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ARTICLES

Characterization of Selected South African Young Cultivar Wines Using FTMIR Spectroscopy, Gas Chromatography, and Multivariate Data Analysis

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The powerful combination of analytical chemistry and chemometrics and its application to wine analysis provide a way to gain knowledge and insight into the inherent chemical composition of wine and to objectively distinguish between wines. Extensive research programs are focused on the chemical characterization of wine to establish industry benchmarks and authentication systems. The aim of this study was to investigate the volatile composition and mid-infrared spectroscopic profiles of South African young cultivar wines with chemometrics to identify compositional trends and to distinguish between the different cultivars. Data were generated by gas chromatography and FTMIR spectroscopy and investigated by using analysis of variance (ANOVA), principal component analysis (PCA), and linear discriminant analysis (LDA). Significant differences were found in the volatile composition of the cultivar wines, with marked similarities in the composition of Pinotage wines and white wines, specifically for 2-phenylethanol, butyric acid, ethyl acetate, isoamyl acetate, isoamyl alcohol, and isobutyric acid. Of the 26 compounds that were analyzed, 14 had odor activity values of >1. The volatile composition and FTMIR spectra both contributed to the differentiation between the cultivar wines. The best discrimination model between the white wines was based on FTMIR spectra (98.3% correct classification), whereas a combination of spectra and volatile compounds (86.8% correct classification) was best to discriminate between the red wine cultivars.

KEYWORDS: Cultivar discrimination; FTMIR spectroscopy; gas chromatography; chemometrics; classification

INTRODUCTION

Traditionally, the only way to discriminate between wines was by sensory evaluation. Due to the subjective nature of this approach, chemical and spectroscopic analyses in combination with statistical techniques were explored and found to be robust, precise, and objective (*1*, *2*).

Many different types of analytical data have been used to investigate the chemical composition of wine in order to distinguish between wines from different cultivars, each providing a unique set of information. Some examples of compositional information that have been used to discriminate between wine cultivars include phenolic compounds (*3*, *4*) and volatile compounds (*5*, *6*). Data obtained with electronic nose and electronic tongue (*7*, *8*) detectors were used to discriminate between wines. In addition, different spectroscopic methods (*9*−*11*) have been applied successfully to discriminate between wine cultivars.

The volatile composition of wines can possibly be linked the strongest to sensory analysis, the traditional method of distinguishing wines, as these compounds are primarily responsible for the distinct flavor of wine. Higher alcohols, esters, and volatile fatty acids are especially useful for investigating differences and similarities between wines, as they appear to be generic to most wine cultivars (*5*). In fact, strong correlations have been found between grape variety and the main byproduct

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of yeast amino acid metabolism, specifically iso-acids and higher alcohols, ethyl esters of iso-acids, and acetate esters of higher alcohols (*5*, *6*).

Fourier transform mid-infrared (FTMIR) spectroscopic data contain a wealth of information on the composition of wine that is not necessarily connected to specific compounds (*2*). The FTMIR spectra of wine samples can therefore be regarded as a compositional fingerprint of the wines.

Data analytical techniques play a vital role in the interpretation of chemical and instrumental properties of wine. The use of chemometrics allows the analyst to gain more insight into complex data sets and to comprehensively represent the multidimensional variability commonly associated with wine (*12*). Several data analysis tools can be used to investigate the intrinsic characteristics of wine. Two methods that are commonly used are principal component analysis (PCA) and linear discriminant analysis (LDA) (*13*, *14*). PCA is an unsupervised classification technique that is used to observe the underlying structure of a data matrix. PCA results typically show the degree of similarity between samples and the influence of variables, such as chemical properties, on these similarities (*15*). LDA is a supervised classification technique that uses the distances between samples in the data space to establish a classification model. Such a classification model can be used to classify unknown samples into sample categories based on their chemical properties (*16*).

Thorough knowledge of South African wine cultivars is especially important, as cultivars play an important role in the South African wine market dynamics. Although the chemical properties of South African cultivar wines have been determined in several studies (*4*, *17*), little is known about the combination of volatile composition and FTMIR spectroscopy as a tool to investigate the differences and similarities that exist between South African cultivar wines.

Therefore, the aim of this paper was to investigate the role of volatile composition and FTMIR spectra in the differentiation between over 400 South African young wines of single-cultivar Pinotage, Merlot, Cabernet Sauvignon, Shiraz, Chardonnay, and Sauvignon Blanc. Young wines were used to exclude variability caused by oak maturation, blending, and bottle aging. Furthermore, the analysis of different instrumental signals with chemometric techniques for classification of young wines into cultivar groupings was investigated. The analytical data generated in this study were used to create a database of the volatile composition of South African young wines. To the authors' knowledge, this is the first report on the volatile composition and FTMIR spectroscopic properties of such a large number of South African young cultivar wines.

MATERIALS AND METHODS

Wines. A total of 496 single-varietal young wines that were entered in the annual South African Young Wine Shows of 2005 and 2006 were collected and analyzed. The wines were made from Sauvignon Blanc, Chardonnay, Pinotage, Merlot, Cabernet Sauvignon, and Shiraz grapes. As determined by the entry requirements of the South African Young Wine Show, the wines were single-cultivar wines that had not undergone aging. The use of young wines for this study limited the variance caused by blending, oak maturation, and bottle aging. **Table 1** shows the distribution of the sample set in terms of cultivar and vintage. As illustrated in **Table 2**, the basic chemical composition of the wines was well within the normal parameters associated with young wines. The average fructose concentrations of the Sauvignon Blanc and Chardonnay wines were similar, but this is probably not significant.

Chemicals, Standards, and Wine Matrix Simulant. *Chemicals and Standards.* Ethyl acetate and isoamyl acetate were purchased from Riedel de Haën (Seelze, Germany). Methanol, hexanol, acetic acid, and 2-phenylethanol as well as diethyl ether, ethanol, and Na_2SO_4 were purchased from Merck (Darmstadt, Germany). Ethyl butyrate, propanol, isobutanol, butanol, hexyl acetate, ethyl lactate, propionic acid, isobutyric acid butyric acid, isovaleric acid, diethyl succinate, valeric acid, 2-phenylethyl acetate, 4-methyl-2-pentanol, and hexane were purchased from Fluka (Buchs, Switzerland). Hexanoic acid, octanoic acid, isoamyl alcohol, ethyl octanoate, and ethyl decanoate were purchased from Aldrich (Steinheim, Germany). Decanoic acid and ethyl hexanoate were purchased from Sigma (St. Louis, MO).

Table 1. Number of Wine Samples in Each Cultivar Group and Their Distribution between the Training and Test Datasets As Used in the Linear Discriminant Analysis Cultivar Classification Model

	2005			2006			
cultivar	total	trainingset	testset	total	training	test	total
Sauvignon Blanc	56	42	14	47	32	15	103
Chardonnay	44	28	16	26	18	8	70
Pinotage	35	23	12	27	18	9	62
Shiraz	52	40	12	37	26	11	89
Cabernet Sauvignon	57	41	16	32	17	15	89
Merlot	49	35	14	34	25	9	83
total	293	209	84	203	136	67	496

Wine Matrix Simulant. The internal standard and volatile standards were dissolved in a wine simulant consisting of 12% v/v ethanol and 2.5 g/L tartaric acid (Merck) in deionized water from a Milli-Q water purifying system from Millipore (Billerica, MA). The pH was adjusted to 3.5 with 0.1 M NaOH (Merck).

