Effect of Storage Time, Temperature and Region on the Levels of 1,1,6-Trimethyl-1,2-dihydronaphthalene and other Volatiles, and on Quality of Weisser Riesling Wines*

J. Marais[1], C.J. van Wyk[2] and A. Rapp[3]

1) Nietvoorbij Institute for Viticulture and Oenology (Nietvoorbij), Private Bag X5026, 7599 Stellenbosch, Republic of South Africa
2) Department of Oenology, University of Stellenbosch, 7600 Stellenbosch, Republic of South Africa
3) Bundesforschungsanstalt für Rebenzüchtung, Geilweilerhof, D-6741 Siebeldingen, Germany

Submitted for publication: January 1992
Accepted for publication: March 1992
Key words: 1,1,6-Trimethyl-1,2-dihydronaphthalene, region, ageing, storage temperature, Weisser Riesling

A survey of the concentration levels of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) in wines of different cultivars, vintages and regions was conducted. The TDN concentrations of South African Weisser Riesling wines were higher than those from Germany and Italy, and those of other cultivars. The effect of storage time and temperature on free and precursor TDN concentrations, on the concentrations of free trans-vitispirane, some monoterpenes, esters and higher alcohols, and on the quality of Weisser Riesling wines was investigated. Three Weisser Riesling wines from different regions were stored at 15°C and 30°C for four years and one year, respectively. These wines were analysed periodically by gas chromatography and evaluated sensorially. The concentrations of TDN, trans-vitispirane, 2,6-dimethyl-7-octen-2,6-diol and trans-1,8-terpin, and the intensity of the bottle-aged kerosene-like character increased significantly with ageing. During the same period, significant decreases occurred in the concentrations of diendiol-1, linalool, i-amyl acetate, ethyl caproate, hexyl acetate, 2-phenethyl acetate, hexanol, 2-phenyl ethanol, and in the intensity of young wine character. alpha-Terpineol showed significant increases followed by decreases under the same conditions. These changes in concentrations were more prominent at 30°C than at 15°C storage. The development of the kerosene character in Weisser Riesling wines was restricted to sensorially acceptable levels by storage at 15°C.

Earlier studies indicated the presence of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) in rum, wine and brandy (Liebich, Koenig & Bayer, 1970; Bertuccioli & Viani, 1976; Schreier *et al.,* 1976; Williams & Strauss, 1977). Simpson (1978) demonstrated that TDN is an important contributor to the bottle-aged kerosene-like character of Weisser Riesling wines. A flavour threshold in wine of 20 ppb was reported. Although TDN is also present in wines of other cultivars, its concentration is too low to be organoleptically detectable. In Weisser Riesling, however, it is widely accepted that the kerosene-like character is beneficial to wine quality when present at low intensities, but becomes undesirable when present at high intensities.

High TDN concentrations, almost exclusively associated with aged Weisser Riesling wines, generated investigations into the origin of this compound. Ohloff (1978) suggested that TDN is formed through carotenoid degradation. Traces of TDN were in fact produced during the photo-oxidation of beta-carotene (Hohler, Nitz & Drawert, 1988). A few intermediates between carotenoids and TDN have been proposed. These are 5,6-epoxy-beta-ionone, 3-oxo-alpha-ionone, 4,4,7-trimethyl-3,4-dihydro-2(1H)-naphthalenone, 3,4-dihydro-beta-ionone, 4-hydroxy-1,1,6-trimethyltetrahydronaphthalene and megastigma-4,7- dien -3,6,9-triol (Stevens, Lundin & Davis, 1975; Davis, Stevens & Jurd, 1976; Enzell, Wahlberg & Aasen, 1977; Di Stefano, 1985; Strauss *et al.,* 1986). Recently it has been demonstrated that a number of TDN precursors are present in Weisser Riesling wine and that they appear to be polar glycosidic derivatives, as well as non-glycosidic compounds (Winterhalter, Sefton & Williams, 1990). Two of the suggested natural precursors of TDN have been identified as the glycosidically bound forms of 2,6,10,10-tetramethyl-1-oxaspiro [4.5] dec-6-ene-2,8-diol, and 3,4-dihydroxy-7,8-dihydro-beta-ionone beta-D-glucopyranoside in Weisser Riesling wine and red currant leaves, respectively (Winterhalter, 1991; Humpf, Winterhalter & Schreier, 1991).

Various factors may influence the development of TDN in wine during ageing. One of these is the potential volatile TDN (TDN precursor) concentration, which has been found to increase during ripening of Weisser Riesling grapes (Strauss *et al.,* 1987; Marais, Van Wyk & Rapp, 1992). It was also found that TDN precursor concentrations were significantly higher in sun-exposed than in shaded Weisser Riesling grapes (Marais *et al.,* 1992). Higher concentrations of TDN were also reported in older compared to younger commercial Weisser Riesling wines (Simpson & Miller, 1983; Rapp & Güntert, 1985). In addition, Simpson & Miller (1983) found higher TDN concentrations when grape juice was heated at a lower pH.

**Part of a Ph. D. (Agric.) dissertation to be submitted by the senior author to the University of Stellenbosch.*
Acknowledgements: The authors wish to express their appreciation to Miss E. Fourie for assistance with the analyses and for preparation of the diagrams, and to Mr D. Capatos and Dr J.H. Randall for assistance with the statistical analyses.

In view of limited knowledge about the development of TDN in wine, further investigation is required. In this study TDN concentrations in South African Weisser Riesling wines were compared to those in wines of cooler countries and other cultivars. In addition, the effect of storage time and temperature on TDN development in Weisser Riesling wines in relation to that of other volatiles, and on wine quality was determined.

MATERIALS AND METHODS

Commercial Weisser Riesling, Chenin blanc, Kerner and Cape Riesling (Crouchen blanc) wines of different vintages and regions in South Africa, as well as Weisser Riesling wines of different vintages and regions in Germany and Italy were collected. The regions, classified according to Winkler *et al.* (1974), and the wine producers are listed in Table 1.

TABLE 1
Regions and wine producers in Germany, Italy and South Africa.

Regions*	Wine producers (co-operatives and estates)
Germany	
Pfalz (I)	Deidesheim; Frankweiler/Rietburg; Geilweilerhof (Research Station)
Italy	
Trentino-South Tyrol (II)	Cornaiano; Hirschprunn; Laimburg
Friuli (III)	Jermann
South Africa	
Constantia (II/III)	Groot Constantia; Klein Constantia
Durbanville (III)	KWV (Weisser Riesling and Kerner grapes)
Stellenbosch (III/IV)	Delheim; Eersterivier; Lievland; Neethlingshof; Nietvoorbij (Research station); Oude Libertas (SFW); Simonsig; Vlottenburg
Paarl (IV)	Boschendal; Nederburg; Simonsvlei
Robertson/Bonnievale (IV)	De Wetshof; Mon Don; Roodezandt; Weltevrede
Worcester/Rawsonville (IV)	Lebensraum; Nuy; Waboomsrivier
Vredendal (V)	Vredendal

* Regions classified according to Winkler *et al.* (1974).

In addition, Weisser Riesling wines of the 1987 vintage were obtained in bulk from three producers, namely KWV (grapes from Durbanville region), Vlottenburg co-operative (Stellenbosch region) and Groot Constantia estate (Constantia region). After bottling, two batches of each wine were stored at 15°C and 30°C, respectively. Samples were removed for analyses and sensory evaluations upon bottling and at eight additional stages over four years for the wines stored at 15°C, and five stages over one year for the wines stored at 30°C.

