Flavour indices for winegrapes

FINAL REPORT to
GRAPE & WINE RESEARCH & DEVELOPMENT CORPORATION
PROJECT NO. UA 2V
Researcher : B. Coombe

Organisation : Faculty of Agricultural and Natural Resource Sciences
Date : 1992

GRAPE AND WINE RESEARCH COUNCIL

Final Report for Project UA 2V

Title: Flavour Indices for Winegrapes

Objectives: To select objective measurements of flavour on harvested grapes that correlate well with subjective assessments of quality of dry table wine made from the grapes.

Staff and facilities: The project was supervised by Dr B G Coombe, Reader in Horticultural Science of the University of Adelaide, Waite Campus, with Dr P J Williams of the Australian Wine Research Institute (AWRI) as an associate supervisor. Most of the funds were used for a Junior Research Fellowship position which was awarded to Ms. Nerida Abbott. Ms Abbott became a PhD candidate in the University of Adelaide. Additional cooperators were M G McCarthy, South Australian Department of Agriculture, who provided grapes from a planting distance experiment at Coonawarra, and A J W Ewart, Roseworthy Agricultural College, who vinified Coonawarra grape samples and assessed their wine quality.

Background: The following two paragraphs, written in February 1987 for the original application, describe the background to the project:-

> Background: The wine industry of Australia differs significantly from that of other countries because of its high proportion of grape-growers who sell grapes to wine-makers i.e. they do not make wine themselves. About 6000 growers (largely un-cooperated) produce about 70% of the grapes made into the wine. The high proportion is partly the result of post-war soldier settlement irrigation schemes, especially in the Riverland, Sunraysia and the MIA. The predominance of independent growers has made difficult the determination of wine-grape prices; the major mechanism of price determination has been by private barter against a minimum price framework, with growers as weak bargainers (Browert 1987, Coombe 1987). Prices determined by these methods have tended to affect prices paid for all winegrapes. Premiums for quality have been paid based on variety, region and flavour tasing (Jordan and Croser, 1983; Wall, 1986) but, despite these trends, the overall average grape price has remained low. A BAE report (Anon, 1986) shows that the average price has depreciated in relation to the consumer price index in every one of the last six years, now being 30% lower than CPI values indexed relative to their 1981 levels.

Grape price is therefore a small proportion of the return for Australian wine, possibly about 5% in most cases. By contrast, values for grapes and wine in Switzerland show a relative figure of 30% (Koblet, 1986, P. Perret, pers.comm.) The reasons for such a large difference are obviously complex and include some of the socio-economic questions referred to by Browett, 1987. But one possible cause for this difference is the ease with which quality is quantified in Switzerland and similar countries (by simple proportion to sugar content), compared with the great difficulty of this task in Australia (Hoare, 1981; Coombe, 1987). Similar difficulties occur in California and Israel where projects similar to the present proposals have been reported (Kasimatis, 1977; Bravdo et al., 1985). We are optimistic of getting more useful results with this present project because of the harnessing of the resources of AWRI, a world leader in wine flavour research.

In the five years since the above was written little has happened to lessen the need for flavour indices; both Hoare (1988) and Coombe (1991) have reiterated the problem. Low wine stocks in 1987 led to a demand scramble, with resultant higher grape prices and a planting surge. Inevitably, low prices and continued industry instability will return. Several patch-up changes have been made to grape pricing mechanisms, especially for irrigated winegrapes (Turkington 1990), but the fact remains that growers are still in a weak and unhealthy bargaining position. Possibly systems based on "third party grading" (Kirby Moulton, UC Berkeley, private communication) could be used in the future to provide bartering support, but objective guides to the potential quality of grapes for wine are seen as the greatest need.

Research on grape flavour chemistry is being pursued in many laboratories especially in France, Germany, Italy, Israel, California and Australia, but no reports have been seen, or heard of, that relate to the aims specified for this project.

Methodology: The variety Shiraz was chosen for this research because we wished to extend the understanding of flavour chemistry beyond white and floral grapes and because Shiraz is an important Australian winegrape whose quality varies widely in response to viticultural conditions.

The research followed the plan set out in the original application. Batches of Shiraz grapes were collected from three wineries during three years with differences in quality (low, medium and high) selected by each winery staff from historical records. These formed the basis of an intensive sequence of

investigations on the chemistry and sensory characteristics of juice, skin and wine, with an emphasis on volatiles in the glycoside fraction.

Finally, some derived analytical methods were tested on samples of grapes from a Department of Agriculture experiment on Shiraz at Coonawarra in which comparisons were made of the effects of vine spacing, crop thinning and soil ripping, in factorial combination; small-lot wines were made and assessed from these eight treatments.