Liquid−Liquid Extraction Procedure. Five milliliters of wine with internal standard, 4-methyl-2-pentanol (100 μL of 0.5 mg/L solution in wine simulant), was extracted with 1 mL of diethyl ether by sonicating the ether/wine mixture for 5 min. The wine/ether mixture was then centrifuged at 3600*g* for 3 min. The ether layer was removed and dried on Na_2SO_4. Each extract was injected into the GC-FID in triplicate. Validation of the method, in terms of selectivity, linearity, limits of detection, limits of quantification, recovery, robustness, and repeatability, has been described (*18*).

Gas Chromatographic Conditions. A J&W DB-FFAP capillary GC column (Agilent, Little Falls, Wilmington, DE) with dimensions 60 m length × 0.32 mm i.d. × 0.5 μm f.t. and a Hewlett-Packard 6890 Plus GC (Little Falls, DE) equipped with a split/splitless injector and an FID detector were used. The initial oven temperature was 33 °C for 17 min, after which the temperature was increased by 12 °C/min to 240 °C, at which it was held for 5 min. Three microliters of the diethyl ether extract was injected at 200 °C. The split ratio was 15:1, and the split flow rate was 49.5 mL/min. The column flow rate was 3.3 mL/min using hydrogen as a carrier gas. The detector temperature was 250 °C. After each sample run, a postrun of 5 min at an oven temperature of 240 °C, with a column flow of 6 mL/min, cleaned the column of high-boiling contaminants.

FTMIR Spectroscopy. Samples were filtered prior to spectroscopic analysis, using a filtration unit (type 79500, FOSS Analytical, Denmark) connected to a vacuum pump to remove coarse particles that could damage the cuvette. The filtration process also limits the amount of CO_2 in the wines, which can cause spectral interferences (*19*).

Filter paper disks graded with pore size of 20−25 μm and a diameter of 185 mm (Schleicher & Schuell, Germany) were used for filtration. A WineScan FT 120 spectrometer equipped with a Michelson interferometer (Foss Analytical) was used to generate spectra in the wavenumber region of 5011−929 cm^{-1}. The samples were scanned at 4 cm^{-1} intervals at 40 °C using a CAF_2-lined cuvette with a fixed path length of 37 μm. FTMIR spectra were recorded in transmittance mode, and a transmittance spectrum of each sample was converted to a linearized absorbance spectrum (*19*). The WineScan is an application instrument designed specifically for wine analysis. The spectral preprocessing is proscribed (*19*) and is therefore not accessible to change by the user. The full spectral range, 5011−929 cm^{-1}, was stored for each wine.

Table 2. Concentration Range, Average, and Standard Deviation of the Major Chemical Parameters of South African Young Wines per Cultivar

cultivar	pH	volatile acids (g/L)	total acids (g/L)	malic acid(g/L)	glucose (g/L)	fructose (g/L)	alcohol (% v/v)
Sauvignon Blanc (103)[a]	3.2−4.0 (3.5 ± 0.1)[b]	0.3−0.8 (0.4 ± 0.1)	5.2−7.6 (6.2 ± 0.5)	2.0−5.8 (3.4 ± 0.7)	0.0−4.1 (0.7 ± 0.7)	0.4−4.3 (1.6 ± 0.9)	10.4−14.7 (12.6 ± 0.7)
Chardonnay (70)	3.4−4.2 (3.7 ± 0.2)	0.2−0.7 (0.4 ± 0.1)	4.3−6.3 (5.5 ± 0.4)	0.4−4.2 (2.7 ± 0.7)	0.0−1.7 (0.3 ± 0.3)	0.4−4.3 (1.6 ± 0.9)	12.4−15.2 (13.9 ± 0.5)
Pinotage (62)	3.5−4.6 (3.9 ± 0.2)	0.4−0.8 (0.6 ± 0.1)	4.2−6.0 (5.1 ± 0.3)	0.0−0.7 (0.2 ± 0.1)	0.0−2.9 (0.5 ± 0.5)	0.4−6.4 (1.3 ± 0.9)	10.8−16.6 (14.2 ± 1.1)
Shiraz (89)	3.3−4.2 (3.8 ± 0.2)	0.3−0.8 (0.5 ± 0.1)	4.4−6.4 (5.3 ± 0.4)	0.0−1.6 (0.3 ± 0.2)	0.0−2.0 (0.8 ± 0.4)	0.0−6.3 (1.2 ± 0.8)	11.8−16.0 (14.3 ± 0.8)
Cabernet Sauvignon (89)	3.4−4.5 (3.9 ± 0.2)	0.1−0.8 (0.4 ± 0.1)	4.5−6.5 (5.4 ± 0.3)	0.1−2.3 (0.4 ± 0.2)	0.0−2.7 (0.2 ± 0.4)	0.0−5.2 (1.1 ± 0.7)	12.0−15.6 (14.1 ± 0.8)
Merlot (83)	3.2−4.3 (3.8 ± 0.2)	0.2−0.8 (0.4 ± 0.1)	4.4−7.3 (5.4 ± 0.4)	0.1−2.1 (0.4 ± 0.3)	0.0−1.3 (0.4 ± 0.3)	0.1−3.8 (1.0 ± 0.6)	12.4−15.2 (13.9 ± 0.5)

[a] Number of samples. [b] Minimum−maximum (average ± standard deviation).

Statistics. *Data Pretreatment.* The wavenumber regions 5011−2970 and 1716−1543 cm^{-1} were omitted in the multivariate data analyses except where specifically stated that the entire spectrum was used. The two regions 1716−1543 and 3627−2971 cm^{-1} contain strong water absorption peaks, whereas the region 5011−3627 cm^{-1} contains very little useful wine-related information (*19*−*21*). In samples having a chemical component that was present below the limit of detection, a concentration value of 0 g/L was used for that particular component in chemometric analysis of the data. The data were centered and scaled to the same variance by standardization throughout all multivariate statistical procedures.

Principal Component Analysis (PCA). PCA was performed with The Unscrambler 9.2 software (CAMO Process AS, Oslo, Norway), using cross-validation (20 segments) as a validation method, in order to observe correlations between observations and variables in the data (*22*).

Linear Discriminant Analysis (LDA). LDA was performed using Statistica 7 (Statsoft Inc., www.statsoft.com) to classify the wines into their respective cultivar groupings. A multiple linear classification approach was used with the assumption of equal covariance matrices. The LDA model was validated using test set validation. For this analysis, the data were randomly divided into a training set and a test set, representing 70 and 30% of the total data set, respectively. Histograms of the cultivar, vintage, and origin distribution of the samples in the training and test sets were plotted in Statistica 7 and compared to ensure that the test and training sets were representative of the original data set. The distribution of the sample set among the training and test sets is shown in **Table 1**.