All wines were extracted with Freon 11 and the extracts analysed for free TDN by gas chromatography (Marais, 1986). The 1987 Weisser Riesling wines stored at 15°C and 30°C were analysed for C_{13}-norisoprenoids, monoterpenes, esters and higher alcohols. The precursors of TDN and a related compound believed to be a hydroxylated TDN (OH-TDN) were isolated on Amberlite XAD-2 resin according to the technique of Gunata *et al.* (1985), as adapted by Versini *et al.* (1987). These two compounds were subsequently liberated from their bound forms by acid hydrolysis for four hours at pH 1, in a waterbath at 50°C. The liberated norisoprenoids were extracted with pentane/dichloromethane (2:1), the extracts concentrated and analysed by gas chromatography. The optimum conditions for acid hydrolysis were determined by monitoring the liberation of TDN from its precursor(s) in a Weisser Riesling grape sample over 30 hours at pH 1 and 2. The abovementioned analyses were not replicated.

Gas chromatography and mass spectrometry: The gas chromatographic analyses were performed, using a Hewlett Packard 5880A instrument with automatic dual integrators. The capillary columns and gas chromatographic conditions used, were:

1. Supelcowax 10 fused silica (60 m x 0,32 mm i.d., film thickness: 0,25 µm); temperature programme: 10 min. at 60°C, 1°C/min. up to 190°C, 30 min. at 190°C; detector: FID; detector temperature: 250°C; injection temperature: 200°C; carrier gas: helium; column flow rate: 1,5 ml/min; split ratio: 60:1.

2. SPB-5 fused silica (60 m x 0,32 mm i.d., film thickness: 0,25 µm); temperature programme: 5 min. at 80°C, 1°C/min. up to 250°C, 20 min. at 250°C; detector temperature: 300°C; other parameters as under 1.

3. Carbowax 20 M fused silica (50 m x 0,32 mm i.d., film thickness: 0,3 µm); temperature programme: 10 min. at 60°C, 1°C/min. up to 190°C, 30 min. at 190°C; other parameters as under 1.

The C_{13}-norisoprenoids were determined on columns 1 and 2 and the monoterpenes, esters and higher alcohols on columns 1 and 3. Concentrations were expressed relative to those of internal standards, 3-decanol (for acid-released volatiles) and 2-ethyl hexanol (for free volatiles). The identities of all compounds were confirmed by comparing their mass spectra and retention times with those of authentic standards, which were analysed under similar conditions and on similar columns on a Finnigan 4600 mass spectrometer.

Sensory evaluations: All the samples of the 1987 Weisser Riesling wines aged at 15°C and 30°C, respectively, were sensorially evaluated by an expert panel of eight judges. They were selected by virtue of their experience as wine judges and their ability to rate the intensity of young wine character and the typical "kerosene" character of aged Weisser Riesling wines. Since samples of the same wine, kept at 15°C and 30°C, were sensorially evaluated repeatedly during storage periods of 199 and 47 weeks, respectively, some of the judges could not be present at each tasting. At two sittings where only four judges were present the evaluations were replicated. Intensities of young wine character and kerosene character as well as overall wine quality were evaluated on a 9-point scale. The descriptive terms for the intensity scale varied from "not detectable (1 point)" to "exceptionally prominent (9 points)", and for the quality scale from "unacceptable (1 point)" to "excellent (9 points)".

Statistical analyses: The significance of the effect of storage time on the concentrations of volatiles in the Weisser Riesling wines was determined by means of linear regression analysis (Snedecor & Cochran, 1980). In some cases log transformation of the data was necessary because of gross inequalities in error variance between the regions. An example is the TDN concentrations of the wines stored at 30°C (Fig. 2).

The sensory evaluation data were analysed by means of a generalised linear model (McCullagh & Nelder, 1983) fitted using the computer program PC-PLUM (Randall, 1989a). In this approach the categories of an ordinal scale were treated as intervals of an imaginary underlying scale and some distribution (in this case the logistic distribution) fitted (Randall, 1989b). The approach is clearly depicted in the vertical axes of Figure 7. The technique supplied a location value for each wine at each time of tasting (the points in the figure) and allowed the fitting of parametric models (the lines in the figure). Notice that the intervals on the vertical axes are of different lengths even though the scores are equally spaced. This reflects the fact that the score numbers are arbitrary but the interval lengths have been fitted to the data.

RESULTS AND DISCUSSION

Survey of relative TDN concentration levels in wines of different cultivars, vintages and regions: The relative concentrations of TDN in wines of different cultivars, vintages and regions are illustrated in Figure 1. Chenin blanc and Cape Riesling (Crouchen blanc) contained relatively low TDN concentrations (Fig. 1A). In general, Kerner (Weisser Riesling x Trollinger) contained higher TDN concentrations than Chenin blanc and Cape Riesling (Fig. 1A). The TDN concentrations of Weisser Riesling wines from Italy were relatively low, while those from the Pfalz (Germany) were higher (Fig. 1B). Compared to the wines from the abovementioned cooler regions, the Weisser Riesling wines from the warmer South African regions had on average 78% higher TDN concentrations (Fig. 1C).

The abovementioned observations confirmed earlier presumptions about differences in TDN concentrations between the cooler European and the warmer South African regions. This phenomenon could be explained by the difference in the rate of development of TDN precursors in grapes of these countries, due to the combined effect of climatic factors and viticultural practices. For example, TDN precursor levels were found to be almost twice as high in sun-exposed grapes than in shaded grapes at similar sampling stages (Marais *et al.*, 1992).

Due to the limited number of samples available for the survey, regions within a country could not be clearly distinguished in terms of TDN levels (Table 1, Fig. 1). However, it appears that the TDN levels of the wines of the same vintage from the cooler South African regions (II/III) were higher than those from the warmer regions (IV) (Table 1, Fig. 1). This phenomenon is in contrast to that observed in Weisser Riesling wines from the cooler European regions which contained lower TDN levels than those wines from the warmer South African regions (Fig. 1). Furthermore, higher TDN levels were observed in older wines than in younger wines of all cultivars (Fig. 1). Deviations from this trend may be ascribed to different TDN precursor levels and different storage temperatures. For example, the TDN concentrations of three Weisser Riesling wines from the 1987 vintage, namely KWV, Vlottenburg and Groot Constantia, which were stored at 15°C, were appreciably lower than those of other 1987 wines (Fig. 1C), not necessarily stored at such low temperatures. It should be emphasized that TDN levels could also be affected by other factors such as clone, crop level, grape maturity at harvest and wine-making techniques.

Effect of storage time and temperature on free TDN and TDN precursor concentrations in Weisser Riesling wines: The effect of storage time and temperature on free TDN concentrations in three Weisser Riesling wines (KWV, Vlottenburg and Groot Constantia) from the 1987 vintage is illustrated in Figure 2. The levels of significance for the effect of storage time on these TDN concentrations are given in Table 2. A significant increase in TDN concentration occurred at 15°C and 30°C storage and in fact confirmed similar trends obtained by analyses of a variety of Weisser Riesling wines from different vintages and origins (Simpson & Miller, 1983; Rapp & Güntert, 1985). The TDN concentrations increased at a faster rate at 30°C than at 15°C, and were followed by slight decreases after about 20 weeks storage (Fig. 2). The latter tendency also occurred at 15°C storage (Fig. 2). Higher levels of TDN were observed in the Groot Constantia Weisser Riesling wines than in the other two wines (Fig. 2). Parts of the Constantia region are cooler than the Durbanville (KWV) and Stellenbosch (Vlottenburg) regions, due to the influence of the sea (Table 1). This phenomenon, namely higher TDN concentrations in cooler South African regions, confirmed the results discussed earlier (Fig. 1C).

