujar-Ortiz et al., 2009). The presence, abundance and various combinations of volatile compounds can be greatly affected by viticultural practices (variety, cultivation, grape thinning etc.), environmental conditions (climate, soil) and oenological measures (fermentation, yeasts, post-fermentation treatments etc.) (Ribéreau Gayon et al., 2006; Welke et al., 2014).

Not all volatile compounds present in wine contribute to aroma (Welke et al., 2014). The influence of volatile compounds on the final aroma depends on their content and the specific perception threshold of each compound. The threshold of olfactory perception is defined as the lowest content capable of producing an olfactory sensation detected by the human nose, and that can be identified by at least 50 % of the judges on a sensory evaluation panel (Welke et al., 2014).

In our research, esters were of particular interest as they are usually responsible for the typical aroma of most not-aromatic varieties of wine (Etievant 1993; Ferreira et al, 1995). One factor that supports the use of this approach is the typical fruity smell of Teran PTP wines, which is correlated to abundant contents of esters. The results of the present study are particularly interesting, since the aromatic profile of Teran PTP wine has never been investigated before and even less over a multi-year period. Previous studies of Teran PTP were mostly concentrated on phenolic compounds and their influence on wine technologies or wine quality (Novak, 2011; Vrščaj Vodošek and Košmerl, 2004).

To determine the volatile compounds in the wine, different analytical techniques were used: discontinuous or continuous liquid-liquid extraction (LLE) (Andujar-Ortiz et al., 2009), solid phase extraction (SPE) (García-Carpintero et al., 2012a; García-Carpintero et al., 2014), solid phase microextraction (SPME) (Revi et al., 2014) and stir bar sorptive extraction (SBSE) (Martínez-Gil et al., 2012; Košmerl and Zlatić et al., 2009). It should be mentioned that the LLE technique is slowly being replaced by more manageable and solvent-free techniques. However, this type of extraction is still a reference technique used for wine aromatic compounds extraction. The main advantages of this technique are its capacity to extract a wide range of compounds of different volatilities (as long as they have an affinity to the solvent), its high repeatability level and the possibility of carrying out simultaneous extractions (Andujar-Ortiz et al., 2009). For determination, gas chromatography (GC) was used, coupled to a flame ionization detector (FID) (Pino and Queris, 2011; Moreno-Pérez et al., 2013) or a mass spectrometer (MS) (Callejón et al., 2009; Pino and Queris, 2011). The mass spectrometer is the most widely used, because it enables unequivocal qualitative and quantitative detection of substances. Quantitative detrermination of the impact of aromatic compounds on the overall aroma of wine can be done by calculating the odor activity value (OAV) and relative odour contribution (ROC). On the other hand, a qualitative evaluation can be done based on the odor descriptors of each component e.g., floral, fruity, green, solvent, plastic, toasted and others (Welke et al., 2014).

The aims of the present work are to present a volatile profile of Teran PTP wine produced in the Primorska winegrowing region (Kras district) in vintages 2011, 2012 and 2013 and a differentiation of an obtained volatile profile from other red wines. We focused our research on the different groups of volatile compounds formed during alcoholic fermentation together with C6 compounds deriving from the grapes. Some wine physico-chemical characteristics were also determined for all samples and presented in the article.

2 MATERIALS AND METHODS

2.1 Samples

The Teran PTP wine samples were collected from the winegrowing district Kras wine producers directly from stainless steel tanks and/or wooden barrels. During a three-year monitoring period, 82 wines were sampled from different producers; 39 samples from the 2011 vintage, 22 samples from the 2012 vintage and 21 samples from the 2013 vintage. The wines were sampled 9 months after fermentation, after the completion of malolactic fermentation and before bottling. Analyses of the volatile compounds and standard wine parameters were performed one month after sampling at the Central Laboratories of the Agricultural Institute of Slovenia.