For the models based on FTMIR spectra, PCA was done on the training set during which the PCA scores were calculated. The optimum number of principal components for this step was calculated with cross-validation. Subsequently, a LDA was done on the PCA scores. Validation was done by calculating the PCA scores of the test set, using the PCA model derived from the training data. These PCA scores were then used as input to the LDA model developed on the calibration set. For the models based on the volatile composition of the wines the variable set was refined using best subset regression based on the calibration data.

Supplementary Statistics. One-way analysis of variance (ANOVA) was performed in Statistica 7, using the Tukey posthoc test, to identify the volatile compounds that occurred at significantly different concentrations between cultivars. Factorial ANOVA was performed to determine whether there were significant interactions between vintages and cultivars. Radar graphs of the volatile compounds present in the cultivar wines were plotted in Excel on the basis of the average concentration per cultivar. The data were standardized to compensate for the large variation in the concentrations at which the different compounds occurred in the wines.

RESULTS AND DISCUSSION

Comparison of the Volatile Composition. Summaries of all the analyzed compounds and their concentration ranges in the white and red wines are given in **Tables 3** and **4**, respectively. **Tables 3** and **4** also show the odor thresholds for each compound as reported in the literature and their odor activity value (OAV) in each cultivar. OAVs were calculated by dividing the mean concentration value of a compound by its odor threshold value as reported in the literature (*23*).

Of the 26 volatile compounds, 14 had OAVs > 1, meaning that they make an active contribution to the odor of the wine. These compounds were isobutanol, isoamyl alcohol, 2-phenylethanol, ethyl acetate, ethyl butyrate, isoamyl acetate, ethyl hexanoate, ethyl octanoate, butyric acid, isovaleric acid, hexanoic acid, and octanoic acid.

Sauvignon Blanc contained significantly higher average concentrations of decanoic acid, hexyl acetate, and octanoic acid when compared to Chardonnay. In turn, Chardonnay contained significantly higher amounts of ethyl hexanoate. Three of these compounds were present in odor active quantities in both Sauvignon Blanc and Chardonnay. The profiles of Sauvignon Blanc and Chardonnay in terms of these compounds are illustrated in **Figure 2**.

The fatty acids decanoic acid and octanoic acid are derived from acetyl-CoA, which is, in turn, formed from pyruvic acid, an important byproduct of alcoholic fermentation (*24*). Hexyl acetate is derived from hexanol, which can be a grape constituent or formed from hexanoic acid (*25*). Hexanoic acid is also the precursor of ethyl hexanoate. It seems as if there are metabolic links between the fermentation compounds responsible for the differences between Chardonnay and Sauvignon Blanc.

No statistical differences were observed between the white cultivars based on the concentrations of the other volatile compounds. This suggests that the volatile composition as determined in this study does not play a very important role in the differentiation between young Sauvignon Blanc and Chardonnay wines. However, other volatile compounds that have not been determined in this study, such as methoxypyrazines, which have been found to play a significant role in Sauvignon Blanc aroma (*26*), might be more appropriate to elicit the differences between these two cultivars.

The Pinotage wines differed significantly from the other red wines with regard to 2-phenylethanol, butyric acid, ethyl acetate, isoamyl acetate, isoamyl alcohol, and isobutyric acid concentration levels. Pinotage wines were in fact more comparable to the two white wine cultivars than the other red wine cultivars in terms of these compounds (**Figure 3**). Apart from isobutyric acid and propionic acid, all of these compounds occurred at odor active quantities in Pinotage. This is not the first study in which Pinotage wines have been found to compare better to white wines than red wines. De Beer et al. (*27*) reported that the antioxidant potential of Pinotage wines was significantly lower than that of other South African red wines. At the time the authors could not relate this phenomenon to the phenolic composition of Pinotage wines, but hypothesized that differences in individual phenolic compounds and/or the ratios at which they occur (*27*) could play a role.

The Merlot wines also differentiated from the other red wines, having significantly lower amounts of 2-phenylethyl acetate and signicantly higher amounts of isobutanol, propionic acid, and valeric acid. In fact, Merlot was the only cultivar in which the compounds propionic acid and isobutanol had an OAV > 1 (**Table 4**). The Shiraz wines differed significantly from the other

Table 3. Odor Threshold Values Reported in the Literature, Concentration Ranges, and Average Concentrations (All in Milligrams per Liter) Determined in This Study, as well as Odor Activity Values for South African Sauvignon Blanc and Chardonnay Young Wines

		Sauvignon Blanc (103)[a]			Chardonnay (70)		
analyte	OTH[a]	range	average	OAV[b]	range	average	OAV
methanol		21.5−180.5	77.83 a[c]		50.6−482.0	105.95 a	
propanol	306 (*30*)	19.2−82.7	36.17 a	0.1	20.6−176.6	56.40 a	0.1
butanol	150 (*31*)	0.3−2.5	0.94 a	0	nd[d]−2.2	1.17 a	0
isobutanol	40 (*23*)	2.3−38.0	16.48 a	0.4	2.3−31.6	15.71 a	0.2
isoamyl alcohol	30 (*23*)	115.4−394.4	177.47 a	5.9	103.7−414.1	162.78 a	1.7
hexanol	8 (*23*)	0.1−3.6	1.19 a	0.1	nd−2.7	1.04 a	0.1
2-phenylethanol	14 (*5*)	6.9−59.3	12.83 a	0.9	5.8−62.1	13.25 a	0.6
ethyl acetate	12.26 (*32*)	30.2−223.6	89.99 a	7.3	20.8−307.5	100.94 a	3.1
ethyl butyrate	0.02 (*23*)	0.2−1.7	0.54 a	27.1	nd−1.9	0.66 a	17.9
isoamyl acetate	0.03 (*23*)	1.1−16.2	5.03 a	167.5	0.5−14.9	4.27 a	82.3
ethyl hexanoate	0.014 (*5*)	0.3−1.4	0.74 b	52.7	0.4−2.3	1.01 a	34.1
hexyl acetate	1.5 (*31*)	nd−1.1	0.22 a	0.1	nd−0.9	0.09 b	0.1
ethyl lactate	154.6 (*32*)	nd−42.8	10.71 a	0.1	nd−130.6	19.61 a	0.2
ethyl octanoate	0.005 (*5*)	nd−2.6	0.73 a	146.7	0.2−0.9	0.50 a	37.2
ethyl decanoate	0.2 (*5*)	nd−0.8	0.18 a	0.9	nd−0.4	0.14 a	0.5
diethyl succinate	200 (*31*)	nd−3.5	0.43 a	0	nd−16.8	1.17 a	0
2-phenylethyl acetate	0.25 (*23*)	nd−0.9	0.16 a	0.6	nd−0.6	0.12 a	0.5
acetic acid	200 (*23*)	101.5−1648.1	408.08 a	2	110.1−1140.3	395.35 a	0.9
propionic acid	20 (*24*)	1.2−43.0	8.82 a	0.4	0.0−53.8	14.96 a	0.9
isobutyric acid	2.3 (*5*)	nd−2.7	1.02 a	0.4	0.1−2.2	1.00 a	0.2
butyric acid	0.173 (*5*)	0.8−3.8	1.83 a	10.6	nd−4.3	2.02 a	3.4
isovaleric acid	0.033 (*5*)	0.2−2.0	0.80 a	24.3	0.1−3.2	0.89 a	15.8
valeric acid		0.0−0.4	0.02 a		0.0−0.4	0.04 a	
hexanoic acid	0.42 (*5*)	3.3−13.7	5.77 a	13.7	1.7−10.4	5.19 a	2.9
octanoic acid	0.50 (*5*)	1.7−10.3	6.17 a	12.4	1.2−9.6	4.70 b	4.2
decanoic acid	1 (*5*)	0.4−3.4	1.42 a	1.4	0.4−2.0	1.07 b	0.4