The decrease in TDN concentration during ageing may be ascribed to its transformation to other compounds. A similar decrease was found when the bound fraction of a Weisser Riesling grape sample was subjected to acid hydrolysis at pH 1 (Fig. 3). A maximum TDN concentration was observed after about 4 hours at 50°C, whereafter a consistent decrease in concentration occurred. A relationship existed between the changes in the concentrations of free TDN and those of the corresponding potentially volatile TDN and OH-TDN in all three Weisser Riesling wines (Fig. 4). As in the case of free TDN, higher levels of TDN and OH-TDN precursors also occurred in the Groot Constantia Weisser Riesling wines than in those of the other two regions. The possibility that the unknown compound, OH-TDN, is also a precursor of TDN was considered in view of its structural relationship with TDN (Marais *et al.*, 1992).

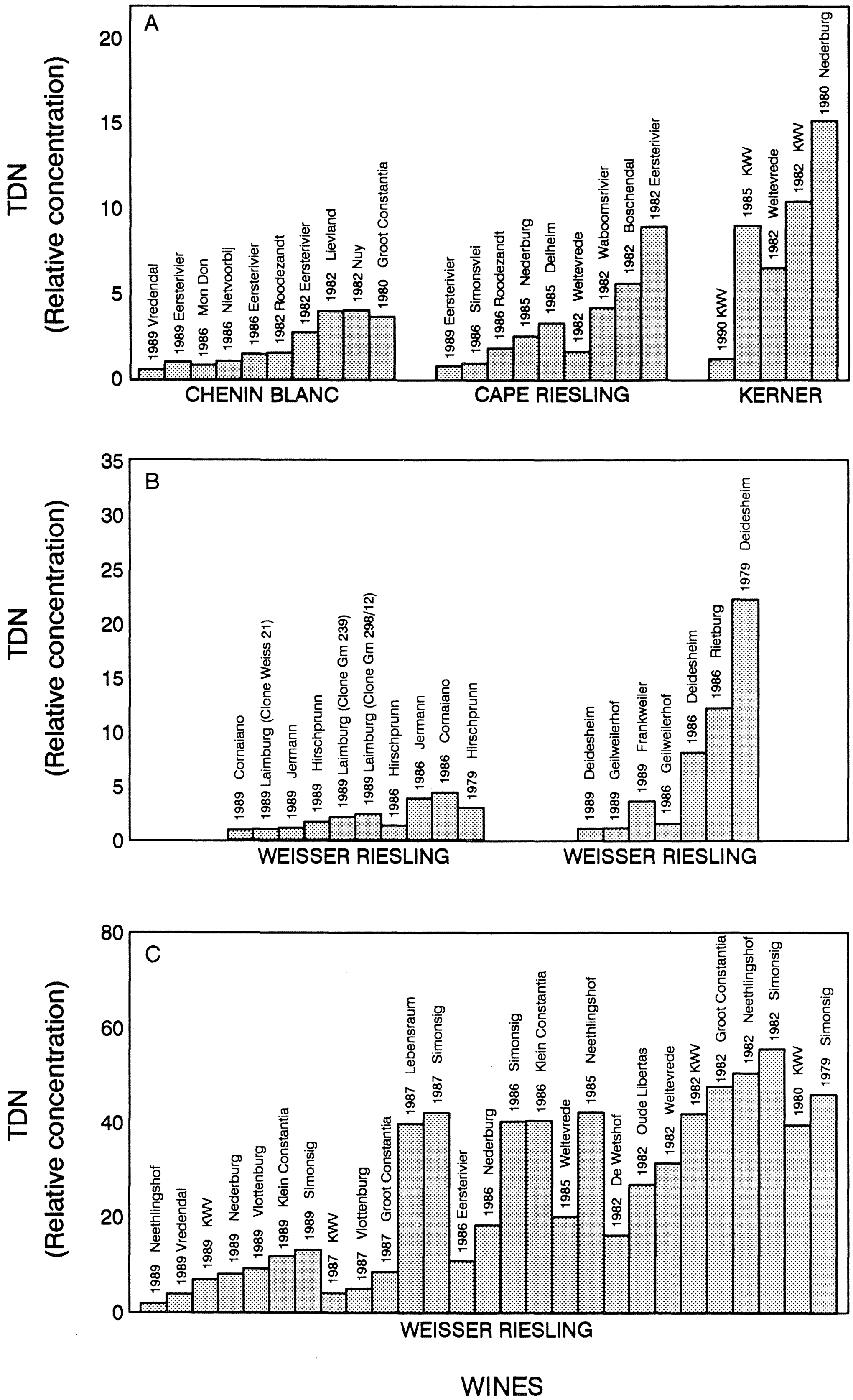

FIGURE 1

A comparison of relative 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) concentrations in wines from cultivars other than Weisser Riesling (A), Weisser Riesling wines from Germany and Italy (B) and from South Africa (C). Wine producers (co-operatives and estates) and vintages are indicated for each wine. The regions within countries, in which the wine producers are situated, are listed in Table 1.

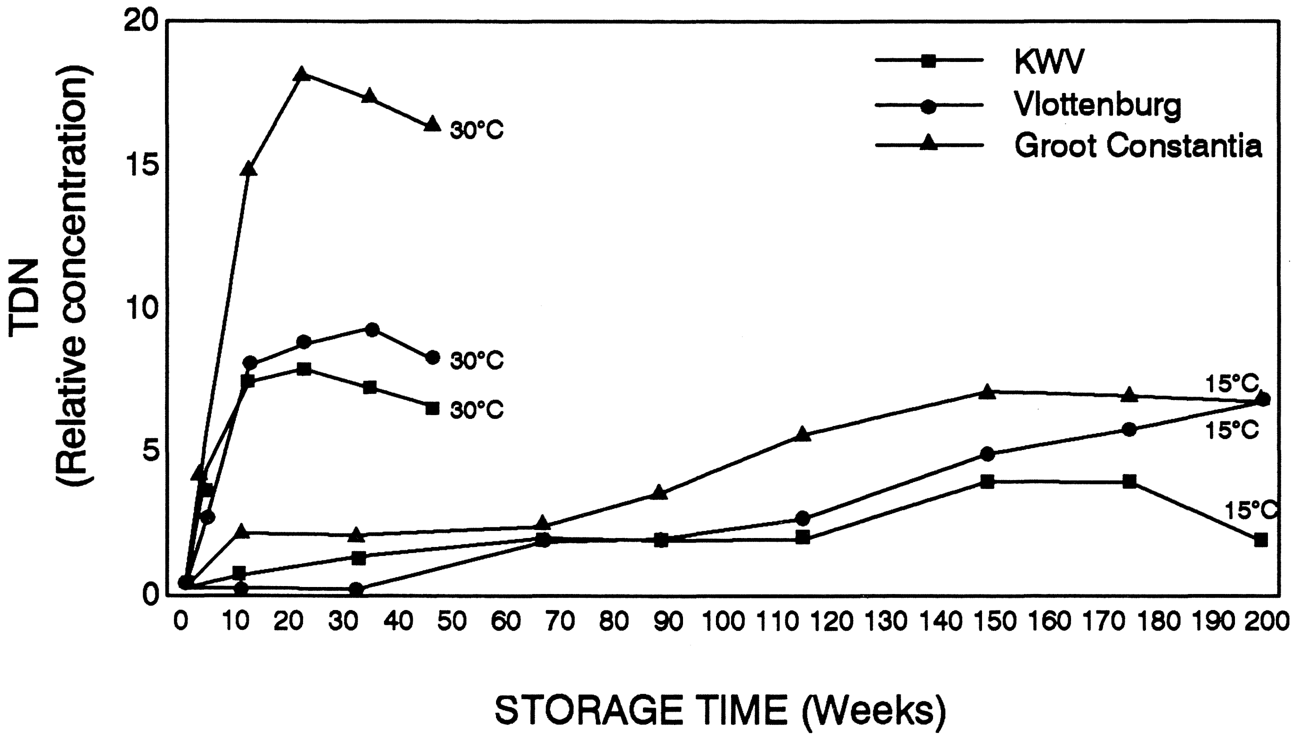

FIGURE 2

Effect of storage time and temperature on the relative concentration of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) in Weisser Riesling wines from three regions, namely Durbanville (KWV), Stellenbosch (Vlottenburg) and Constantia (Groot Constantia). Significance of results is given in Table 2.

