Vitis 18, 31—39 (1979)

Oenological and Viticultural Research Institute, Stellenbosch, Republic of South Africa

Objective quality rating of Pinotage wine

by

J. MARAIS, P. C. VAN ROOYEN and C. S. DU PLESSIS

Objektive Beurteilung der Weinqualität bei der Sorte Pinotage

Zusammenfassung. — Die Beziehungen zwischen der Weinzusammensetzung und drei Parametern der Weinqualität wurden untersucht, wobei das statistische Modell einer mehrfachen linearen Regression verwendet wurde. Zu diesem Zweck wurden die bei 17 Weinen der Sorte Pinotage gewonnenen Analysenergebnisse über 6 Fettsäureester in ein Computerprogramm zur optimalen Kurvenanpassung eingegeben. Durch ein Gutachtergremium wurden die Gesamt-Weinqualität, der Geschmack und der Geruch bewertet; die Daten dieser Qualitätsbeurteilung wurden als abhängige Veränderliche benützt. Es wurde festgestellt, daß 2 Ester, nämlich n-Hexylacetat und Äthyl-n-octanoat eine ausgezeichnete Vorhersage der Weinqualität ermöglichten, wenn ihre Werte in Mehrfachregressions-Gleichungen eingesetzt wurden.

Introduction

Wine quality is generally accepted to consist of several distinct facets frequently separated into colour, aroma, taste, balance, roundness and other subjective characteristics. An overall quality rating generally integrates these factors. Presently and historically all these facets are and were determined by taste panels. In search of an objective quality rating of wines, research workers have in the past few years endeavoured to identify, and simultaneously quantify, chemical components responsible for favourable and adverse qualities in wine. In this way the important contribution of esters to wine aroma and overall quality has been confirmed by various research workers (CHAUVET 1950, POSTEL *et al.* 1972, REINHARD 1972, SUOMALAINEN and NYKÄNEN 1972, CONNELL and STRAUSS 1974, SCHREIER and DRAWERT 1974, JOBBÁGY and HOLLÓ 1976). Although the locally bred Pinotage is one of the most important red cultivars in South Africa, research in this regard on its wine has had very limited attention. VAN WYK *et al.* (in press) have indicated the importance of iso-amyl acetate in relation to the varietal character as far as aroma is concerned.

The subjectivity associated with wine quality evaluation by sensory test panels could lead to divergent opinions; instrumental analysis of aroma components, largely by gas chromatography, and subsequent relation to sensory evaluation has not been very successful. Visual inspection or even simple mathematical evaluation of a gas chromatogram is often fruitless in relating sensory ratings to chemical composition (POWERS and KEITH 1968). The exceptional complexity of quality-component interrelationships has been stressed by prominent research workers in this field (RAPP *et al.* 1973, ROTHE 1976). An important observation by POWERS and KEITH (1968) is that principally due to a lack of suitable methods for correlating this objective-subjective type of data, the utilization of gas chromatographic information has not kept pace with its generation.

Studies in this regard have shown that with subtle flavour differences multivariate statistical analysis is necessary to relate objective measurements to sensory quality (YOUNG *et al.* 1970). It was also observed by POWERS and QUINLAN (1974) that from a practical viewpoint mere statistical significance is not adequate for predictive purposes and has utility only in cases of exceptionally high correlations. Furthermore, it is stressed that computerization of gas chromatographic data in relating it to sensory quality is a field which offers considerable promise in developing instrumental means to approximate sensory judgment (POWERS and QUINLAN 1974).

In an attempt to resolve some of the problems outlined above, especially with regard to the development of a method by which further studies on other wines could be undertaken, a number of Pinotage wines were analysed, and their sensory qualities determined by a trained taste panel.

Materials and methods

1. Material

The analyses and sensory evaluations were performed on 17 dry red wines of the Pinotage cultivar (Pinot noir × Cinsaut) from the 1975 and 1976 seasons, which were all obtained from the same vineyard. Grapes were harvested periodically over approximately 6 weeks in various stages of ripeness to induce variations in quality. Wines were made in duplicate under standard controlled conditions at the Oenological and Viticultural Research Institute.

