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Investigation on the Role Played by Fermentation Esters in the Aroma of Young Spanish Wines by Multivariate Analysis

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Abstract: The role played by ethyl esters of fatty acids and by acetates of higher alcohols on the aroma of young wines from neutral grape varieties has been investigated. The statistical methods used have been stepwise linear regression and principal components analysis. Very significant conclusions have been reached. The role played by these compounds depends on the type of wine. In white wines their main role is in the perception of tree fruit and tropical fruit notes. It has been demonstrated that the former notes are linked to ethyl esters, while the latter are linked mainly to acetates of higher alcohols. In rosé wines the intensity of tree fruit aroma was correlated with ester content, however no clear conclusion was reached about the role of various compounds on the perception of quality. Finally, in red wines these compounds do not determine the intensity of fruit aromas, and they only play a modulating role on aroma quality. This indicates that red grape varieties must have other aroma compounds which are responsible for the fruity characteristics of wines.

Key words: wine flavour, aroma, esters, multivariate data analysis.

INTRODUCTION

The valuable contribution of ethyl esters of fatty acids and acetates of higher alcohols to wine aroma has been known for some time. First of all, their concentration is above their sensory detection threshold (Salo 1970a, 1970b; De Wet 1978; Ribereau-Gayon 1978; Simpson 1979; Shinohara 1984; Simpson and Miller 1984); and secondly, some of the descriptors used in sensory evaluation of wines coincide with the aroma of these compounds (Maarse and Visscher 1989; Etievant 1991). These compounds are synthesised during must fermentation in concentrations usually higher than those theoretically to be expected from their hydrolysis/synthesis equilibria. This means that they are hydrolysed to a significant degree in the early stages of wine maturation, following a kinetic behaviour well described by Ramey and Ough (1980). Thus, they are particularly important in young wine bouquet; albeit they still can play a significant role in an aged wine. A significant amount of work has been done in this field. Wagener and Wagener (1968), found highly significant correlations between the quality of a white wine and its content of these compounds; Van Wyk *et al* (1979) demonstrated that isoamyl acetate was strongly correlated with the characteristic aroma components of young wine from Pinotage variety; Van der Merwe and Van Wyk (1981) were able to reproduce the quality and intensity of a dearomatised wine by addition of esters; Marais (1978) and Marais and Pool (1980) found good statistical correlations between wine quality and ester content in Colombar, Chenin blanc and Riesling wines.

However, the exact contribution of these compounds to wine aroma is not perfectly elucidated. It is not clear what aroma perception is induced by a certain combination of esters, or what influence the remaining wine compounds have on the perception of these esters. Several studies have been done in that direction, but the results are sometimes contradictory and are limited largely to wines from white grape varieties. Van der

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Merwe and Van Wyk (1981) showed that isoamyl acetate is the compound that contributes the most to wine aroma, and that ethyl esters may have a suppressor effect on the aroma intensity of acetates; however, they contribute positively to the general quality of wine. These investigators concluded that none of the esters added separately will restore the aroma intensity or the overall quality of the original wine. On the other hand, Keith and Powers (1968) found the elimination of one of the esters did not have any significant effect on aromatic perception. Du Plessis (1975) found that adding ethyl octanoate and ethyl decanoate did not improve wine quality. From all the esters considered by De Wet (1978), isoamyl acetate and ethyl hexanoate are those that played a major role in the aroma of young white wines. Similar conclusions were reached by Romano *et al* (1989); they showed that a simple linear model could explain the intensity of caramel/apple/acetate notes of Chardonnay wines as a function of their acetate content, mainly isoamyl acetate. However, the model did not explain the perception of tropical fruit notes which are attributed to ethyl esters of fatty acids. Van Rooyen *et al* (1982) could not interpret in a clear way what composition corresponded to a guava note in some high quality Chenin blanc wines; however, they concluded that it was related to the relative ester composition, mainly to the concentration of ethyl butyrate and the ethyl ester ratios butyrate/decanoate and butyrate/octanoate.

The reason why these results do not offer any definitive conclusion may be due to the complex interactions that may take place among these and other aroma compounds, and even among them and various matrix compounds. Piggot and Findlay (1984) showed, by means of a study on binary mixtures of esters, that at certain concentrations there are synergistic or antagonistic relations. The interaction among these compounds and ethyl acetate (Ribereau-Gayon 1978; Van der Merwe and Van Wyk 1981; Bertuccioli *et al* 1983) and ethanol (Williams and Rosser 1981) have been studied. Based on these works and on recent studies related to the effects of fining, also for consideration are possible association with proteinaceous or other macromolecular elements which would diminish the effective concentration of the odour compounds in the headspace (Voillei *et al* 1990). Nevertheless, another more important reason could be the fact that many researchers analysed samples of relatively similar characteristics, and therefore the composition variability was not great enough (Romano *et al* 1989). Also, in most cases, the authors tried to get results of univariant type, or considered compounds which are at concentrations way below their threshold, or the study concerned the effect on overall quality more than the explanation of particular aroma notes.