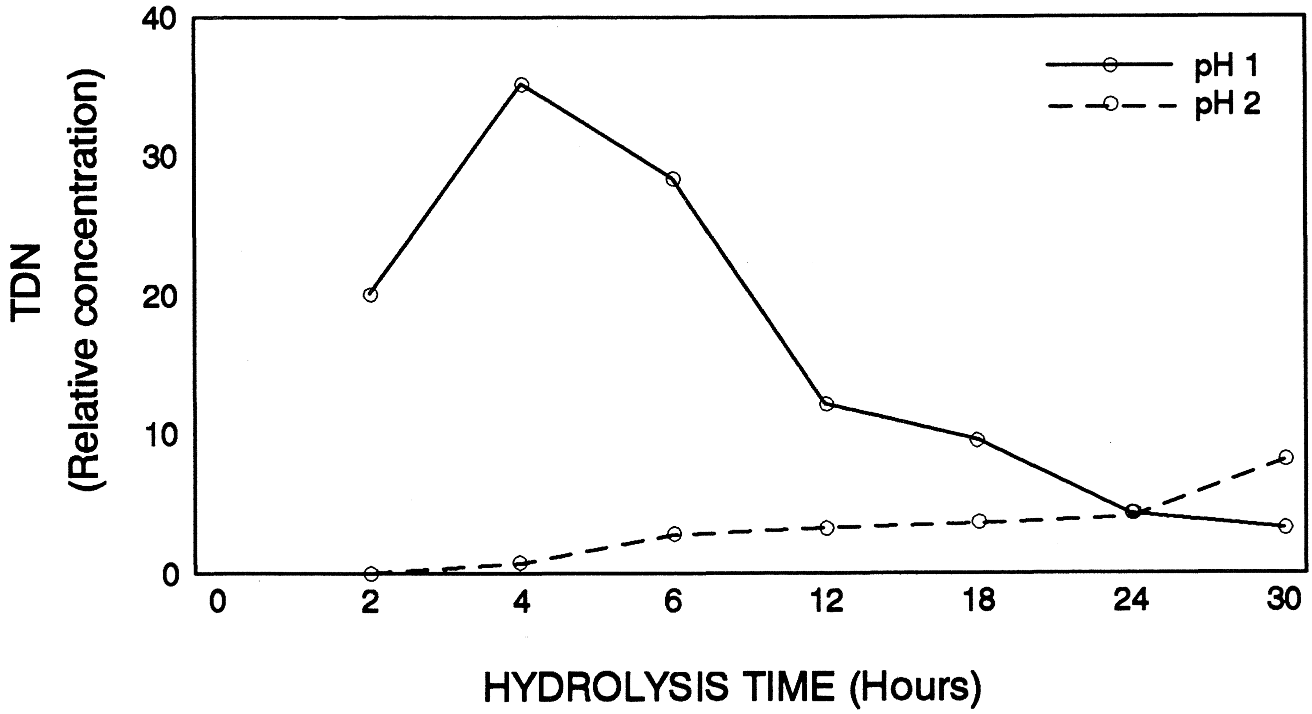

FIGURE 3

Effect of hydrolysis time and pH on the liberation of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) from its bound forms, isolated from Weisser Riesling grapes.

TABLE 2
Significance of the effect of storage time on volatile compound concentrations in Weisser Riesling wines from three regions.

Compound	15°C storage for 199 weeks			30°C storage for 47 weeks		
	KWV	Vlottenburg	Groot Constantia	KWV	Vlottenburg	Groot Constantia
1,1,6-Trimethyl-1,2-dihydronaphthalene	*	**	**	**	**	**
trans-Vitispirane	**	**	**	*	*	NS
Diendiol-1	NS	NS	*(-)	**(-)	*(-)	**(-)
Hydroxylinalool	**	**	**	NS	*	**
trans-1,8-Terpin	**	**	**	*	**	**
Linalool	**(-)	**(-)	**(-)	**(-)	**(-)	**(-)
alpha-Terpineol	**	**	**	**(-)	*(-)	*(-)
i-Amyl acetate	**(-)	**(-)	**(-)	**(-)	**(-)	**(-)
Hexyl acetate	**(-)	**(-)	**(-)	**(-)	**(-)	**(-)
Ethyl caproate	NS	NS	NS	**(-)	**(-)	**(-)
2-Phenethyl acetate	** (-)	**(-)	**(-)	**(-)	**(-)	**(-)
Hexanol	NS	NS	**	*(-)	**(-)	NS
2-Phenyl ethanol	NS	*(-)	NS	**(-)	**(-)	**(-)

** = Highly significant ($p \leq 0{,}01$).
* = Significant ($p \leq 0{,}05$).
NS = Not significant.
(-) = Decreases in concentration.
KWV = Grapes from the Durbanville region.
Vlottenburg = Stellenbosch region.
Groot Constantia = Constantia region.

Effect of storage time and temperature on other volatile compound concentrations in Weisser Riesling wines: The effect of storage time on the concentrations of trans-vitispirane, terpenes, esters and higher alcohols, which are known to contribute to aroma, was also determined in this investigation. The levels of significance for these changes are given in Table 2 and typical concentration changes are illustrated in Figures 5 and 6.

Significant increases occurred in the concentrations of trans-vitispirane, 2,6-dimethyl-7-octen-2,6-diol (hydroxylinalool) and trans-1,8-terpin (Table 2, Fig. 5). It has been claimed that these compounds may also contribute to the bottle-aged character of terpene-rich wines (Simpson, Strauss & Williams, 1977; Simpson & Miller, 1983; Rapp, Güntert & Ullemeyer, 1985). Significant decreases were observed in the concentrations of diendiol-1, linalool, i-amyl acetate, hexyl acetate, ethyl caproate, 2-phynethyl acetate, hexanol and 2-phenyl ethanol (Table 2, Figs. 5 and 6). In a few cases these decreases occurred only at 30°C and not at 15°C storage. alpha-Terpineol showed a significant increase, followed by a decrease in concentration under the same conditions. This tendency was especially prominent at 30°C storage and could be explained by the conversion of linalool, nerol and geraniol via alpha-terpineol to cis-1,8-terpin (Rapp *et al.,* 1985). In general, terpenes present in older Weisser Riesling wines are produced by acid-catalysed conversions of volatile monoterpene alcohols initially present in the young wines, as well as produced from the less volatile hydroxylated linalool derivatives and glycosides (Usseglio-Tomasset & Di Stefano, 1980; Williams, Strauss & Wilson, 1980; Di Stefano, 1981; Williams *et al.,* 1982a, 1982b). Decreases in the concentrations of the acetate esters, *e.g.* i-amyl acetate (Fig. 6) were prominent. It is doubtful that these esters, which are recognised for their contribution to the fermentation bouquet or young wine character, could have interacted appreciably with the kerosene character of TDN, since the latter normally becomes pronounced at a stage when the fruity fermentation bouquet is rather weak. As in the case of free TDN and its precursors, volatile compound concentrations were higher in the Groot Constantia Weisser Riesling wines than in the other wines (Figs. 2, 4, 5 and 6) which is in accordance with the more complex wines produced in this relatively cool region. The abovementioned volatiles were considered in this study, since they are known to contribute to the aroma of wine, and some may have a masking or strengthening effect on the kerosene character of TDN.