2. Extraction of fatty acid esters from wine

The fatty acid esters were determined by a gas chromatographic method developed by DE VRIES (1962) which was slightly modified to adapt to local laboratory conditions. Precisely 2.0 cm^3 internal standard (ethyl nonanoate, 400 mg/l in 96 vol% ethanol) was added to 200 cm^3 wine. The wines were extracted with 3 × 50 cm^3 purified ether, the extracts being washed firstly for 3 min with 2 × 10 cm^3 0.5 n NaOH solution and finally with 4 × 20 cm^3 distilled water. The extracts were dried overnight on 5 g anhydrous $MgSO_4$ and concentrated to approximately 0.5 cm^3 at 39 °C.

3. Gas chromatography

Detectors:	Dual hydrogen flame ionization
Columns:	Dual 3 m × 3 mm stainless steel
Stationary phase:	5 % Apiezon M plus 0.15 % (of stationary phase) purified Manoxol OT on chromosorb G, D.M.C.S., 60—80 mesh
Injection port temperature:	200 °C
Detector temperature:	250 °C
Temperature programme:	15 min isothermal at 60 °C, 60—120 °C at 6 °C min^{-1}, 8 min isothermal at 120 °C, 120—180 °C at 7.5 °C min^{-1}
Carrier gas flow:	Nitrogen at 30 cm^3 min^{-1}.

4. Sensory evaluation

The wines were evaluated by a panel of 15—20 experienced judges. The system used was developed at the Oenological and Viticultural Research Institute (TROMP

1977), and the data used as dependent variables in this study were overall quality as well as aroma and taste quality, all on a percentage scale.

5. Statistical methods

A linear least squares curve fitting programme (DANIEL and WOOD 1971) was used to process the data. This method, apart from providing normal multiple regression statistics, enables the user to search for candidate equations via a so-called "Cp search". Cp is an index of the total squared error, and allows the identification of other equations having less independent variables than the full regression equation, but still giving the same predictive capability. Moreover, frequently the choice is left to the user which equation (compatable with previous experience or literature study) he wants to use for predicting the dependent variable. The identification of an equation having for example 4 instead of 10 variables, but still predicting wine quality as adequately as the latter equation, also allows hypotheses to be set up concerning which components (fatty acid esters in this case) influence wine quality. This approach could lead to the eventual analysis of only those components having an influence on wine quality and the reduction in analyses of non-relevant compounds.

Table 1

Independent variables for two possible equations to predict overall wine quality
Unabhängige Veränderliche für zwei mögliche Gleichungen zur Vorhersage der Gesamt-Weinqualität

Equation	Number of variables (P)	Total squared error (Cp)	Independent variables in equation
1	6	5.6	nHA, nHA^2, EC_8, EC_8^2, EC_{10}
2	7	7.1	iAA, EC_6^2, EC_8, EC_8^2, EC_{10}, EC_{10}^2

Table 2

Equation terms [1]) for prediction of overall wine quality from ester concentrations
Gleichungsgrößen für die Vorhersage der Gesamt-Weinqualität aus den Esterkonzentrationen

Variable	b-coefficients (intercept = −24.01)	t-value
nHA	−204.89	3.4
nHA^2	523.38	3.1
EC_8	177.69	5.6
EC_8^2	−137.56	4.9
EC_{10}	242.70	4.2

[1]) From equation 1 of Table 1.
F = 16.20 (significant at 99 % confidence level).
R^2 = 0.88.
Average error of prediction = 3.91 %.

Results and discussion

The sensory evaluations gave data which included overall quality as well as aroma and taste ratings. These were treated as dependent variables and their relation to the independent variables (ester concentrations) examined.

The wines were analysed for the following fatty acid esters. The concentration ranges are given for each component. (Peak areas were calculated from the peak height times, the width at half peak height and quantified by the internal standard technique.)