The knowledge of the combination of compounds that produce certain aroma notes is of great importance in a market demanding original products. The use of certain standardised winemaking practices—including the use of commercial yeast strains—is leading to an overall increase in the ester concentration in young wines. If this means a general increase in wine quality, it is also true that the lack of comprehension of how these compounds affect wine characteristics, when coinciding with grapes and winemaking areas of low individual character, is leading to a situation in which 'standard' fruity wines are unable to penetrate in a highly competitive market. The objective of the present work is to study the existing relation between wine ester composition and the sensory perception of aroma intensity and quality. The investigated notes (descriptors) are grouped under the first-order term fruity (Noble *et al* 1987). The starting hypothesis is that the various aroma notes are due not only to the absolute ester composition, but also to the relative composition of esters, that is, the profile of such composition. We have studied how different global compositions correspond to different aroma perceptions. For this purpose we have used principal component analysis.

MATERIALS AND METHODS

Commercial wines, 32 white, 20 rosé and 20 red, from the 1990 harvest, and from various Spanish denominations of origin, were analysed. Wines showing some defect or an ethyl acetate concentration higher than 80 mg litre^{-1} were rejected. Sensory analysis was performed during April and May of 1991 by a group of 18 experts from the Unión Española de Catadores (Spanish Association of Tasters). After three preliminary sessions the following sensory descriptors and intensity scores were chosen by consensus according to the standard terminology proposed by Noble *et al* (1987):

- White wines: First-order descriptor: fruity. Intensity: null (0), light (1), intense (2), very intense (3). Second-order descriptors: tree fruit, tropical fruit (same scales).
- Rosé wines: First-order descriptor: fruity. Intensity: null (0), light (1), intense (2), very intense (3). Second-order descriptors: tree fruit, tropical fruit, red berry (same scales).
- Red wines: First-order descriptor: fruity. Intensity: null (0), light (1), intense (2), very intense (3). Second-order descriptors: black berry, red berry (same scales).

Each wine was tasted twice in 10 different sessions. In each session only wines of the same type (white, rosé or red) were tasted.

For ester analysis reference compounds of analytical grade from Chemservice (West Chester, PA, USA) were used. Freon 113 HPLC grade was from Aldrich

(Wisconsin, USA). Aroma components were extracted and analysed by microextraction with Freon 113 as proposed by Ferreira *et al* (1993). Aroma analyses were performed during the same period of time as the tasting. Analysis were carried out in duplicate. Statistical treatments were performed with Statview package by Apple Macintosh, 3.02 version.

RESULTS AND DISCUSSION

Chemical data

The results on the composition of esters in the wines are shown in Tables 1–3. Absolute compositions clearly distinguish rosé and white wines from red wines as can be seen in the ANOVA in Table 1. Red wine ester contents were significantly different from those of rosé and white wines. When the aerobiosis level is higher during fermentation, as happens in red wines, the synthesis of these compounds is reduced (Nordstrom 1964). The only difference observed between white and rosé wines was the ethyl butyrate content. With respect to relative ester composition, rosé and white wines are rather similar, even though in rosé wines the ethyl ester content is slightly higher. The main differences are found when comparing red with white and rosé wines. The ethyl ester profile of a red wine is significantly different from that of other types of wine: ethyl butyrate is particularly high, while ethyl hexanoate and ethyl octanoate are low. This is in agreement with the observation by Bertrand (1968): different aeration levels bring about a different relative ester composition. Hence, from a taxonomic point of view we can consider red wines as subjects rather different from rosé and whites. For this reason in Tables 2 and 3, only data from white and rosé wines are compiled, otherwise a strong bias would be introduced.

Regional differences are important as can be seen in Table 2. Significant differences appear among the regions for all the compounds, except ethyl laurate and isobutyl acetate. Even more, the coefficient ethyl esters/acetates, that constitutes a rough measurement of the relative composition, is linked to the geographical origin dividing regions in three groups. Wines from the centre are the only ones with a coefficient below one. In wines from Galicia and Canarias this coefficient takes values close to one, while in wines from Castilla and Ebro takes values around two. It is beyond the scope of this paper to build a discriminant function but data in Table 2 show that this is possible. It should be noted that the relative ester composition is going to change due to the natural tendency to reach the equilibrium ester/acid + alcohol. On the other hand grape variety seems to have a minor effect on the absolute ester composition (see data in Table 3). However, the effect on the relative ester composition, as defined by the coefficient ethyl esters/acetates, is still important. It is remarkable that the factor origin is in reality a mixture of several factors: soil, climate, cultural practices and technological practices (plus in some cases, the grape variety), so the results are not surprising and it is not possible with the data handled in this study to separate the variances into simpler factors. The only thing we can say is that the ester composition is first a function of the presence of skins during the fermentation (the most important effect of which is, probably, an increase of the aerobic level), second a function of the factors included in the origin factor and third, and with far less importance, a function of the grape variety.

Sensory data

Tables 4–7 condense the statistical validity of the sensory data. To check if the replications differed significantly, a paired comparison test was conducted between sensory data obtained in different sessions. t-values from this experiment showed (data not given) that replications did not differ significantly. For the first-order terms, the precision of the measurements of each taster, as defined by S of replications, ranked from 0·53 (white wines) to 0·55 (red wines). To test if there were significant interactions between judges and wines a two factor ANOVA was performed. The observed S between replications was taken as a measurement of the error and was used to compare the size of the mean squares (see Tables 4–7). F values were obtained for the interaction $J \times W$ terms. Data show that there is no evidence of significant interaction at least for the first-order terms. However, when considering the second-order terms for rosé and red wines the F-interaction values are quite high, showing that some kind of interaction may take place. A study of the residuals (graphics not shown) leaded to the same conclusions. There is no evidence of interaction neither for the first-order terms, nor the white wine second-order terms. But the residual versus estimates graph for the rosé wines second-order term showed a clear funnel shape. This implies that the linear model is not adequate to study this particular set of results.

