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Flavour in "Pedro Ximénez" grape musts subjected to maceration processes

by

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S u m m a r y : Crushed grapes of Vitis vinifera cv. Pedro Ximénez were macerated at 10, 15 and 25 °C for 4, 16, 24 and 48 hours. The musts obtained after pressing were used for the determination of higher alcohols, esters and terpene compounds. The data was subjected to discriminant analysis, obtaining three functions of difficult interpretation. A fruitiness index (Σ favourable aromas / Σ unfavourable aromas) x 100 and the total of phenolic compounds were subjected to variance and multiple range analyses which revealed significant differences ($p<0.01$) for maceration times and temperatures. Taking into account the fruitiness index and phenolic compound values, as well as the significant differences obtained by multifactorial (time-temperature) variance analysis, the 24 h-10 °C, 4 h-15 °C, 16 h-15 °C and 24 h-15 °C were the best conditions.

K e y w o r d s : grape must, maceration, flavour, terpenols, esters, higher alcohols, polyphenols.

Introduction

At present, it is accepted that the fruity flavour of white table wines is a complex sensory perception essentially determined by their terpene and ester contents, and adversely affected by higher alcohols owing to their sensory "hardiness". Most of the alcohols and esters in wine are produced by yeasts during fermentation while terpenes originate mainly from the grapes (Cordonnier and Bayonove 1974; Rapp *et al.* 1982; Bayonove 1986; Wilson *et al.* 1986; Baumes *et al.* 1988, 1989), though part of them may be synthesized and/or released from their glucoside prior to and during fermentation (Fagan *et al.* 1981; Williams *et al.* 1982 a, b; Bayonove *et al.* 1984; Nykanen 1986; Dubourdieu *et al.* 1988). This last amount, however, seems to be negligible relative to the first (Wilson *et al.* 1986).

Skin maceration enhances the fruity flavour of the resulting wine favouring the transfer of terpene compounds to the must. This technique provides generally good results depending on grape variety and experimental conditions, being more effective with aromatic varieties (Ough and Berg 1971; Arnold and Noble 1979; Cooke and Berg 1983; Dubourdieu *et al.* 1986; Test *et al.* 1986; Baumes *et al.* 1988; Moyano *et al.* 1991). However, contact of the must with grape skins favours polyphenol extraction, and, depending on the maceration conditions, the resulting must and wine are more or less sensitive to browning (Ough 1969; Ough and Berg 1971; Noble *et al.* 1975; Singleton *et al.* 1975; Test *et al.* 1986). Different combinations of maceration, temperatures and times, can lead to musts and wines of very similar quality (Baumes *et al.* 1989), although some of these combinations may be economically undesirable. For this reason, the results obtained in maceration processes should be objectified.

Must from *Vitis vinifera* cv. Pedro Ximénez can be classified as moderately rich in terpene compounds (Moreno 1986), so maceration may enhance the aroma of the wines. The purpose of this work was to determine the best maceration conditions for Pedro Ximénez grapes in order to increase the content of aroma compounds in the resulting musts and hence their fruity flavour while maintaining a low level of polyphenols to avoid oxidation processes as far as possible.

Material and methods

M a c e r a t i o n : 100 kg of Pedro Ximénez grapes were harvested at a semi-ripe stage (the sugar content in the resulting must was 177.0 ± 7.6 g/l) in the Montilla-Moriles region (Córdoba, Southern Spain) where ripe grapes of this variety are commonly used to produce Sherry white wines, while semi-ripe grapes yield white table wines.

The collected grapes were divided into homogeneous batches that were crushed and macerated in triplicate at 10, 15 and 25 °C for 4, 16, 24 and 48 h. Every batch was supplied with 75 mg SO_2/kg as potassium metabisulfite prior to processing. After the treatment was finished, the grapes were pressed and the resulting musts analysed.

G L C a n a l y s i s : The fraction composed of terpenes, higher alcohols and esters was isolated by continuous extraction with Freon-11 for 24 h and subsequently quantified by injecting the concentrated extracts into a Perkin-Elmer Sigma 3 chromatograph furnished with a SP-1000 capillary column (60 m; 0.32 mm), using 2-octanol as internal standard.

S t a t i s t i c a l a n a l y s i s : Statistical calculations were carried out by using the programme Statgraphics Statistical Computer Package. Data for various aroma frac-

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tions obtained under the different maceration conditions were subjected to discriminant analysis by direct method. *F* values for the time and temperature were obtained by applying the sub-programme Multifactor Analysis of Variance to data for the different fractions.