[a] Number of samples. [b] OTH, odor threshold. The numbers in parentheses refer to the literature source. [c] Odor activity value. [d] Tukey HSD values: different letters in the same row indicate significant differences in the average concentration of the respective cultivars. [e] Not detected.

Table 4. Odor Threshold Values Reported in the Literature, Concentration Ranges, and Average Concentrations (All in Milligrams per Liter) Determined in This Study, as well as Odor Activity Values for South African Red Cultivar Young Wines

		Pinotage (62)[a]			Cabernet Sauvignon (89)			Merlot (83)			Shiraz (89)		
analyte	OTH[b]	range	average	OAV[c]	range	average	OAV	range	average	OAV	range	average	OAV
methanol		70.7−284.8	157.75 c[d]		82.0−407.9	207.73 b		124.7−406.7	253.50 a		nd[e]−433.1	236.94 a	
propanol	306 (*30*)	4.8−213.7	94.64 a	0.3	3.3−97.5	45.41 bc	0.1	17.4−85.1	41.71 c	0.1	2.6−180.2	53.33 b	0.2
butanol	150 (*31*)	0.8−3.3	2.05 a	0	1.1−5.0	1.99 a	0	1.0−3.4	1.91 a	0	1.0−8.0	2.15 a	0
isobutanol	40 (*23*)	3.4−54.8	24.75 b	0.6	2.3−84.5	24.03 b	0.6	24.9−97.9	58.48 a	1.5	4.5−68.8	24.89 b	0.6
isoamyl alcohol	30 (*23*)	119.6−331.1	216.77 c	7.2	159.5−580.3	379.44 a	2.3	206.1−642.3	360.42 a	12	194.6−487.6	320.75 b	10.7
hexanol	8 (*23*)	0.2−2.1	1.06 b	0.1	0.7−5.4	1.79 a	0.1	0.3−4.4	1.27 b	0.2	0.5−5.5	1.89 a	0.2
2-phenylethanol	14 (*5*)	7.8−47.3	18.87 c	1.3	24.5−142.1	68.73 a	1.7	18.8−155.4	66.99 a	4.8	16.9−96.3	44.08 b	3.1
ethyl acetate	12.26 (*32*)	30.3−158.5	85.04 a	6.9	3.7−103.4	62.97 b	1.3	27.7−119.3	65.76 b	5.4	20.2−127.1	68.54 b	5.6
ethyl butyrate	0.02 (*23*)	nd−7.3	0.35 a	18	nd−2.0	0.16 a	10.7	nd−1.9	0.23 a	11.6	nd−4.4	0.19 a	9.5
isoamyl acetate	0.03 (*23*)	0.3−7.7	2.65 a	88.6	nd−5.8	0.96 b	24.4	0.2−4.7	1.30 b	43.5	0.2−5.8	1.39 b	46.2
ethyl hexanoate	0.014 (*5*)	0.1−0.8	0.34 a	24.2	nd−0.5	0.20 b	8.4	nd−0.9	0.39 a	28.1	nd−1.6	0.49 a	35
hexyl acetate	1.5 (*31*)	nd−1.6	0.03 a	0	nd	nd a	0	nd	nd a	0	nd	nd a	0
ethyl lactate	154.6 (*32*)	51.2−210.7	125.26 a	0.8	19.6−194.7	100.61 b	0.2	4.1−182.4	83.67 c	0.5	23.5−208.1	100.53 b	0.7
ethyl octanoate	0.005 (*5*)	0.1−0.8	0.27 ab	53.9	nd−0.3	0.09 c	11.6	nd−0.7	0.32 a	64.5	nd−3.4	0.12 bc	23.1
ethyl decanoate	0.2 (*5*)	nd−0.3	0.10 b	0.5	nd−0.2	0.02 c	0.2	nd−0.6	0.15 a	0.8	nd−0.2	0.02 c	0.1
diethyl succinate	200 (*31*)	1.3−22.3	8.24 b	0	2.1−19.4	10.87 a	0	1.0−17.6	8.07 b	0	1.3−19.6	10.15 a	0.1
2-phenylethyl acetate	0.25 (*23*)	nd−0.4	0.15 ab	0.6	nd−1.3	0.19 a	0.8	nd−0.4	0.06 c	0.3	nd−1.5	0.13 b	0.5
acetic acid	200 (*23*)	268.7−889.2	597.52 a	3	251.8−1011.5	526.89 ab	0.6	39.8−1122.1	491.27 b	2.5	336.0−945.6	568.43 a	2.8
propionic acid	20 (*24*)	1.7−127.6	17.17 b	0.9	0.8−4.3	2.79 c	0	2.0−357.0	40.89 a	2	1.9−6.1	3.43 c	0.2
isobutyric acid	2.3 (*5*)	0.3−2.6	1.43 b	0.6	0.8−7.8	2.02 a	0.4	0.6−7.3	2.18 a	0.9	0.5−4.3	1.88 a	0.8
butyric acid	0.173 (*5*)	0.6−3.3	1.30 a	7.5	nd−1.8	0.98 b	1.6	0.4−1.9	0.97 b	5.6	0.4−2.6	0.97 b	5.6
isovaleric acid	0.033 (*5*)	0.4−2.6	1.38 c	41.7	0.9−4.6	2.84 a	24.4	0.8−8.0	2.73 a	82.8	0.8−3.8	2.06 b	62.4
valeric acid		0.0−0.7	0.14 b		0.0−0.3	0.05 c		0.0−1.6	0.31 a		nd	nd c	
hexanoic acid	0.42 (*5*)	0.8−4.3	1.94 a	4.6	nd−3.1	1.57 ab	0.9	0.5−2.6	1.50 ab	3.6	nd−2.5	1.43 b	3.4
octanoic acid	0.50 (*5*)	0.8−4.1	1.77 ab	3.5	0.6−407.9	1.45 ab	1.1	0.3−3.1	1.81 a	3.6	0.4−3.8	1.29 b	2.6
decanoic acid	1 (*5*)	nd−1.7	0.62 ab	0.6	nd−1.1	0.57 b	0.5	nd−1.7	0.79 a	0.8	nd−1.0	0.19 c	0.2

[a] Number of samples. [b] OTH, odor threshold. The numbers in parentheses refer to the literature source. [c] Odor activity value. [d] Tukey HSD values: different letters in the same row indicate significant differences in the average concentration of the respective cultivars. [e] Not detected.

red wines in terms of decanoic acid, 2-phenylethanol, isoamyl alcohol, and isovaleric acid, although decanoic acid did not occur at odor active quantities in the any of the red wines. Cabernet Sauvignon was comparable to at least one red cultivar except in terms of ethyl hexanoate, of which it contained significantly lower amounts. The differences between the volatile profiles of the red cultivars are shown in **Figures 3** and **4** There were no significant differences between the red cultivars in terms of butanol, ethyl butyrate, or hexyl acetate levels.