The confidence intervals for the final averages of each wine (as defined by $s_j/\sqrt{n}$) rank thus from 0·14 (white wines first-order term) to 0·15 (rosé wines first-order term) and from 0·16 (white wines tree fruit second-order term) to 0·28 (rosé wines tree fruit second-order term).

The statistical analysis was divided in two parts: first, a general stepwise linear regression. In this first approximation a linear model was used since the sensory response within the range of concentrations of these compounds is approximately linear and corresponds to the first ascending part of the sigmoidal curve (Romano *et al* 1989). The authors have tried to find general tendencies which could be confirmed later. In the second

TABLE 1

Wine ester composition and one-factor ANOVA (factor = type: white, red or rosé)

Compound	*White wines (n = 32)*				*Rosé wines (n = 20)*				*Red wines (n = 20)*				*ANOVA*[a]		
	$\bar{X}$	*s*	*max*	*min*	$\bar{X}$	*s*	*max*	*min*	$\bar{X}$	*s*	*max*	*min*	*F*	*p*	*Category*[b]
Ethyl butyrate	0·851	0·45	2·194	0·371	1·107	0·27	1·666	0·671	0·667	0·27	1·292	0·246	7·55	0·001	rd versus rs rd versus wt
Ethyl hexanoate	1·152	0·54	2·731	0·428	1·256	0·36	1·811	0·701	0·387	0·21	0·990	0·179	26·5	0·0001	rd versus rs rd versus wt
Ethyl octanoate	1·303	0·57	2·636	0·440	1·573	0·49	2·692	0·836	0·507	0·32	1·342	0·230	26·1	0·0001	rd versus rs rd versus wt
Ethyl decanoate	0·345	0·20	0·821	0·106	0·426	0·17	0·720	0·116	0·186	0·12	0·486	0·072	10·2	0·0001	rd versus rs rd versus wt
Ethyl laurate	0·008	0·01	0·034	0·001	0·009	0·07	0·028	0·001	0·023	0·02	0·062	0·001	7·64	0·001	rd versus rs rd versus wt
Isobutyl acetate	0·161	0·09	0·366	0·037	0·235	0·13	0·653	0·133	0·131	0·061	0·257	0·055	8·19	0·0007	rd versus rs rs versus wt
Isoamyl acetate[c]	3·018	2·58	7·354	0·430	2·840	2·12	8·704	0·837	1·411	1·23	5·434	0·279	3·71	0·029	rd versus rs rd versus wt
Hexyl acetate	0·146	0·11	0·405	0·007	0·137	0·084	0·316	0·016	0·030	0·023	0·096	0·004	12·4	0·0001	rd versus rs rd versus wt
Phenylethyl acetate	0·308	0·21	0·744	0·079	0·407	0·29	1·204	0·098	0·179	0·118	0·525	0·049	5·67	0·005	rd versus rs rd versus wt
$\sum$ Ethyl esters	3·734	1·58	7·218	1·221	4·371	1·08	6·797	2·691	1·771	0·84	3·601	0·910	22·1	0·0001	rd versus rs rd versus wt
$\sum$ Acetates	3·714	2·90	10·46	0·594	3·633	2·33	9·971	1·173	1·752	1·39	6·253	0·474	4·46	0·015	rd versus rs rd versus wt
$\sum$ Esters	7·337	4·43	16·75	2·230	8·004	2·53	15·39	5·043	3·523	1·99	8·781	1·512	10·9	0·0001	rd versus rs rd versus wt
Ethyl esters/acetates	1·473	0·77	3·353	0·404	1·635	0·92	3·71	0·421	1·306	0·64	2·436	0·406	0·88	0·41	

[a] Significant differences after minimum significant difference method.
[b] rd, red wines; rs, rosé wines; wt, white wines.
[c] IUPAC name: isopentyl acetate.

TABLE 2
White and rosé wines ester composition and one-factor ANOVA (factor = geographical origin: Centre, Galicia, Castilla, Ebro or Cataluña)