2.2 Materials used for determining the volatile compounds

The standard volatile compounds, with the highest available purity (minimum of 98 %), were obtained from Merck, Sigma Aldrich, Fluka and SAFC. Stock solutions of each of the standard volatile compounds in pure dichloromethane were prepared with contents ranging from 1.8 to 2.5 g l^{-1}. From the stock solutions, one mixed solution of all the minor volatile compounds was prepared. The final standards were prepared with proper dilutions from this flask. Internal standard 4-nonanol (0.12 g dissolved in 100 ml dichloromethane) was added using a 0.05 ml Hamilton syringe to 10 ml of dichloromethane standard solution and mixed.

2.3 Extraction and determination of volatile compounds

For the extraction of minor volatile compounds (μg l^{-1}), discontinuous liquid-liquid extraction (LLE) with dichloromethane (Sigma-Aldrich) was used. The wine (100 ml) was then transferred into a 250 ml Erlenmeyer flask. To this, 23 μg of 4-nonanol was added as an internal standard, using a 0.05 ml Hamilton syringe from the corresponding ethanol solution. Dichloromethane (40 ml) was added and the mixture was stirred at 350 rpm for 20 min. Then the mixture was centrifuged (8500 g, 10 min) and the organic phase was recovered. The aqueous phase was re-extracted twice, using the same method. Finally, the organic phases were combined and dried over sodium sulphate. They were concentrated to a final volume of 1 ml with a rotary evaporator and nitrogen gas flow prior to GC–MS analysis. This method is described in detail in other articles (Bavčar et al., 2011a; Bavčar et al., 2011b; Bavčar and Baša Česnik, 2011).

2.4 Calculation of odour activity value and relative odour contribution

The OAV is a quantitative approach for determining the impact that volatile compounds have on the aroma of wine. The OAV is obtained from the ratio between the content of an individual compound and its perception threshold. A volatile compound contributes to aroma when its content in wine is above the perception threshold. Therefore, only compounds with an OAV>1 can be perceived. (Pino and Queris, 2011; Welke et al., 2014). Another quantitative factor is the relative odor contribution (ROC), which is the percentage of the impact of a particular aroma compound. It is the ratio of the OAV percentage of each individual compound and the sum of the OAV of compounds that showed OAV>1 (Welke et al., 2014).

2.5 Statistical analysis

Data were collected and edited using Excel (Microsoft Office Professional Plus 2010) and analysis of variance (one-way ANOVA) was performed on physico-chemical characteristics and aromatic compounds data using Statgraphics® Centurion XVI statistical software package (StatPoint Technologies).

3 RESULTS AND DISCUSSION

Over a three-year period, we also monitored the basic parameters of Teran PTP wine. The results of the wine physico-chemical characteristics were obtained by adhering to standard EEC methods (European Union, 1990). These results are presented in Table 1. Most of statistically different physico-chemical characteristics were found in wines from 2011 vintage. But differences between the 2011, 2012 and 2013 vintages are not extensive and most probably caused only by different climatic conditions (Ribéreau Gayon et al., 2006; Vodopivec, 1999). We can confirm that Teran PTP wines contain moderate levels of alcohol (12 vol %), are high in total dry extract and acidity levels, and have surprisingly low contents of both free and total sulphur dioxide in correlation with regulation's demands (Pravilnik, 2004).

Table 1: Average physico-chemical characteristics of Teran PTP wines for the 2011, 2012 and 2013 vintages

Preglednica 1: Povprečne fizikalno-kemijske značilnosti vin Teran PTP letnikov 2011, 2012 in 2013