These results are in agreement with previous reports. The differences observed between Pinotage and Cabernet Sauvignon wines are similar to the results from a previous study conducted

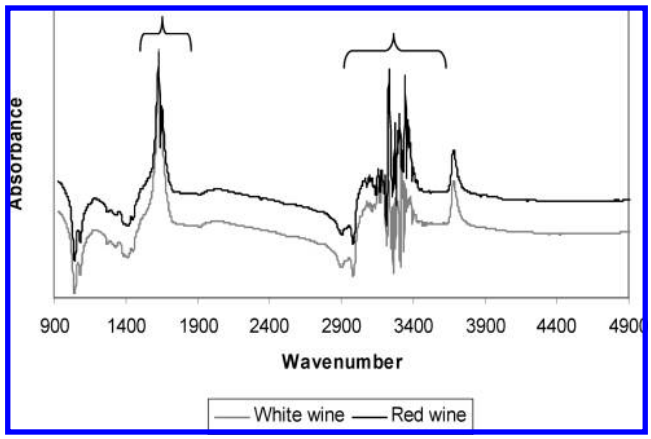

Figure 1. Typical FTMIR spectrum of a young red wine and a young white wine. The indicated wavenumber regions 1716−1543 and 3627−2971 cm^{-1}, respectively, are characterized by strong water absorption peaks. The red wine spectrum was plotted with an offset of 0.5 unit for the sake of clarity, and therefore the values on the *y*-axis are not shown.

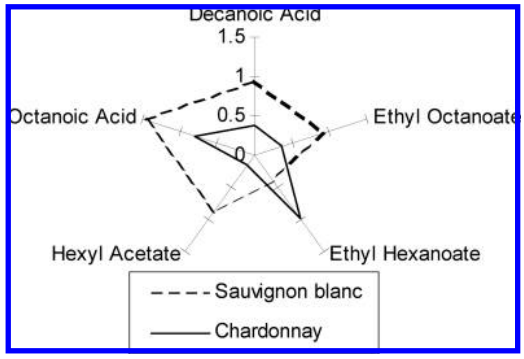

Figure 2. Volatile composition profiles of Chardonnay and Sauvignon Blanc wines based on the average concentration per cultivar for some significant compounds.

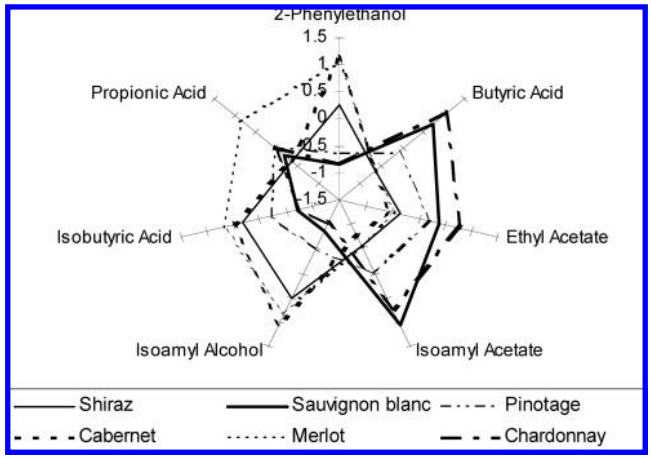

Figure 3. Volatile composition profiles of the six wine cultivars based on the average concentration per group. The Pinotage profile is more comparable with the white wines than the other red wines.

on South African wines, except in the case of ethyl lactate and 2-phenylethyl acetate (*17*). Furthermore, a previous study has shown that the fusel alcohol acetates, iso-acids, and fusel alcohols discussed above contributed significantly to the differences between grape varieties (*5*). These compounds are linked to the amino acid metabolism of yeast cells and, as Ferreira et al. (*5*) suggested, the differences in the concentration of these yeast metabolites could be due to the unique amino

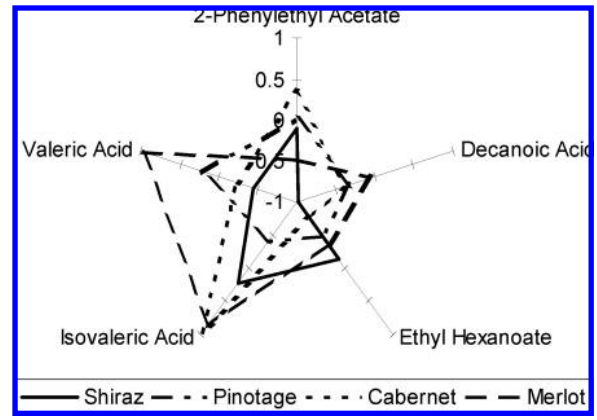

Figure 4. Volatile composition profile of the four red wine cultivars based on the average concentration per group for some significant compounds.

acid profiles of the cultivars. The fact that many of the compounds discussed above have common amino acid precursors supports this statement.

Contribution of FTMIR Spectra and Volatile Composition to the Differentiation between Cultivars. PCA was performed to investigate and interpret the contribution of FTMIR spectra to the differentiation between cultivar wines. Separation, with some degree of overlap, was observed between the Chardonnay and Sauvignon Blanc wines on the basis of their spectra (**Figure 5**). The first two principal components explained 90% of the variance in the data. The loading plot showed that the wavenumbers with high loadings were distributed over the entire wavenumber range and included a large sequence of continuous wavenumbers. The degree of differentiation between the two white cultivars decreased when volatile compounds were included in the variable set (data not shown). These results suggested that the differentiation between the Chardonnay and Sauvignon Blanc wines could be attributed to the wines' chemical composition as a whole and not only to the volatile compounds. This observation was supported by the fact that only four of the volatile compounds occurred at statistically different levels between the Chardonnay and Sauvignon Blanc wines, as discussed before.

The opposite was noted for the red wines, where the volatile components contributed more to the differences between cultivars than the spectra. No cultivar groupings could be observed with PCA of the reds when only the spectra were used as variables (data not shown). It has previously been reported that poor differentiation was observed between red wine cultivars on the basis of their MIR spectra using PCA (*14*), as well as with hierarchical cluster analysis and SIMCA (*9*). Spectroscopic differentiation between red wine cultivars has been reported to be more successful when focusing on the phenolic composition of the wines by the analysis of their phenolic extracts either with MIR spectroscopy or with UV−vis spectroscopy (*9*, *11*).

