

The Contribution of Hydrolyzed Flavor Precursors to Quality Differences in Shiraz Juice and Wines: An Investigation by Sensory Descriptive Analysis

N. A. ABBOTT¹, B. G. COOMBE², and P. J. WILLIAMS^{3*}

Volatile components liberated by hydrolysis of C-18 reversed phase isolates from *Vitis vinifera* cv. Shiraz juice were evaluated by sensory descriptive analysis. The isolates were hydrolyzed at pH 3.2 or by treatment with a non-selective glycosidase enzyme. Shiraz juices assigned as high and low 'quality', each sourced from two regions and sampled in 1988 and 1989, were studied. Wines made from the 1989 juices were also subjected to descriptive analysis. The results showed that for one pair of wines and all but one pair of hydrolysates, the quality differences could be distinguished and quantified. The glycosidic hydrolysates prepared by both methods were found to contribute non-berry attributes to wine such as 'stalky', 'earthy', and 'cigar/tobacco'. Wines considered to be of high quality were rated higher in these non-berry attributes than their low quality counterparts, and it may be deduced that glycosidic hydrolysates contain aroma compounds that are important to high quality Shiraz wine.

KEY WORDS: Shiraz, sensory analysis, quality, enzyme hydrolysis, acid hydrolysis, flavor precursor

The role of glycosidic conjugates of volatile compounds as precursors of flavor in grapes and wine is now better understood (8,9). Analysis of volatiles liberated by either acid or glycosidase enzyme hydrolysis of the glycosidic fraction has provided some insight into the flavor compounds responsible for the sensory properties of non-floral varieties (9). To date, however, this approach of precursor analysis has been confined to comparisons of the volatile composition of white wine grape varieties.

We have recently adapted this approach to attempt a more quantitative determination of 'quality' in a black variety, *Vitis vinifera* cv. Shiraz (1). The grapes were sampled from commercial vineyards under different viticultural management regimes and from three different climatic regions. The high and low 'quality labels' were given to the Shiraz samples by both winemakers and viticulturists based on their experiences with the wines made from the respective vineyards (see **Materials and Methods**). The study is still at a preliminary stage, but has indicated that Shiraz grapes of high quality, when compared with grapes of lesser quality, yield a greater concentration of volatiles as enzyme-liberated products and a greater number of volatiles deconjugated by acid hydrolysis of the respective precursor fractions (1).

In conjunction with the chemical analysis of the volatile components released from the conjugates, it is

necessary to investigate the flavor properties of the volatiles bound in the precursor fraction of Shiraz. Specifically, there is a need to determine the contribution made by the deconjugated volatiles to the sensory properties of Shiraz and to give sensory validation to the premise on which the research is based, *i.e.* that samples from vineyards traditionally yielding fruit varying in quality can objectively be distinguished. These aims necessitate the application of sensory descriptive analysis (4) to base wines spiked with the acid and enzyme hydrolysates. The aims also require comparison of the sensory properties of the spiked samples with those of wines made from the grapes from which the precursor fractions were derived. This paper reports the results of these sensory studies.

Materials and Methods

Samples: The juice samples were selected from three viticultural regions and of three different qualities. The word 'quality' as used in this paper relates to expected market value as wine. The assignments of 'high', 'medium', and 'low' quality were obtained from: (a) the winemakers' evaluation of the fruit; (b) the commercial and, where appropriate, show records of wines from the vineyards; and (c) the viticultural characteristics of the vineyards. The yield from the vineyards assigned as being of low quality was two to three times greater than that from the high quality vineyards for both regions and years. The high quality fruit came from vineyards which supplied grapes used in premium wine production. Low quality fruit was used for bulk wine production.

The four wines were prepared commercially from high and low quality grapes from the Coonawarra and the Barossa Valley regions in 1989. They were sampled directly after fermentation and had received no wood treatment.

¹Department of Plant Physiology, Waite Agricultural Research Institute, The University of Adelaide, Glen Osmond, South Australia, 5064; and ²The Australian Wine Research Institute, Glen Osmond, South Australia, 5064.

*Author to whom correspondence should be addressed.

This research was conducted at The Australian Wine Research Institute. We thank the staff members of The Australian Wine Research Institute for participating on the sensory panel, industry members who contributed both wine and grape samples and the Grape and Wine Research Council for funding the research.

Manuscript submitted for publication 19 July 1990.

Copyright © 1991 by the American Society for Enology and Viticulture. All rights reserved.

Extraction of volatiles from juice precursor fractions: Precursor fractions isolated from Shiraz juice (500 mL) by retention on C-18 reversed phase silica gel were subjected to acid or enzyme hydrolysis as previously described (1) with the exception that no internal standards were added. The enzyme added was Rohapect C, a commercial pectinase preparation containing glycosidase activities (3). The hydrolysis products were isolated by continuous extraction with dichloromethane. Solvent was removed from these extracts by distillation through a column of Fenske's helices to give a concentrate of *ca* 100 μ L. The concentrate was taken up in water (10 mL), and the aqueous solution was rotary evaporated *in vacuo* at room temperature for 10 minutes to remove the solvent residue. Each sample was adjusted to a volume of 20 mL with water and stored at -20°C .