Compound	*Centre* (*n* = 11)		*Galicia* (*n* = 8)		*Castilla* (*n* = 5)		*Ebro* (*n* = 13)		*Cataluña* (*n* = 12)		*ANOVA*[a]		
	$\bar{X}$	*s*	$\bar{X}$	*s*	$\bar{X}$	*s*	$\bar{X}$	*s*	$\bar{X}$	*s*	*F*	*p*	*Category*[b]
Ethyl butyrate	1·197	0·53	0·835	0·27	0·573	0·21	1·127	0·29	0·856	0·31	4·01	0·004	cn versus gl and cst and ct cst versus eb
Ethyl hexanoate	1·151	0·52	1·282	0·41	0·684	0·25	1·351	0·348	1·321	0·529	2·86	0·025	gl versus cst cst versus eb and ct
Ethyl octanoate	1·235	0·57	1·679	0·54	1·074	0·45	1·682	0·51	1·353	0·47	2·77	0·029	cn versus eb gl versus cst cst versus eb
Ethyl decanoate	0·316	0·21	0·511	0·21	0·32	0·15	0·457	0·19	0·315	0·10	2·64	0·035	cn versus gl gl versus ct
Ethyl laurate	0·007	0·007	0·012	0·012	0·012	0·010	0·007	0·008	0·006	0·005	0·98	0·44	
Isobutyl acetate	0·267	0·12	0·171	0·032	0·199	0·14	0·192	0·051	0·167	0·17	1·43	0·23	
Isoamyl acetate	5·432	2·81	3·900	2·02	1·194	0·71	1·635	0·73	2·504	2 ·06	6·76	0 ·0001	cn versus cst and eb and ct gl versus cst and eb
Hexyl acetate	0·208	0·13	0·186	0·082	0·043	0·056	0·108	0·062	0·147	0·089	3·5	0·009	cn versus cst and eb gl versus cst cst versus ct
Phenylethyl acetate	0·449	0·23	0·441	0·21	0·475	0·49	0·199	0·083	0·329	0·22	2·4	0·05	cn versus eb gl versus eb cst versus eb
∑ Ethyl esters	3·906	1·70	4·319	1·37	2·664	1·03	4·626	1·16	3·852	1·30	2·7	0·03	gl versus cst cst versus eb
∑ Acetates	6·357	3·10	4·698	2·22	1·912	1·31	2·137	0·83	3·15	2·30	6·47	0·0001	cn versus cst and eb and ct gl versus cst and eb
∑ Esters	11·01	4·04	9·094	3·93	4·567	2·27	6·763	1·80	6·929	3·53	4·55	0·002	cn versus cst and eb and ct gl versus cst
Ethyl esters/acetates	0·679	0·26	1·060	0·45	1·836	0·97	2·319	0·63	1·585	0 ·66	9·77	0 ·0001	cn versus cst and eb and ct gl versus cst and eb eb versus ct

[a] Significant differences after minimum significant difference method.
[b] cn, Centre; gl, Galicia; cst, Castilla; eb, Ebro; ct, Cataluña.

TABLE 3

Wine ester composition and one-factor ANOVA (factor = main grape variety: grenache, tempranillo, grenache + tempranillo, airen, macabeo or albariño)

Compound	Grenache ($n = 8$)		Tempranillo ($n = 2$)		Mix of G + T ($n = 9$)		Macabeo ($n = 8$)		Albariño ($n = 5$)		Airen		ANOVA[a]		
	$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s	$\bar{X}$	s	F	p	Category[b]
Ethyl butyrate	1·239	0·32	1·131	0·33	0·978	0·16	0·814	0·43	0·835	0·27	1·090	0·73	1·41	0·23	
Ethyl hexanoate	1·397	0·36	1·401	0·45	1·159	0·31	1·183	0·44	1·282	0·41	0·878	0·46	0·76	0·61	
Ethyl octanoate	1·777	0·58	1·769	0·11	1·428	0·35	1·251	0·39	1·679	0·54	1·009	0·67	2·31	0·05	gr versus mc and air alb versus air
Ethyl decanoate	0·511	0·18	0·474	0·004	0·351	0·16	0·287	0·099	0·511	0·21	0·355	0·29	3·01	0·01	gr versus mc mc versus alb
Ethyl laurate	0·006	0·007	0·012	0·003	0·009	0·008	0·006	0·007	0·012	0·011	0·008	0·008	0·74	0·62	
Isobutyl acetate	0·223	0·074	0·254	0·077	0·227	0·097	0·127	0·11	0·171	0·032	0·220	0·11	1·13	0·36	
Isoamyl acetate	2·433	1·72	5·342	4·75	2·837	1·78	1·915	2·38	3·900	2·02	4·305	3·43	1·29	0·28	
Hexyl acetate	0·134	0·095	0·190	0·070	0·137	0·083	0·127	0·12	0·186	0·82	0·144	0·13	0·41	0·87	
Phenylethyl acetate	0·272	0·14	0·734	0·023	0·474	0·35	0·227	0·19	0·441	0·21	0·347	0·28	2·66	0·026	temp versus gr and mc and air t + g versus mc mc versus alb
∑ Ethyl esters	4·931	1·19	4·788	0·89	3·9626	0·81	3·541	1·27	4·319	1·37	3·34	2·09	1·44	0·21	
∑ Acetates	3·064	1·99	6·522	4·88	3·674	1·93	2·404	2·77	4·698	2·23	5·017	3·66	1·38	0·24	
∑ Esters	7·994	2·07	11·31	5·77	7·600	1·82	5·811	4·10	9·095	3·93	9·743	5·10	1·29	0·28	
Ethyl esters/acetates	2·076	0·98	0·948	0·57	1·410	0·85	2·159	0·72	1·061	0·45	0·794	0·37	3·62	0·005	gr versus alb and air temp versus mc g + t versus mc mc versus alb and air

[a] Significant differences after minimum significant difference method.
[b] gr, grenache; temp, tempranillo; g + t, mixture of grenache + tempranillo; mc, macabeo; alb, albariño; air, airén.

TABLE 4
Variance table for the sensory data of white wines (first-order descriptor: fruity)

Source of variation	*Sum of squares*	*Degree of freedom*	*Mean squares*	*F quotients*
Between wines	517·14	31	16·69	58·44
Between judges	6·17	17	0·363	1·271
Interactions $W \times J$	59·06	527	0·1121	0·393
Replications (error)	164·5	576	0·2856	
Total	746·87	1151		

part, principal component analysis was performed using all the variables with the exception of ethyl laurate since, among all the analysed compounds, this was the only one found in concentrations below its detection threshold (see Meilgaard 1975); therefore, it was not taken into consideration for statistical analysis.