	Vintage 2011	Vintage 2012	Vintage 2013
	n=39	n=22	n=21
Alcohol (vol. %)	12.01±0.60 A	11.95±0.58 A	12.06±0.46 A
Extract (g l^{-1})	30.0±2.4 B	27.3±1.7 A	27.1±2.6 A
Total acidity (g l^{-1} as tartaric)	7.5±0.7 A	8.0±0.8 B	7.5±0.8 AB
Volatile acids (g l^{-1}as acetic)	0.62±0.17 B	0.45±0.11 A	0.73±0.13 C
Free SO_2 (mg l^{-1})	13±3 B	12±1 A	12±4 A
Total SO_2 (mg l^{-1})	43±6 B	40±9 B	35±7 A
pH	3.37±13 B	3.26±0.12 A	3.33±0.14 AB
Relative density	0.9958±0.0001 B	0.9948±0.0007 A	0.9946±0.0008 A
Lactic acid (g l^{-1})	2.1±0.4 B	1.5±0.4 A	2.5±0.6 C
Reducing sugar (g l^{-1})	2.5±0.7 B	1.2±0.3 A	1.3±0.7 A

n = number of samples
all data present mean value ± standard deviation
significant differences between vintages are indicated A, B, C at $p \leq 0.05$

The focus of our research was to determine the presence of certain volatile compounds in Teran PTP wines from the 2011, 2012 and 2013 vintages. The results are presented in Table 2. We found that Teran PTP wine contains high amounts of 1-hexanol (the mean value of the three vintages was 1292 µg l^{-1}) and γ-butyrolactone (the mean value of the three vintages was 12920 µg l^{-1}). We also found significant amounts of 2-phenyl-ethyl-acetate (the mean value of the three vintages was 49 µg l^{-1}), isoamyl acetate, benzaldehyde, benzyl alcohol, *cis*-3-hexen-1-ol, ethyl butyrate, ethyl decanoate, ethyl dodecanoate, ethyl hexadecanoate, ethyl hexanoate and ethyl octanoate.

Table 2: Contents (µg l^{-1}) of volatile compounds in Teran PTP wines from years 2011, 2012 and 2013 and their threshold values according to ((a) Li et al., 2008; (b) Duarte et al., 2010; (c) García-Carpintero et al., 2012a; (d) Rocha et al., 2004, 2005, (e) Sánchez-Palomo et al., 2012; (f) García-Carpintero et al., 2014; (g) Welke et al., 2014)

Preglednica 2: Vsebnosti (µg l^{-1}) hlapnih spojin v vinih Teran PTP letnikov 2011, 2012 in 2013 in njihovi pragovi zaznave kot navedeno v ((a) Li et al., 2008; (b) Duarte et al., 2010; (c) García-Carpintero et al., 2012a; (d) Rocha et al., 2004, 2005, (e) Sánchez-Palomo et al., 2012; (f) García-Carpintero et al., 2014; (g) Welke et al., 2014)