Sensory studies, general aspects: The samples and reference standards were prepared fresh each morning. All samples were presented to the panel in 20-mL aliquots in coded, clear, tulip-shaped glasses. Panelists assessed the samples by aroma only, before midday, in isolated booths under red light at $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

For both duo-trio difference tests and descriptive analyses, the precursor hydrolysates were presented to the panel in a neutral base Shiraz wine at a concentration equivalent to that at which the precursor glycosides were present in the original juice. For the purpose of comparing spiked samples, a neutral base wine exhibiting minimal background aroma was required. This base

wine was chosen and prepared to generate a matrix as close to a red wine medium as possible. It was prepared by rotary evaporating 300 mL of commercial bulk Shiraz wine *in vacuo* at room temperature for three hours to a final alcohol strength of *ca* 8%. The wine samples were taken from a fresh bottle for each replicate.

Duo-trio difference tests: These tests were conducted by the procedure described by Amerine *et al.* (2). The neutral base wine was used as the reference in difference tests for the precursor hydrolysates. The reference used in difference tests involving wine samples was one of the pair under evaluation. Two sets of duo-trio tests were evaluated at each session, each sample being assessed only once by a panel of 26 staff members of The Australian Wine Research Institute. The significance of the duo-trio tests were determined from detailed statistical tables for one-tailed tests, $p = 1/2$ (7).

Descriptive analyses: Fourteen staff members from the Institute were selected to take part in the descriptive analyses according to their availability and interest in the project. All panel members had participated in the duo-trio tests and were familiar with the samples. The initial training session involved the assessment of several commercially available Shiraz wines. The aroma descriptors suggested in this session formed the basis for the development of a range of descriptive standards. Wines and precursor hydrolysates were presented at a further twelve training sessions during which these descriptive standards were assessed and modified. Twelve attributes were considered by the

Table 1. Descriptive attributes and composition of stock mixtures and reference standards.

Attribute code	Attribute	Composition of stock mixture	Portion used in reference standard
H/R	Honey/raisin	Raisins (10 g) were steeped in water (20 mL) for 48 h and combined with a 1:2 mixture of honey (Adelaide Hills) and water (20 mL)	2 mL
BER	Berry	Blackberry jam (Beerenberg, 15 g), black current jam (Cottee's, 15 g), Ribena cordial (2 mL), and blackberry juice (John West, 2 mL) were added to 15 % ethanol (23 mL)	5 mL
STR	Strawberry	Strawberry jam (home made)	4 g
R/V	Rose/violet	20 μ g/L α -ionone plus 2-phenethanol (0.1 mL) in ethanol (20 mL)	0.1 mL 0.05 mL
CIT	Citrus	E30817 VMane Fils natural passion fruit flavor (0.1 mL) in ethanol (10 mL) with 99.9% lemon juice (Berri, 0.2 mL)	1 mL
SPC	Spice	Whole cloves (20) steeped in ethanol (7.5 mL, 24 h), removed, and liquor made up to 20 mL with ethanol	0.01 mL
		Whole pimentos (10) steeped in ethanol (7.5 mL, 24 h), removed, and liquor made up to 10 mL with ethanol	0.2 mL
PEP	Pepper	Black peppercorns (10) crushed and steeped in ethanol (10 mL, 24 h), then diluted 1:1 with ethanol	0.2 mL
STK	Stalky	Geranium stalks Cut grass	1 g 200 mg
EAR	Earthy	Mushroom compost (1 g) in water (20 mL) Earth/bark	1 mL 500 mg
C/T	Cigar/tobacco	Short panatella cigars (Henri Winterman, 700 mg) steeped in a mix of water (20 mL, 24 h) and ethanol (1 mL) Cigarette tobacco (500 mg) steeped in water (20 mL, 24 h)	4 mL 4 mL
LIC	Licorice	Licorice strand	4 g
CHOC	Chocolate	Cooking chocolate (Cadbury Bourneville, 23.8 g) and cocoa (Cadbury Bourneville, 1 g) suspended in water (40 mL)	2 mL

¹Portion of stock mixture made up in base wine (60 mL).

panel as necessary to describe the sensory properties across the samples. The composition of the standards used to describe the twelve attributes is given in Table 1.

The 20 samples selected for descriptive analysis were presented in a random order with no two samples being evaluated together more than once. All samples were presented in duplicate except the base wine which was randomly presented on five occasions throughout the study. At each session three samples were evaluated. The twelve reference standards were present in each booth along with the samples. Panelists were asked to smell the standards individually in the order given in Table 1 and then rate the intensity of each aroma in the samples. Aroma intensities were rated on a 10-point scale 0 to 9 where 0 = no attribute present and 9 = high, *i.e.* equal to the aroma of the standard. The aroma intensity of the standards were not sufficiently great to present any obvious interference to the test samples.