PCA of the volatile compounds in 2005 differed from the analysis of those of 2006 (**Figures 6** and **7**). As can be noted for both vintages, the variances explained by the first two components of both of these models are relatively moderate. In each vintage it was found that the Pinotage wines separated from the rest of the red cultivars, correlating well with the PCs where isoamyl acetate had high positive loadings and the iso-acids and isoamyl alcohol had high negative loadings (**Figures 6** and **7**). It has been established that isoamyl acetate plays an important role in the varietal characteristics of Pinotage wines (*28*). The high negative correlation between isoamyl alcohol

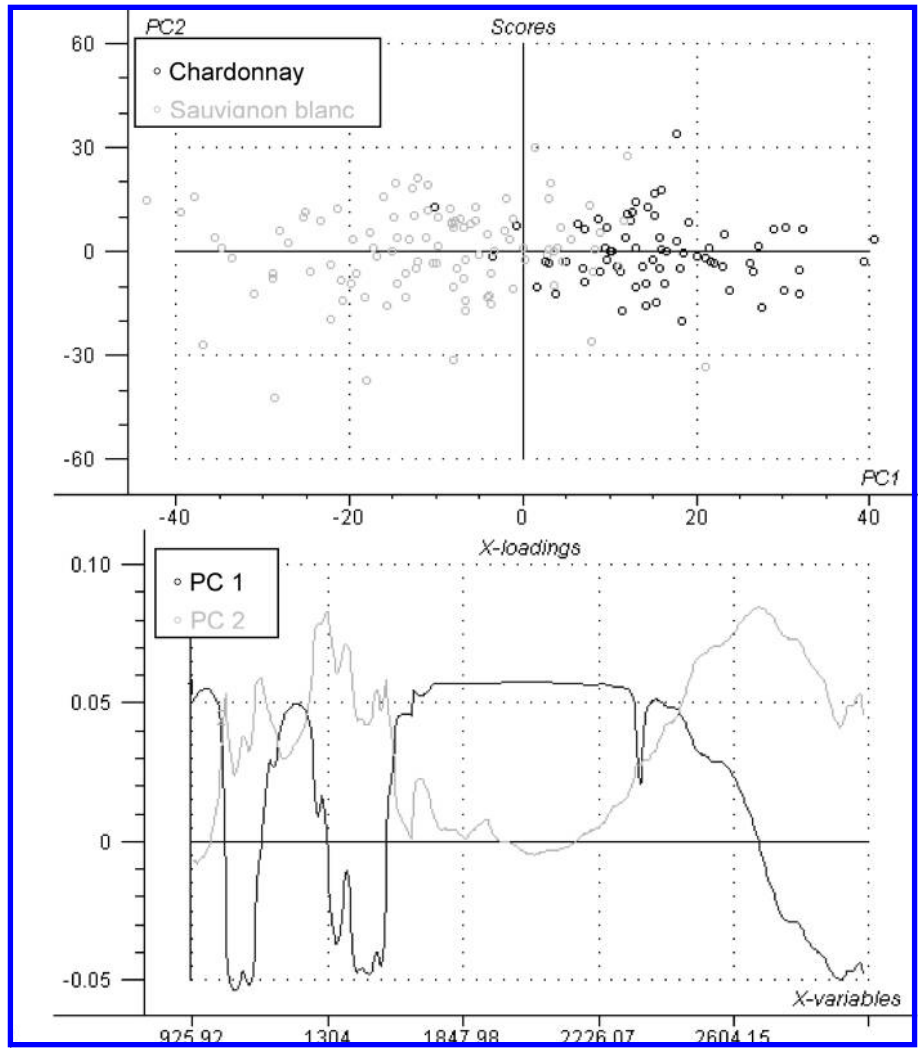

Figure 5. PCA score and loading plots showing the differentiation between Sauvignon Blanc and Chardonnay samples based on their FTMIR spectra. PC 1 and PC 2 explain 62 and 28% of the total variance in the data set, respectively.

and the iso-acids and Pinotage is consistent with the results from the ANOVA tests. PCA of the red wines of vintage 2005 showed that the Merlot wines formed a clear group based on high positive loadings of propionic and decanoic acids and high negative loadings of 2-phenylethyl acetate. However, for the 2006 vintage, the Merlot wines could not be separated from the Shiraz or Cabernet Sauvignon wines (**Figure 7**). The Shiraz and Cabernet Sauvignon wines from the 2005 vintage also separated better from each other than those from the 2006 vintage. In both vintages, the separation between the Shiraz and Cabernet Sauvignon wines was mainly due to high loadings of 2-phenylethanol, isovaleric acid, and isoamyl alcohol. These compounds were negatively correlated with Shiraz. These results are also consistent with the results from ANOVA tests.

To investigate whether the use of volatile compounds is useful for discrimination between red cultivars, despite the observed year differences, a PCA using volatile composition of both years was done. Results showed that the Pinotage wines again clearly separated from the other red cultivars (data not shown). These results highlighted the need for using a multivariate data analysis approach for cultivar characterization.

Factorial ANOVA of the volatile composition of the wines showed that there were significant vintage to cultivar interactions for almost all of the volatile compounds analyzed, indicating that the variation over vintages was not consistent for each cultivar. Therefore, it is understandable that differences in the degree of separation between cultivars were observed between the two vintages.

Classification of Cultivars Based on Chemical and Spectroscopic Properties. The two-dimensional plots generated with PCA are useful for interpretation, but information useful for discrimination may also be found in components with lower explained variance. Therefore, LDA was also applied to classify the wines into their respective cultivar classes. Generally good classification results were achieved between the cultivar wines.

Results for Red Wines. For the classification of the red wines, an average classification success rate of 68% was achieved when the entire spectral range (5011−929 cm^{-1}) was used (**Table 5**). The average classification success rate of the red wines increased to 77% when wavenumbers 5011−2970 and 1543−1716 cm^{-1} were excluded from the analyses. These wavenumbers are generally associated with spectral noise largely caused by water absorbance. A subset of five volatile compounds was selected with best subset regression for discriminant analysis. This subset included decanoic acid, ethyl hexanoate, isoamyl acetate, isobutanol, and isoamyl alcohol. These compounds were identified as significant compounds in the differentiation between the red cultivar wines according to ANOVA results as discussed in the second part of this Results section. Isoamyl acetate is