Effect of storage time and temperature on quality parameters of Weisser Riesling wines: The changes in young wine character intensity, kerosene character intensity and overall wine quality of the wines at the two tempera-

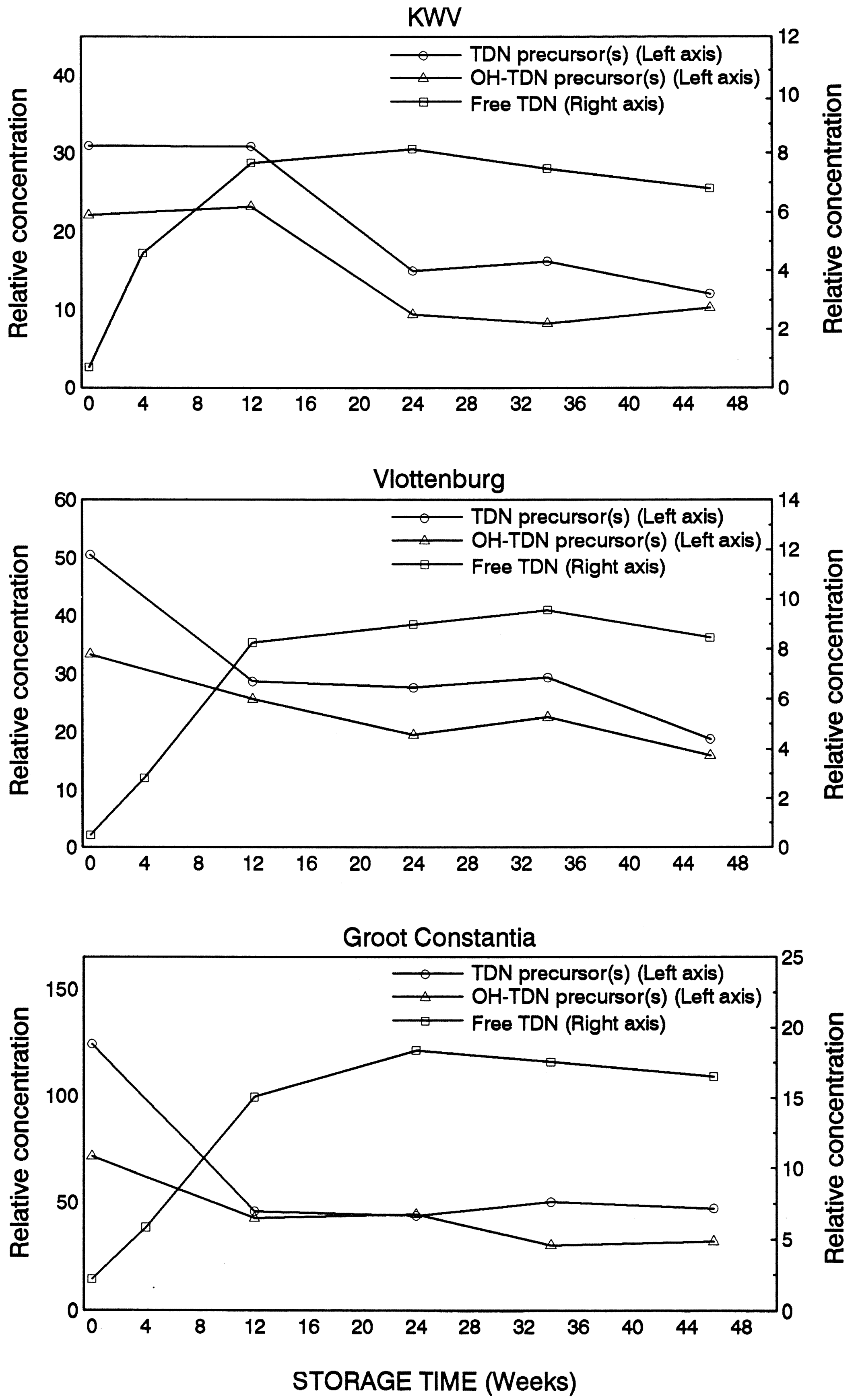

FIGURE 4
Effect of storage time and temperature (30°C) on the relative concentrations of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) and OH-TDN (unknown compound) precursors, and on free TDN in Weisser Riesling wines from three regions, namely Durbanville (KWV), Stellenbosch (Vlottenburg) and Constantia (Groot Constantia).