White wines
Highly significant correlations between fruit notes and ester composition of the aroma were obtained by the use stepwise linear regression. These data can be seen in Table 8. The first-order term: fruity, is strongly correlated with the total amount of esters. The tree fruit aroma term is of second order and contains the third-order notes apple, pear, cherry and peach. All the studies indicate that ethyl esters are the main compounds which contribute to the tree fruit aroma note and it is an aroma note perceived in wines with low total ester content. When considering individual ester concentration, again this term appears correlated with the main ethyl esters. It should be taken into account that as these compounds are strongly correlated between themselves, the coefficients that appear in the corresponding equations do not show the actual contribution of each compound to the perception, but the predictive value of the equations is fairly good, with a standard error of estimates (SEE) ranking between 0·44 and 0·48. The tree fruit note is probably the result of the action of all of them together, this fact being supported by the strong similarity in their olfactory descriptors (see Etievant 1991).

Tropical fruit is a second order term which groups the tertiary terms pineapple, banana, and melon. In this case the correlations obtained were higher (see Table 8) and the predictive ability of the model, as measured by the corresponding SEE, is still better than the one obtained with the tree fruit note, ranking from 0·41 to 0·44. We may conclude that the tropical fruit term is highly correlated to acetate content. It is interesting to point out that the role played by ethyl esters on perception of this aromatic note is a negative one as can be seen in the coefficient with these compounds entered in the equation. This result is in accordance with those of Van der Merwe and Van Wyk (1981). In this case, given the great concentration differences between isoamyl acetate and the rest, it does not make sense to study the contribution of each individual compound since they are also highly correlated among themselves.

TABLE 5
Variance table for the sensory data of rosé wines (first-order descriptor: fruity)

Source of variation	*Sum of squares*	*Degree of freedom*	*Mean squares*	*F quotients*
Between wines	297·12	19	15·64	53·86
Between judges	7·13	17	0·419	1·443
Interactions $W \times J$	38·32	323	0·1186	0·408
Replications (error)	104·51	360	0·2903	
Total	447·08	719		

TABLE 6
Variance table for the sensory data of red wines (first-order descriptor: fruity)

Source of variation	*Sum of squares*	*Degree of freedom*	*Mean squares*	*F quotients*
Between wines	318·2	19	16·75	55·77
Between judges	6·59	17	0·388	1·292
Interactions $W \times J$	32·37	323	0·1002	0·334
Replications (error)	180·12	360	0·3003	
Total	465·28	719		

TABLE 7
Condensed variance table for the sensory data of second-order descriptors

	F between wines	*F between judges*	*F inter-action*	*S replic-ations*
White wines				
Tropical fruit	42·53	1·36	0·483	0·57
Tree fruit	36·21	1·19	0·632	0·61
Rosé wines				
Tree fruit	16·2	2·12	1·95	0·82
Red berry	49·17	1·34	1·21	0·49
Tropical fruit	28·33	1·75	0·994	0·62
Red wines				
Black berry	41·82	1·73	1·07	0·54
Red berry	26·46	1·67	1·37	0·72

TABLE 8
Stepwise correlation analysis—white wines

Equation	*n*	*r*	*F*	*p*	*SEE*
First-order term: fruity					
$I = 0{\cdot}46 + 0{\cdot}16 \sum_{esters}$	32	0·889	86·54	0·001	0·385
Second-order term: tree fruit					
$I = 0{\cdot}14 + 0{\cdot}33 \sum_{ethyl\ esters}$	32	0·788	37·79	0·01	0·441
$I = 0{\cdot}17 + 0{\cdot}31 \sum_{ethyl\ esters} + 0{\cdot}02 \sum_{acetates}$	32	0·790	18·24	0·05	0·454
$I = 0{\cdot}26 + 1{\cdot}44 \sum_{ethyl\ esters} + 1{\cdot}19 \sum_{acetates} - 1{\cdot}17 \sum_{esters}$	32	0·805	12·86	0·05	0·450
$I = 0{\cdot}28 + 0{\cdot}93\ C_{ethyl\ hexanoate}$	32	0·748	29·31	0·01	0·480
$I = 0{\cdot}21 + 0{\cdot}40\ C_{ethyl\ butyrate} + 0{\cdot}65\ C_{ethyl\ hexanoate}$	32	0·778	16·90	0·05	0·465
$I = 0{\cdot}13 + 0{\cdot}40\ C_{ethyl\ butyrate} + 0{\cdot}33\ C_{ethyl\ hexanoate} + 0{\cdot}38\ C_{ethyl\ octanoate}$	32	0·802	11·76	0·05	0·463
Second-order term: tropical fruit					
$I = 0{\cdot}44 + 0{\cdot}25 \sum_{acetates}$	32	0·873	73·72	0·001	0·436
$I = 0{\cdot}62 - 0{\cdot}09 \sum_{ethyl\ esters} + 0{\cdot}29 \sum_{acetates}$	32	0·879	37·43	0·01	0·435
$I = 1{\cdot}14 - 0{\cdot}31 (\sum_{ethyl\ esters}/\sum_{acetates}) + 0{\cdot}19 \sum_{acetates}$	32	0·891	42·37	0·01	0·414

The sensory terms considered in this study are also correlated between themselves. The first-order term fruity, that includes the two second-order terms, tree fruit and tropical fruit, is strongly correlated with both of them (0·85 and 0·84 for the tropical and tree fruit, respectively) while the correlation founded between the two second-order descriptors was 0·55. These values are however, below the correlation coefficients found between these compounds (total amount of esters versus acetates is 0·974; versus ethyl esters is 0·904, and acetates versus ethyl esters is 0·786).