Statistical analyses: Statistical analyses were performed using NH Analytical software 'Statistix' (Roseville, MN). The consulting services of Lindsay Veitch Inc. were employed.

No judges were removed from the panel, therefore, the mean scores of the 14 assessors for each attribute and for each sample were used in all analyses.

The 1988 and 1989 samples were processed as one data set as the error structure for both years was expected to be the same even though there was an added treatment, *i.e.*, wine in the second year. Consequently, the experimental design was non-orthogonal and multiple regression analysis (MRA) rather than the usual analysis of variance (AOV) was performed on the data. If AOV had been chosen as the method for statistical analysis, separate analyses would have been necessary for each of the two years, leading to difficulties in any subsequent comparisons. A further benefit of the MRA was that an assessment of any carry-over effect was possible to determine if the intensity of the aroma of any samples biased the results of another sample assessed in the same set. This carry-over effect could not be calculated using AOV.

A design matrix was thus established to enable the data to be analyzed as a single data set and to allow differences in quality between samples to be investigated. This design matrix was, therefore, constructed to include the main variables: *i.e.*, year, y (1988 and 1989), region, r (Barossa and Coonawarra), quality, q (high and low), and treatment, st 1 and st 2 (enzyme hydrolysis, acid hydrolysis, and wine)

and all possible interactions among them. Thus, the main effects were y, r, q, (st 1 and st 2) with degrees of freedom 1, 1, 1, and 2, respectively. Additionally, allowance was made for a possible carry-over effect, c, taking one degree of freedom. The first order interactions were $y \times r$, $y \times \text{st 1}$, $r \times q$, ($r \times \text{st 1}$ and $r \times \text{st 2}$) and ($q \times \text{st 1}$ and $q \times \text{st 2}$). The term $y \times \text{st 2}$ was omitted because it was linearly dependent on y, st 1, and $y \times \text{st 1}$. Thus, first order interactions used 1, 1, 1, 1, 2, and 2 degrees of freedom, respectively. Second order interactions were $y \times r \times q$, $y \times r \times \text{st 1}$, $y \times q \times \text{st 1}$, and ($r \times q \times \text{st 1}$ and $r \times q \times \text{st 2}$) with 1, 1, 1, and 2 degrees of freedom, respectively. The terms $y \times r \times \text{st 2}$ and $y \times q \times \text{st 2}$ were omitted because of their linear dependency on the other variables. Finally, for the third order interaction there was $y \times r \times q \times \text{st 1}$ with one degree of freedom; $y \times r \times q \times \text{st 2}$ being omitted because of linear dependency on the other variables. Hence, the forty observations provided 1, 5, 1, 8, 5, 1, and 19 degrees of freedom for the grand mean, main effects, possible carry-over effect, first order, second order, and third order interactions and error, respectively. All significance tests used the error mean square on 19 degrees of freedom.

Results and Discussion

Duo-trio data: The duo-trio difference test results reported in Table 2 demonstrate that for most samples the volatiles released from the bound fractions of Shiraz juices, either by acid or enzyme hydrolysis, conferred on the base wine sensory properties significantly different from those of the control (a neutral base Shiraz wine without any addition). It is important to note that not all

Table 2. Results of the duo-trio difference tests for aroma of enzyme hydrolysates (EH) and acid hydrolysates (AH) compared to that of the base wine.

Quality	Region	Year	EH		AH	
			No. of correct responses	Sig	No. of correct responses	Sig.
High	Barossa	1988	20/28	**	21/28	**
High	Barossa	1989	19/24	***	20/28	**
Mid	Barossa	1988			21/29	***
Mid	Barossa	1989	20/29	*	19/28	*
Low	Barossa	1988	18/24	**	21/29	***
Low	Barossa	1989	24/27	***	20/30	**
High	Coonawarra	1988	21/24	***	19/27	*
High	Coonawarra	1989	21/24	***	24/28	***
Mid	Coonawarra	1988	14/22	ns	19/25	**
Mid	Coonawarra	1989	21/27	***	17/29	ns
Low	Coonawarra	1988	23/27	***	20/28	**
Low	Coonawarra	1989	13/27	ns	19/28	*
High	Langhorne Ck.	1988	22/24	***	17/30	ns
High	Langhorne Ck.	1989	13/24	ns	16/26	ns
Mid	Langhorne Ck.	1988	16/28	ns	20/25	***
Low	Langhorne Ck.	1988	22/27	***	10/25	ns
Low	Langhorne Ck.	1989	18/27	ns	17/30	ns

*, **, *** = significance at $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively.

ns = no significant difference.

Where no values are shown, sample not analyzed.

Table 3. Results of duo-trio difference tests between two pairs of hydrosylates.