Ester	mg/l
i-Amyl acetate (iAA)	1.22—7.21
Ethyl hexanoate (EC_6)	0.34—0.89
n-Hexylacetate (nHA)	0.00—0.37
2-Phenyl ethyl acetate (PEA)	0.08—0.52
Ethyl-n-octanoate (EC_8)	0.15—1.08
Ethyl-n-decanoate (EC_{10})	0.14—0.37

1. Overall wine quality

An initial computer run employing all 6 independent variables was carried out, and inspection of independent variables versus residual variance plots showed indications of non-linearity in relation to wine quality with regard to EC_6, nHA, EC_8

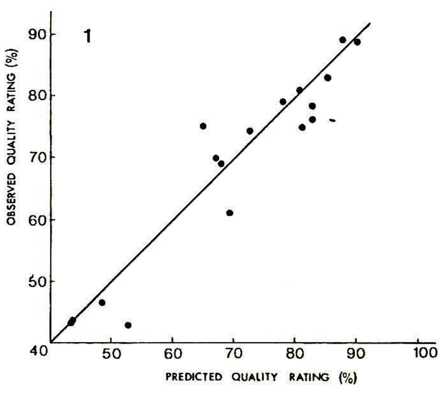
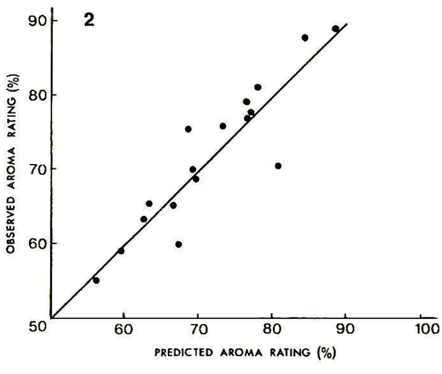
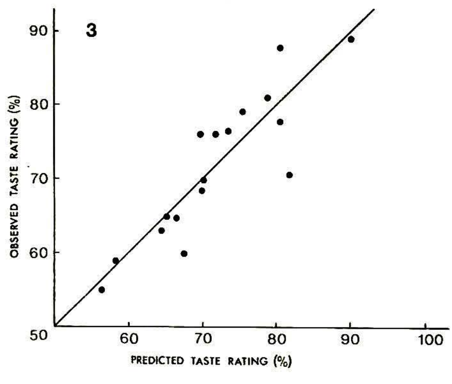


Fig. 1: Plot of observed versus predicted overall quality ratings.
Fig. 2: Plot of observed versus predicted aroma ratings.
Fig. 3: Plot of observed versus predicted taste ratings.

Abb. 1: Die Beziehungen zwischen den sensorisch ermittelten und den errechneten Werten der Gesamt-Weinqualität.
Abb. 2: Die Beziehungen zwischen den sensorisch ermittelten und den errechneten Werten des Weinaromas.
Abb. 3: Die Beziehungen zwischen den sensorisch ermittelten und den errechneten Werten des Weingeschmacks.





and EC_{10} esters. In a subsequent multiple regression analysis the quadratic components of these esters, e.g. EC_6^2, nHA^2, EC_8^2 and EC_{10}^2 were also included, bringing the total number of variables to 10. A "Cp search" was simultaneously conducted, aiming at reducing the unfavourable ratio of independent variables to number of observations. By inspection of the Cp versus P plot (P being the total number of variables in the equation), two equations were selected on basis of closest approximation of Cp and P (Daniel and Wood 1971). The first equation incorporated 3 esters (nHA, EC_3 and EC_{10}), as well as the squared values of the first 2. The second equation contained 4 esters and 3 quadratic components, viz. iAA, EC_3, EC_{10}, EC_6^2, EC_8^2 and EC_{10}^2 (Table 1). On the basis of the near equality of the P and Cp values it was clear that overall quality could be satisfactorily predicted by either of the two equations. The regression coefficients (b), intercept and t-values for equation 1 are given in Table 2. From the F and multiple correlation coefficient (R) values for this equation for instance, it can be concluded that for this set of data overall quality could be adequately predicted by utilising concentrations of 3 esters, giving a highly significant correlation and a multiple coefficient of determination of 0.88. A plot of the relationship between observed and predicted values for equation 1 is given in Fig. 1.