Results of principal component analysis are shown in Figs 1 and 2. The two diagrams were produced using only the chemical information and the sensory information was then superimposed, on this occasion considering the wines as belonging to different categories. The quantitative categories (see Fig 1) were directly extracted from the first-order term information. Wines with a score bigger than 2·3 were designated strongly fruity wines with a score between 1·3 and 2·3 fruity, those between 0·5 and 1·3 slightly fruity, and those below 0·5 not fruity. The qualitative categories were assigned in the following way: if the score of one of the two second-order terms was 1·5 points above the other, the wine was considered as belonging to the category that scored higher; if the difference was below 1·5 it was assigned to the category 'tropical and tree fruits'. Finally, the wines that were considered in the previous diagram as not fruity were assigned to this same category. The advantage of these diagrams is that we can correlate a certain region of the chemical hyperspace that contains the wines (now reduced through PCA to a smaller dimension) with the possession of a particular attribute of aroma intensity and quality, solving with this approach the problems derived from the collinearity between the variables. The two first com-

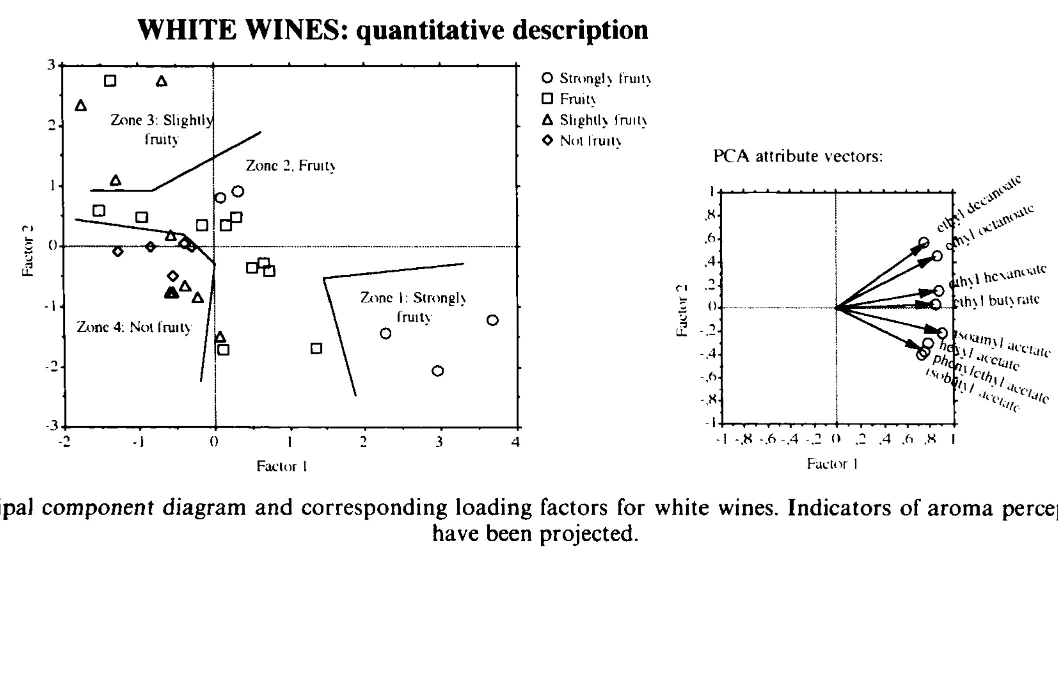

Fig 1. Principal component diagram and corresponding loading factors for white wines. Indicators of aroma perception intensity have been projected.

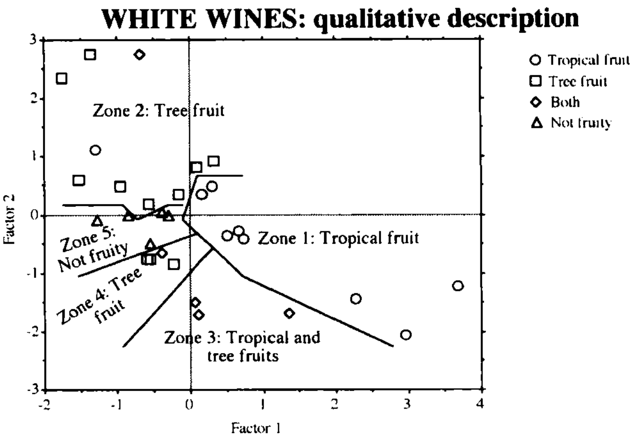

Fig 2. Principal component diagram from white wines. Indicators of aroma quality perception have been projected.

ponents account for 78% of the total variance, the first component accounts for 61% . It can be observed that all variables have positive weights in the first component. With respect to fruity aroma intensity, the highest (zone 1) corresponds to those samples with high total ester content, particularly acetates, while the null aroma intensity (zone 4) corresponds to samples with a low total ester content, particularly ethyl esters, or with a ethyl ester/acetate ratio of approximately 1/1. Comparatively it can be said that wines with higher proportion of ethyl esters have higher aroma intensities than analogous wines with higher proportion of acetates; there seems to be a zone where ethyl esters and acetates have antagonistic effects. This implies that a large amount of all esters results in an intense aroma perception, but the opposite is not true. The composition profile also plays an important role so that wines with richer ethyl ester profile need a smaller amount of total esters in order to reach an intense perception.