Hydrosylate comparison	Samples ¹	Significance
AH vs. EH	M and E	***
AH vs. AH	I and M	***

AH = acid hydrolysis product.

EH = enzyme hydrolysis product.

¹Refer to Table 5 for sample codes.

*** = significance at $p < 0.001$.

the samples could be distinguished in these tests; *i.e.*, most of those from Langhorne Creek were not distinguished from the control by the panel. Because of the almost uniformly positive difference responses given by the panel to the high and low quality hydrolysates from Barossa and Coonawarra juices, these samples were chosen for descriptive analysis. Although the 1989 low quality enzyme hydrolysis sample from Coonawarra was not significantly different from the base wine, for completeness of the data set it was included in the descriptive analyses.

Previous studies of the sensory properties of precursor hydrolysates from non-floral grapes have shown that only the acid hydrolysates could be detected when these were back-added to a base wine (9). Products given by glycosidase hydrolysis from Chardonnay (5,9) and from Sauvignon blanc and Semillon (9) were not detectable when assessed at a concentration near to that at which the precursor glycosides occurred in the original wine. In contrast, most of the Shiraz samples examined gave both acid and enzyme hydrolysates with sensory properties detectable at single strength in a base wine. As the previous investigations of the acid- and enzyme hydrolysates involved only single samples for each variety, this present finding for Shiraz suggests that examination of the enzyme hydrolysates from a wider range of samples of non-floral white varieties may yet allow observation of positive duo-trio responses.

Duo-trio data in Table 3 confirm that the panel could distinguish between the volatiles released from a precursor fraction by hydrolysis with a glycosidase enzyme, and those released by acid hydrolysis. Furthermore, the acid hydrolysates liberated from a high quality juice were perceived by the panel as being significantly different from those liberated from a low quality juice. The wines prepared from the high quality grape samples were significantly different from those prepared from the low quality grape samples for both the

Table 4. Results of duo-trio difference tests for the aroma of high vs. low quality wine samples from two regions.

Region	Samples ¹	Significance
Barossa	Q and S	**
Coonawarra	R and T	***

** and *** indicate significance at $p < 0.01$ and $p < 0.001$, respectively.

¹Refer to Table 5 for sample codes.

Table 5. Codes of samples evaluated by descriptive analysis.

	1988	1988	1989	1989
	Barossa	Coonawarra	Barossa	Coonawarra
Low quality EH	A	B	C	D
High quality EH	E	F	G	H
Low quality AH	I	J	K	L
High quality AH	M	N	O	P
Low quality wine			Q	R
High quality wine			S	T

EH = enzyme hydrolysis products.

AH = acid hydrolysis products.

Barossa and Coonawarra regions (Table 4). The identification codes for the 20 samples chosen for descriptive analysis are given in Table 5.

Statistical analyses: Multiple regression analyses (MRA) were executed on the mean scores of the fourteen assessors for each attribute for the entire model. As a possible means of simplifying the interpretation of the data, principal component analyses (PCA) were run on the correlation matrix from the fitted values of all samples. The first two principal components (PCs) are described in Figure 1 and account for 91.2% of the total variance of the data. This principal component diagram demonstrates a separation of the hydrolysates from the wine samples along PC1 and a separation of the acid hydrolysates from the enzyme hydrolysates along PC2.

The eigenvectors calculated from the correlation matrix describe the relative positions and loadings of the twelve attributes as used by the panel and are illustrated in Figure 2. The vectors indicate how each attribute was used by the panel in the descriptive analysis over all the samples; note that all attributes were used by the panel as significant descriptors for the

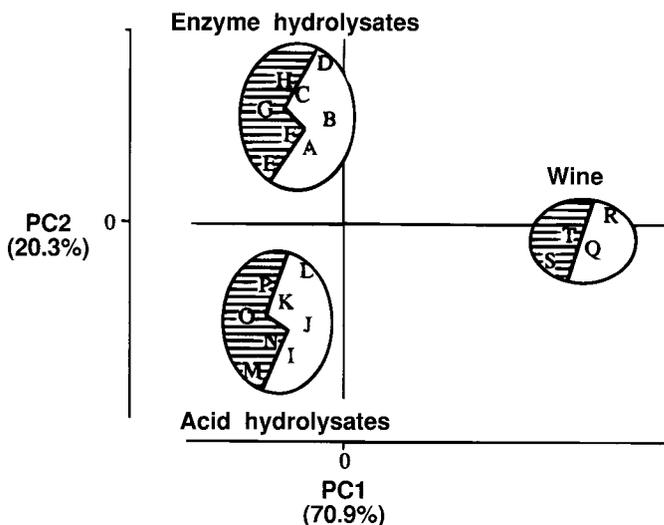


Fig. 1. Projection of sensory descriptive data for all samples (A to T) on principal components PC1 and PC2. Refer to Table 5 for sample identification codes. The high quality samples are represented by the shaded portion.