Table 3

Independent variables for six equations to predict aroma quality
Unabhängige Veränderliche für sechs Gleichungen zur Vorhersage der Geruchsqualität

Equation	Number of variables (P)	Total squared error (Cp)	Independent variables in equation nHA	nHA^2	EC_6	EC_6^2	EC_8	EC_8^2	EC_{10}	PEA
1	4	3.9	+	+	−	−	+	−	−	−
2	5	5.0	+	+	−	−	−	−	+	+
3	5	5.0	+	+	+	−	+	−	−	−
4	5	5.0	+	+	+	−	−	−	−	+
5	5	5.0	+	+	−	−	−	+	−	+
6	5	5.1	+	+	−	+	+	−	−	−

Table 4

Equation terms [1]) for the prediction of aroma quality from ester concentrations
Gleichungsgrößen für die Vorhersage der Geruchsqualität aus den Esterkonzentrationen

Variable	b-coefficient (intercept = 50.20)	t-value
nHA	−119.63	3.3
nHA^2	267.10	2.8
EC_8	40.23	7.3

[1]) From equation 1 of Table 3.
F = 21.2 (significant at 99 % confidence level).
$R^2 = 0.83$.
Average error of prediction = 2.82 %.

2. Aroma quality

Employing the same method used for the overall quality rating, non-linear relationships were detected when aroma quality as determined by sensory evaluation was regressed on the same 6 ester concentrations.

Results from a computer run incorporating all 10 variables comprising of 6 esters plus 4 quadratic components as before, showed that a good predictive equation could be constructed, resulting in a R^2 value of 0.92 and a highly significant F-value. For the same reason as stated before, a Cp search for candidate equations was used to select equations with fewer variables still giving a satisfactory low error of prediction. The P versus Cp plot generated by the programme revealed that six equations would give satisfactory prediction (Table 3). In fact, for all practical purposes, any of the equations listed in Table 3 would give similar predictive power for this data set. The independent variables, b-coefficients and t-values for equation 1 (Table 3) are given in Table 4. To illustrate the marked predictive ability of this equation ($R^2 = 0.83$) a plot of observed versus predicted values is given in Fig. 2. It is of interest to note that only 2 esters viz. nHA and EC_8 are required for this equation.

From the independent variables in the six equations presented in Table 3 the importance of nHA is obvious, since it occurs in all the equations. The second most important ester in this case was EC_8, occurring four times (equations 1, 3, 5 and 6). Furthermore, the absence of iAA, a component which has been shown to contribute markedly to the varietal character of Pinotage wine (VAN WYK *et al.* 1977), is at this

Table 5

Independent variables for two equations to predict taste quality
Unabhängige Veränderliche für zwei Gleichungen zur Vorhersage der Geschmacksqualität

Equation	Number of variables (P)	Total squared error (Cp)	Independent variables in equation
1	7	6.8	iAA, nHA, EC_6^2, EC_8, EC_8^2, EC_{10}
2	8	8.0	iAA, nHA, EC_6^2, EC_8, EC_8^2, EC_{10}, EC_{10}^2

Table 6

Equation terms for prediction of taste quality from ester concentrations
Gleichungsgrößen für die Vorhersage der Geschmacksqualität aus den Esterkonzentrationen

Variable	b-coefficient (intercept = 30.34)	t-value
iAA	− 0.19	0.2
nHA	−16.42	1.0
EC_6^2	27.21	2.5
EC_8	62.93	2.6
EC_8^2	−46.65	1.9
EC_{10}	75.17	1.6

F = 9.1 (significant at 99 % confidence level).
$R^2 = 0.85$.
Average error of prediction = 2.87 %.

stage inexplicable but noteworthy. Under conditions where the established non-linear relationships are ignored and therefore only linear components are fitted, iAA was included in a predictive equation, leading to a drop in R^2 from 0.83 to 0.78.

3. Taste quality

The same approach as that applied in the previous two sections led to a good predictive equation when all 10 variables were included ($R^2 = 0.94$) but the same unsatisfactory ratio between number of independent variables and number of observations made another Cp search necessary. From this analysis two equations emerged having adequate predictive abilities as well as an acceptable number of independent variables (Table 5). Again the closeness of specific P and Cp values served to discriminate between candidate equations. Equation 2 differs from equation 1 only in that the quadratic term of EC_{10} is included in the latter. The P and Cp values for an equation utilising only 3 independent variables, instead of the 6 for the selected equation in Table 6, were 4 and 5.2, respectively, compared to 7 and 6.8 for equation 1 (Table 5). Although the total error is higher than that of the equation in Table 6, R^2 is still satisfactory. This equation is presented in Table 7.