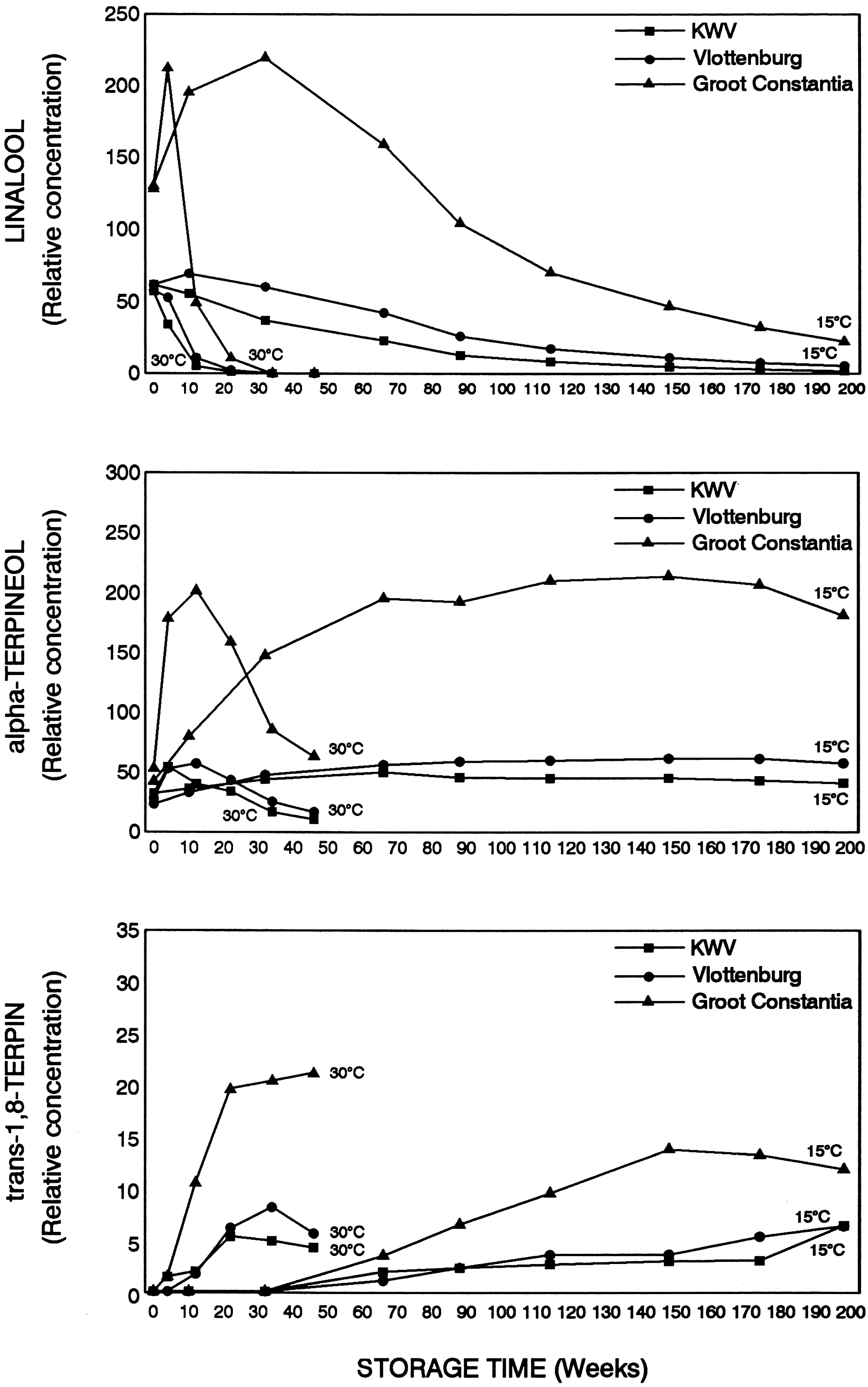

FIGURE 5
Effect of storage time and temperature on the relative concentrations of linalool, alpha-terpineol and trans-1,8-terpin in Weisser Riesling wines from three regions, namely Durbanville (KWV), Stellenbosch (Vlottenburg) and Constantia (Groot Constantia). Significance of results is given in Table 2.

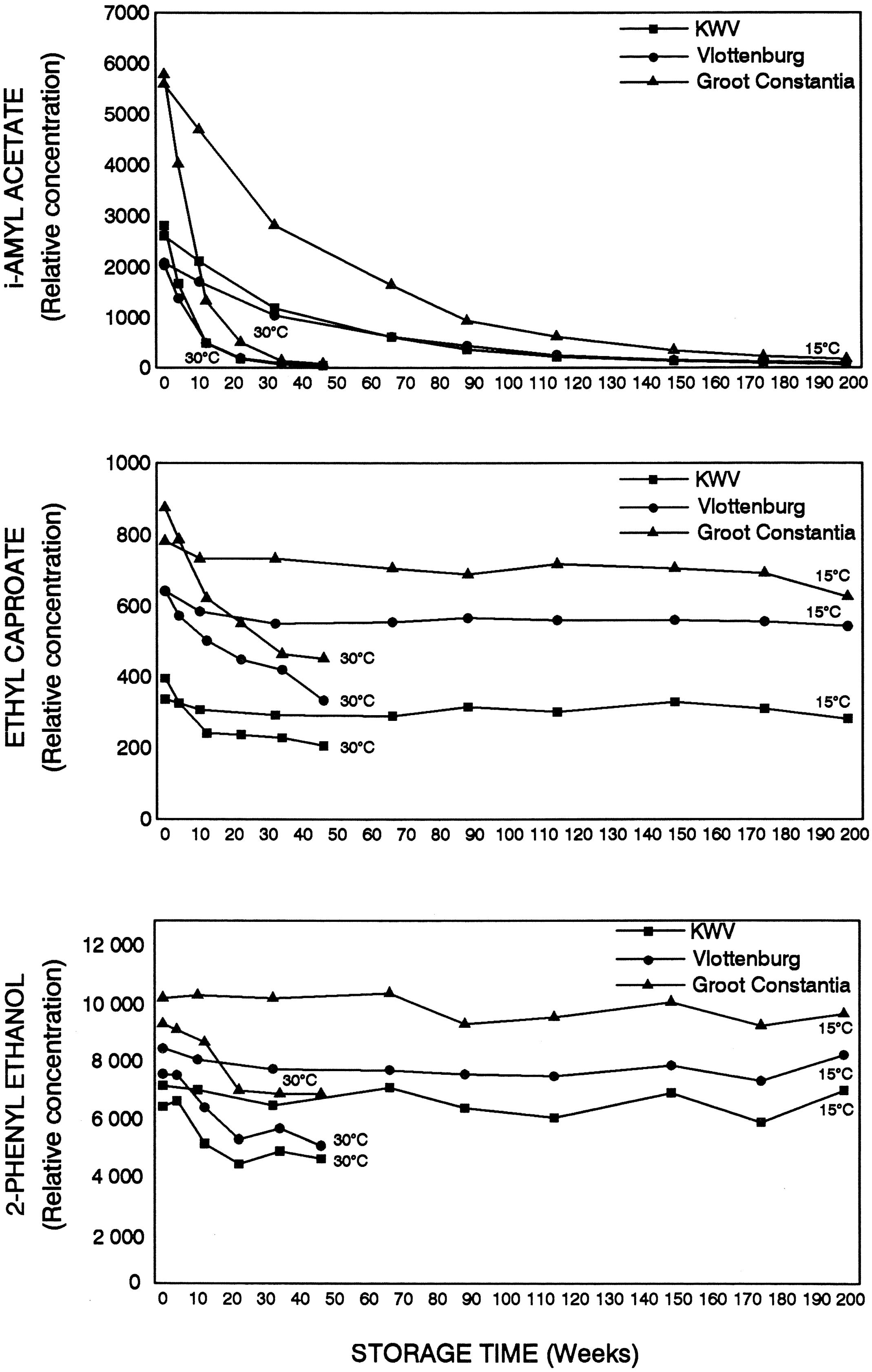

FIGURE 6

Effect of storage time and temperature on the relative concentrations of i-amyl acetate, ethyl caproate and 2-phenyl ethanol in Weisser Riesling wines from three regions, namely Durbanville (KWV), Stellenbosch (Vlottenburg) and Constantia (Groot Constantia). Significance of results is given in Table 2.