	Vintage 2011		Vintage 2012		Vintage 2013		Sensory treshold
	min - max	average±std	min - max	average±std	min - max	average±std	
ALDEHYDES							
n-Hexaldehide (Capronaldehide)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Benzaldehyde	n.d. - 91	8±18 A	<LOQ - 10	4±3 A	<LOQ - 75	16±20 B	350 (c, e, f)
Benzyl alcohol	42 - 799	164±152 A	67 - 474	163±90 A	42 - 842	285±210 B	200000 (c)
C6 COMPOUNDS							
1-Hexanol	310 - 2538	1205±454 A	632 - 2218	1227±462 AB	598 - 3008	1522±672 B	8000 (a, b, c, e, f)
Cis-3-hexen-1-ol	15 - 125	50±24 A	18 - 190	55±35 A	23 - 278	103±67 B	400 (c, e, f)
ESTERS							
2-Phenyl-ethyl-acetate	13 - 108	51±24 B	15 - 72	35±16 A	41-90	62±14 C	250 (b, c, e, f)
Ethyl butanoate (Ethyl butyrate)	30 - 301	116±52 B	57 - 104	80±14 A	37 - 245	108±44 B	20 (a, b, c, e, f)
Ethyl decanoate (Ethyl caprate)	29 - 237	84±45 B	23 - 84	56±16 A	73 - 291	184±57 C	200 (a, b, c, e, f)
Ethyl dodecanoate (Ethyl laurate)	n.d. - 46	29±25 A	n.d. - 13	8±4 A	n.d. - 56	40±14 A	3500 (f)
Ethyl hexadecanoate (Ethyl palamitate)	<LOQ - 717	84±141 A	1 - 152	26±42 A	2 - 751	92±163 A	1500 (a, f)
Ethyl hexanoate (Ethyl caproate)	81 - 304	186±49 B	84 - 211	157±36 A	132 - 300	191±43 B	14 (a, b, c, e, f)
Ethyl octanoate (Ethyl caprylate)	105 - 376	216±59 B	88 - 259	170±41 A	118 - 253	187±41 A	5 (a, b, c, e, f)
Hexyl acetate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1500 (a, c, e, f)
Isoamyl acetate	163 - 803	393±143 B	163 - 563	264±82 A	232 - 609	406±98 B	30 (c, e, f)
LACTONES							
γ-Butyrolactone	6840 - 18907	14036±3408 B	4444 - 12999	9423±2449 A	8401 - 19879	14512±2983 B	5000 (d)
KETONES							
β-Ionone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.5 (b)

n.d. - not detected
<LOQ - below limit of quantification
significant differences between vintages are indicated A, B, C at $p \leq 0.05$

A comparison between the three vintages shows that the 2012 vintage has a lower content of 2-phenyl-ethyl-acetate, isoamyl acetate, ethyl butyrate, ethyl decanoate, ethyl hexanoate and γ-butyrolactone than the 2011 and 2013 vintages. The lowest volatile contents were mostly found in wines from vintage 2012.

OAV and ROC values were calculated to estimate the sensory contribution of the aromatic compounds to the overall aroma of the wine. According to these calculations the most important volatile compound for Teran PTP wines was ethyl octanoate which reminiscent of sweet red cherry fruity. The second most abundant compound was isoamyl acetate reminiscent of banana, fruity and sweet smell and ethyl hexanoate with fruity, apple and strawberry odour. Important were also ethyl butyrate, with fruity odour and γ-butyrolactone described as sweet, toast and caramel. These results are presented in Table 3.

Table 3: OAV and ROC (%) values and their standard deviations for volatile compounds significant for the aroma of Teran PTP wines from the 2011, 2012 and 2013 vintages

Preglednica 3: OAV in ROC (%) vrednosti in njihovi standardni odkloni za hlapne spojine, ki so signifikantne za vonj vin Teran PTP letnikov 2011, 2012 in 2013