A high level of significance is obtained with $R^2 = 0.78$ in the same order of magnitude (0.85) as for the former equation. A plot of observed versus predicted taste ratings is given in Fig. 3, giving a visual appreciation of the predictive capabilities of the final equation. It must be stressed, however, that the final equation differs in predictive power considerably from the one given in Table 6, its only advantage being the utilisation of only 3 independent variables.

Table 7

Equation terms for the prediction of taste quality from ester concentrations
Gleichungsgrößen für die Vorhersage der Geschmacksqualität aus den Esterkonzentrationen

Variable	b-coefficient (intercept = 49.93)	t-value
nHA	−29.43	1.9
EC_6^2	14.62	1.8
EC_8	28.71	3.8

F = 15.4 (significant at 99 % confidence level).
$R^2 = 0.78$.
Average error of prediction = 3.32 %.

Conclusions

The relatively good regression equations for the prediction of all three facets of wine quality which emerged from this study were in all probability due to a certain extent to favourable experimental conditions. The fact that all the wines were made according to a standard technique from a single cultivar originating from the same vineyard, eliminated factors such as diverse soil types and cellar techniques. These facts made the detection of ester-sensory evaluation relationships possible with relatively few observations.

In all the regression equations set up for the prediction of overall quality, aroma and taste ratings, 2 esters viz. nHA and EC_8 figured prominently. In the light of research by VAN WYK *et al.* (1977), the fact that iAA could not be proved to contribute to a greater extent is not clear at this stage. Although YOUNG *et al.* (1970) pointed out that gas chromatographic analysis in itself could not be overlooked as a possible contributing factor to non-correlation, iAA recovery in the method used in this study was relatively constant in the order of 70—80 % and could therefore be excluded as a source of error.

Where iAA was found to contribute to the taste rating, however, its relative contribution as evaluated by the magnitude of its b-coefficient in the regression equation was of the order of 10 times lower than that of the next least significant factor (Table 6), its value varying so much that a non-significant t-value of 0.2 was assigned to it. In contrast, the nHA and EC_8 ester concentrations were weighted to a far greater extent, confirming their relative importance in this predictive equation.

Regarding the prediction of aroma rating, the identification of nHA and EC_8 as being the most important contributors of the 6 esters with pleasant olfactory properties could be a significant finding. The non-linear relationship found for the former compound suggests a minimum concentration for positive correlation with aroma. Further research is needed to clarify this aspect. Some uncertainty surrounds the direct contribution of EC_8 to the Pinotage aroma. DU PLESSIS (1975) found high correlations for this ester with wine quality, but concluded that its direct contribution could not be proved. He also pointed out that correlation coefficients relating a single component to wine quality could not logically be expected to give satisfactory results in this type of research, although excellent correlations may be found as reported by NOBLE (1977). Whether EC_8 contributes directly to the Pinotage wine aroma or acts as indicator of some unmeasured compound has not been proved in this study, but that it certainly is an important factor in the prediction of this aroma cannot be overlooked.

On the whole, promising results were obtained in the search of an objective rating parameter for wines of the Pinotage cultivar, calculated from ester analysis. In the course of the study it became obvious that simple correlation coefficients or even regression equations containing only linear relationships would not be able to perform this function. Evidence points towards a complex non-linear relationship based on at least 3 independent variables. Further studies will indicate whether climatic, cellar technological or other external factors will necessitate the introduction of other independent variables into predictive equations for the quality of Pinotage wines. It is clear that there is a definite need for a better understanding of the relationship between sensory and physicochemical factors, as has been frequently pointed out (VON SYDOW 1971, POWERS and QUINLAN 1974). However, since it appears that the generation of gas chromatographic data of wines has outstripped its utilisation, the use of computer technology and advanced statistical techniques coupled with programmed and systematic data collection should make it possible to make great advances in the field of subjective-objective relationships.

Summary

Relationships between wine composition and three quality parameters were investigated employing a linear multiple regression statistical model. For this purpose a least squares curve fitting computer programme was applied to analyses of

17 Pinotage wines for 6 fatty acid esters. Overall quality, taste and aroma ratings were determined by a taste panel and utilized as dependent variables. It was found that 2 esters viz. n-hexylacetate and ethyl-n-octanoate allowed excellent prediction equations to be set up for the quality ratings when incorporated into multiple regression equations.