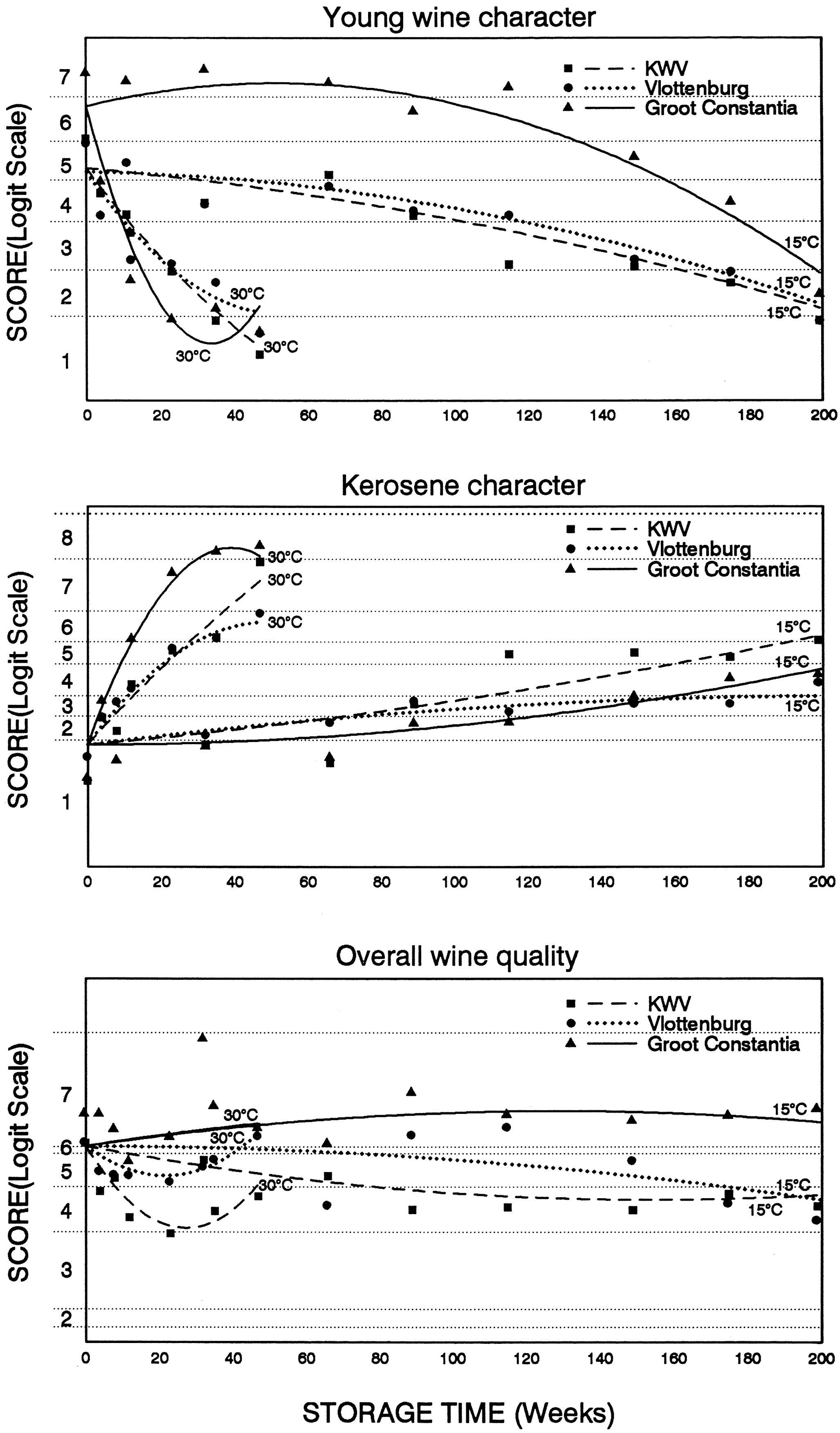

FIGURE 7
Effect of storage time and temperature on the intensities of young wine character and kerosene character, and on overall wine quality of Weisser Riesling wines from three regions, namely Durbanville (KWV), Stellenbosch (Vlottenburg) and Constantia (Groot Constantia). Significance of results is given in Table 3.

TABLE 3
Significance of the effect of storage time on sensory evaluation data of Weisser Riesling wines from three regions.

Quality characteristics	KWV		Vlottenburg		Groot Constantia	
	Coefficient[a]		Coefficient[a]		Coefficient[a]	
	Quadratic	Linear	Quadratic	Linear	Quadratic	Linear
15°C storage for 199 weeks						
Young wine character	-1,1 NS	-6,2**	-1,7 NS	-5,6 **	-4,8 **	-5,2**
Kerosene character	1,1 NS	9,0**	-1,2 NS	5,3 **	2,0 *	5,6**
Overall wine quality	1,7 NS	-4,3**	-1,0 NS	-2,6 **	-1,6NS	3,9**
30°C storage for 47 weeks						
Young wine character	0,6 NS	-7,5**	1,4 NS	-6,8 **	5,6 **	-9,6**
Kerosene character	-0,6 NS	11,1**	-2,7 **	10,3 **	-6,2 **	12,1**
Overall wine quality	4,0 **	-4,5**	2,4 *	0,1NS	-0,1NS	2,3 *

a = Value of highest order coefficient fitted (Randall, 1989a, 1989b).
** = Highly significant (p≤0,01).
* = Significant (p≤0,05).
NS = Not significant.
KWV = Grapes from the Durbanville region.
Vlottenburg = Stellenbosch region.
Groot Constantia = Constantia region.

tures and after different storage times are depicted in Figure 7. The lines in the figure were drawn according to the best-fitting quadratic function. While the curvature of these lines was not always significant, the slope of a straight line was highly significant in most cases (Table 3). Although quadratic functions represented the general tendency observed adequately, the line for the young wine character of Groot Constantia at 30°C warned against too literal an interpretation.

Highly significant decreases in young wine character intensity occurred in all of the wines during ageing (Table 3). This phenomenon was accompanied by highly significant decreases in the concentrations of acetic acid esters (Table 2, Fig. 6), which are known to be key contributors to fermentation bouquet (Van der Merwe & Van Wyk, 1981) and young wine character. The decrease in esters in wine during ageing is due to acid catalysed hydrolysis (Nordström, 1964) and will be enhanced by an increase in temperature (Marais & Pool, 1980). This accounts for the higher rate of decrease in young wine character intensity at 30°C (Fig. 7).

The decrease in young wine character intensity was accompanied by a significant increase in kerosene character intensity in all of the wines (Table 3). This may be attributed to the significant to highly significant increase in the concentrations of TDN (Table 2), the main contributor to this odour (Simpson, 1978).

During ageing the quality of the KWV and Vlottenburg wines decreased significantly at 15°C (Table 3). The significant changes at 30°C could be ascribed to the abovementioned loss of quality-enhancing fermentation bouquet and gain in less attractive kerosene character. Under the same conditions, however, the Constantia wine showed a significant to highly significant increase in quality at both temperatures. This phenomenon occurred despite highly significant decreases in quality-enhancing fermentation bouquet substances (acetate esters) and highly significant increases in the concentration of the kerosene-like TDN (Table 2). These contradictory findings could probably be attributed to the presence of higher levels of other quality-enhancing aroma constituents, such as terpenes and C_{13}-norisoprenoids. These compounds may be released during ageing and thus contribute to a more complex aroma, which in turn could mask the kerosene character of the TDN. This phenomenon may occur more readily in the relatively cool Constantia region, which is well known for its more complex flavourful Weisser Riesling wines.

CONCLUSIONS

The development of the kerosene-like bottle-aged character of Weisser Riesling wines, and TDN which is an important contributor to this character was influenced by the region, storage time, temperature and probably by the concentrations of the TDN precursors. By varying the storage temperature, wines can be aged at different rates, and wines with different kerosene character intensities and wine styles can be obtained. However, the perception of the kerosene character in Weisser Riesling wines may depend on the complexity of the wine and on the changes in concentration of terpenes and other C_{13}-norisoprenoids during ageing.

LITERATURE CITED

BERTUCCIOLI, M. & VIANI, R., 1976. Red wine aroma: Identification of headspace constituents. *J. Sci. Food Agric.* **27**, 1035-1038.

DAVIS, D.L., STEVENS, K.L. & JURD, L., 1976. Chemistry of tobacco constituents. Oxidation of alpha-ionone and the acid-catalyzed rearrangement of 5-keto-alpha-ionone. *J. Agric. Food Chem.* **24**, 187-189.

DI STEFANO, R., 1981. Terpene compounds of white Muscat from Piemonte. *Vini Ital.* **23**, 29-43.

DI STEFANO, R., 1985. Presenza di caratteri organolettici favoreoli in vini bianchi lungamente invecchiati. Indagine sui composti volatili e su alcuni parametri chimici e fisici di Riesling prodotti in Germania. *Riv. Vitic. Enol.* **4**, 228-241.

ENZELL, C.R., WAHLBERG, I. & AASEN, A.J., 1977. Isoprenoids and alkaloids of tobacco. *Fortschritte d. Chem. org. Naturst.* **34**, 1-79.

GUNATA, Y.Z., BAYONOVE, C.L., BAUMES, R.L. & CORDONNIER, R.E., 1985. The aroma of grapes. I. Extraction and determination of free and glycosidically bound fractions of some grape aroma components. *J. Chromatogr.* **331**, 83-90.