Results and discussion

In Tab. 1 the contents of favourable aroma compounds of the musts are listed. The overall of terpenols include linalool, nerol and α-terpineol. These compounds endow the wine with pleasant floral odours and are largely responsible for their varietal aroma (CORDONNIER and BAYONOVE 1981); they were extracted in the greatest amounts in the macerations at 10 °C.

Eugenol is a phenol of low molecular weight, the concentration of which increases with the time of maceration (especially at 10 °C). Its pleasant spicy odour, resembling those of cinnamon and clove, warrants inclusion of this compound in the group of substances enhancing the primary aroma of grapes.

Esters provide delicate odours resembling those of fruits and flowers. Among the different ester families analysed, only butyl, isoamyl, n-amyl and 2-phenethyl acetates were found to be present at detectable concentrations. The overall of esters concentration detected was maximal for the macerations carried out at 15 °C for 24 and 48 h. Based on the overall concentration of favourable compounds (terpenes + eugenol + esters), extraction of these substances from semi-ripe Pedro Ximénez grapes was maximal for the macerations performed at 10 °C for 16, 24 and 48 h.

In Tab. 2 the contents of unfavourable aroma compounds are listed. This group is composed of aliphatic and aromatic alcohols, which are readily distinguished by their strong odour and pungent flavour, and make up the major class of aroma compounds in quantitative terms. The C_6 n-hexanol, E-3-hexenol and Z-2-hexenol are of special significance according to CORDONNIER and BAYONOVE (1981); they occur in the musts as a result of pre-fermentation treatments of the grapes, and are largely responsible for herbaceous odours and flavours. These alcohols were present at their highest concentrations during the macerations at 10 °C.

Table 1

Influence of maceration conditions on the composition of the musts in the favourable aromas (μg/l)

	T	0 HOURS	4 HOURS	16 HOURS	24 HOURS	48 HOURS
Linalool +	10°C	14.4±3.67	18.2±1.67	100±17.7	108±10.1	83.9±9.22
Nerol +	15°C	14.4±3.67	16.6±4.67	11.7±2.0	11.4±3.1	11.0±1.4
α-terpineol	25°C	14.4±3.67	6.0±0.81	8.19±0.63	8.61±0.88	11.8±1.64
	10°C	12.7±2.16	14.1±1.75	20.2±1.75	43.2±2.8	46.9±2.82
Eugenol	15°C	12.7±2.16	13.2±1.84	14.5±0.73	15.5±0.5	17.5±3.46
	25°C	12.7±2.16	17.4±0.99	17.8±3.34	18.0±4.91	29.6±5.8
	10°C	6.3±0.23	N.D.	N.D.	26.9±8.11	38.7±5.55
Σ Esters	15°C	6.3±0.23	22.4±3.9	23.9±3.49	66.3±10.1	83.9±6.93
	25°C	6.3±0.23	50.6±9.6	38.2±3.21	49.3±8.03	35.1±6.26
	10°C	37.1±3.19	32.3±0.28	121±17.0	177±56.4	169±3.78
Σ FAVOURABLE	15°C	37.1±3.19	52.2±9.26	50.2±3.02	93.2±7.47	112±7.69
AROMAS	25°C	37.1±3.19	73.9±9.75	64.1±4.28	75.9±3.15	76.4±9.48

N.D. = Not detected

Table 2

Influence of maceration conditions on the composition of the musts in the unfavourable aromas (μg/l)

	T	0 HOURS	4 HOURS	16 HOURS	24 HOURS	48 HOURS
n-hexanol +	10°C	184±10.1	197±21.4	234±13.4	214±13.4	293±37.6
E-3-hexenol +	15°C	184±10.1	143±14.4	221±37.7	155±8.13	144±31.7
Z-2-hexenol	25°C	184±10.1	161±19.2	127±1.32	142±3.80	259±35.4
Σ alcohols scarcely	10°C	992±362	3062±736	2446±652	2149±983	3402±755
affected by	15°C	992±362	156±23.2	202±22.8	570±102	524±210
fermentation	25°C	992±362	437±85.6	310±86.6	324±24.0	390±44.5
Σ alcohols markedly	10°C	931±68.1	1087±92.4	933±298	1369±259	1522±246
affected by	15°C	931±68.1	870±65.1	905±346	1411±256	1684±70.6
fermentation	25°C	931±68.1	1668±293	1455±281	1605±137	1485±263
	10°C	2107±291	4347±805	3625±951	3719±750	5155±872
Σ UNFAVOURABLE	15°C	2107±291	1168±93.3	1328±349	2136±259	2364±282
AROMAS	25°C	2107±291	2266±370	1892±232	2071±162	2157±210

The remainder of alcohols were classified according to changes in their contents during alcoholic fermentation into those scarcely affected and those markedly affected by the process. It is well known that the concentrations of 1-butanol, 1-pentanol, 1-octanol and benzyl alcohol change very little during alcoholic fermentation (scarcely affected), whereas those of isobutyl, isoamyl and 2-phenylethyl alcohol change considerably during the fermentation process by effect of yeasts (markedly affected). Scarcely affected alcohols occurred at their highest concentrations in the macerations carried out at 10 °C, though the concentrations of the markedly affected peaked in the macerations at 25 °C. On the whole, the overall concentration of aroma-detracting compounds was lowest at 15 and 25 °C.