Results and discussion: Only a small part of the large array of results are mentioned here, sufficient to illustrate their scope and the value of the conclusions reached.

1. **Sensory descriptive analysis** was performed on the volatiles liberated by hydrolysis of a C-18 isolate from Shiraz juices (this is the first such study done on black grapes for red wine). Hydrolysates from high and low quality samples were added to a neutral base wine and the aroma attributes adjudged by statistically-acceptable panel methods. The quality differences were discerned; glycoside hydrolysates from high quality juice contributed greater amounts of the non-berry attributes - 'stalky', 'earthy' and 'cigar/tobacco' (Figure 1). It was concluded that this fraction was most appropriate for further work.

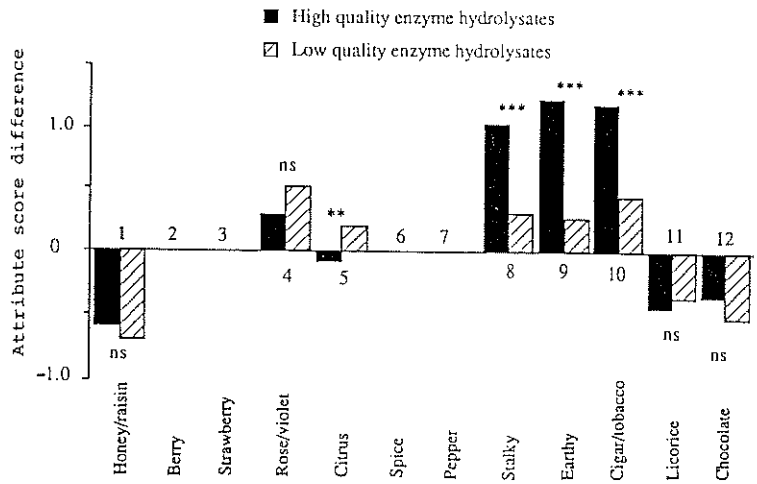


Figure 1 *Each histogram shows the difference between the mean attribute score for a hydrolysate and the corresponding base wine score, for those attributes in which either one or both mean scores differ significantly from zero i.e the base wine. ns, *, ** and *** indicate differences between the high and low quality hydrolysates are not significant, significant at p < 0.05, 0.01 and 0.001*

2. **Study of the identity of compounds** was a major part of the project since little information was available in the literature on Shiraz, or indeed of many black-berried varieties. Using gas chromatography-mass spectrometry analysis of the glycoside hydrolysate fraction, 177 compounds were identified and another 23 tentatively identified. Classification of these compounds showed that there were four major classes, as shown below, with two classes predominating - substituted benzene derivatives (which arise from the shikimic acid pathway) and nor-isoprenoids (degraded terpenes arising from the carotenoid pathway). This array differs significantly from that found in white grapes.

The table shows their relative total abundance (ppb) in Shiraz skin, juice and wine.

Class	Skin	Juice	Wine
Subs. benzene derivatives	28[a] / 542[b]	8 /318	3 /2020
Nor-isoprenoids	670/1823	105/297	17/3365
Monoterpenoids	10 /315	13 / 95	0 /474
Aliphatics	1444/124	22 /25	1 /174

a.= ppb of free compounds of the class, found in extracts of skin glycoside fractions

b.= ppb of compounds of the class, released after glucosidase treatment of skin glycoside fractions

A valuable finding is that analysis of the juice serves as a suitable indicator, qualititatively and quantitatively, of the volatile compounds in the whole sample. Further it was also shown that hydrolysed samples amplify the quantities of materials available for analysis (as had been found with white grapes).

3. **Differences between high and low quality juices** were examined quantitatively by comparing the amounts of key volatile

compounds released by acid- or enzyme hydrolysis. This effort was unsuccessful although it is considered that, with a larger number of samples and more sustained analytical input, the approach could bring rewards and it should not be discarded. The alternative approach was pursued of comparing the sum total amount of all compounds released by hydrolysis from different samples. In one series it was possible to correlate such a measure with a quantified quality index called the Value Index (a number that derives from the classification by winemakers of young wines to a range of premiums which express the anticipated value in the market of each grape parcel). The direct correlation shown in Figure 2 between "released volatiles" and "value index" is encouraging; the lack of difference found in 1989 was not unexpected and was attributed to that season's weather conditions. An important outcome of this experiment was the realization that an analysis of the glucose released from the hydrolysed glycosides would give a complementary measure of the bound volatiles. Thus analysis of glycosyl-glucose should serve the same purpose as analysis of the glycosyl-volatiles with the immense advantage of simplicity.