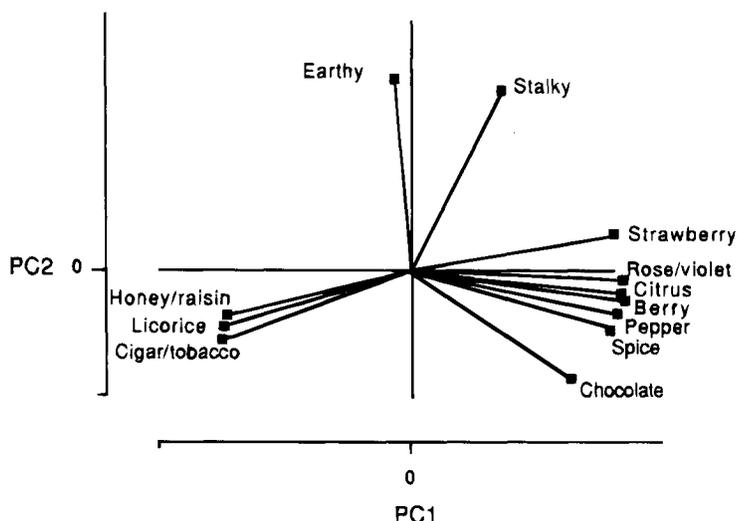


Fig. 2. Relative positions and loadings of the twelve attributes used in the descriptive analysis for samples A to T on principal components PC1 and PC2. Refer to Table 5 for sample identification codes.

samples being tested. The vector diagram (Fig. 2) corresponds to the PC diagram (Fig. 1); superimposition indicates which attributes were used by the panel to describe the sample groups.

The wine samples were separated from the juice hydrolysates along PC1 in terms of the attributes berry, strawberry, rose/violet, citrus, and pepper which were collectively important to the wines and the opposing earthy and cigar/tobacco attributes which were important to the hydrolysates. The major attributes contributing to the separation of the hydrolysates along PC2 were cigar/tobacco, honey/raisin, stalky, and earthy. It is interesting to note that for both hydrolysate groups the high quality samples are positioned on the left indicating that they are being displaced from the low quality by a common attribute or attributes.

Interactions of independent variables: The MRAs of the full model over the twelve attributes

showed that many of the first and second order interactions were significant. To simplify the description of the data, it was decided to ignore any interactions which did not exhibit significance when analyzed as an entire group: *e.g.*, all first order interactions together, *etc.* To determine if the independent variables made a significant contribution to the overall model, F-ratios were calculated for each group over the 20 samples and for each attribute and are presented in Table 6 with their significant differences.

Year was a significant factor for five attributes and region for six attributes. This result was not unexpected: the two years experienced different weather patterns during grape ripening, and the two regions have different climate and soil types and also different canopy management regimes. Quality was significantly different for seven of the twelve attributes studied indicating that the panel was able to distinguish the high from the low quality samples.

Treatment was a significant variable for the majority of attributes over all the samples, the implication of which shall be discussed below. The first order interactions contributed significantly to the model for five of the attributes analyzed - honey/raisin, strawberry, citrus, stalky, and cigar/tobacco. There were no significant second order interactions, and the third order interactions were barely significant for three attributes - berry, strawberry, and stalky. The relative magnitudes of the F-ratios in Table 6 justify confining attention to the main variables, hence the significant first and third order interactions will not be discussed further.

The source of the significance within each group of independent variables in Table 6 can be determined from the pooled means of the fitted values for the component parts of each year (*i.e.*, 1988 and 1989), region (Coonawarra and Barossa), quality (high and low), and treatment (enzyme hydrolysates, acid hydrolysates and wine) groups. The pooled means of the fitted

Table 6. F-ratios of significant independent variables for the 12 attributes over 20 samples with degrees of freedom (df) and significance.

Attribute	Year	Region	Quality	Treatment	1 st order	2 nd order	3 rd order
Honey/raisin	38.11 ***			15.49 ***	3.89 **		
Berry	12.51 **	6.37 *	13.07 **	7.99 **			5.70 **
Strawberry		41.97 ***	27.01 ***	10.76 ***	5.34 **		7.94 **
Rose/violet				7.93 **			
Citrus		98.02 ***	53.82 ***	26.76 ***	4.56 **		
Spice				19.57 ***			
Pepper	13.90 ***	4.47 *	26.49 ***	9.04 **			
Stalky		14.72 ***	22.81 ***	7.93 **	3.60 *		5.26 **
Earthy			13.10 **				
Cigar/tobacco	37.97 ***		71.90 ***		3.24 *		
Licorice	13.45 **			5.86 **			
Chocolate		21.17 ***					
df	1	1	1	2	8	5	1

*, **, *** indicate significance at $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively. The residual mean squares have 19 degrees of freedom.