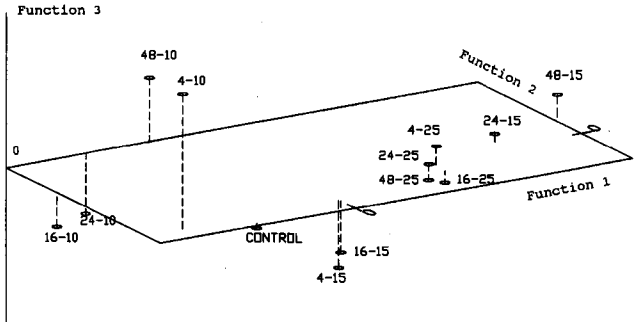

Fig.1: Discriminant analysis of different maceration conditions (time-temperature).

Fig. 1 shows the results of the discriminant analysis to which the overall concentrations of higher alcohols, esters and terpenes + eugenol were subjected. The first two discriminant functions account for 92.69% of the whole variance. Based on the values for the different discriminant function coefficients, the esters have a marked effect on function 1 (0.977 for the esters, -0.397 for terpenes + eugenol and -0.219 for higher alcohols), while terpenes + eugenol influence function 2 (0.811 for the terpenes + eugenol, 0.312 for the esters and 0.161 for higher alcohols). For terpenic and eugenol compounds, the 24 h-10 °C and 48 h-10 °C conditions are optimal, followed by 16 h-10 °C and 48 h-15 °C. All other conditions are considerably poor in terpenes + eugenol, even though most of them are richer in esters (particularly samples 48 h-15 °C and 24 h-15 °C). On the other hand, samples are scattered around function 3 since conditions 24 h-10 °C and 16 h-10 °C are negative, whereas 48 h-10 °C and 48 h-15 °C are positive, which suggests a different contribution from higher alcohols in the former two conditions compared to the latter two, taking into account that function 3 is strongly influenced by the alcohols (discriminant function coefficient for these is 1.055, in opposite to -0.613 for the terpenes + eugenol and 0.030 for the esters).

However, while function 1 arises mostly from the contribution of the ester fraction, the coefficients for the other two aroma fractions should not be underestimated. This problem is similar with the functions 2 and 3. In addition, the adverse influence of polyphenol extraction is rather difficult to include in a discriminant analysis since it gives rise to 4 functions, with a complex interpretation. In order to objectify the results, it is worth defining a "fruitiness index" including the two aroma fractions studied and increasing with the concentration of fruitiness-enhancing compounds (and decreasing with increasing contents of aroma-hardening substances). It can be calculated from the expression (Σ favourable aromas / Σ unfavourable aromas) x 100. This index can be questioned because only take account of fractions as a whole and includes no multiplicative factors considering quantitative aspects. Nevertheless, available knowledge on the individual contribution of each compound to the overall aroma is still limited and wine flavour is perceived "as a whole", so the balance between fractions is more often of greater interest than is the absolute contribution of each. In fact, this criterion has been used for other enological purposes such as determining the optimal temperature for fermentation of white table wines.

Table 3

Multifactor (time-temperature) analysis of variance and multiple range analysis for fruitiness index and polyphenolic compounds

FRUITINESS INDEX				POLYPHENOLIC COMPOUNDS			
LEVEL	PERCENT COUNT	CONFIDENCE INTERVALS AVERAGE	HOMOG.GROUPS	LEVEL	PERCENT COUNT	CONFIDENCE INTERVALS AVERAGE	HOMOG.GROUPS
4h-10°C	3	0.733	*	4h-10°C	3	375.466	*
CONTROL	3	1.600	*	16h-10°C	3	377.500	*
48h-10°C	3	3.300	*	CONTROL	3	378.566	*
4h-25°C	3	3.366	*	4h-15°C	3	385.333	*
16h-25°C	3	3.400	*	24h-10°C	3	403.666	**
48h-25°C	3	3.400	*	16h-15°C	3	404.333	**
16h-10°C	3	3.433	*	24h-15°C	3	451.400	**
24h-25°C	3	3.666	*	4h-25°C	3	464.800	*
16h-15°C	3	4.000	**	48h-10°C	3	471.800	*
4h-15°C	3	4.433	**	48h-15°C	3	560.366	*
24h-15°C	3	4.433	**	16h-25°C	3	562.166	*
24h-10°C	3	4.700	**	24h-25°C	3	726.600	*
48h-15°C	3	4.766	*	48h-25°C	3	773.700	*

Analysis of variance. F-ratio: Index: 11.636 ($p<0.01$). Polyphenolic compounds: 20.132 ($p<0.01$).