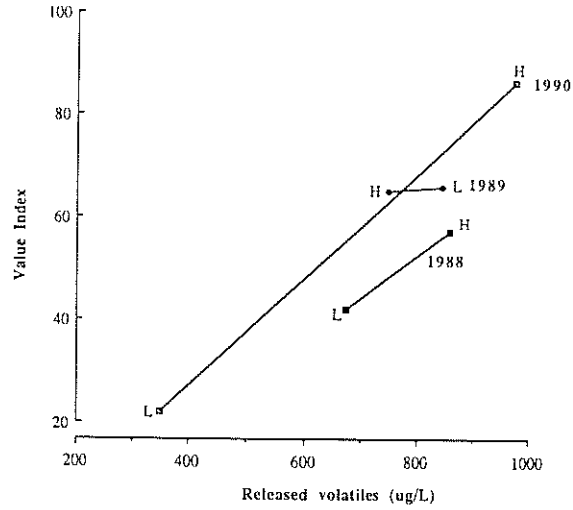


Figure 2 *Relationship between the concentration of released volatile secondary metabolites (ppb) and the grape Value Index for three sets of high and low quality samples over three years.*

4. **A method for the assay of glycosyl-glucose** was needed to enable further testing of the conclusions reached in point 3. A protocol for a batch-type assay was established but is not discussed here because it is the subject of a provisional patent application.

5. **Preliminary testing of the glycosyl-glucose assay** (the G-G assay). Grape samples from a replicated field experiment of the S.A. Department of Agriculture were examined. This Shiraz experiment compared high and low vine density, ± bunch thinning and ± soil ripping. G-G analyses could be related to the quality assessment of small-lot wines, however a confounding with the Brix values of the samples has complicated interpretation of these data. Figure 3 compares measures of released glucose versus released volatiles averaged from each of the eight treatments; the good correlation is encouraging.

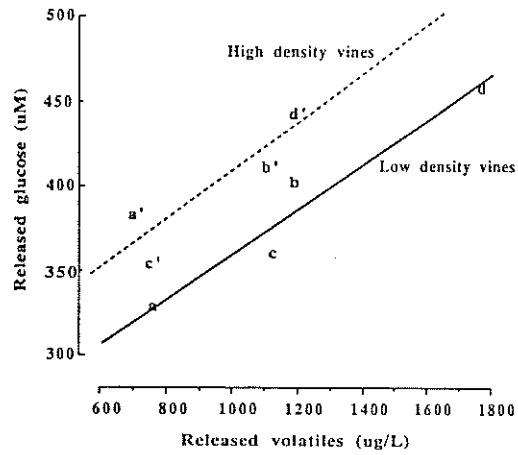


Figure 3 Relationship between glycosidically bound glucose and concentration of released volatiles for the control (a', a), ripped (b', b), thinned (c', c), and thinned plus ripped (d', d) plots for the high and low density vines respectively. THe linear regression of the four plots for the high density planting is r^2= 0.844 and r^2 = 0.945 for the low density planting.

Conclusions: Arguments are presented for the need for flavour indices to help quantify the quality of winegrapes. This work suggests that glycosylated compounds contain flavour compounds that are important to high quality Shiraz. and that it should be possible to quantify them to provide a flavour index. This could not be done by quantifying selected volatile compounds, but a measure of total glycosyl-glucose appears to be a promising indicator of quality. Such an assay should be adaptable for industry use and could become the basis of a "flavour-meter". The principle could well be useful for fruits other than winegrapes.

Significance: The project has met the objectives (more successfully than was thought possible); the significance for the wine industry might be profound. Publicity of the development will initially be subject to patenting constraints.

Acknowledgments: We thank Penfolds, Mildara and Wolf Blass wine companies for the provision of grape samples, and Penfolds for the information on the Value Indices of their samples. We also thank Council for the grants during these four years.

References:

Anon, (1986). Real average grape prices decline further says BAE reports. Australian Grapegrower and Winemaker. Dec. 1986. p.12.

Bravdo, B., Hepner, Y., Loinger, C., Cohen, S. and Tabocman, H. (1985). Effect of crop level and crop load on growth, yield, must and wine composition and quality of Cabernet Sauvignon, **36,** Amer. J. Enol. & Vitic. 125-131.

Browert, J. (1987). The South Australian Wine Industry: a retrospective view. Proc. 6th Aust. Wine Industry Technical Conference. pp.12-16.

Coombe, B.G. (1987). Viticultural research and technical development in Australia. Proc. 6th Aust. Wine Industry Technical Conference. pp.20-24.

Coombe, B.G. (1991). From grape juice to vascular bundles. Aust. N.Z. Wine Industry J., **6,** 41-42.