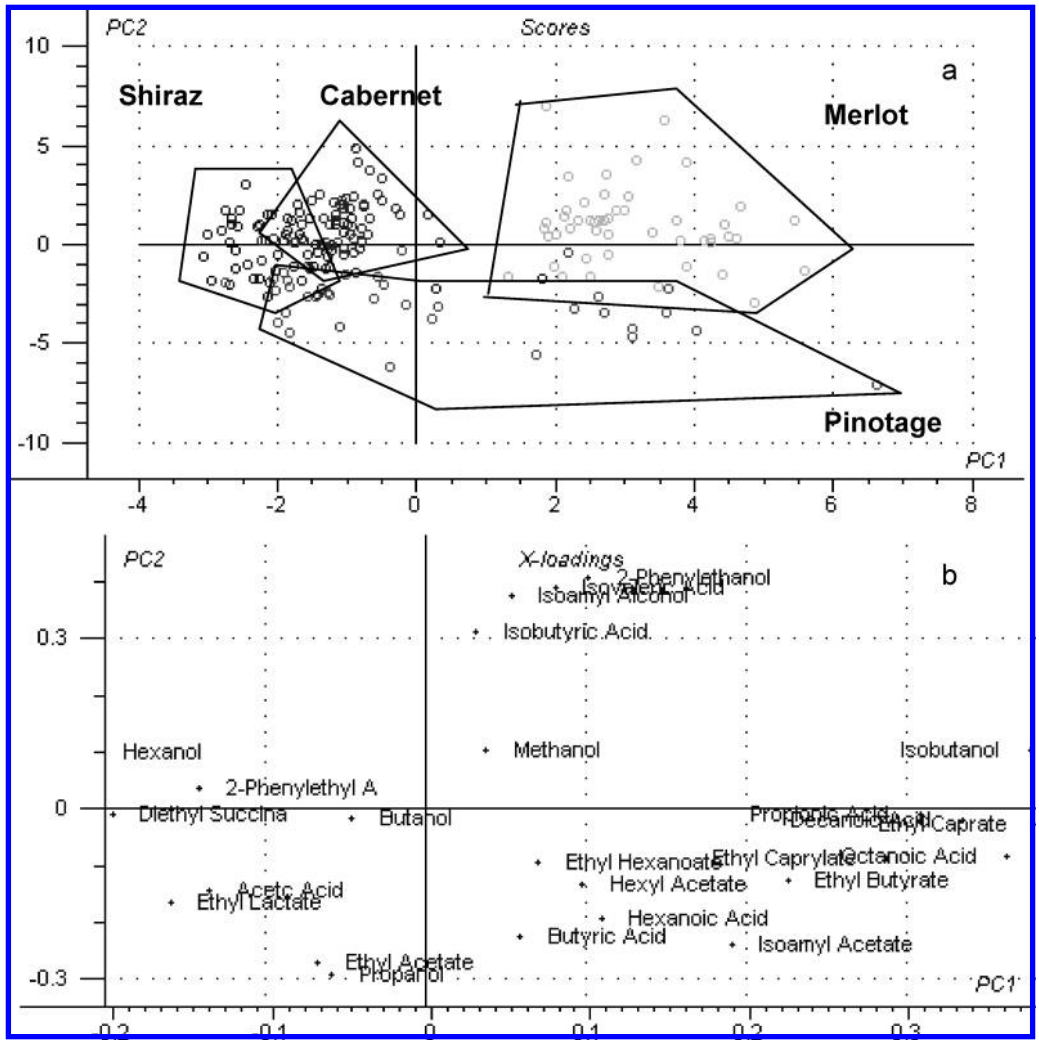

Figure 6. PCA score and loading plots showing the differentiation between red cultivar wines from the 2005 vintage based on their volatile composition. On the score plot (**a**), each symbol denotes a wine sample, whereas the line shapes indicate the location of samples of the same cultivar in the plot. PC 1 and PC 2 each explain 21 and 18% of the total variance, respectively. The loading plot (**b**) shows the relative influence of the volatile compounds in the differentiation between the wines.

particularly characteristic of Pinotage wines, although isoamyl alcohol also differentiated this cultivar from the other red wines. The inclusion of ethyl hexanoate in this subset is also interesting, as this compound was significantly lower in Cabernet Sauvignon wines than in the other red wines. Isobutanol and decanoic acid played significant roles in differentiating Merlot and Shiraz wines from the other wines, respectively. Decanoic acid is the only compound in the subset that did not have an OAV > 1 for any of the red wine cultivars. This subset of volatile compounds resulted in a discriminant analysis model with an average correct classification rate of 71%. The best result, 86% average correct classification, was achieved using a combination of the entire spectral range as discussed above and all 26 volatile compounds. This is not the first case of better discrimination being observed between red wine cultivars on the basis of their MIR spectra using LDA, whereas poor discrimination was observed using PCA on the same wines (*14*).

Bevin et al. reported a similar case with Australian wines; they were able to correctly classify 93% of red wine cultivars on the basis of their MIR using LDA even though they observed little discrimination between the cultivars with PCA (*14*).

Results for White Wines. The spectroscopic data, the compositional data, and combinations thereof could all successfully be used to discriminate between Sauvignon Blanc and Chardonnay wines. A 98% correct classification rate was obtained using the entire spectral range. In contrast to the modeling of the red wines, the average classification success rate of the white wines dropped to 93% when the wavenumbers associated with noise (5011−2970 and 1543−1716 cm^{-1}) were excluded from the analyses. Some possible functional groups that could have absorbance bands in these regions are the −CH stretches of alkanes, alkenes, and alkynes. In addition, the −CH and C═C stretches of aromatic compounds as well as the primary and secondary −NH stretch of amines and the −C═O stretch and −NH stretch and bend of amides are also found in this region (*29*).

However, there is only a 5% difference in the classification rate obtained when using the entire spectra versus selected wavenumbers (**Table 5**), and the white cultivars could therefore successfully be classified without the contribution of functional groups that strongly absorb in the 5011−2970 and 1543−1716 cm^{-1} wavenumber regions. The improvement of the classification model by the use of a larger wavenumber region highlights the value of FTMIR spectra as an information-rich and nonselective instrumental signal.

Best subset regression identified butanol, decanoic acid, ethyl hexanoate, isoamyl alcohol, methanol, propanol, and propionic acid as the most influential compounds for the discrimination