	OAV			ROC (%)		
	2011	2012	2013	2011	2012	2013
ALDEHYDES						
n-Hexaldehide (Capronaldehide)	0	0	0	/	/	/
Benzaldehyde	0.02 ± 0.05	0.012 ± 0.008	0.05 ± 0.06	/	/	/
Benzyl alcohol	0.0008 ± 0.0008	0.0008 ± 0.0005	0.001 ± 0.001	/	/	/
C6 COMPOUNDS						
1-Hexanol	0.15 ± 0.06	0.15 ± 0.06	0.19 ± 0.08	/	/	/
Cis-3-hexen-1-ol	0.13 ± 0.06	0.14 ± 0.09	0.26 ± 0.17	/	/	/
ESTERS						
2-Phenyl-ethyl-acetate	0.20 ± 0.09	0.14 ± 0.06	0.25 ± 0.06	/	/	/
Ethyl butyrate (Ethyl butanoate)	5.8 ± 2.6	4.0 ± 0.7	5.4 ± 2.2	7.4 ± 0.1	6.7 ± 0.1	7.4 ± 0.1
Ethyl decanoate (Ethyl caprate)	0.4 ± 0.2	0.28 ± 0.08	0.9 ± 0.3	/	/	/
Ethyl dodecanoate (Ethyl laurate)	0.008 ±0.007	0.002 ± 0.001	0.011 ± 0.004	/	/	/
Ethyl hexadecanoate (Ethyl palamitate)	0.06 ± 0.09	0.02 ± 0.03	0.06 ± 0.11	/	/	/
Ethyl hexanoate (Ethyl caproate)	13.3 ± 3.5	11.2 ± 2.5	13.7 ± 3.1	17.0 ± 0.1	18.8 ± 0.2	18.8 ± 0.2
Ethyl octanoate (Ethyl caprylate)	43.1 ± 11.7	33.9 ± 8.2	37.3 ± 8.3	55.2 ± 0.4	56.7 ± 0.6	51.2 ± 0.5
Hexyl acetate	0	0	0	/	/	/
Isoamyl acetate	13.1 ± 4.8	8.8 ± 2.7	13.5 ± 3.3	16.8 ± 0.2	14.7 ± 0.2	18.6 ± 0.2
LACTONES						
γ-Butyrolactone	2.8 ± 0.7	1.9 ± 0.5	2.9 ± 0.6	3.59 ± 0.02	3.15 ± 0.04	3.99 ±0.04
KETONES						
β-Ionone	0	0	0	/	/	/

Many of the analyzed volatile compounds in Teran PTP are below OAV. Despite this, they could express a synergistic effect with a positive character to the wine aroma. It is known, that the OAV does not provide a definitive answer to the impact that different compounds can have on the overall aroma of a wine (Benkwitz et al., 2012). The content of some compounds may significantly differ between samples, but this has little or no impact on the sensory properties of these wines. This may be due to the masking and/or enhancing effects of other volatile and nonvolatile components within the wine, found also at various content-levels (Benkwitz et al., 2012).

Although it is difficult to compare volatile compounds of Teran PTP with publish data as each author used specific method, samples were analyzed at different aging time and wines were vinificated with different technologies, we have compared volatile compounds of some other varieties with volatiles of Teran PTP (Table 4).

Table 4: Comparison of volatile compound contents in Teran PTP wines (average of three sequential vintages and their standard deviations) with the volatile compound values of a selection of Spanish red wines (μg l^{-1}) ((a) García-Carpintero et al., 2012b (average of four consecutive vintages); (b) Moreno-Pérez et al., 2013 (6 months after fermentation); (c) García-Carpintero et al., 2014 (control wine of oak treatment), New Zealand Pinot Noirs from Central Ottago (average of three regions) ((d) Imre et al., 2012) and French red wines with their standard deviations ((e) Antalick et al., 2014)

Preglednica 4: Primerjava vsebnosti hlapnih spojin v vinih Teran PTP (povprečje treh zaporednih letnikov in njihovi standardni odkloni) z vrednostmi hlapnih spojin določenih v izbranih španskih rdečih vinih (μg l^{-1}) ((a) García-Carpintero et al., 2012b (povprečje štirih zaporednih letnikov); (b) Moreno-Pérez et al., 2013 (6 mesecev po fermentaciji); (c) García-Carpintero et al., 2014 (kontrolno vino po tretiranju s hrastom), New Zealand Pinot Noirs iz Central Ottago (povprečje treh območij) ((d) Imre et al., 2012) in francoskih rdečih vin z njihovimi standardnimi odkloni ((e) Antalick et al., 2014)