The fruitiness index and polyphenolic compounds were subjected to variance analysis and multiple range analysis as a function of the maceration temperature and time. The results show that the fruitiness index is markedly dependent on the maceration time and temperature ($p \leq 0.01$), as are the polyphenolic compounds which increase with the duration of skin contact and temperature, even though the differences between the milder conditions are insignificant. On the other hand, the fruitiness index is maximum at 24 h, but similar to that obtained at 48 h. As to the temperature, the index peaks at 15 °C.

In variance analysis previously accomplished the means for all the samples at a constant value of one factor are used; a statistical classification of all the samples according to their contents is better established by carrying out a multifactor (time-temperature) analysis of variance and multiple range analysis of the values for their triplicates. The results thus obtained are given in Tab. 3. As can be seen, the samples yielding the highest fruitiness indices were those obtained at 48 h-15 °C, 24 h-10 °C, 24 h-15 °C, 4 h-15 °C and 16 h-15 °C, with no significant differences between them. On the other hand, the best samples in terms of the polyphenolic compounds were those with the lowest values (4 h -10 °C, 16 h-10 °C, 4 h-15 °C, 24 h-10 °C, 16 h-15 °C and 24 h-15 °C) with no significant differences between them, nor with the unmacerated must.

The mean values for the fruitiness index and polyphenolics compounds in each of the maceration conditions are plotted in Fig. 2. Left of the vertical line is the zone where no significant differences are observed between the minimun values for the polyphenolic compounds. The upper zone of the horizontal line shows the same for the maximun values of the fruitiness index. The samples obtained at 24 h-10 °C, 4 h-15 °C, 16 h-15 °C and 24 h-15 °C, lie in a common zone, so all of them give rise to the same aroma to phenol ratio since neither index differs significantly between them.

In conclusion, macerating musts from semi-ripe Pedro Ximénez grapes in order to enhance the fruity flavour while minimizing the adverse effects of polyphenols is best done at 15 °C, which results in maximal extraction of aroma-enhancing compounds, except for too long maceration period (48 h). Similar result is obtained at 10 °C, but only at a fairly long time (24 h). Of these 4 possible conditions, the best choice will be determined by economic or industrial reasons in each case.

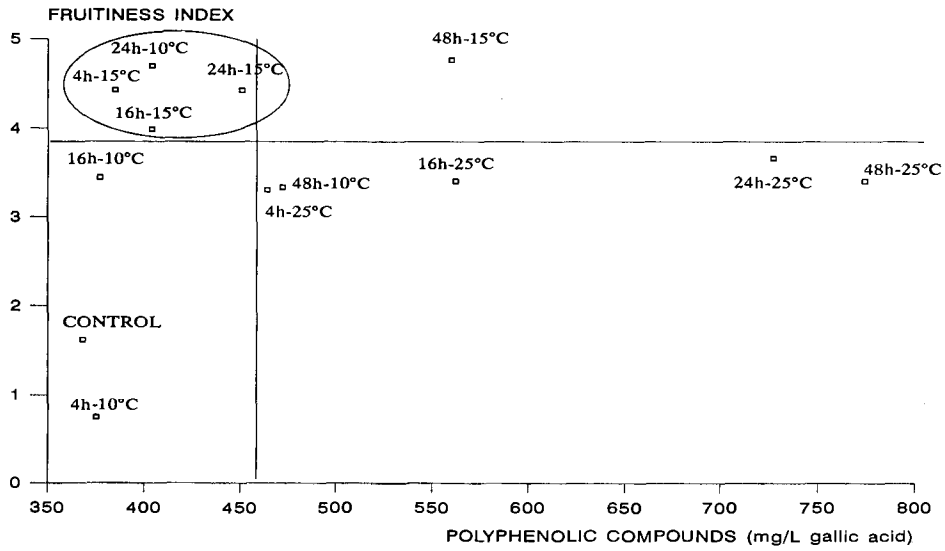

Fig.2: Fruitiness index, (Σ favourable aromas / Σ unfavourable aromas) x 100, *vs.* polyphenolic compounds (mg/l gallic acid), for the different maceration conditions.

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