Table 7. Pooled means of fitted values for the significant main variables - year, region, juice, and treatment - and the significant differences across the variables for the 12 aroma attributes.

	Mean values												
	Year			Region			Quality			Treatment			
	1989	1988	Sig.	Cw	Bar	Sig.	Low	High	Sig.	Enzyme	Acid	Wine	Sig.
	(n = 24)	(n = 16)		(n = 20)	(n = 20)		(n = 20)	(n = 20)		t1	t2	t3	
Honey/raisin	2.355	2.386	ns							2.331	2.702	1.788	** ** *
Berry	2.298	2.239	ns	2.321	2.212	ns	2.345	2.187	ns	2.099	2.175	2.838	ns *** **
Strawberry				1.936	1.579	**	1.852	1.662	*	1.661	1.578	2.363	ns *** **
Rose/violet										1.390	1.465	2.872	ns *** **
Citrus				1.516	1.229	*	1.489	1.255	*	1.116	1.146	2.388	ns *** **
Spice										0.990	1.099	1.888	ns *** **
Pepper	1.876	1.794	ns	1.903	1.769	ns	1.772	1.898	ns	1.707	1.756	2.305	ns *** **
Stalky				1.639	1.409	*	1.442	1.605	ns	1.776	1.262	1.597	*** ns ns
Earthy							1.489	2.113	*				
Cigar/tobacco	2.051	2.569	**				2.032	2.467	**				
Licorice	1.391	1.194	*							1.103	1.341	1.688	** *** **
Chocolate				0.968	1.232	*							

Cw = Coonawarra; Bar = Barossa.

*, **, *** indicate significance at the $p < 0.1$, $p < 0.01$, and $p < 0.001$, respectively.

ns = no significant difference.

values and their significant differences are presented in Table 7.

The results for the comparisons amongst the three treatments, *i.e.*, enzyme hydrolysates (samples A to H), acid hydrolysates (samples I to P), and wines (samples Q to T) over both regions and both years show that both the acid hydrolysates and enzyme hydrolysates when compared with the wines were significantly different for all attributes except stalky; the enzyme and acid hydrolysates differed only for three attributes, honey/raisin, stalky, and licorice. Nevertheless, the level of significant difference in the three distinguishing attributes indicated that the hydrolysate types should be treated separately.

Differences among the samples: Fischer's LSD test (6) was used to determine the significance of the differences between individual samples hence allowing an investigation into the source of the differences shown in Table 7.

Comparisons between high and low quality enzyme hydrolysates (*i.e.* samples A to H) and the high and low quality acid hydrolysates (*i.e.* samples I to P) (Table 8) demonstrated that, for both the two regions and the two years, qualities were significantly different for at least one attribute for all samples except I and M. Most of the differentiating attributes in both the acid and enzyme hydrolysis products were rated quantitatively higher for the high quality samples.

With regard to the differences between the high and low quality wines, the panel found that the Coonawarra pair were significantly different (Fig. 3). The high quality Coonawarra wine was rated higher for the non-berry-type attributes, *i.e.*, stalky, earthy, cigar/tobacco, and licorice, while the low quality wine was rated higher

in berry, strawberry, and citrus. The high and low quality Barossa wines (samples Q and S) could not be differentiated by descriptive analysis even though they were found to be significantly different in the duo-trio tests (Table 4). Descriptive analysis data for the Barossa wines are not shown.

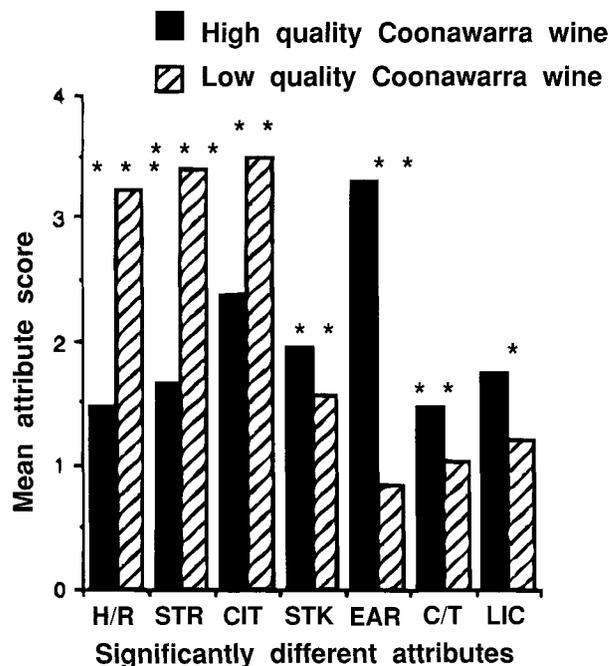


Fig. 3. Mean attribute scores for seven attributes showing significant differences between high and low quality Coonawarra wines (samples T and R). *, ** and *** indicate that differences are significant at $p < 0.05$, 0.01 , 0.001 , respectively. Refer to Table 1 for attribute codes.