HOHLER, A., NITZ, S. & DRAWERT, F., 1988. Über die Bildung und die sensorischen Eigenshaften flüchtiger Nor-Carotinoide. I. Photooxidation von beta-Carotin in N,N-Dimethylformamid. *Chem. Microbiol. Technol. Lebensm.* **11**, 115-126.

HUMPF, H.-U., WINTERHALTER, P. & SCHREIER, P., 1991. 3,4-Dihydroxy-7,8-dihydro-beta-ionone beta-D-glucopyranoside: Natural precursor of 2,2,6,8-tetramethyl-7,11-dioxatricyclo [6.2.10^{1,6}] undec-4-ene (Riesling acetal) and 1,1,6-trimethyl-1,2-dihydronaphthalene in red currant (*Ribes rubrum* L.) leaves. *J. Agric. Food Chem.* **39**, 1833-1835.

LIEBICH, H.M., KOENIG, W.A. & BAYER, E., 1970. Analysis of the flavor of rum by gas-liquid chromatography and mass spectrometry. *J. Chrom. Sci.* **8**, 527-533.

MARAIS, J., 1986. A reproducible capillary gas chromatographic technique for the determination of specific terpenes in grape juice and wine. *S. Afr. J. Enol. Vitic.* **7**, 21-25.

MARAIS, J. & POOL, H.J., 1980. Effect of storage time and temperature on the volatile composition and quality of dry white table wines. *Vitis* **19**, 151-164.

MARAIS, J., VAN WYK, C.J. & RAPP, A., 1992. Effect of sunlight and shade on norisoprenoid levels in maturing Weisser Riesling and Chenin blanc grapes and Weisser Riesling wines. *S. Afr. J. Enol. Vitic.* **13**, 23-32.

McCULLAGH, P. & NELDER, J.A., 1983. Generalized linear models. Chapman and Hall, London.

NORDSTRÖM, K., 1964. Studies on the formation of volatile esters in fermentation with Brewer's Yeast. *Svensk Kem. Tidskri.* **76**, 9-43.

OHLOFF, G., 1978. Recent developments in the field of naturally-occurring aroma components. *Fortschritte d. Chem. org. Naturst.* **35**, 431-527.

RANDALL, J.H., 1989a. PC-PLUM Manual (Version 2). Dept. of Biometry, University of Stellenbosch, Stellenbosch, Republic of South Africa.

RANDALL, J.H., 1989b. The analysis of sensory data by generalized linear model. *Biom. J.* **31**, 781-793.

RAPP, A. & GÜNTERT, M., 1985. Changes in aroma substances during the storage of white wines in bottles. In: CHARALAMBOUS, G. (ed.). The shelf life of foods and beverages. Proc. 4th Int. Flavor Conf., 23-26 July, Rhodes, Greece. pp. 141-167.

RAPP, A., GÜNTERT, M. & ULLEMEYER, H., 1985. Über Veränderungen der Aromastoffe während der Flaschenlagerung von Weissweinen der Rebsorte Riesling. *Z. Lebensm. Unters.-Forsch.* **180**, 109-116.

SCHREIER, P., DRAWERT, F., KERENYI, Z. & JUNKER, A., 1976. Gaschromatographisch-massenspektrometrische Untersuchung flüchtiger Inhaltsstoffe des Weines. VI. Aromastoffe in Tokajer Trockenbeerenauslese (Aszu)-Weinen. a) Neutralstoffe. *Z. Lebensm. Unters.-Forsch.* **161**, 249-258.

SIMPSON, R.F., 1978. 1,1,6-Trimethyl-1,2-dihydronaphthalene: an important contributor to the bottle aged bouquet of wine. *Chem. Ind.* **1**, 37.

SIMPSON, R.F. & MILLER, G.C., 1983. Aroma composition of aged Riesling wine. *Vitis* **22**, 51-63.

SIMPSON, R.F., STRAUSS, C.R. & WILLIAMS, P.J., 1977. Vitispirane: a C_{13} spiro-ether in the aroma volatiles of grape juice, wines and distilled grape spirits. *Chem. Ind.* **15**, 663-664.

SNEDECOR, G.W. & COCHRAN, W.G., 1980. Statistical methods (7th Edition). The Iowa State University Press, Ames, Iowa, U.S.A.

STEVENS, K.L., LUNDIN, R. & DAVIS, D.L., 1975. Acid catalyzed rearrangement of beta-ionone epoxide. *Tetrahedron* **31**, 2749-2753.

STRAUSS, C.R., DIMITRIADIS, E., WILSON, B. & WILLIAMS, P.J., 1986. Studies on the hydrolysis of two megastigma-3,6,9-triols rationalizing the origins of some volatile C_{13} nor-isoprenoids of *Vitis vinifera* grapes. *J. Agric. Food Chem.* **34**, 145-149.

STRAUSS, C.R., WILSON, B., ANDERSON, R. & WILLIAMS, P.J., 1987. Development of precursors of C_{13} nor-isoprenoid flavorants in Riesling grapes. *Am. J. Enol. Vitic.* **38**, 23-27.

USSEGLIO-TOMASSET, L. & DI STEFANO, R., 1980. Profilo aromatico del Moscato bianco del Piemonte. *Riv. Vitic. Enol.* **33**, 58-68.

VAN DER MERWE, C.A. & VAN WYK, C.J., 1981. The contribution of some fermentation products to the odor of dry white wines. *Am. J. Enol. Vitic.* **32**, 41-46.

VERSINI, G., DALLA SERRA, A., DELL'EVA, M., SCIENZA, A. & RAPP, A., 1987. Evidence of some glycosidically bound new monoterpenes and norisoprenoids in grapes. In: SCHREIER, P. (ed.). Bioflavour '87. Analysis. Biochemistry. Biotechnology. Proc. Int. Conf., 29-30 September, Würzburg, Germany. pp. 161-170.

WILLIAMS, P.J. & STRAUSS, C.R., 1977. Apparatus and procedure for reproducible, high-resolution gas chromatographic analysis of alcoholic beverage headspace volatiles. *J. Inst. Brew.* **83**, 213-219.

WILLIAMS, P.J., STRAUSS, C.R. & WILSON, B., 1980. Hydroxylated linalool derivatives as precursors of volatile monoterpenes of muscat grapes. *J. Agric. Food Chem.* **28**, 766-771.

WILLIAMS, P.J., STRAUSS, C.R., WILSON, B. & MASSY-WESTROPP, R.A., 1982a. Novel monoterpene disaccharide glycosides of *Vitis vinifera* grapes and wines. *Phytochemistry* **21**, 2013-2020.

WILLIAMS, P.J., STRAUSS, C.R., WILSON, B. & MASSY-WESTROPP, R.A., 1982b. Studies on the hydrolysis of *Vitis vinifera* monoterpene precursor compounds and model monoterpene beta-D-glucosides rationalizing the monoterpene composition of grapes. *J. Agric. Food Chem.* **30**, 1219-1223.

WINKLER, A.J., COOK, J.A., KLIEWER, W.M. & LIDER, L.A., 1974. General Viticulture. Univ. Calif. Press, Berkeley.

WINTERHALTER, P., 1991. 1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN) formation in wine. I. Studies on the hydrolysis of 2,6,10,10-tetramethyl-1-oxaspiro [4.5] dec-6-ene-2,8-diol rationalizing the origin of TDN and related C_{13}-norisoprenoids in Riesling wine. *J. Agric. Food Chem.* **39**, 1825-1829.

WINTERHALTER, P., SEFTON, M.A. & WILLIAMS, P.J., 1990. Volatile C_{13}-norisoprenoid compounds in Riesling wine are generated from multiple precursors. *Am. J. Enol. Vitic.* **41**, 277-283.