Hoare, R. (1985). A study of wine grape pricing systems and viticultural trends in South Africa, France, Italy, Germany and USA. Churchill Fellowship Report, Farm 1773, Stanbridge, NSW.

Hoare, R. (1988). Winegrape quality and winegrape pricing: a review of some systems. Proc. 2nd Int. Cool Climate Vitic. & Oenol. Symposium, Auckland. pp.188-190.

Jordan, A.P. and Croser, B.J. (1983). Determination of grape variety by aroma/flavour assessment. Proc. 5th Aust. Wine Industry Technical Conference. pp.261-274.

Kasimatis, A.N. (1977). Differnetial cropping levels of Zinfandel vines - a progress report on some effects of vine growth, fruit composition and wine quality. O.I.V. Syrup in Quality of the Vintage Capetown. pp.189-194.

Koblet, W. (1986). Herbstversammlung des Schweiz. Weinbauvereins. Schweiz Z. Obst- und Weinbau **122,** 715-720.

Turkington, C.R. (1990). Pricing of irrigated winegrapes produced in the Murrumbidgee and Murray districts. Aust. Grapegrower & Winemaker. No. 322, pp.9-13.

Wall, P. (1986). Yalumba's grape quality assessment system is raising wine quality. Aust. Grapegrower and Winemaker, Dec. 1986, 20-22.

Publications from the project

Part of the work described in this thesis has been reported in the following publications:

Abbott, N.A.; Coombe, B.G.; Sefton, M.A.; Williams, P.J. Composition of Shiraz grapes in relation to the quality of table wine. In: *Proceedings of the 4e Symposium International d'Oenologiques;* 15-17 Juin, 1989, Bordeaux, France, Dunod, France, **1990a**, 94-99.

Abbott, N.A.; Coombe, B.G.; Williams, P.J. The flavour of Shiraz as characterised by chemical and sensory analysis. *Aust. N.Z. Wine Ind. Journal* **1990b**, 5(4), 315-319.

Abbott, N.A.; Coombe, B.G.; Sefton, M.A.; Williams, P.J. The secondary metabolites of Shiraz grapes as an index of table wine quality. In: *Proceedings of the Seventh Australian Wine Industry Technical Conference*; 13-17 August, 1989, Williams, P.J.; Davidson, D.M.; Lee, T.H. Eds.; Australian Industrial Publishers, Adelaide, SA; **1990c**, 117-120.

* Abbott, N.A.; Coombe, B.G.; Williams, P.J. The contribution of hydrolysed flavour precursors to quality differences in Shiraz juice and wines: an investigation by sensory descriptive analysis. *Am. J. Enol. Vitic.* **1991**, 42(3), 167-174.

Abbott, N.A.; Coombe, B.G.; Williams, P.J. Development of a rapid analytical technique for the estimation of the concentration of potential volatile flavour compounds and hence quality of *Vitis vinifera* Shiraz grapes. Provisional patent No. PK 7216, 16th July 1991.

Other papers are being prepared.

* This paper has been selected as the best enology paper for 1991 by the American Society for Enology and Viticulture

Publications from the project

Part of the work described in this thesis has been reported in the following publications:

Abbott, N.A.; Coombe, B.G.; Sefton, M.A.; Williams, P.J. Composition of Shiraz grapes in relation to the quality of table wine. In: *Proceedings of the 4e Symposium International d'Oenologiques;* 15-17 Juin, 1989, Bordeaux, France, Dunod, France, **1990a**, 94-99.

Abbott, N.A.; Coombe, B.G.; Williams, P.J. The flavour of Shiraz as characterised by chemical and sensory analysis. *Aust. N.Z. Wine Ind. Journal***1990b**, 5(4), 315-319.

Abbott, N.A.; Coombe, B.G.; Sefton, M.A.; Williams, P.J. The secondary metabolites of Shiraz grapes as an index of table wine quality. In: *Proceedings of the Seventh Australian Wine Industry Technical Conference*; 13-17 August, 1989, Williams, P.J.; Davidson, D.M.; Lee, T.H. Eds.; Australian Industrial Publishers, Adelaide, SA; **1990c**, 117-120.

Abbott, N.A.; Coombe, B.G.; Williams, P.J. The contribution of hydrolysed flavour precursors to quality differences in Shiraz juice and wines: an investigation by sensory descriptive analysis. *Am. J. Enol. Vitic.* **1991**, 42(3), 167-174.

Abbott, N.A.; Coombe, B.G.; Williams, P.J. Development of a rapid analytical technique for the estimation of the concentration of potential volatile flavour compounds and hence quality of *Vitis vinifera* Shiraz grapes. Provisional patent No. PK 7216, 16th July 1991.

Other papers are being prepared.