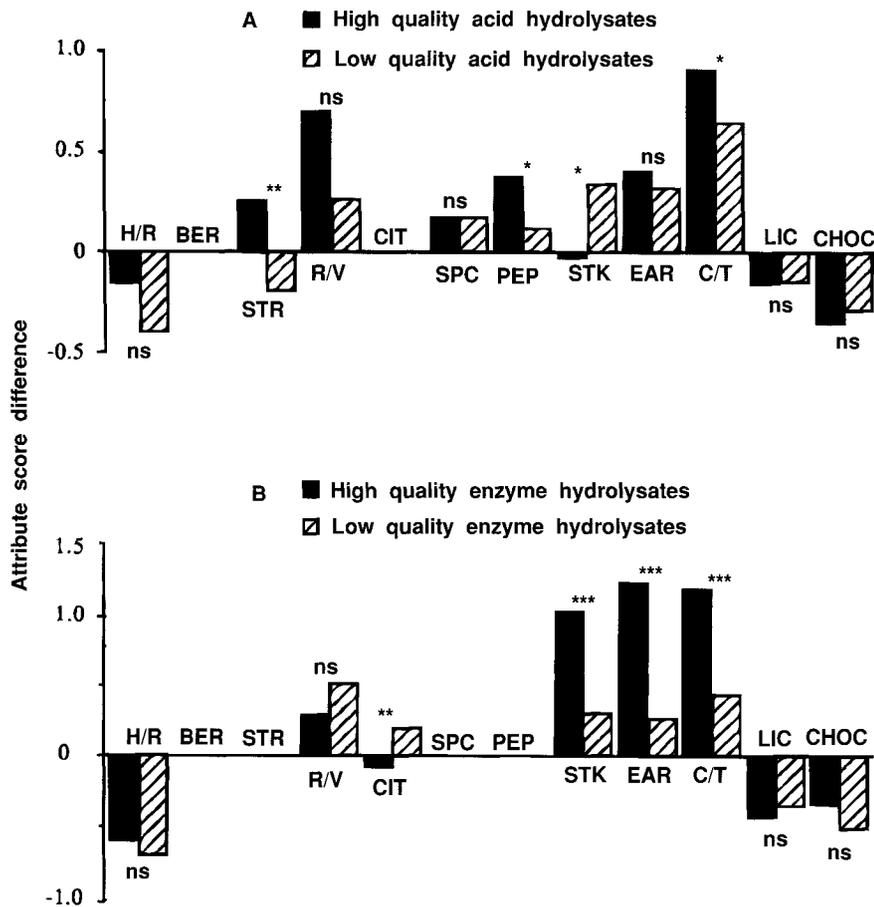


Fig. 4. Each histogram shows the difference between the mean attribute score for a hydrolysate and the corresponding base wine score, for those attributes in which either one or both mean scores differ significantly from zero *i.e.*, the base wine. Acid hydrolysates are shown in A and enzyme hydrolysates in B. ns, *, ** and *** indicate differences between the high and low quality hydrolysates are not significant, significant at $p < 0.05$, 0.01 and 0.001 , respectively. Refer to Table 1 for attribute codes.

Relationships between sensory data for precursor hydrolysates and wines: To focus on the effects of hydrolysate addition to the base wine, the mean attribute scores of the hydrolysates were subtracted from the corresponding base wine scores (Figure 4). The base wine is represented in Figures 4A and 4B as zero on the y-axis. Histograms are shown for the attributes where either one or both of the hydrolysate pairs were significantly different from the base wine.

tobacco, which were quantitatively dominant in the high quality enzyme hydrolysates and, in the case of the last attribute was also dominant in the high quality acid hydrolysates, were the same as those characterizing the high quality wine from Coonawarra. This common sensory feature of the high quality samples was also observable from the data in Table 6 which showed that cigar/tobacco and earthy were significant quality determinants across all treatments.

At least one of the attribute scores for the quality pairs of the acid hydrolysates, presented in Figure 4A was rated significantly higher than the base wine for seven attributes - strawberry, rose/violet, spice, pepper, stalky, earthy, and cigar/tobacco. The high quality acid hydrolysates were given a higher mean score for strawberry, pepper, and the quantitatively-important attribute cigar/tobacco than their low quality counterparts.

Five attributes were scored higher than the base wine for at least one of the enzyme hydrolysate quality pairs (Fig. 4B). These were rose/violet, citrus, stalky, earthy, and cigar/tobacco. The high and low quality enzyme hydrolysates were significantly different for the last four of these attributes. Of these, stalky, earthy, and cigar/tobacco were scored significantly higher for the high quality samples. These aroma characteristics of the enzyme hydrolysates, and particularly the dominance of the non-berry-type attributes in the high quality samples were observable qualitatively in the PC and vector diagrams in Figures 1 and 2.