	Teran PTP	Cabernet Sauvignon (b)	Syrah (b)	Monastrell (b)	Bobal (c)	Moravia Dulce (a)	Rojal (a)	Tortosí (a)	Pinot noir (d)	young red wines (e)	aged red wines (e)	Beaujolais Noveau red wines (e)
ALDEHYDES												
n-Hexaldehide (Capronaldehide)	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Benzaldehyde	10±17	n.a.	n.a.	n.a.	7	27	3	9	n.a.	n.a.	n.a.	n.a.
Benzyl alcohol	195±164	n.a.	n.a.	n.a.	688	234	278	438	n.a.	n.a.	n.a.	n.a.
C6 COMPOUNDS												
1-Hexanol	1292±531	1020	1500	1481	1375	1835	1938	1547	583	n.a.	n.a.	n.a.
Cis-3-hexen-1-ol	65±47	33	102	9	81	146	178	35	39	n.a.	n.a.	n.a.
ESTERS												
2-Phenyl-ethyl-acetate	49±22	56	442	115	297	960	80	70	12	58±19	37±16	311±195
Ethyl butanoate (Ethyl butyrate)	104±45	n.a.	n.a.	n.a.	85	60	60	90	31	177±42	147±32	367±95
Ethyl decanoate (Ethyl caprate)	102±65	n.a.	n.a.	n.a.	125	70	70	70	20	108±45	53±33	364±120
Ethyl dodecanoate (Ethyl laurate)	22±19	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3±3	0.6±0.7	13±10
Ethyl hexadecanoate (Ethyl palamitate)	70±131	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ethyl hexanoate (Ethyl caproate)	179±46	189	93	10	631	360	380	420	43	387±94	326±72	793±158
Ethyl octanoate (Ethyl caprylate)	196±53	99	25	n.d.	428	330	420	430	66	479±106	365±95	1001±221
Hexyl acetate	n.d.	5	15	14	9	3670	2670	4350	10	2±2	2±1	23±15
Isoamyl acetate	362±132	511	644	57	1076	240	240	580	177	507±142	324±98	3190±1788
LACTONES												
γ-Butyrolactone	12920±3712	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
KETONES												
β-Ionone	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.2	n.a.	n.a.	n.a.

n.a. means not analysed, n.d. means not detected

Comparing our samples with other red wines shows that Teran PTP did not contain hexyl acetate, which is responsible for green and floral aromas, and was found in other red wines (García-Carpintero et al., 2012b; Moreno-Pérez et al., 2013; García-Carpintero et al., 2014). This was also possible because of its typical decomposition in months following alcoholic fermentation as our samples were analyzed at least 9 months after its completion (Ramey and Ough, 1980). A further comparison with other articles shows that 1-hexanol, a compound with intensive herbal, woody aroma is present in all red wines, including Teran PTP.

Antalick et al. (2014) showed that young (one year old) red wines from Bordeaux, Loire valley and the Rhône's southern region (n=19) contain substantial amounts of ethyl butyrate (mean content 177 μg l^{-1}), ethyl hexanoate (mean content 387 μg l^{-1}), ethyl octanoate (mean content 479 μg l^{-1}), ethyl decanoate (mean content 108 μg l^{-1}) and isoamyl acetate (mean content 507 μg l^{-1}). Substantial amounts of these esters were also found in Teran PTP wines. They are of additional interest, as they are known to give a positive, synergistic effect on the wine odour (Ferreira et al., 1998).

The Teran PTP contained isoamyl acetate at slightly higher contents than the three Spanish varieties from the Jumilla Controlled Appellation – 'Moravia Dulce' and 'Rojal' (García-Carpintero et al., 2012b), higher contents than the 'Monastrell' (Moreno-Pérez et al., 2013) and Pinot noir (Imre et al., 2012), but lower contents than the 'Cabernet Sauvignon' and 'Syrah' (Moreno-Pérez et al., 2013), 'Bobal' (García-Carpintero et al., 2014), 'Tortosí' (García-Carpintero et al., 2012b), the young French red wines (Antalick et al., 2014) and the 'Beaujolais Noveau' red wines (Antalick et al., 2014). The Teran PTP contained isoamyl acetate at approximately the same content as the aged French red wines (Antalick et al., 2014).