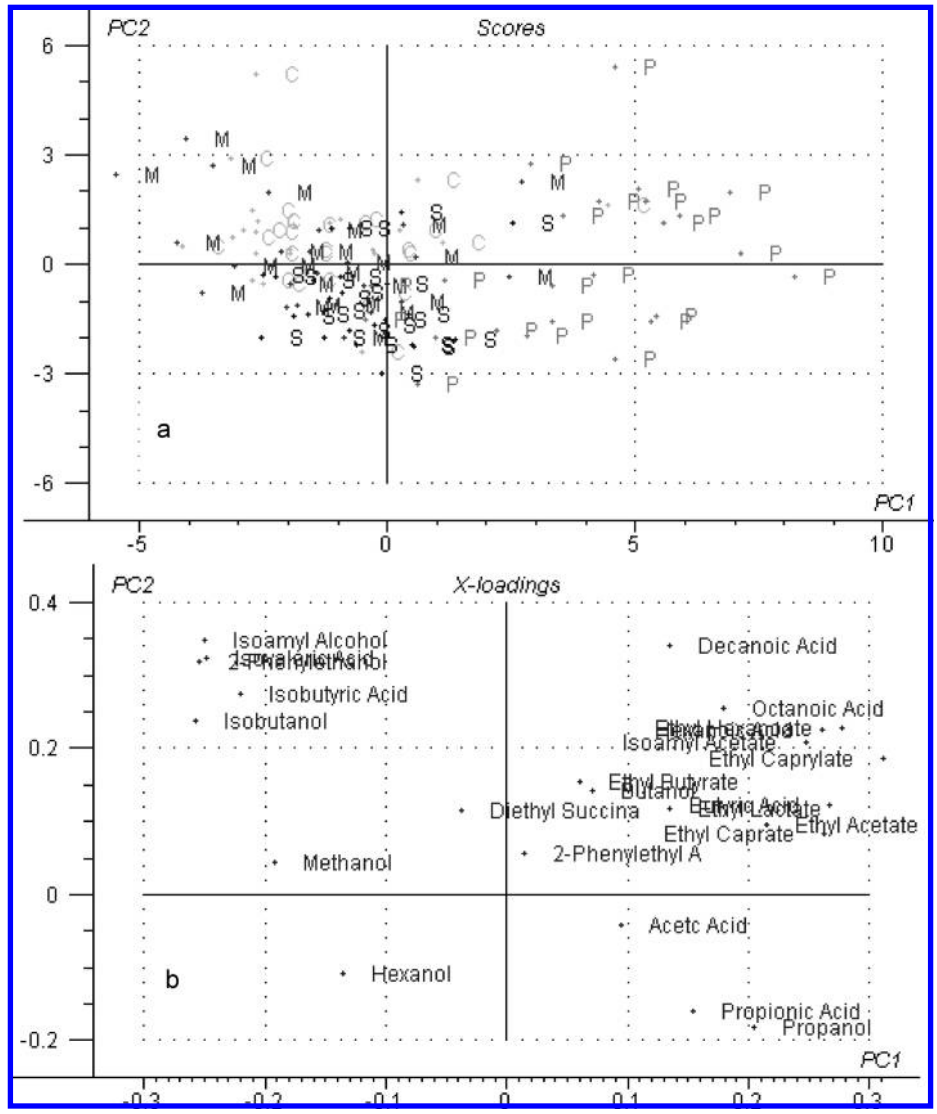

Figure 7. Score plot (**a**) of the PCA done on the volatile composition of the 2006 red wines shows that there was little differentiation between the Cabernet Sauvignon (C), Shiraz (S), and Merlot (M) wines of this vintage. Pinotage (P) wines separated slightly from the other red wines on PC 1. PC 1 and PC 2 each explain 34 and 11% of the total variance, respectively. The loading plot (**b**) shows the influence of the respective volatile components in the positioning of the wines on the score plot.

between the two white cultivars. Of these compounds only decanoic acid and ethyl hexanoate were significantly different between Sauvignon Blanc and Chardonnay according to ANOVA. Decanoic acid, ethyl hexanoate, and isoamyl alcohol were the only compounds in the subset that were odor active in the white wines. Nevertheless, a combination of these compounds resulted in a discrimination model with an 83% correct classification rate. A combination of the entire set of spectroscopic data and all 26 volatile compounds could be used to correctly discriminate between Sauvignon Blanc and Chardonnay wines at an average correct classification rate of 93%. The negative effect of the volatile compounds on the white wine classification model is in accordance with the results of the PCA that showed that the spectroscopic data had a larger influence on the differences between Sauvignon Blanc and Chardonnay wines.

There are of course many other data modeling options that can be explored to optimize the classification success rate and stability of a classification model. However, it is important to note that both the FTMIR spectra and the volatile composition each contribute to the classification of South African cultivar wines. Different variable sets, such as spectroscopic measure-

Table 5. Percentage of Correct Classification between Cultivar Wines Obtained with Linear Discriminant Analysis with Different Variable Sets after Test Set Validation

cultivar	entire spectra[a]	selected wavenumbers[b]	volatile compounds[c]	volatile compounds[d] + entire spectra
		Red Cultivars		
Cabernet	48.6	68.6	62.9	71.4
Pinotage	84.0	76.0	88.0	100.0
Shiraz	50.0	83.3	66.7	86.7
Merlot	95.8	83.3	70.8	95.8
total	66.7	77.2	71.1	86.8
		White Cultivars		
Chardonnay	100.0	86.2	72.4	93.1
Sauvignon Blanc	96.9	100.0	93.9	93.9
total	98.3	93.5	83.8	93.5

[a] FTMIR spectra from 5011 to 929 cm^{-1}. [b] FTMIR spectra where the wavenumbers regions 5011−2970 and 1716−1543 cm^{-1} have been omitted. [c] Compounds selected by best subset regression. [d] Volatile compounds, standardized.

ments and chemical compounds, have been shown to contribute uniquely to the variability in samples (*33*). This has important practical implications. Although the simple and rapid method of FTMIR spectroscopy is sufficient for the classification of Sauvignon Blanc and Chardonnay wines, the volatile composition, which is more time-consuming to determine, is necessary for reliable discrimination of the red wine cultivars. The viability of using a sample preparation procedure to remove further interfering compounds prior to FTMIR analysis can be investigated because it has been found that the MIR spectra of phenolic extracts of red wines are more useful for discrimination between red cultivar wines than of untreated wines (*9*). Such a method could be compared to the GC-FID analysis used in this study in terms of the quality of the discrimination models, practicality, and cost effectiveness. The current work included only six of the most important cultivars in the South African wine industry, and it would be interesting to investigate the contribution of FTMIR spectroscopy and GC-FID analysis on the discrimination models with other cultivars included. The discriminant power of FTMIR spectroscopy on white wine cultivars should especially be tested by including more white wine cultivars. Because the current study was done on young wines only, additional discrimination models could also be developed for matured wines.

In conclusion, the results of this study confirmed that South African Sauvignon Blanc, Chardonnay, Merlot, Pinotage, Cabernet Sauvignon, and Shiraz wines differ significantly in terms of yeast-derived volatile components and FTMIR spectra. Statistical differences were found in the volatile compositions of the cultivar wines. Fourteen of the volatile compounds analyzed were present at odor active quantities. Similarities were observed between Pinotage wines and white wines. On the basis of PCA, it seemed that most of the differences between red wines were due to the volatile constituents, although the FTMIR spectra contributed considerably to distinction between the white wines. This trend followed through in the discriminant models for the classification of the red and white wine cultivars. The most successful classification rate for the red wines was achieved with a combination of the entire infrared spectra and volatile compounds, whereas the best discriminant model for the white wines was based on only the spectroscopic data, showing that both FTMIR spectra and volatile components play a role in the differentiation between young South African cultivar wines.

ABBREVIATIONS USED

ANOVA,analysis of variance; FID, flame ionization detection; FTMIR, Fourier transform mid-infrared; GC, gas chromatography; GC-FID, gas chromatography with flame ionization detection; LDA, linear discriminant analysis; nd, not detected (below limit of detection); MIR, mid-infrared; OAV, odor activity value; OTH, odor threshold; PC, principal component; PCA, principal component analysis; SIMCA, soft independent modeling of class analogies; UV−vis, ultraviolet−visible.

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