Importantly, when the data in Figure 3 are interpreted in relation to those in Figures 4A and 4B it can be seen that the non-berry-type attributes, stalky, earthy, and cigar/tobacco, which were quantitatively dominant in the high quality enzyme hydrolysates and, in the case of the last attribute was also dominant in the high quality acid hydrolysates, were the same as those characterizing the high quality wine from Coonawarra. This common sensory feature of the high quality samples was also observable from the data in Table 6 which showed that cigar/tobacco and earthy were significant quality determinants across all treatments.

Conclusions

The data presented confirm that the quality differences assigned to the samples were distinguishable by sensory analysis and, for all but one pair of wines and one pair of acid hydrolysates, these differences could be described and quantified. The major contributions made by both the acid- and enzyme hydrolysates from Shiraz grapes to wines of this variety are non-berry-type sensory attributes. It is significant that the precursor hydrolysates from high

Table 8. Sensory attributes found to be significant for the comparison between high and low quality enzyme- and acid hydrolysis products.

Enzyme hydrolysis products		Acid hydrolysis products	
Samples ¹	Attributes	Samples	Attributes
A and E	Honey/raisin [#] , Pepper	I and M	ns
C and G	Stalky [#] , Earthy [#]	K and O	Stalky
B and F	Strawberry, Stalky [#] , Cigar/tobacco [#]	J and N	Cigar/tobacco [#]
D and H	Spicey [#] , Cigar/tobacco [#]	L and P	Strawberry [#] , Pepper [#]

¹See Table 5 for sample identification codes.

[#]Attribute for which the high quality sample is more intense.

ns = no significant difference.

quality grapes, particularly those prepared enzymatically, as well as the wine made from these grapes were rated higher in non-berry attributes than low quality samples. Accordingly, it may be deduced that the precursor hydrolysates contain aroma compounds which are important to high quality wines of this variety.

These observations justify further studies into the chemical composition of the acid and enzyme hydrolysates of Shiraz. It is evident that these studies should allow observation of quantitative, and possibly qualitative, differences which can be related to wine quality. It remains to be determined if the increase in non-berry sensory attributes which are observable in Shiraz and other red wines on maturation can be ascribed to hydrolysis and slow release of glycosidically-bound flavor compounds from the fruit.

Literature Cited

1. Abbott, N. A., B. G. Coombe, M. A. Sefton, and P. J. Williams. Secondary metabolites of Shiraz grapes as an index of table wine quality. *In: Proceedings of the 7th Australian Wine Industry Technical Conference, Adelaide*, S. A. P. J. Williams, D. Davidson, and T. H. Lee (Eds.). Australian Industrial Publishers, Adelaide, (In press, 1990).
2. Amerine, M. A., R. M. Pangborn, and E. B. Roessler. Principles of Sensory Evaluation of Food. p 333. Academic Press, New York (1965).
3. Aryan, A. P., B. Wilson, C. R. Strauss, and P. J. Williams. The properties of glycosidases of *Vitis vinifera* and a comparison of their β -glucosidase activity with that of exogenous enzymes. An assessment of possible applications in enology. *Am. J. Enol. Vitic.* 38:182-8 (1987).
4. Noble A. C. Analysis of wine sensory properties. *In: Modern Methods of Plant Analysis*. Vol. 6. Wine Analysis. J. F. Jackson and H. F. Linskens (Eds.). pp 9-28. Springer-Verlag, Berlin (1988).
5. Noble, A. C., C. R. Strauss, P. J. Williams, and B. Wilson. Sensory evaluation of non-volatile flavor precursors in wine. *In: Flavor Science and Technology: Proceedings of the 5th Weurman Flavor Research Symposium*. M. Martens, G.A. Dalen, and H. Russwurm Jr. (Eds.). pp 383-90. John Wiley and Sons, New York (1987).
6. O'Mahoney, M. Sensory evaluation of food. Statistical methods and procedures. S. R. Tannenbaum, and P. Walstra (Eds.). Marcel Dekker Inc., New York (1986).
7. Roessler, E. B., R. M. Pangborn, J. L. Sidel, and H. Stone. Expanded statistical tables for estimating significance in paired-preference, paired-difference, duo-trio and triangle tests. *J. Food Sci.* 43:940-7 (1978).
8. Strauss, C. R., B. Wilson, P. R. Gooley, and P. J. Williams. Role of monoterpenes in grape and wine flavor. *In: Biogenesis of Aromas*. T. H. Parliment, and R. Croteau (Eds.). pp 222-42. ACS Symposium Series 317, American Chemical Society, Washington, DC (1986).
9. Williams, P. J., M. A. Sefton, and B. Wilson. Nonvolatile conjugates of secondary metabolites as precursors of varietal grape flavor components. *In: Flavor Chemistry: Trends and Developments*. R. Teranishi, R. G. Buttery, and F. Schahidi (Eds.). pp 35-8. ACS Symposium Series 388. American Chemical Society, Washington, DC (1989).