Literature cited

CHAUVET, J., 1950: L'arôme de vins fins. Bull. Inst. Natl. Appel. Orig. Vins et Eaux-de-Vie. 34, 8—17.

CONNELL, D. W. and STRAUSS, C. R., 1974: Major constituents of fusel oils distilled from Australian grape wines. J. Sci. Food Agricult. 25, 31—44.

DANIEL, C. and WOOD, F. S., 1971: Fitting equations to data. Wiley Interscience, New York.

DU PLESSIS, C. S., 1975: Fermentation-formed components in relation to wine quality. Proc. 4th Intern. Enol. Symp., May 26—29, 1975, Valencia, Spain.

JOBBÁGY, A. und HOLLÓ, J., 1976: Über die gaschromatographische Duftqualifizierung von Weinen. 2. Mitt. Entwicklung einer Maßzahl zur Qualifizierung des Duftes durch Bestimmung des Zusammenhanges mit den Peakflächen und Anwendungsbedingungen. Die Nahrung. 20, 295—305.

NOBLE, A. C., 1977: Correlation of instrumental analysis of flavors with sensory data. Proc. Bienn. Intern. Codata Conf. 5th, 109—111.

POSTEL, W., DRAWERT, F. und ADAM, L., 1972: Gaschromatographische Bestimmung der Inhaltsstoffe von Gärungsgetränken. III. Flüchtige Inhaltsstoffe des Weines. Chem. Mikrobiol. Technol. Lebensm. 1, 224—235.

POWERS, J. J. and KEITH, ELIZABETH S., 1968: Stepwise discriminant analysis of gas chromatographic data as an aid in classifiying the flavor quality of foods. J. Food Sci. 33, 207—213.

— — and QUINLAN, M. C., 1974: Refining of methods for subjective-objective evaluation of flavour. J. Agr. Food Chem. 22, 744—749.

RAPP, A., HOVERMANN, W., JECHT, U., FRANCK, H. und ULLEMEYER, H., 1973: Gaschromatographische Untersuchungen an Aromastoffen von Traubenmosten, Weinen und Branntweinen. Chemiker-Ztg. 97, 29—36.

REINHARD, C., 1972: Zur Bestimmung der höheren Ester und des 2-Phenyläthanols in Weinen und Brennweinen. Chem. Mikrobiol. Technol. Lebensm. 1, 236—240.

ROTHE, M., 1976: Aroma values — a useful concept? Die Nahrung 20, 259—266.

SCHREIER, P. und DRAWERT, F., 1974: Gaschromatographisch-massenspektrometrische Untersuchung flüchtiger Inhaltsstoffe des Weines. Chem. Mikrobiol. Technol. Lebensm. 3, 154—160.

SUOMALAINEN, H. and NYKÄNEN, L., 1970: Investigations on the aroma of alcoholic beverages. Naeringsmiddelindustrien (1-2), 1—16. [Abstr.: Amer. J. Enol. Viticult. 23 (1972), 134.]

SYDOW, E. VON, 1971: Flavor — a chemical or psychophysical concept? Food Technol. 25, 40—44.

TROMP, A., 1977: The evaluation of wine with an effective score card (Afric.). Wynboer (549), 52—53.

VRIES, M. J., DE, 1962: Extraction of higher fatty acid esters in alcoholic beverages and their determination using gas liquid chromatography (Afric.). S. Afr. J. Agricult. Sci. 5, 395—400.

WYK, C. J. VAN, AUGUSTYN, O. P. H., WET, P. DE and JOUBERT, W. A. (in press): The role of isoamyl acetate in the typical fermentation bouquet of *Vitis vinifera* cultivar Pinotage. Proc., S. Afr. Soc. Enol. Viticult., Symp. Cape Town, Nov. 21—22, 1977.

YOUNG, L. L., BARGMANN, R. E. and POWERS, J. J., 1970: Correlation between gas chromatographic patterns and flavor evaluation of chemical mixtures and of cola beverages. J. Food Sci. 35, 219—223.

Eingegangen am 19. 12. 1978

J. MARAIS
Oenological and Viticultural
Research Institute
Private Bag X5026
Stellenbosch 7600
Republic of South Africa