There are five different zones from the point of view of qualitative perception (see Fig 2). Zone 1 corresponds to large amounts of esters and acetate-rich profiles; it groups wines showing mainly tropical fruit aromas. Zone 2 corresponds to small or medium total ester content and ethyl ester-rich profiles; it groups wines with tree fruit aromas. Zone 3 appears to be a transition zone, it is defined by medium total ester content and profiles dominated by acetates; perception is of a mixture of tropical and tree fruits. Zone 4 groups wines whose predominant aroma is again tree fruit, and corresponds to small amounts of total esters and profiles slightly higher in acetates. Zone 5 groups samples with null intensities.

It seems therefore that high acetate contents determine tropical fruit perception, but minimal amounts of ethyl esters are also needed to sustain the perception. In zone 3, which is poorer than zone 1 in ethyl esters, perception was mixed, while in zone 4 the tree fruit note was perceived, indicating that when the total amount of esters is small, perceived aroma tends to be tree fruit independently of aroma profile, with the exception of a 1/1 profile where the perceived aroma is null. On the contrary, ethyl esters do not seem to require acetates so the perceived aroma is tree fruit when the aroma profile is richer in ethyl esters.

Rosé wines

In this case there is a much more complex behavior than that observed in white wines as was already anticipated when red berry, which does not coincide with aroma descriptors for fermentation esters, was chosen as a descriptor. Other aroma components in this type of wine may play an important role by overlaying, opposing or complementing the ester role. Results of this study can be seen in Table 9. The correlations found are poorer, but are better for individual compounds than for the summation of esters. Significant correlations for the first-order term fruit intensity have been found, but not for second-order terms. The SEE rank between 0·68 and 0·69 for the model containing the global parameters; they rank between 0·55 and 0·59 when the individual compounds are considered. It is worth mentioning the equations that best fit the first-order sensory data are rather similar to the ones found when working with white wines and the second-order term tropical fruit. That is to say, the ethyl esters seem to have in this case only a secondary role in the perception of fruitness in a rosé wine. A second consequence arises from the fact that the total amount of acetates could not be correlated with the tropical fruit content. These facts seem to indicate that a rosé wine is rather

TABLE 9

Stepwise correlation analysis—rosé wines

Equation	*n*	*r*	*F*	*p*	*SEE*
First-order term: fruity					
$I = 0{\cdot}13 + 0{\cdot}237 \sum_{\text{acetates}}$	20	0·692	10·12	0·05	0·677
$I = 0{\cdot}867 - 0{\cdot}27 (\sum_{\text{ethyl esters}}/\sum_{\text{acetates}}) + 0{\cdot}157 \sum_{\text{acetates}}$	20	0·717	5·28	0·1	0·687
$I = -0{\cdot}0897 + 7{\cdot}772\, C_{\text{hexyl acetate}}$	20	0·775	16·6	0·05	0·593
$I = -0{\cdot}252 + 0{\cdot}133\, C_{\text{isoamyl acetate}} + 5{\cdot}84\, C_{\text{hexyl acetate}}$	20	0·828	10·87	0·05	0·553
$I = -0{\cdot}157 + 0{\cdot}076\, C_{\text{ethyl hexanoale}} + 0{\cdot}131\, C_{\text{isoam acetate}} + 5{\cdot}89\, C_{\text{hexyl acetate}}$	20	0·828	6·55	0·1	0·582

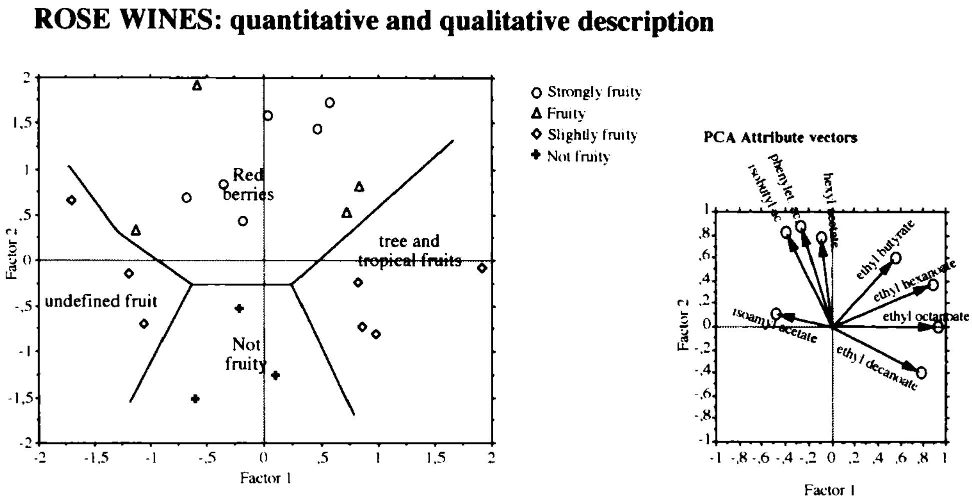

Fig 3. Principal component diagram and corresponding loading factors for rosé wines. Indicators of aroma intensity have been projected. The separated regions indicate different qualitative perceptions.

different from a white wine from the point of view of sensory perception.