García-Carpintero et al. (2014) studied the volatile profile of 'Bobal' wine from the La Macha region (Spain) and the influence of oak chips added during vinification. Other authors have shown that the addition of oak chips before the start of alcohol fermentation increases the amount of ethyl esters from straight chain fatty acids. In comparison with Teran PTP wine, which is traditionally vinificated without oak chips, the Bobal wines showed higher amounts of isoamil acetate, ethyl hexanoate and ethyl octanoate. Teran PTP on the other hand, contained higher contents of ethyl butyrate than 'Bobal' (García-Carpintero et al., 2014), 'Moravia Dulce', 'Rojal' and 'Tortosí' (García-Carpintero et al., 2012b).

During four consecutive vintages (2006-2009) García-Carpintero et al., (2012b), analyzed the volatile profile of three red minor varieties: 'Moravia Dulce', 'Rojal' and 'Tortosí', grown in the La Mancha region (Spain). All three varieties showed a higher content of C6 compounds, ethyl hexanoate and ethyl octanoate. On the other hand, comparing the volatile profile of Teran PTP with the 'Pinot Noir' from Central Otago (New Zealand) (Imre et al., 2012), the Teran PTP wines showed a higher content of both esters and C6 compounds.

Cerdan et al. (2004) showed that ethyl butyrate decreased during the aging of 'Merlot' and 'Cabernet Sauvignon' in American oak barrels. After 18 month of aging in oak barrels its content was lower compared to the three-year aging average of Teran PTP. The ethyl hexanoate content in Teran PTP was higher than in the 'Syrah', 'Monastrell' (Moreno-Pérez et al., 2013) and 'Pinot Noir' (Imre et al., 2012) wines. Its content was approximately the same as in the 'Cabernet Sauvignon' (Moreno-Pérez et al., 2013) and lower than the young French red wines (n=22) (Antalick et al., 2014), aged French red wines (n=61) and the 'Beaujolais Nouveau' red wines (n=19) (Antalick et al., 2014). As reported by Cerdan et al. (2004), the content of ethyl hexanoate did not alter during the first six months of aging in oak barrels, but subsequently it increased until it reached a maximum at 12 months of aging. After one year, the contents of this compound diminished. On the other hand, Antalick et al. (2014) showed that contents of ethyl esters of fatty acids (EEFA) decrease with the age of wines only when the EEFA have the longest carbon chain, such as ethyl decanoate and dodecanoate. Ethyl butyrate, hexanoate and octanoate contents were, for the most part, unaltered by the age of wines.

Teran PTP contained lower contents of ethyl octanoate than the 'Bobal' (García-Carpintero et al., 2014), 'Moravia Dulce', 'Rojal' and 'Tortosí' wines (García-Carpintero et al., 2012b), the young French red wines, the aged French red wines and the 'Beaujolais Noveau' red wines (Antalick et al., 2014). But it contained higher contents than the 'Cabernet Sauvignon', 'Syrah' (Moreno-Pérez et al., 2013) and 'Pinot Noir' (Imre et al., 2012). Cerdan et al. (2004) showed that ethyl octanoate increased during the first six months of aging in oak barrels. Then it remained practically constant until it decreased due to hydrolysis. The same authors have also shown that changes in ethyl esters during the aging of 'Merlot' and 'Cabernet Sauvignon' in oak barrels were not related to the alcohol contents and pH values of the wine.

4 CONCLUSIONS

According to the results of our study, esters are a very influential aromatic group in Teran PTP wines and do contribute to its typical fruity aroma. The aromatic profile of Teran PTP wines was most affected by ethyl octanoate, which reminiscent of a fruity sweet red-cherry. The second most important ester was ethyl hexanoate, with its fruity apple and strawberry odour. The third was isoamyl acetate, with a fruity sweet banana odour and was followed ethyl butyrate with fruity smell. A comparison of our results with red wines from other varieties showed some differences in ester contents. However, like for other wines esters were found to be one of the most important volatile compounds in Teran PTP.

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