The results obtained by principal component analysis are shown in Fig 3. The two first components account for 68% of total variance, 39% corresponds to the first component, and 29% to the second one. Intensity is in this case related to the second component, where isobutyl, hexyl and phenylethyl acetates have the highest loadings. With respect to aroma perception quality, the zone where the predominant fruit note is red berry is a zone of high ester content, and a ester profile slightly richer in acetates than in ethyl esters. The zone where tree and tropical fruit notes predominate is a zone of high relative content of ethyl esters. In this case aroma intensities were very weak. The zone that groups samples of high isoamyl acetate content and low ethyl ester content are also zones of very low aromatic perception, where none of the fruit notes appeared clearly defined. The zone occupied by samples with no fruit aroma corresponds to wines with low ester content.

Therefore, it should be concluded that esters play a main part in aroma perception, since in the chemical space defined by them wines are grouped following certain sensory criteria. However, the behaviour or these compounds is very different from that we found in the case of the white wines. In all caes wines that scored high in fruit also scored high in the second-order term red berry. On the other hand, no wine scored high in tree or tropical fruits. These facts may indicate that in these wines there is not a lineal sensory response for the second order terms. If this is due to the interaction of these compounds with some other compound in the matrix (altering in any case the headspace composition), or to the direct effect of a third compound or class of compounds (altering then the impression in the pituitary) is a question that remains open and that requires further research.

Red wines

Red wines differed from the other two groups in their lower ester content. It has been impossible to find a significant correlation between ester content and intensity of fruit aroma perceptions in these samples.

Figures 4 and 5 show principal component analysis. The plane of the two first components accounts for 81·1% of the total variance: 65·7% by first component, and 16·1% by the second one. The ester content plays a negative role on fruit aroma perception. Samples with higher ester content are those with null fruit aroma intensity. Samples with high ester content are those which underwent high levels of anaerobiosis which resulted in low-quality wines with off aromas. There is not much to say about qualitative aroma perception due to the high polarisation introduced by the previous factor. In any case it has been demonstrated that the intensity of the fruit notes it is not related to the ester content of a red wine. Therefore, it should be conclude that there are some other different compounds directly responsible for the fruit notes in the red wines.

CONCLUSIONS

Fermentation esters play a main role on fruit notes of white wine aroma, and determine the intensity as well as the quality of aroma perception. The ratio of ethyl esters to acetates, and the total ester content seem to be the variables that better express the system. In rosé wines the role played by esters is still important, but it is not as clear as the one observed in white wines. Other components different from the esters must take part in the fruit notes of these wines. Finally, in red wines esters play a supporting role in aromatic perception, and other compounds play a main role.

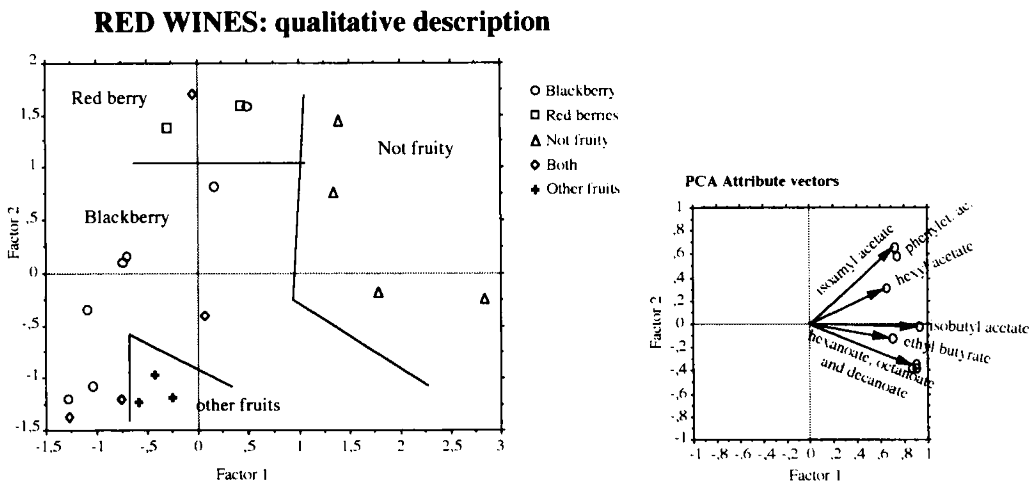

Fig 4. Principal component diagram and corresponding loading factors for red wines. Indicators of aroma perception quality have been projected.

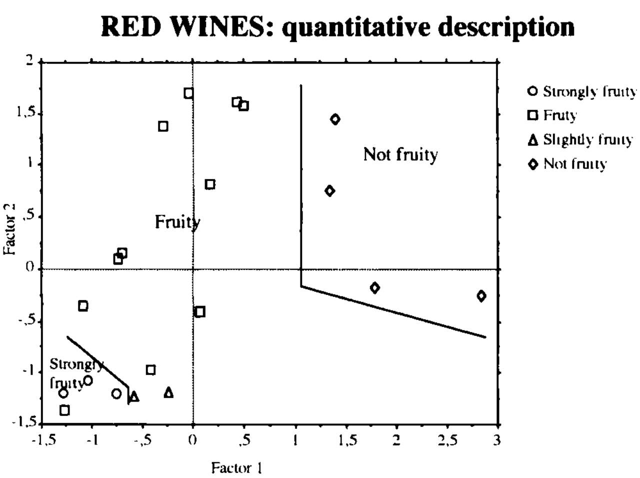

Fig 5. Principal component diagram for red wines. Indicators of aroma perception intensity have been projected.

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